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MOLYBDENUM AND TUNGSTEN MONONITROSYL COMPLEXES

FOR

MOLECULAR ELECTRONICS

by

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SYNOPSIS

The primary objective of this thesis is the preparation and characterisation of molybdenum and tungsten mononitrosyl complexes designed to exhibit nonlinear optical (NLO) effects. A part of this work has also been directed at the synthesis of molybdenum mononitrosyl complexes designed to possess liquid crystal phases. Novel materials displaying such "molecular electronic" properties are required for the creation of opto-electronic devices to be used in computing and communications systems of the 21st century. All of the new metallo-organic compounds described have been fully characterised by standard physical techniques including i.r. and ^{1}H n.m.r. spectroscopy. Cyclic voltammetry and electronic absorption spectroscopy have also been used extensively to investigate molecular electronic properties.

Nine aryl amino- or hydroxy-ligands bearing *para*-ferrocenyl substituents have been synthesised and used to prepare a total of thirty two heterobimetallic complexes of the form [M(NO)L*(X)(Y)] (where M = Mo, X = F, Cl, Br, I, alkoxide, or arylferrocenyl ligand (ArFc), Y = ArFc; M = W, X = Cl or ArFc, Y = ArFc; L* = tris(3,5-dimethylpyrazolyl)hydroborate). In such complexes the ferrocenyl group acts as an electron donor and the 16-electron {M(NO)L*} centre is an electron acceptor. All of these complexes have been tested for powder second harmonic generation (SHG) using modifications of a standard test procedure, and referring the efficiency of the material for SHG to that of urea, taken as unity (Ξ = 1). At least nine complexes have been found to exhibit highly efficient doubling of a 1,907 nm laser wavelength, several showing activities similar to the organic compound DAN which has a Ξ value of about 115.

A single crystal X-ray structure of the complex [Mo(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] shows that this molecule, which gives a Ξ value of 123, crystallises in the noncentrosymmetric space group $P2_1$ with only one configuration of the chiral metal centre present. The analogous tungsten complex [W(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] gives a Ξ value of 53 and has a crystal structure

identical to its molybdenum analogue. Results of powder SHG tests show that the isostructural change of replacing Mo by W always leads to lower SHG efficiencies. This is thought to be because the greater electron density of W renders it a poorer electron acceptor. Powder X-ray diffraction has been used to investigate isostructural and non-isostructural changes in this class of complexes, and to relate these to observed SHG signals.

The nitroarylferrocenyl ligand precursors have also been tested for SHG at 1,907 nm, but only the stilbene compound 4-Fc-$C_6H_4CH=CHC_6H_4$-4-NO_2 shows any frequency doubling. A crystal structure of the related compound 4-Fc-$C_6H_4N=NC_6H_3$-2-CH_3-4-NO_2 shows that this molecule crystallises in the centrosymmetric space group $P2_1/c$ in which dipole cancellation precludes the observation of bulk NLO effects.

A number of stilbenyl and diphenylazo ligands bearing dimethylamino or methoxy substituents have been synthesised and used to prepare forty one {M(NO)L*} complexes. The lack of powder SHG from any of these complexes is thought to be a result of unfavourable structural effects.

Several stilbenyl and biphenyl ligands bearing long alkyl chain substituents have been synthesised and used, along with two mono-aryl ligands, to prepare twenty five donor-acceptor {Mo(NO)L*} complexes. Three molybdenum complexes of the cholesterolate ligand have also been prepared. All of these complexes have been investigated for liquid crystalline behaviour using DSC and polarising microscopy, but no evidence of any mesophases has been found. This is likely to be because the bulky nature of the tripodal L* ligand prevents the fluid ordering found in mesogenic materials.

Four {Mo(NO)L*} complexes containing the chiral resolved ligand (-)-2-(6-methoxy-2-naphthyl)-1-propoxide have been prepared, and a single diastereomer of the complex [Mo(NO)L*(HNC_6H_3-3-CH_3-4-$N=NC_6H_4$-4-Fc){(-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3}] isolated by column chromatography. The complex [Mo(NO)L*(OR)(HNC_6H_3-3-CH_3-4-$N=NC_6H_4$-4-Fc)] (R = cholesterolate) has also been prepared but not resolved. These complexes have not been tested for SHG.

Several homobimetallic {Mo(NO)L*} complexes have been

synthesised along with six complexes of the form [Mo(NO)L*(Cl)(OAr-4-NO_2)] (where Ar = phenyl, stilbenyl, or diarylazo), and these have been reduced chemically using cobaltocene. This was intended to produce complexes in which the reduced paramagnetic 17-electron Mo centre behaves as an electron donor in NLO-active compounds, but the reduction products have not been adequately characterised.

A retinal-derived aniline has been synthesised and used to prepare the first {Mo(NO)L*} complex of a polyene ligand. This complex does not appear to show second-order NLO effects, but may be of interest for third-order effects.

Some reactions of the related cationic mononitrosyl dihalide complexes $[Mo(NO)L^N(X)_2]^+.PF_6^-$ (where L^N = N,N',N"-trimethyl-1,4,7-triazacyclononane, and X = Br or Cl) with potential aryl ligands have also been investigated. However, only one complex, $[Mo(NO)L^N(Br)_2(H_2NC_6H_3\text{-}3\text{-}CH_3\text{-}4\text{-}N{=}NC_6H_4\text{-}4\text{-}Fc)]^+.PF_6^-$, has been isolated. This contains a seven coordinate paramagnetic 18-electron Mo centre bearing a neutral amino ligand, but does not show detectable powder SHG. These studies have shown that the cationic {Mo(NO)L^N} dihalides do not display the extensive amide and phenoxide derivative chemistry associated with their L* counterparts.

To

Emz, Mum, Dad, and Tanis

and

to the Glory of God

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"I want to run, I want to hide
I want to tear down the walls that hold me inside
I want to reach out and touch the flame
Where the streets have no name"

(U2)

"You broke the bonds
You loosed the chains
You carried the cross
And my shame
And my shame
You know I believe it...
But yes I'm still running"

(U2)

"You may find a better way
You may find the reasons for it all
You may hold a better hand
All your pride and understanding
Never really feeling love at all...
So you challenge everyone you meet
Crying out to fill a void in you
What are you running from my love?
What's this thing you're guilty of?
Follow me and never be accused
But you never do believe a word I say
And you never did believe there'd be a day of reckoning
So you run and you run and you run and you never stop
And you work and you work and you work until you drop
You're in over your head and the pressure just don't quit
But you can't escape the reach of love"

(The Call)

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Note: Complexes of the L^* ligand which are chiral at the metal centre are represented as only one enantiomer when in fact all such compounds were initially isolated as racemates. The only figures in which the metal configuration is intentionally specified are those depicting molecular structures derived from X-ray crystallographic studies.

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ABBREVIATIONS

VLSI	very large-scale integration
STM	scanning tunnelling microscopy
NLO	nonlinear optics/nonlinear optical
SHG	second harmonic generation
THG	third harmonic generation
D	(electron) donor
A	(electron) acceptor
EFISH	electric field induced SHG
PM	phase matching/phase matched
PMSHG	phase matched SHG
L-B	Langmuir-Blodgett
LC	liquid crystal/liquid crystalline
CT	charge-transfer
MLCT	metal-to-ligand charge-transfer
TCNQ	tetracyanoquinodimethane
TCNE	tetracyanoethylene
TTF	tetrathiafulvalene
KDP	potassium dihydrogen phosphate
ADP	ammonium dihydrogen phosphate
mNA	*meta*-nitroaniline
MAP	methyl-(2,4-dinitrophenyl)-aminopropanoate
MNA	2-methyl-4-nitroaniline
POM	3-methyl-4-nitropyridine-N-oxide
DAN	3-acetamido-4-dimethylaminonitrobenzene
NPP	N-(4-nitrophenyl)-(L)-prolinol
NPPA	N-(5-nitro-pyridyl)-(*S*)-phenylalaninol
DCNP	3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole
MMONS	3-methyl-4-methoxy-4'-nitrostilbene
MBADNP	2-N-(α-methylbenzylamino)-5-nitropyridine
TPP	tetraphenylporphyrin
pz	1-pyrazolyl
L*	tris(3,5-dimethylpyrazolyl)hydroborate
Cp	cyclopentadienide
thf	tetrahydrofuran

Fc	ferrocenyl = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$
DIBAL	diisobutylaluminium hydride
DMSO	dimethylsulphoxide
DCM	dichloromethane
DMF	dimethylformamide
Me	methyl
Et	ethyl
Ph	phenyl
t.l.c.	thin layer chromatography
i.r.	infra-red
u.v.	ultra-violet
n.m.r.	nuclear magnetic resonance
e.p.r.	electron paramagnetic resonance
m.s.	mass spectrometry
EI	electron impact
FAB	fast atom bombardment
SCE	standard calomel electrode
DSC	differential scanning calorimetry

Terms used to describe ^1H n.m.r. spectra:

δ	chemical shift
ppm	parts per million
s	singlet
d	doublet
t	triplet
q	quartet
qn	quintet
sx	sextet
m	multiplet
c	complex
br	broad
vbr	very broad
dd	doublet of doublets
td	triplet of doublets

Terms used to describe i.r. spectra:

s	strong
m	medium
w	weak
br	broad

INTRODUCTION

I-1 TOWARDS 'MOLECULAR ELECTRONICS'

The comparatively recent discovery and utilisation of electricity heralded a revolution in almost every area of human society. In particular, the activities of communication and calculation, which had relied upon solely mechanical means for the vast majority of mankind's history, have been completely transformed in a remarkably short period of time. Indeed, it is only in the last 50 or so years that electronic technology has evolved. The war-time vacuum electronics was quickly superseded by solid state science which has developed to yield microelectronic and VLSI (*i.e.* 'silicon chip') devices. An ever decreasing scale of operation has been accompanied by faster and faster processing speeds making pocket computers and almost instantaneous global communication present day realities.

However, the modern world, especially the advanced postindustrial ('information-based') societies, has pressing demands for an ever increasing amount of information processing and communication. This necessitates further rapid advances in technology, and in recent years the inherent limitations of microelectronic systems have begun to become significant as barriers to progress. The rate of movement of electrical current and inter-wire interference effects serve to set limits on the speed and scale of operation respectively, and the natural progression to overcome these factors is to begin to use light rather than electricity for processing. Current device-orientated research in this context is directed at hybrid opto-electronic systems which use light beams in conjunction with electrical signals, but for some purposes the ultimate aim is to achieve all-optical operation.

As a consequence of this newly emerging emphasis, considerable attention has been turned away from conventional metals and semiconductors to the study of the optical and electronic

properties of molecular organic materials. In this electronic science is beginning to shift its focus from the present day solid state inorganics towards a closer mimicking of natural biological systems, and the area of "molecular electronics" has arisen as a young and rapidly growing inter-disciplinary research field.

Clearly, the realisation of the desired advances will depend to a large extent upon the discovery and investigation of new materials possessing the necessary opto-electronic properties as well as on the design and fabrication of novel devices. Hence, the synthetic chemist will have an integral role to play in the development of the science of molecular electronics.

I-1.1 MOLECULAR ELECTRONICS: DEFINITIONS

It should be recognised that there are in fact two distinct senses in which the term "molecular electronics" may be used:

(i) **Molecular materials for electronics;** this concerns the use of the macroscopic (bulk) properties of molecular materials and represents a more immediately applicable science since results may feed directly into new device technology.

(ii) **Electronics at the molecular level;** this involves the manipulation of single molecules and developing means of controlling charge and energy distribution within molecules or supramolecular arrays. This topic is of long term fundamental scientific interest and is unlikely to provide rapid applications.

Description *(i)* embraces a wide variety of areas including: organic metals, semiconductors, and superconductors; nonlinear optics; liquid crystals; photo/electro-chromics; piezo/pyro-electrics. Description *(ii)* involves less well developed aspects such as: biological system analogues; assembly (*e.g.* film technology); charge and energy processes including photo-excitation and emission; charge injection (via scanning tunnelling microscopy, STM); function (logic) and architecture (parallel computation, neural networks, *etc.*). For the purposes of this study definition *(i)* is of most relevance and in particular the area of nonlinear optics which will now be addressed in detail.

I-2 NONLINEAR OPTICS

I-2.1 A BRIEF HISTORY

Interest in the area of Nonlinear Optics (NLO) received a huge boost from the discovery of optical laser action in ruby by T. H. Maiman in 1960.[1] This event made possible the observation and study of a variety of optical phenomena which previously had been regarded merely as theoretical curiosities. Although such "nonlinear processes" as the Pockels, Kerr, and Faraday effects had been observed at the turn of the century, the demonstration of Second Harmonic Generation (SHG = frequency doubling) from the 694 nm fundamental of a ruby laser in crystalline quartz by Franken *et al.* in 1961[2] effectively marked the birth of the field.

Following this initial discovery, a large number of other inorganic materials were found to give far greater doubling efficiencies of visible and infra-red laser light including potassium dihydrogen phosphate (KDP = KH_2PO_4),[3] lithium niobate ($LiNbO_3$),[4] and barium sodium niobate ($Ba_2NaNb_5O_{15}$).[5] These experimental results were accompanied by a development of the mathematical theory of NLO properties as well as the observation and study of other effects such as the linear electro-optic (Pockels) effect (electric field dependent refractive index),[6] parametric amplification (frequency mixing),[7] and third harmonic generation (THG).[8]

During the 1960's a small number of organic compounds including benzopyrene[9] and hippuric acid[10] were investigated, but it wasn't until the end of the decade, after a new standard semiquantitative testing procedure for the SHG efficiency of powder samples had been defined,[11] that a more systematic approach was adopted (Table I). The adoption of SHG as a useful experimental probe of NLO activity arose from its early theoretical understanding along with an ease of measurement.

Extensive powder as well as single crystal testing for SHG in conjunction with theoretical developments helped to establish the basic microscopic and bulk requirements for significant NLO

effects. A number of organic compounds (Table II) including urea [1],[12] 2-methyl-4-nitroaniline (MNA) [4],[13] methyl-(2,4-dinitrophenyl)-aminopropanoate (MAP) [3],[14] and 3-methyl-4-nitropyridine-N-oxide (POM) [5][15] were thoroughly studied, and it became evident that molecular species could often exhibit much higher nonlinear responses than purely inorganic materials.[16,17] This, along with other positive factors such as ultrafast response times in the femtosecond (10^{-15} sec.) time domain, good optical damage resistance, the prospect of chemical modification to optimise the bulk properties and the possiblity of theoretical prediction to guide synthetic programmes, has led to an extensive investment of both capital and research skills in the study of organic NLO materials.[18] This work involves both academic and industrial institutions and brings together scientists from such diverse disciplines as physics, chemistry and engineering.

TABLE I

Some Early Examples of Materials Exhibiting SHG

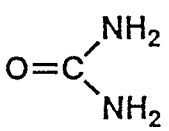
Year first tested for NLO	Substance	Powder SHG of 1.064 μm relative to quartz[11]
1961[2]	quartz (α-SiO_2)	1
1962[3]	KDP (KH_2PO_4)	16
1963[19]	ADP ($NH_4H_2PO_4$)	15
1964[4]	lithium niobate ($LiNbO_3$)	600
1968[11]	silver mercury iodide (Ag_2HgI_4)	1500
1968[11]	lead titanate ($PbTiO_3$)	2400
1968[11]	urea [1] 	400

TABLE II

Examples of Aromatic Organics Exhibiting SHG

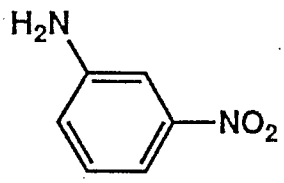
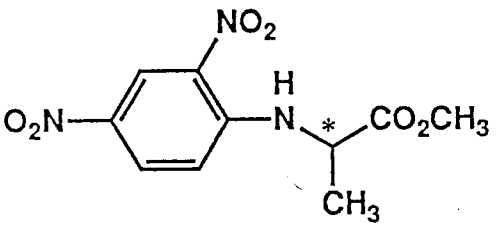
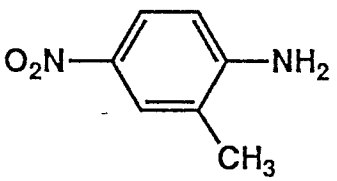
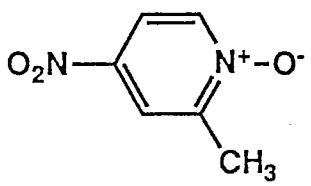
Year first tested for NLO	Compound	Powder SHG (fundamental/μm) relative to urea
1971[20]	m-nitroaniline (mNA) [2] 	0.13 (1.064)[16]
1977[14]	methyl-(2,4-dinitrophenyl) -aminopropanoate (MAP) [3] 	10 (1.064)[16]
1979[13]	2-methyl-4-nitroaniline (MNA) [4] 	22 (1.064)[16]
1981[15]	3-methyl-4-nitropyridine-N-oxide (POM) [5] 	13 (1.32)[21]

TABLE II

(Continued)

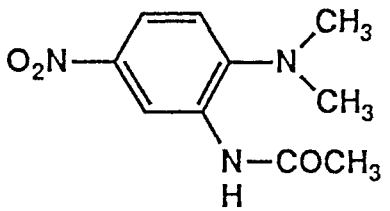
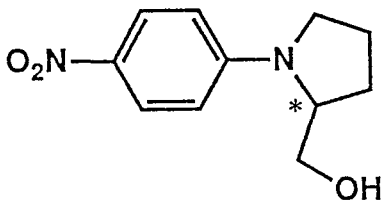
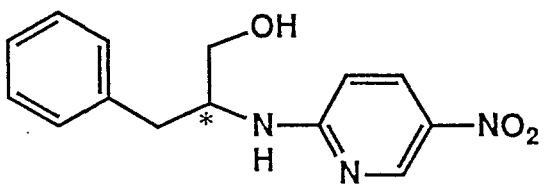
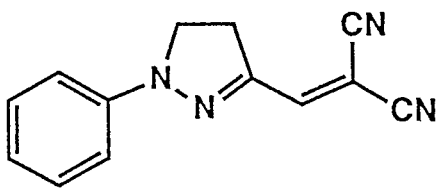
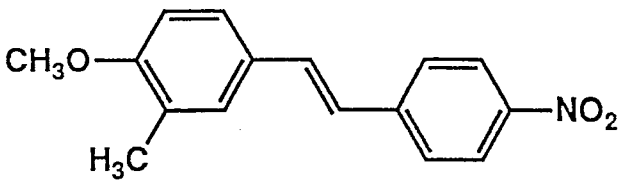
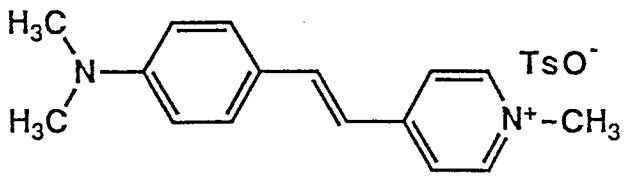
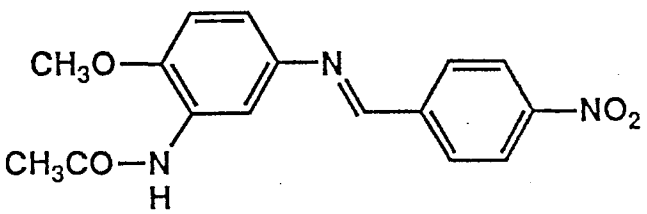
Year first tested for NLO	Compound	Powder SHG (fundamental/μm) relative to urea
1983[22]	3-acetamido-4-dimethylamino nitrobenzene (DAN) [6] 	115 (1.064)[16]
1984[23]	N-(4-nitrophenyl)-(L)-prolinol (NPP) [7] 	160 (1.064)[16]
1985[24]	N-(5-nitro-pyridyl) -(*S*)-phenylalaninol (NPPA) [8] 	130 (1.064)[24]
1988[25]	3-(1,1-dicyanoethenyl)-1-phenyl -4,5-dihydro-1H-pyrazole (DCNP) [9] 	100 (1.064)[26]

TABLE II

(Continued)

Year first tested for NLO	Compound	Powder SHG (fundamental/μm) relative to urea
1989[27]	3-methyl-4-methoxy-4'-nitrostilbene (MMONS) [10] 	1250 (1.064)[27]
1989[28]	4'-dimethylamino-N-methyl -stilbazolinium tosylate [11] 	1000 (1.907)[28]
1990[29]	3-acetamido-4-methoxy -4'-nitrobenzylideneaniline [12] 	230 (1.064)[29]

I-2.2 PHYSICAL ORIGIN OF MOLECULAR NLO EFFECTS

I-2.2(a) Simplified Physical Basis

When a molecule experiences an applied electric field *E* its electronic charges are perturbed from equilibrium *i.e.* an induced

polarisation P (= dipole moment per unit volume) occurs which can be expressed as a power series in the local field E by

$$P = \alpha E + \beta E^2 + \gamma E^3 + \ldots \quad (1)$$

The first tensor coefficient α is the linear molecular polarisability and is the origin of the refractive index if the field E is associated with electromagnetic radiation in the optical frequency range. At low E field strengths the higher coefficients β and γ (known as the first and second molecular hyperpolarisabilities) are negligible and only the first linear term in the expansion need be considered. This situation then describes "linear" optical effects such as refraction, *etc.*

However, as the field strength increases the higher coefficients become significant and the polarisation response becomes nonlinear in character. The advent of lasers made possible the creation of coherent light sources far brighter than any hitherto available incoherent sources. Hence extremely high power densities of greater than 10^9 W/cm^2 became available which correspond to an electric field strength of 10^6 V/cm. Since this is within the range of atomic field strengths, large deviations from linear behaviour can result.

Second-order (quadratic) effects which arise from the hyperpolarisability tensor coefficient β are generally greater in magnitude than third-order (cubic) effects due to γ and are better understood due to the large amount of research effort applied to this topic over the last 30 years. Interest in γ effects is growing, but since the study described here has been directed almost exclusively at second-order effects only these will be considered in detail.

I-2.2(b) Mathematical Origin of SHG

It is a comparatively simple matter to demonstrate how the nonlinear response defined in equation (1) can give rise to harmonic frequencies of the incoming laser light.

The a.c. applied field due to an electromagnetic wave is of the form

$$E = E_o.\sin\omega t \qquad (2)$$

where ω is the fundamental laser frequency. Substitution of equation (2) into equation (1) gives

$$P = \alpha E_o.\sin\omega t + \beta E_o^2.\sin^2\omega t + \gamma E_o^3.\sin^3\omega t + \ldots \qquad (3)$$

and using the trigonometric identities $2\sin^2x = 1 - \cos2x$ and $4\sin^3x = 3\sin x - \sin3x$ it can be shown that

$$P = \alpha E_o.\sin\omega t + \beta E_o^2(1 - \cos2\omega t)/2 - \gamma E_o^3(\sin3\omega t)/4 + \ldots \qquad (4)$$

The interesting terms in this expansion are those involving 2ω and 3ω which represent dipole moments (per unit volume) induced in the molecule oscillating at frequencies two and three times the incident frequency. By the classical laws of electromagnetism these oscillating dipoles themselves act as sources of electromagnetic radiation, generating waves which correspond to the second and third harmonics of the fundamental frequency. Hence we have a mechanism for Second Harmonic Generation (SHG) and Third Harmonic Generation (THG).

[An alternative description of SHG from a quantum mechanical point of view is that a photon of high energy ($h2\omega$) is created every time the simultaneous annihilation of two low energy ($h\omega$) occurs].[30,31]

I-2.2(c) Catalytic Nonlinearities

At this point it should be made clear that all of the second-order NLO effects of relevance to this study fall under the general heading of "passive" effects. This means that the NLO response does not involve any actual interchange of light energy with the medium, and all that occurs is a rearrangement of the incoming photons. Fundamental frequencies which do not correspond

to either vibrational or electronic excitations are used, and the material is said to function as an 'optical catalyst'.[32] NLO effects in which the medium plays a more active role such as Raman scattering[33] will not be covered here.

I-2.3 CHEMICAL ORIGIN OF MOLECULAR NLO EFFECTS

Experimental and theoretical results have led to a clear understanding of the molecular properties which are required to give rise to significant NLO responses.[34] Firstly, the molecule must be dipolar *i.e.* have an overall asymmetry in its charge distribution, and secondly it must be polarisable which means that its charge distribution can be altered readily. In practice this is achieved when the molecule contains an electron-rich portion linked via an unsaturated system to an electron-deficient portion. The electron-rich portion can then act as a donor (D) of charge to the electron-deficient portion which is an acceptor (A). Unsaturated bridges give the best conduction of charge from D to A because their delocalised π-electrons are far more mobile than σ-framework electrons.

The classification of substituent groups into acceptors and donors is as follows:

I-2.3(a) Acceptor (A) Groups

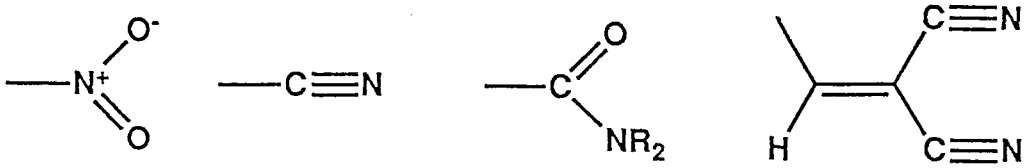
If a substituent has vacant low energy π-orbitals it can attract electrons from a conjugated system and is classed as an acceptor (Fig. 1); the larger the electronegativity of the group, the stronger its acceptor character.

I-2.3(b) Donor (D) Groups

If a substituent has occupied high energy π-orbitals, it can share some of its electronic charge with a conjugated system and is classed as a donor (Fig. 2). In practice this generally

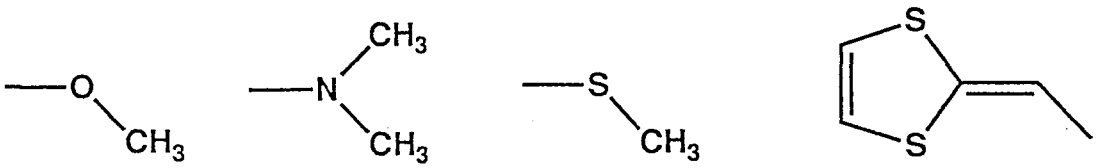
involves the lone pairs of non-bonding electrons found on atoms such as N, O, and S.

Fig. 1
Some Common Acceptor Groups



nitro cyano alkylamido dicyanovinyl

Fig. 2
Some Common Donor Groups



methoxy dimethylamino methylthio dithiolylidenemethyl

The fully charged phenyl ring substituents such as O^- (phenoxide) and N_2^+ (aryl diazonium ion) are among the most potent D and A groups, but have found very limited use in NLO organic materials to date.

I-2.3(c) Linking Groups

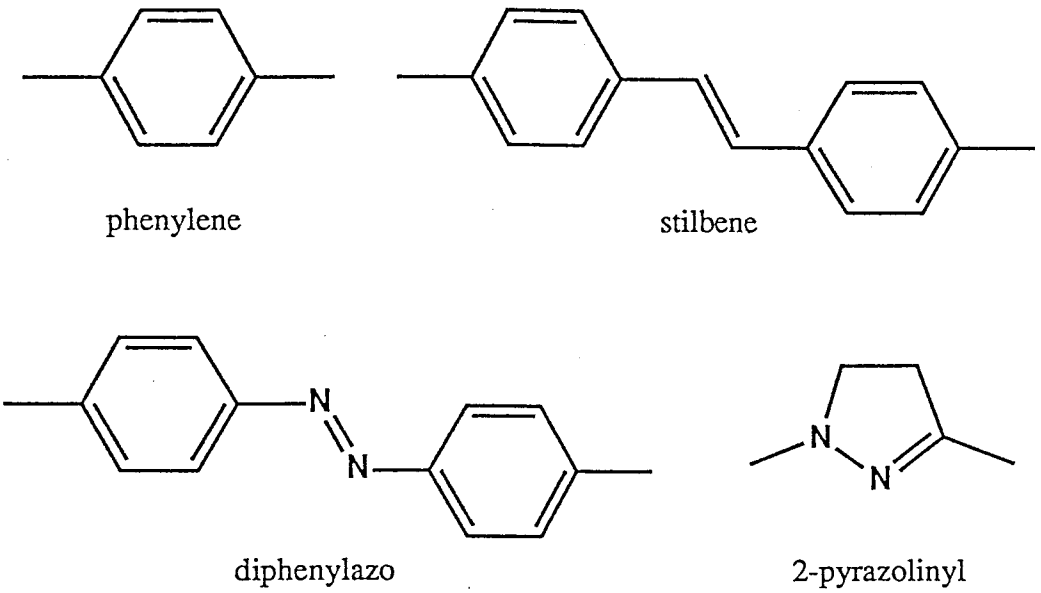
Any π-delocalised system, either all-carbon or hetero-substituted, can function as a link between donor and acceptor groups. Generally cyclic systems are prefered for second-order effects with extended polyene chains often the choice for third-order effects. However, many high β molecules contain links made up of both cyclic and linear unsaturated portions and clear distinctions do not exist. Some common examples of linking groups giving rise to high β values are shown in Fig. 3.

Amongst these there is some evidence to suggest that the

diphenylazo group should be the best possible connector of D and A groups for optimizing electron transmission effects.[35]

Fig. 3

Some Common Linking Groups



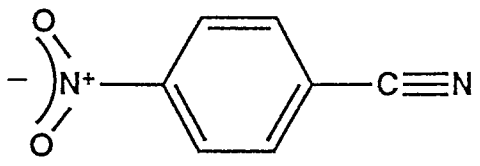
phenylene stilbene

diphenylazo 2-pyrazolinyl

It is worth pointing out that some molecules which at first sight do not appear good candidates can exhibit significant NLO effects. For example, the molecule 4-nitrobenzonitrile [13] (Fig. 4) contains two acceptor groups and yet has been found to give a powder SHG of some two times urea.[36] Structural studies have shown the crystal packing (discussed later) to be favourable,[37] but clearly the molecule itself possesses the necessary electronic properties for NLO. Such examples should act as a warning against the adoption of a strictly dogmatic approach when seeking molecules for NLO.

Fig. 4

4-Nitrobenzonitrile

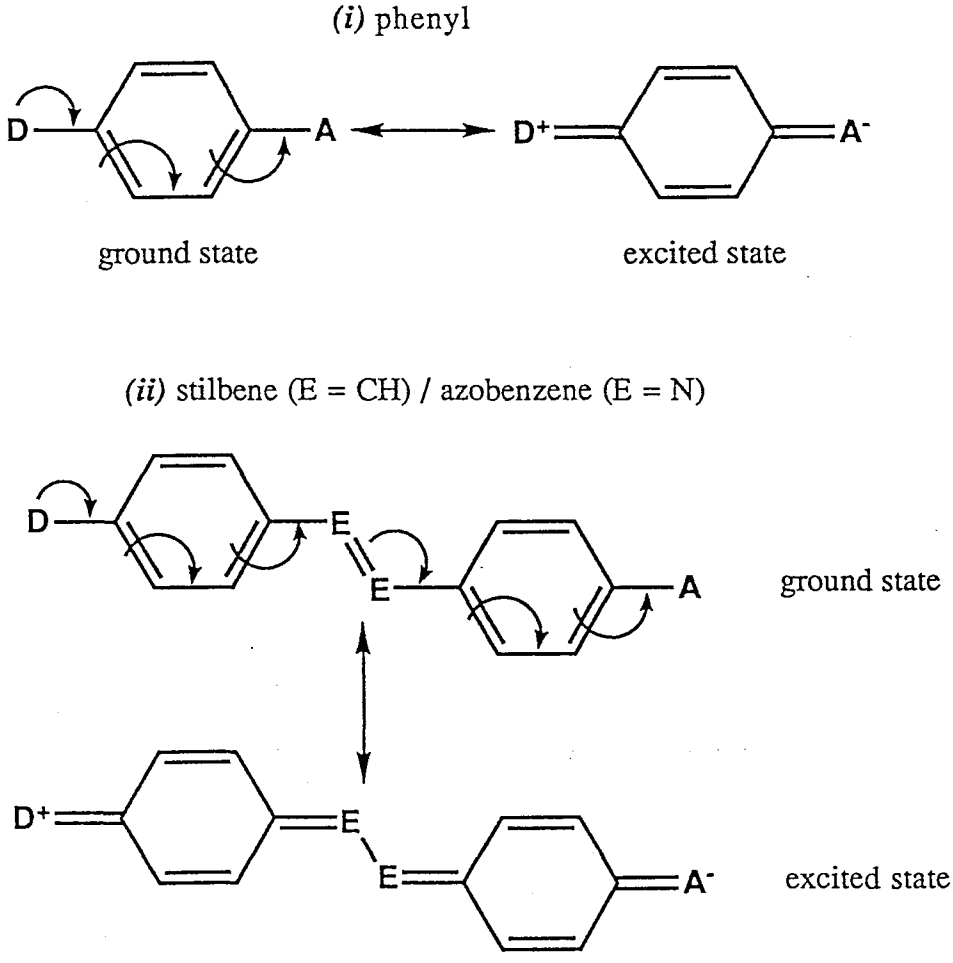
[13] 

SHG = 2 x urea

I-2.3(d) Intramolecular Charge-Transfer

A situation where a mesomeric interaction results in a net transfer of electron density from D to A is known as a charge-transfer state, and if the overall electron distribution is perturbed from that found in the equilibrium or ground state then the result is called an intramolecular charge-transfer excited state. This is illustrated in Fig. 5 using classical valence-bond Mulliken resonance forms.

Fig. 5
Charge-Transfer Excitation in Aromatic Molecules



The excited states shown in Fig. 5 are the maximal charge-transfer states in which one whole electron is transferred from donor to acceptor. However, such representations are an

oversimplification, and in any real D-π-A molecule the actual ground and excited states are essentially combinations of the extreme resonance structures depicted.

Despite their crude nature, the Mulliken resonance structures in Fig. 5 clearly demonstrate how a dipole moment (μ) change occurs upon charge-transfer excitation given by

$$\Delta\mu = \mu \text{ (excited state)} - \mu \text{ (ground state)} \qquad (5)$$

It is a large $\Delta\mu$ resulting from an electronic excitation with a small transition energy gap near to (but not including) 2ω and a large oscillator strength which will give rise to large values of the second order molecular hyperpolarisability tensor β. A molecule which has a centre of symmetry has zero dipole moment, and this leads to the result that for β to be non-zero the molecule must be non-centrosymmetric.[16] It should be noted that this condition does not apply to the third-order coefficient γ, which can be non-zero in centrosymmetric polarisable molecules.

I-2.4 THE SECOND-ORDER HYPERPOLARISABILITY β

The β coefficient is a third-rank tensor which is complex in nature *i.e.* composed of real and imaginary parts. Its mathematical nature will not be further described here, save to say that from a chemical point of view β is often separated into two parts,

$$\beta = \beta_{add} + \beta_{CT} \qquad (6)$$

where β_{CT} is that part arising from intramolecular charge-transfer processes and β_{add} is an additive part due to substituent-induced asymmetry in the charge distribution ("inductive effects").[30] In the charge-transfer molecules considered here, β_{CT} will be considerably larger than β_{add}.

Both the experimental measurement and theoretical calculation of β coefficients are of great interest in the search for highly NLO-active organic materials.

I-2.4(a) Theoretical Calculation of β

Reliable theoretical predictions of the magnitude of molecular susceptibilities, intended largely as a guide to synthetic organic chemistry programmes, have attracted considerable attention over the last 10 or so years.[38,39] When it comes to a realistic description of the electronic polarisation involved in an NLO response, the crude nature of qualitative valence-bond theory means that various molecular orbital approaches have to be adopted. Although the relative complexity of the molecules involved generally necessitates the use of semi-empirical rather than *ab initio* calculations, the results obtained with the aid of advanced computers are usually found to be in fairly good agreement with empirical β values and are certainly accurate enough for molecule assessment purposes.

I-2.4(b) Experimental Measurement of β

Although the procedure is non-trivial, β can be measured in a centrosymmetric gas, liquid or solid phase using a technique called Electric Field Induced SHG (EFISH). In the case of liquids or solutions this involves the application of a d.c. field which is synchronised to a laser pulse so as to statistically orientate the molecules of interest and allow the emission of a second-harmonic signal.[40] The β value, which is the vector part of the hyperpolarisability tensor projected along the dipolar axis of the molecule, is then derived from this signal.[41] Its magnitude will be slightly different from that in the crystal phase since the cooperative effects of intermolecular interactions are likely to be much less important in the liquid state.

I-2.5 MACROSCOPIC NLO EFFECTS

A microscopic description of NLO effects is of far greater use for molecular than inorganic ionic compounds since molecules are known to retain their geometric shape and properties to a large extent

upon aggregation to form a molecular crystal.[42] However, it is still necessary to develop the basic molecular theory to describe how the individual molecules act together to give the NLO effects which may be observed experimentally.

Hence, the polarisation induced in a bulk molecular medium by an external electric field is given by

$$P = \chi^{(1)}.E + \chi^{(2)}.E^2 + \chi^{(3)}.E^3 + \ldots \qquad (7)$$

where the χ coefficients are now the macroscopic equivalents of the molecular α, β and γ tensors described earlier, $\chi^{(2)}$ being the coefficient which gives rise to second-order effects.

I-2.5(a) The Kurtz Powder Test for SHG

Originally devised in 1968,[11] this semi-quantitative test is employed to assess the extent to which a particular compound exhibits second-order NLO effects. This can be done at an early stage, before single crystals of significant size are available. By studying the effects of variations in grain-size and wavelength, it is possible to detect the occurrence of phase-matching (see later) and to derive estimated $\chi^{(2)}$ values.

The basic procedure used in the early work is as follows: the output of a laser is passed through a beam-splitter so that one ray passes through a powdered sample mounted on a glass slide whilst the other passes through a similarly mounted reference powder of known efficiency. Filters behind the samples are used to remove the fundamental frequency to leave only the second-harmonic signals which are detected by photomultiplier tubes. A ratio of sample to reference signal is then produced and displayed.

The commonly used laser frequency is that of an Nd:YAG near i.r. laser at 1.064 μm which can be Raman-shifted by a high pressure hydrogen cell to give a fundamental at 1.907 μm. These frequencies will then give rise to second-harmonics at 0.532 μm (green) and 0.954 μm respectively. Tunable dye-lasers which cover the entire visible range (400-700 nm) are sometimes used for single crystal studies of frequency doubling into the u.v. region,

but rarely in powder testing. The reference material used in the original powder SHG studies was powdered quartz (silica; α-SiO_2), but currently the usual choice as a standard for organics is urea.

The powder SHG observed for any given sample will vary with a large number of parameters including laser wavelength and bandwidth, particle size (from very fine powders to more efficient larger crystallites), temperature, crystallisation solvent and technique, and other aspects of sample history. Hence, it must be stressed that results obtained from the Kurtz powder test are at best semi-quantitative and caution should be exercised in making comparisons of SHG efficiency. It transpires that a difference in powder SHG by a factor of two is not generally significant, and even greater differences may result from the factors listed above.[43] The real value of the powder technique lies in the screening of large numbers of samples in order to pick out any which display significant NLO activity. These may then be subjected to further more precise study either as single crystals or molecular films.

A schematic diagram of the experimental set-up used to measure powder SHG at Durham University, which represents a modified version of Kurtz's original apparatus,[11] is shown in Fig. 6.

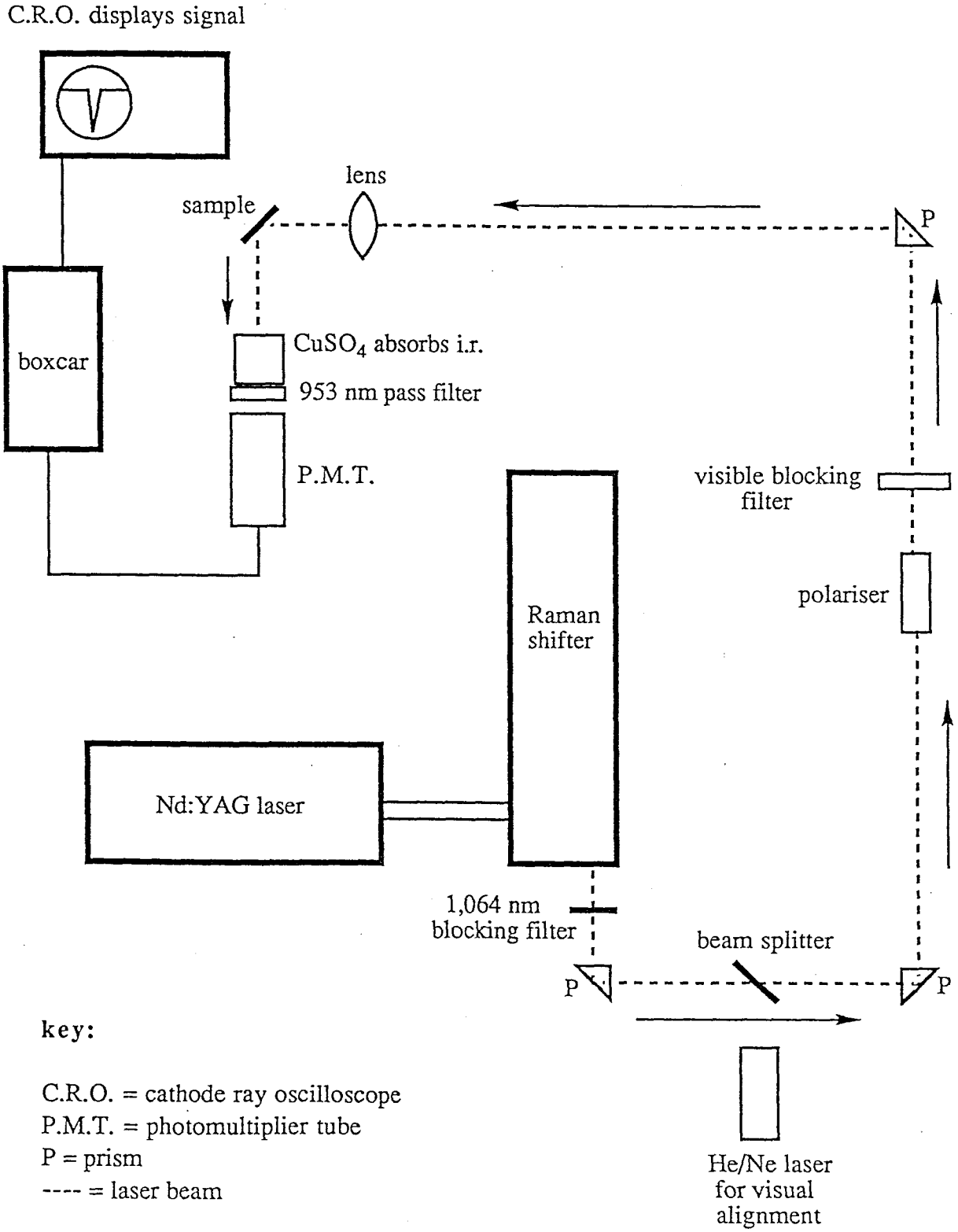
I-2.5(b) Absolute SHG Efficiencies

Although SHG efficiencies are usually quoted as emitted harmonic intensities relative to a standard material, it is useful to have some idea of how much of the fundamental laser light is actually converted to its second-harmonic.

The earliest studies on quartz crystals produced very low energy conversion efficiencies of typically 10^{-6} - 10^{-4}% from the 694 nm ruby laser fundamental.[3] Vastly greater efficiencies were later reported, *e.g.* 51% for KDP and 21% for $LiNbO_3$ from the 1.064 μm Nd:YAG laser,[44] and even 100% conversion of this wavelength has been claimed by placing a $LiIO_3$ crystal inside the laser cavity.[45] As far as organics are concerned, SHG conversion efficiencies of *ca.* 20% are readily attainable and, for example, DAN [6] can give around 30% conversion from a 1 mm crystal.[46]

Fig. 6

Apparatus used for Powder SHG Measurements at Durham University



I-2.5(c) The Macroscopic $\chi^{(2)}$ Coefficient

It should be emphasised that the same symmetry restrictions that apply to the molecular hyperpolarisability β also apply to the bulk coefficient $\chi^{(2)}$, *i.e.* $\chi^{(2)}$ can only be non-zero for macroscopic structures which lack a centre of symmetry. Hence, molecules with high β can only give rise to $\chi^{(2)}$ if they pack together in one of the non-centrosymmetric crystal space groups. Since roughly 75% of all organic molecules crystallize in centrosymmetric space groups,[47] this criterion serves to reduce greatly the number of organic crystals with observable bulk NLO properties.

Due to the present inability to predict how even simple organic molecules will pack together in a crystal[48] the theoretical prediction of $\chi^{(2)}$ is not feasible, but its magnitude can be measured experimentally. The most accurate determination is achieved by single crystal SHG studies (*e.g.* for MNA [4]),[13] but $\chi^{(2)}$ may also be estimated using powder SHG tests[16] described earlier.

I-2.6 FACTORS AFFECTING $\chi^{(2)}$: CRYSTAL-PACKING FACTORS

Assuming that the individual molecular units have high β, then the most important factors which affect $\chi^{(2)}$ will be those which determine the crystal packing and symmetry.

The simplest and most basic forces which hold neutral molecules together in a crystal are weak intermolecular electronic attractions resulting from quantum fluctuations in the electronic distributions of adjacent molecules.[49] It is the coherence of these charge fluctuations which gives rise to net attractive forces often referred to as van der Waals interactions.[50] The energy involved in such interactions is small compared to the forces which hold together ionic crystals or metals. Other important factors which affect molecular crystal packing are summarised as follows:

I-2.6(a) Dipole-Dipole Interactions

Although this is an area which is not well understood, it is clear that as the molecular ground-state dipoles become larger, so the electrostatic interaction between adjacent molecules increases and this will make the pairing and consequent cancellation of dipoles more energetically favourable. This dipole cancellation will serve to reduce or completely destroy the bulk $\chi^{(2)}$ and is therefore undesirable for second-order effects.

One way of getting around this problem lies in the use of molecules which have a lower dipole moment in the ground-state (g.s.) than in the excited state(s). POM [5] is an example of an efficient NLO material which possesses a vanishing g.s. dipole moment.[15]

I-2.6(b) Hydrogen-Bonding

Hydrogen-bonds (H-bonds) are more energetic by one or two orders of magnitude than van der Waals and dipole-dipole interactions, while being only a little more than one order of magnitude below intramolecular bond energies. Hence they can play a very important role in influencing the packing of molecules which possess both electron-deficient hydrogen atoms and atoms having non-bonding electron pairs such as O and N.

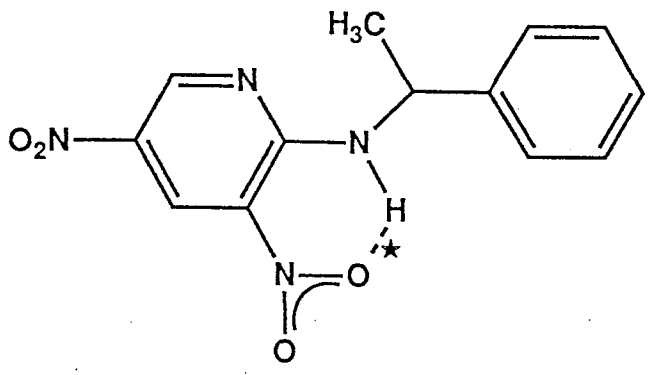
H-bonds can be made to overcome dipolar interactions in molecules of the appropriate structure, and hence may be used to encourage the adoption of packing arrangements suitable for $\chi^{(2)}$. They may be either intermolecular as in DAN [6],[22] or intramolecular as in 2-N-(α-methylbenzylamino)-5-nitropyridine (MBADNP) [14],[51] shown in Fig. 7.

Aside: As well as having such profound structural effects, spectroscopic studies clearly show that H-bonding (both inter- and intra-molecular) can also influence the local electronic situation. Although the molecules do retain their individualities, the resulting effects on molecular hyperpolarisability are not presently well understood.[52] However, it is known that large

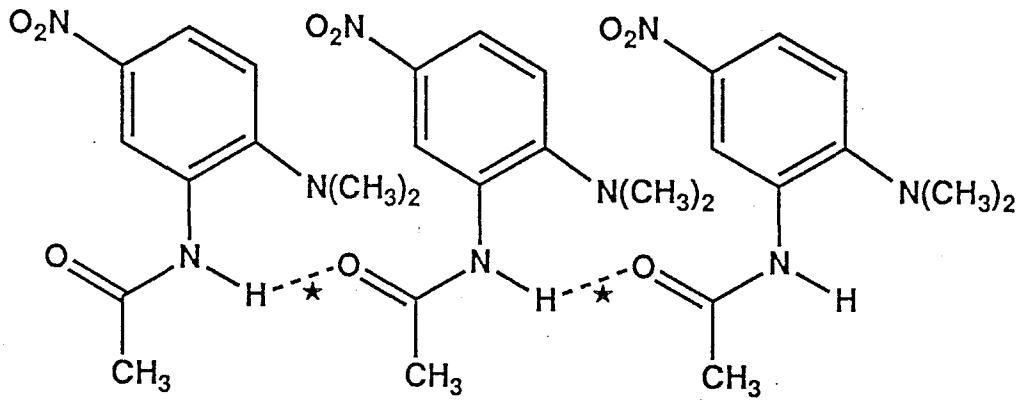
modifications in β can result, as has been shown for urea where β is thought to be enhanced by this intermolecular H-bonding.[53]

Fig. 7

Hydrogen-Bonding in NLO-Active Compounds



(i) Intramolecular H-bonding in MBADNP, [14]



(ii) Intermolecular H-bonding in DAN, [6]

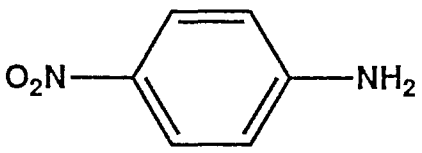
(★ = H-bond)

I-2.6(c) Molecular Substituents and Steric Effects

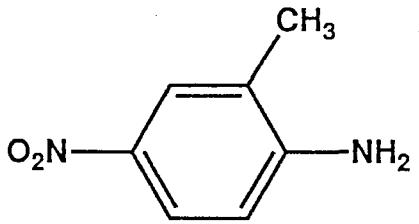
It is often found that a molecule with a high β, but which exhibits no bulk NLO effects, can be rendered active by the addition of a simple substituent which has little or no effect on the hyperpolarisability. This is due to the adoption of a favourable non-centrosymmetric crystal packing by the more asymmetric substituted molecule, and the classic example of this

effect is *p*-nitroaniline [15] (Fig. 8). Although possessing a high β, this molecule exhibits no bulk SHG because of dipolar cancellation in a centrosymmetric lattice. However, its methyl derivative MNA [4][13] is highly active as the steric bulk of the methyl group causes the molecules to pack in a different non-centrosymmetric fashion.

Fig. 8
Substituent Effects in Nitroanilines



(i) *p*-nitroaniline **[15]**
centrosymmetric crystal
SHG inactive



(ii) 2-methyl-4-nitroaniline (MNA) **[4]**
noncentrosymmetric crystal
SHG = 22 x urea (1.064 μm)

Substituents can have large direct electronic effects on the molecular β as discussed earlier, but it is sometimes found that their steric or space-filling properties can exert less obvious effects which may have a large impact on the molecular chromophore, dipole moment and ultimately the hyperpolarisability. The most important of these is known as steric inhibition of mesomerism. This is seen when ortho substituents on a benzene ring serve to force D or A groups out of the ring plane and hence reduce the degree of possible mesomeric interaction between them. This will reduce the dipole moment and hence β, and is exemplified by the addition of a second methyl group in the POM molecule [5].[15,54]

I-2.6(d) Chirality

Much attention has been focused on this aspect of molecular structure since the presence of a chiral centre ensures that a molecule lacks a centre of symmetry, and this can produce acentric

crystal structures.

Initial studies focused on natural substances such as amino acids and sugars[55] and were later extended to other classes including steroids (cholesterol) and terpenoids (menthol).[11] A very thorough study of the powder efficiencies of a variety of biological molecules has subsequently been reported.[56] Only rather low SHG efficiencies have generally been found, and this is because such molecules do not contain the necessary conjugation and polar functionality required for large (hyper)polarisability. However, notable successes have since been achieved by the attachment of chiral auxiliary functions to polarisable aromatic molecules, the earliest example of which being MAP [3][14] in which the amino acid (*S*)-(+)-alanine was employed as its methyl ester.

It is found that if a chiral substance is crystallised as a racemate then a centrosymmetric space group is almost invariably adopted due to pairing of enantiomers within the unit cell. The isolation of a compound as one pure enantiomer does ensure a noncentrosymmetric crystal structure,[57] but it should be noted that this is not a guarantee of NLO activity since molecular dipoles can still align antiparallel in an acentric environment and therefore self-cancel.[58] Resolution is usually achieved chemically by using only one configuration of the chiral group, thus precluding the need for any physical resolution using, for example, column chromatographic techniques. It may sometimes occur that a racemate will resolve itself by producing discrete crystallites each containing only one enantiomer.

Two drawbacks of using chiral auxiliaries are the possible accompanying synthetic complications, and also the fact that, by increasing the molecular volume per chromophore, the auxiliary produces an inevitable dilution of the NLO effect. Clearly, the latter would cease to be a problem if the chiral group were involved in the π-delocalised system of the molecule, but this is unfortunately not possible for tetrahedral sp^3 carbon centres. However, the exploitation of other chirality classes such as asymmetric heteroatoms, asymmetric octahedral sites, and restricted rotation of dissymmetric planes could overcome this

problem and is likely to provide useful NLO materials with novel structures.[59]

I-2.6(e) Structural Complications

Aside from these main aspects, several minor factors can complicate the ideal situation and these include:

(i) If β is very large any slight deviation from centrosymmetry in an otherwise centrosymmetric crystal structure may give rise to appreciable SHG.[60]

(ii) Defects or even surface effects can give similar results in centrosymmetric crystals.[61]

(iii) It is sometimes found that a given molecule is capable of adopting different crystal forms either from one sample to another or even within a single sample. This phenomenon is called polymorphism[62] and can be caused by changes in solvent, temperature and rate of crystallisation. Its effects on the observed SHG and other NLO properties of organic molecules have often been found to be of great significance.[58]

I-2.7 FACTORS AFFECTING $\chi^{(2)}$: OTHER PHYSICAL FACTORS

Along with the aforementioned crystal-packing factors, a number of other important aspects will determine whether efficient bulk NLO (especially SHG) is possible. The two major considerations are phase-matching and absorption which will be discussed briefly in the following two sections.

I-2.7(a) Phase Matching

Efficient SHG can only occur in a birefringent medium *i.e.* one in which refractive index is directionally dependent or anisotropic. In practice this requires large biaxial (triclinic, monoclinic or orthorhombic) crystals so orientated that the fundamental frequency propagates as an o-ray (ordinary ray -

refractive index independent of crystallographic direction) and the harmonic propagates as an e-ray (extraordinary ray - refractive index varies with crystallographic direction) or vice versa. The crystal orientation is adjusted so that the o-ray and the e-ray propagate at the same speed, *i.e.* their refractive indices (n) are equal:

$$n_o^{\omega} = n_e^{2\omega} \qquad \text{(index matching)} \qquad (8)$$

Thus, power is coupled from the fundamental to the harmonic as the two rays propagate in phase through the crystal. Meeting this condition is known as phase-matching (PM).[63,64]

If a crystal shows PM then maximum SHG will be detected at various set angles between the fundamental laser beam, crystal and detector.[12] As mentioned previously, the Kurtz powder method can be used to detect the occurrence of PM by measuring the total second-harmonic output as a function of crystallite size. A saturation of output as crystallite size is increased is observed for phase-matchable samples, whilst non phase-matchable materials exhibit a sharp decrease in output after a certain crystallite size is exceeded. Quartz is an example of a non-phase matchable material, a crystal of which cannot give rise to efficient frequency conversion since only a small fraction of the crystal length, the coherence length, contributes to the nonlinear process. In a phase-matchable crystal, the coherence length goes to infinity and the entire length of the crystal cumulatively contributes to the nonlinear interaction.

It has been established, using mathematical theory, that for a given crystal space group ideal molecular orientations exist for maximum possible PMSHG.[65] The important quantity is the angle θ_m formed between the molecular polarisation axis and the principal crystallographic axis (*e.g.* the c two-fold axis in the space group Fdd_2). Empirical studies of the packing and SHG efficiencies of various organics have provided confirmation of this general principle.[66]

I-2.7(b) Absorption (Resonance) Effects

As has already been explained, for the observation of catalytic quadratic NLO effects the laser wavelengths used generally fall in the transparent region of the molecular absorption spectrum, where no light energy is actually removed from the incoming beam by either electronic (u.v.-visible) or vibrational (i.r.) excitation processes. This situation is described as working off-resonance and non-resonant β processes involve virtual rather than the actual transitions of molecular photon absorption.

The β coefficient is wavelength dependent, and it is found that its magnitude can be greatly increased by working with either the fundamental or harmonic wavelength close to a resonance absorption. This phenomenon is known as "resonance enhancement" of the nonlinear response.[32] Further enhancement can be achieved if both the fundamental and harmonic are close to resonance which gives rise to "double resonant SHG".[67] However, due to the occurence of photon absorption and possible resulting thermal damage to the sample, operating very close to resonance is likely to have overall deleterious effects on the second-harmonic process and is rarely encountered in practice. This trade-off between the magnitude of the β coefficient and the corresponding optical loss due to absorption is a crucial factor in the optimisation and exploitation of molecular materials for NLO, and is referred to as the "efficiency-transparency trade-off".

I-2.8 MOLECULAR ENGINEERING

Molecular engineering has been defined as "the planned synthesis of materials having prescribed bulk properties".[68] For NLO properties the aim then is to synthesise molecules which have optimised β coefficients and which simultaneously form bulk phases which produce high $\chi^{(2)}$ values.

The good theoretical level of understanding of quadratic molecular effects along with advanced organic synthetic techniques

make the preparation of high β molecules relatively straightforward,[25] but the large number of factors which determine crystal structure mean that it is not currently possible to predict *ab initio* how a molecule will crystallise. The utilisation of chirality, H-bonding, and low g.s. dipoles can prove helpful,[69] but the area is still largely governed by empirical observation and serendipity.

Some effort has been directed at establishing rules whereby the optical absorption bands of a molecule can be hypsochromically shifted by "tuning" the chromophore without significant loss of hyperpolarisability.[70] This facilitates the production of laser light sources operating further into the blue and u.v. parts of the spectrum where naturally occuring laser lines are rare, and could have important applications in areas such as laser induced nuclear fusion.[71]

It is important to note that, although the often narrow transparency range of CT molecules may be prohibitive for frequency generation applications, it is less important for applications to electro-optic modulation,[72] which only requires good transparency at the fundamental frequency. Such applications are of considerable current interest to the telecommunications industry (see below).

I-2.9 CURRENT AIMS OF NLO RESEARCH AND DEVICE RELATED CONSIDERATIONS

It has been known for many years that organic materials can exhibit significantly larger intrinsic nonlinearities than inorganic dielectric and semiconductor crystals. However, although such materials as lithium niobate and KDP have found application in various devices[73,74] which exploit their harmonic generation, parametric amplification, and linear electro-optic properties, no organic materials have yet found their way into commercial NLO devices.

This situation is certain to change in the near future due to the needs of the telecommunications and computing industries for

increased speed and efficiency of high bandwidth signal processing via fast switching, amplification, and modulation of optical signals. Over the last 5 or so years there has been a surge in the establishment of organic NLO research programmes in industry and academia in the USA, Europe, and Japan, and this has been accompanied by a massive increase in patent activity.[26]

Recent work of interest in the area of second-order effects has involved the use of novel approaches such as inclusion complexes (guest-host species),[75] Langmuir-Blodgett (L-B) multilayer techniques,[76] liquid crystals,[77] and various types of polymers.[16,78] The latter have attracted particular attention due not only to their high NLO responses, but also to their good mechanical properties and hence fabrication possibilities for incorporation into wave-guiding and other devices. Problems with crystal growth and handling serve to rather limit the potential of crystalline materials for practical application, and it is highly likely that the first commercial organic NLO devices will make use of molecularly doped, electrically poled, or liquid crystalline polymer materials.[79]

A number of prototype organic NLO devices have been developed,[80] and a few of their most immediate applications are as follows:

(i) SHG from an 830 nm solid state semiconductor diode laser to give 415 nm blue light for use in optical data storage applications.

(ii) The conversion of electrical to optical information using an electro-optic modulator device (Mach-Zehnder interferometer). Polymer systems can give ultrafast modulation frequencies of >50 GHz at low input powers.

(iii) The production of powerful coherent light sources further into the u.v. is of considerable interest for a number of reasons. At present the limit is *ca.* 220 nm for certain nitropyridine derivatives.[81]

Clearly, when considering a substance for device application many factors besides its NLO susceptibility have to be taken into account. These include mechanical and fabrication properties,

chemical and physical stability (w.r.t. fields, light, heat, *etc.*), toxicity, and specialised application-related requirements. For these reasons the derivation and utilisation of "figures of merit" is often undertaken to facilitate the comparison of various materials with all pertinent factors taken into consideration.

I-3 LIQUID CRYSTALS

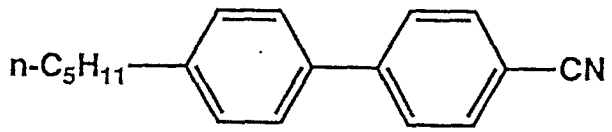
Since this work has concentrated largely on NLO effects, the extensive field of liquid crystals will be discussed here only briefly. Many other detailed texts on the subject[82] are readily available.

A liquid crystal (LC) phase is a phase in between a crystalline solid and an isotropic melt. Such a phase is called a mesophase and substances which exhibit this behaviour are referred to as mesogenic. As the 3-dimensional ordering of a molecular crystal is broken up, a transition to a fluid phase possessing 2- or 1-dimensional order occurs prior to the complete loss of order characteristic of a melt. Because LC phases are ordered fluids they combine some fluid properties with anisotropic (directionally dependent) mechanical, electrical, magnetic, and optical properties.

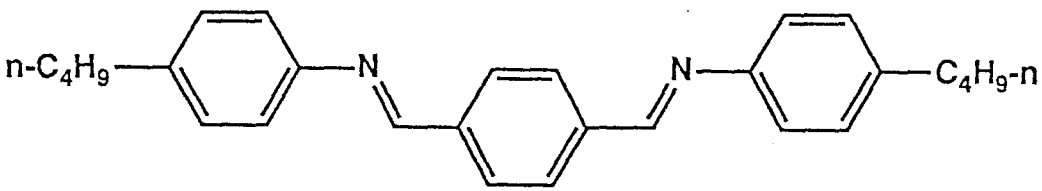
Since the first observations of LC behaviour in soaps towards the end of the last century[83] it has been found that approximately 5% of all known organic compounds possess LC phases of various types.[84] These may be broadly divided into thermotropic, which change phase on heating or cooling, and lyotropic which undergo phase changes on the addition of solvent, usually water. Within these two areas there exist many sub-classifications which will not be detailed here. The classification of thermotropic LCs was originally proposed in 1922,[85] but for a long time LCs were regarded merely as experimental novelties. However, during the last 30 years the development of microelectronic technology has meant that their unusual properties have come to be exploited to great effect primarily in electro-optical display devices.[86]

Thermotropic LCs have been thoroughly studied and some rules for their molecular origin established.[87] The most common type are rod-like mesogens which consist of elongated molecules containing a rigid core, a flexible tail and a polarisable function as shown in the examples in Fig. 9.

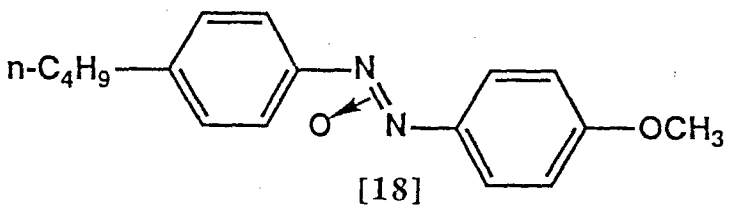
Fig. 9
Some Well Studied Thermotropic Liquid Crystals



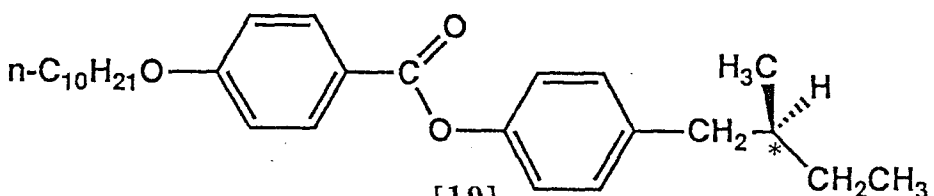
[16]



[17]



[18]



[19]

[16] = 4-n-pentyl-4'-cyanobiphenyl[87]

[17] = *p*-bis(4-n-butylphenyliminomethyl)benzene[84]

[18] = 4-methoxy-4'-n-butylazoxybenzene[84]

[19] = (*S*)-4-(2-methylbutyl)phenyl-4'-decyloxybenzoate[87]

Current research interest is largely directed at compounds with novel structures including chiral[88] and discoidal[89] molecules and the engineering of mesogens with useful properties such as ferroelectric[90] and NLO effects.[77] LC polymer systems, both main-chain and side-chain, have also been discovered and are receiving attention for device applications.[91,92] In such systems the LC behaviour is useful primarily as a way of ordering the molecular components so that their other physical properties can be exploited in the bulk phase.

I-4 THE MOLECULAR ELECTRONIC PROPERTIES OF ORGANOMETALLIC AND COORDINATION COMPOUNDS

The incorporation of metal atoms or ions into molecular organic compounds produces species which often exhibit various interesting and useful physical properties. In particular, the presence of outer shell electrons in d- and f-orbitals for transition metals and lanthanides and actinides respectively gives rise to structural, electronic, magnetic, and optical effects rather different to those found in purely organic or inorganic compounds. In some cases the molecular ligand framework plays an essentially passive role in simply holding the metal in a particular spatial environment, but usually the mixing of metal and ligand atomic orbitals means that both are actively involved in the overall molecular electronic properties.

The vast majority of study in this area to date can be classed under the three overlapping general headings of mixed-valence compounds, photochemically-active redox systems, and molecular ferromagnets. Each of these will now be given brief consideration.

I-4.1 MIXED-VALENCE COMPOUNDS

Mixed-valence compounds, which contain an element in more than one oxidation state, have attracted the interest of chemists for many

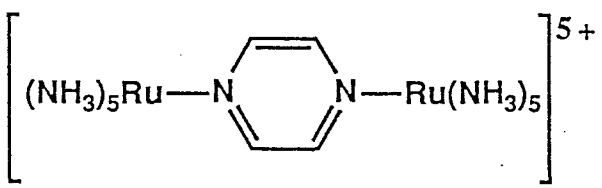
years,[93,94] the earliest example being Prussian blue or Turnbull's blue first discovered in 1724.[95] It has been clear for some time that these two blue substances are in fact the same compound, iron(III) hexacyanoferrate(II), $Fe^{3+}[Fe^{2+}(CN)_6^{4-}]$. The intense colour of this bimetallic salt arises because visible light absorption induces electron transfer from Fe^{II} to Fe^{III}, a phenomenon possible only in the mixed-valence material where both oxidation states are present.

Since this very early discovery, the subject of mixed-valence chemistry has broadened greatly to include more complicated metal-containing molecules. Interest in such systems results from their other physical properties such as electrical conductivity in addition to their spectral properties mentioned above. A point of focus for much of the recent work has been the Creutz-Taube ion [20] (Fig. 10),[96] a diruthenium pyrazine-bridged complex.

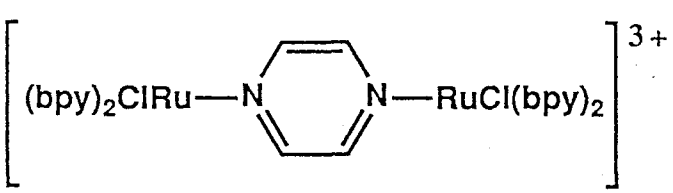
Fig. 10

Diruthenium Complexes Exhibiting Mixed-Valence Behaviour

[20]



[21]



bpy = 2,2'-bipyridyl

The question at issue in such species is whether the Ru valences of II and III are localised (trapped), one at each end, thus making the ends nonequivalent, or whether there is delocalisation through the bridging ligand to make the whole ion symmetrical.

In an effort to rationalise mixed-valence compounds, three broad classes have been distinguished[97] on the basis of the interaction between the two metal centres: In a Class I (valence localised) compound the interaction between the metal centres is so weak that the material exhibits only the properties associated with the isolated mononuclear metal complexes. In Class III (fully

delocalised), the opposite extreme is found: Interaction between the two centres is so great that the two behave as one unit. Class II materials fall in between these two extremes whereby some degree of metal-metal interaction occurs which may be accompanied by some electronic exchange between the metal centres. A Class II compound exhibits some properties not attributable to the isolated metal centres, but is not truly delocalised. Detailed physical descriptions of the kinetics, thermodynamics, and quantum theory of mixed-valence electron transfer interactions can be found elsewhere.[98]

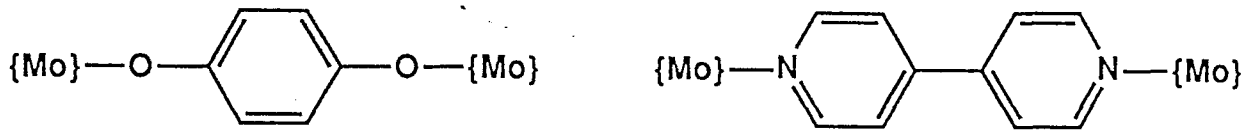
A variety of physical techniques have been used in the study of mixed-valence compounds. These include the study of intervalence transfer absorption bands in the near i.r., u.v.-visible absorption spectroscopy, electrochemistry, and e.p.r. spectroscopy. Kinetic and thermodynamic information may be derived from one of or combinations of these and other techniques. Because different physical processes operate on different timescales, conflicting conclusions as to the electronic nature of [20] have been reported since its discovery. While similar complexes such as [21] (Fig. 10) have been classed as clearly valence-trapped,[99] the original ion itself remains a matter for controversy. Some degree of delocalisation does seem to be present, but it is still uncertain whether the molecule is a true Class III system. Other studies involving a variety of aromatic diamine bridged ruthenium bimetallics[100] and also iron[101] and osmium[102] species have been reported, but most have revealed Class I or Class II behaviour.

Over the last few years, cyclic voltammetric and e.p.r. studies involving bimetallic molybdenum and tungsten mononitrosyl complexes (see later) have shown that very strong metal-metal interactions can occur in species such as [22] (Fig. 11).[103] In such molecules both 16-electron metal centres can undergo reversible one electron reduction processes, and the extent of coupling may be estimated from the separation, ΔE, between the two reduction waves. Systems having ΔE between 500 and 1000 mV reveal strong interactions, those in the range 100-400 mV are regarded as intermediate, whereas those where ΔE is less than 100 mV hardly interact at all.[104]

Fig. 11

Bimetallic Molybdenum Nitrosyl Complexes

[22] [23]



{Mo} = {Mo(NO)L*Cl}; L* = tris(3,5-dimethylpyrazolyl)hydroborate

formally Mo^{II}/Mo^{II}; 1-electron reduction to Mo^{II}/Mo^{I}

formally Mo^{I}/Mo^{I}; 1-electron reduction to Mo^{0}/Mo^{I}

Reduction of diamagnetic [22] electrochemically or by cobaltocene affords the corresponding paramagnetic monoanion.[105] E.p.r. study of this species at room temperature reveals that the unique electron is delocalised on the e.p.r. timescale, but cooling to liquid nitrogen temperatures results in localisation of the extra charge on one metal (*i.e.* Class II behaviour). Similar treatment of the *meta*-isomer has shown that the monoanion exhibits valence-trapped behaviour at room temperature.

Very recently, unusually large interactions across bipyridyl bridging ligands have been observed upon reduction of neutral 17-electron systems[106] such as [23] (Fig. 11).

I-4.2 PHOTOCHEMISTRY

Investigations into the photochemical properties of both natural biological and synthetic coordination complexes have been seriously underway for nearly three decades, and a fairly high level of understanding of their photophysics and excited state reactivity has been developed.[107] Such study has helped to provide a better understanding of the properties and reaction mechanisms of coordination compounds, and is also of interest for potential applications to light-capturing reactions. However, the photochemical properties of organometallic compounds, with the

exception of the metal carbonyls, have received rather less study and understanding is less well developed.[108] This situation has been rapidly changing over the last decade due largely to the development of advanced time-resolved laser spectroscopic techniques coupled with improved methodology suitable for the study of unstable and transient species.[109]

The early development of the photochemistry of transition metal carbonyls was a result of the use of photoinduced ligand substitution reactions as a tool in their synthesis since the late 1950s. The majority of the d-block metals are known to form photoreactive carbonyl complexes; a large number of excited-state decay processes have been observed and are still attracting study today.[110] Other classes of organometallics with established photochemistry include alkene, arene, cyclopentadienyl, isocyanide, hydride, and alkyl complexes.[108]

As mentioned above, many coordination compounds have extensive photochemistry and some particularly well studied examples are complexes of the $[Ru(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridyl) unit which is extensively used as a sensitiser in photodriven chemical and physical processes.[111] The electronic structure of the excited ion $^*[Ru(bipy)_3]^{2+}$ appears to result from transfer of an electron from a metal t_{2g} orbital to a ligand π^*-orbital.[112] This excited state, which may be described as Ru^{III}-L^-, reverts to the ground state by photoemission without chemical reaction unless suitable reactants called quenchers are present. In contrast to this behaviour, the simple ammine complexes of ruthenium, $[Ru(NH_3)_5L]^{2+}$, respond to photoexcitation by promptly aquating or oxidising.[113] Recent work in the bioinorganic field has involved the attachment of the pentaammineruthenium unit to protein molecules such as myoglobin.[114]

A number of prototype molecular electronic devices which utilise the photochemical properties of coordination complexes have recently been demonstrated. These include a $Ru(bipy)_3^{2+}$-viologen complex-polypyrrole film as a molecular photoelectrode,[115] molecular photodiode films containing ferrocenyl and porphyrin derivatives,[116] and a photochromic silver tetracyanoquinodimethane (AgTCNQ) complex exhibiting bistable optical switching which shows

promise for high speed optical logic and data storage applications.[117] The field of optical data storage is of great industrial importance,[118] and systems using metal-organics and dye lasers have attracted much recent attention particularly in Japan where metal bis(1,2-dithiolene) complexes as well as metal substituted dye molecules have received patent protection.[119] Another area of potential practical application for photochemically active metal compounds is that of "water splitting". This is a process whereby the direct conversion of solar energy to split water into hydrogen and oxygen is achieved.[120] An effective photolysis of this nature would have considerable industrial value, but as yet no artificial system has been found which rivals the efficiency of catalytic chlorophyll in the natural photosynthetic scheme.

Recent exploratory work in coordination complex photochemistry has involved the attachment of redox-active molybdenum mononitrosyl centres (see later) to photochemically and redox-active porphyrin and metalloporphyrin molecules. Electrochemical studies on tetraphenylporphyrin (TPP) derivatives such as [31] (Fig. 12) reveal no interaction with the peripheral molybdenum when the molecule is in its ground state. However, laser spectroscopic studies indicate that the molybdenum centre can act to quench fluorescence from the porphyrin once excitation at 510 nm has taken place.[121] This work is currently ongoing, and extensive physical measurements on a number of molecular variations are needed to give a clear picture of the photochemical processes involved.

I-4.3 MOLECULAR FERROMAGNETS

Metal-containing molecular ferromagnets are of two general types, the first consisting of neutral metal coordination complexes. These usually involve the alignment of mononuclear or oligonuclear complex species to give linear ferrimagnetic chains which order either ferro- or antiferro-magnetically. Magnetic coupling occurs between either a single paramagnetic metal and an organic radical

species or between two different types of paramagnetic metal ion. An example of a heterobimetallic system is that in which d^9 copper(II) (spin = ½) and d^5 manganese(II) (spin = 2½) ions are magnetically coupled.[122] Ferromagnetic coupling in a heterotrinuclear compound is a rare phenomenon, but has recently been observed in an Fe(III)-porphyrin-dicopper(II) complex. The d^5 (spin = ½) iron(III) in the porphyrin ring couples simultaneously via imidazolate groups to two d^9 (spin = ½) copper(II) ions which are complexed by chelate ligands.[123]

The second class of molecular ferromagnetic compounds contains metal-organic intermolecular charge-transfer (CT) salts.

Organic CT salts have been known since the 1960s and are of interest because they often possess useful electrical (semiconduction, metallic conduction, or even superconduction), magnetic (ferromagnetism), or optical (electrochromism, thermochromism) properties.[124] They are composed of 1:1 mixtures of an electron rich donor, (D), molecule such as tetrathiafulvalene (TTF) and an electron deficient acceptor, (A), molecule such as tetracyanoquinodimethane (TCNQ). When these are mixed complete intermolecular transfer of an electron from donor to acceptor occurs to produce salts which are made up of stacked linear chains $D^+A^-D^+A^-D^+A^-$ within the crystal lattice. It is the possibility of cooperation between the molecular ions within chains that gives rise to the unusual physical properties mentioned above.

Ferromagnetic behaviour has been searched for recently in species in which either or both the donor and acceptor molecules are coordination or organometallic compounds. Much of this work has involved the readily oxidised decamethylferrocene molecule as the donor in conjunction with TCNQ or TCNE (tetracyanoethylene) as acceptor,[125] and the TCNE-decamethylferrocene material does indeed exhibit a ferromagnetic ground state. Very recently, species have been prepared containing decamethylferrocene and metal bis(1,2-dithiolene) complexes as acceptor,[126] but bulk ferromagnetic coupling has yet to be reported in such systems.

The study described here is primarily aimed at the preparation of metal-organic compounds designed to exhibit NLO effects. Having

already discussed in some detail the basis for such properties in molecular organic systems, a brief review of the published work to date involving metal compounds will now be included. Since the practical application of NLO materials may involve liquid crystal films, the preparation of complexes designed to possess NLO properties along with mesogenic behaviour forms a minor part of this study. Accordingly, a review of the field of metal-containing LCs follows directly after the section on NLO.

I-5 METAL-ORGANIC COMPOUNDS FOR NLO

Although organic compounds have attracted much attention as NLO materials for the past two decades, until very recently little corresponding study had been undertaken on organometallic or coordination compounds. As has been discussed previously, metal-organic species are known to exhibit various interesting molecular electronic properties, and the incorporation of metals into molecular NLO materials is of interest because it offers the potential for combining magnetic and electron transfer properties with optical properties.

The observation of intense metal to ligand or ligand to metal CT bands in the u.v.-visible absorption spectra of both organometallic and coordination compounds shows that such molecules can possess low-lying excited electronic states.[111] To a large extent, these bands arise from excellent overlap of the diffuse metal d-orbitals and the ligand π-orbitals, and since such molecules can contain extended π-systems, they could be expected to possess large molecular hyperpolarisabilities. Also, the alteration of oxidation states and/or the metal ligand environments can be used to tune the electron density at the metal centre thus imparting upon it either electron accepting or donating properties. Changes in ligands will also affect the steric and other crystal packing properties, and hence may be used to encourage the adoption of a non-centrosymmetric crystal structure necessary for a large $\chi^{(2)}$.

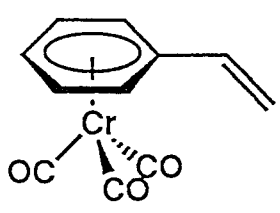
Following these principles, initial investigations focused on arene metal carbonyl complexes and showed that such compounds could produce low but significant SHG from a 1.064 μm laser.[127,128] Of rather greater interest, compounds containing ferrocenyl moieties have been found to exhibit powder SHG efficiencies as high as 62 and 220 times urea.[129,28] Other work on quadratic effects has been carried out using organometallic L-B films,[130] inclusion complexes,[131] and aryl metal compounds.[132] More recently, the field has begun to expand rapidly with reports of second-order effects in aryl-substituted polysilanes,[133] transition metal acetylides,[134] ruthenium(II) arene salts,[135] and nitrido polymers of molybdenum and tungsten.[136] Some molecular orbital β calculations have also been carried out on a number of ferrocenyl and metal carbonyl compounds.[137] Various representative examples of metal-organics exhibiting second-order NLO effects are shown in Fig. 12.

Third-order $\chi^{(3)}$ effects in organometallic platinum poly-yne systems,[138] phthalocyanine complexes,[139] nickel dithiolene complexes,[140] and vinyl ferrocene derivatives[141] have also been investigated. In the area of non-metal inorganic molecular compounds, there have been reports of SHG in phosphorus-boron donor-acceptor molecules[142] and also some theoretical work on third-order effects in conjugated phosphazene polymers.[143]

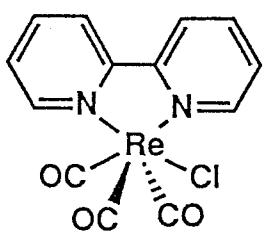
Clearly, the versatility of metal-organic compounds along with their proven NLO properties, ensures that this field will continue to expand at an ever increasing rate in the years to come.

Fig. 12

Metal-Organics Exhibiting Second-Order NLO Effects

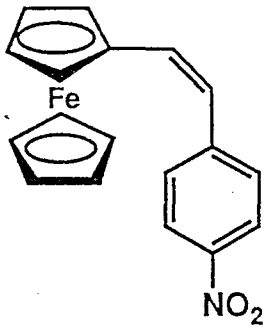


[24] (1986)
SHG = 1.8 x ADP (1.064 μm)[127]

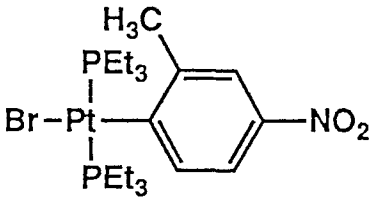


[25] (1987)
SHG = 3.0 x urea (1.064 μm)[128]

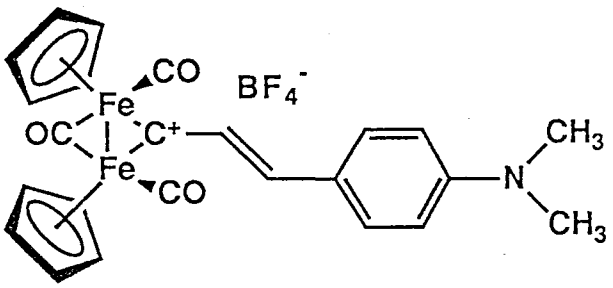
Fig. 12 (*Continued*)



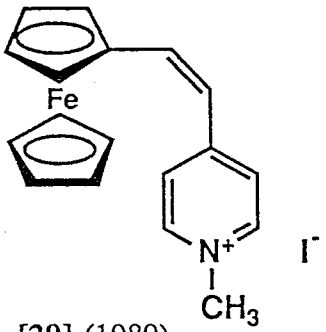
[26] (1987)
SHG = 62 x urea (1.907 μm)[129]



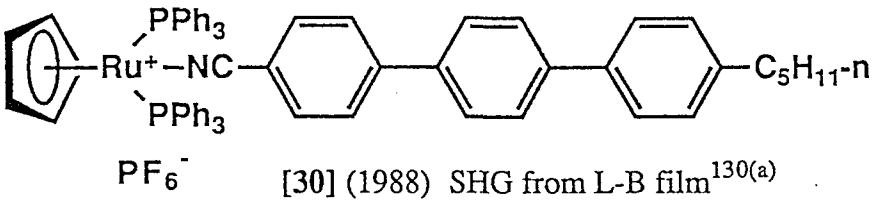
[27] (1988)
SHG = 14 x urea (1.064 μm)[132]



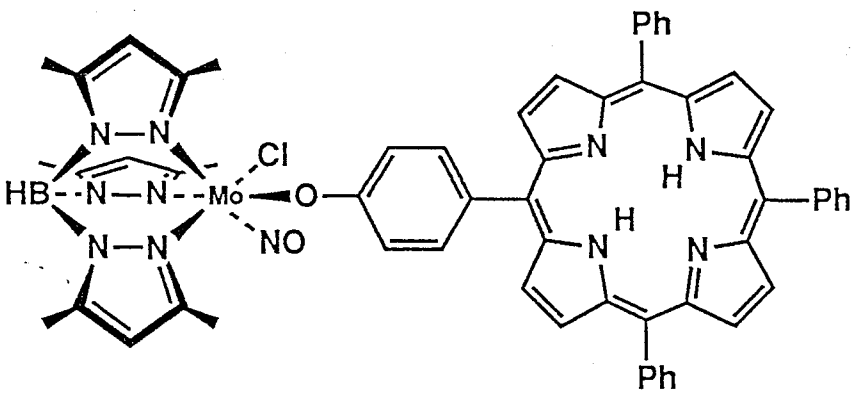
[28] (1988)
SHG = 0.77 x urea (1.907 μm)[144]



[29] (1989)
SHG = 220 x urea (1.907 μm)[28]

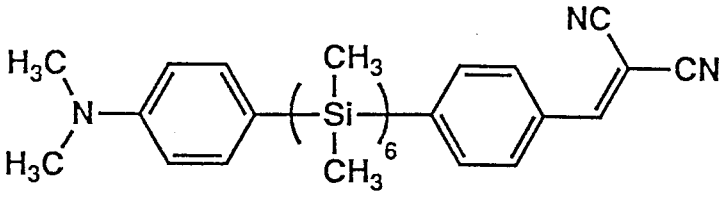


[30] (1988) SHG from L-B film[130(a)]

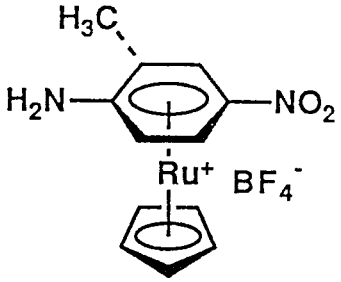


[31] (1989) SHG = 1.93 x urea (1.907 μm)[145]

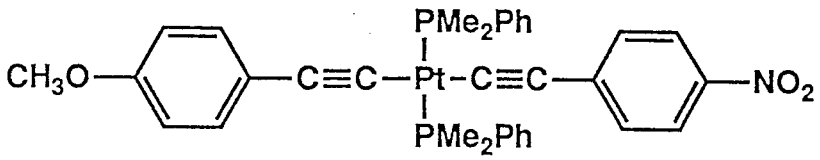
Fig. 12 (*Continued*)



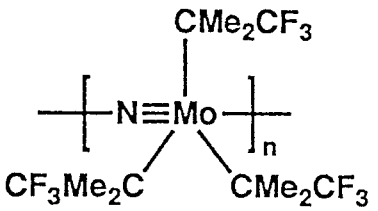
[32] (1990)
high solution β from EFISH[133]



[33] (1991)
SHG = 1.0 x urea (1.064 μm)[135]



[34] (1990)
SHG = 0.67 x urea (1.064 μm)[134]



[35] (1991)
SHG = 0.35 x urea (1.064μm)[136]

Notes: All SHG values from powder tests; dates refer to first reported test.

I-6 METALLOMESOGENS

Over the last 5 or so years interest has burgeoned in the creation and properties of LCs containing metal ions.[146] Early work in the 1980s included studies on, for example, bis(*p*-alkyl-phenyl-dithiolate)nickel and -platinum complexes,[147] *ortho*-palladated azobenzenes,[148] as well as some metal-containing β-diketonates,[149] carboxylates,[150] and phthalocyanines.[151] Since that time the term "metallomesogens" has been adopted to describe all metal-containing LCs, and this new science has begun to spread beyond its initial focus in European academic institutions (mainly in France and Italy) to reach both Japan and the USA. Although

lyotropic metal soaps represent the earliest metallomesogens and have been known for many years, the current interest was stimulated by and is largely aimed at the preparation of thermotropic systems.

The incorporation of metals into mesophases can affect a multitude of properties including: optical (*e.g.* birefringence, colour, NLO); mechanical (elasticity, *etc.*); electrical; thermal (phase temperatures, *etc.*); and magnetic (*e.g.* paramagnetism). Ferroelectric metallomesogens have been discovered,[152] and recent interest has focused on paramagnetic nematic phases since they represent materials which can be easily ordered in a magnetic field.[153] Furthermore, the use of organometallic and coordination compounds makes possible the exploration of various interesting geometries and this is continually expanding knowledge of what shapes of molecules can produce LC phases.

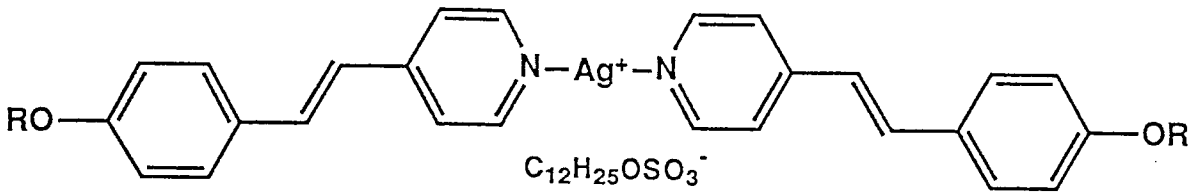
Most of the metallomesogens discovered thus far contain late transition metals such as cobalt,[154] rhodium,[155] iridium,[156] nickel,[146] palladium,[152] platinum,[146] copper,[89] silver,[146] gold,[146] and zinc,[146] but vanadium,[153] iron,[157] lead,[154] alkali-metal,[158] and lutetium[159] containing LCs have also been recently reported. The range of ligands has been extended to include stilbazoles,[160] porphyrins,[161] and crown ethers,[158] and organometallic alkene complexes[162] as well as metal-containing LC polymers[163] have been investigated. Very recently, bimetallic tetracarboxylate complexes of molybdenum have been found to exhibit discotic LC phases,[164] and physical studies have shown that metallomesogens can exhibit greatly enhanced electronic polarisabilities.[165] This latter observation is clearly of interest with respect to the creation of NLO-active metallomesogens.

Since the field is still very young it is unrealistic to talk of metallomesogen devices within the near future, but the challenges presented are sure to stimulate increasing research effort to discover species which possess desirable properties.

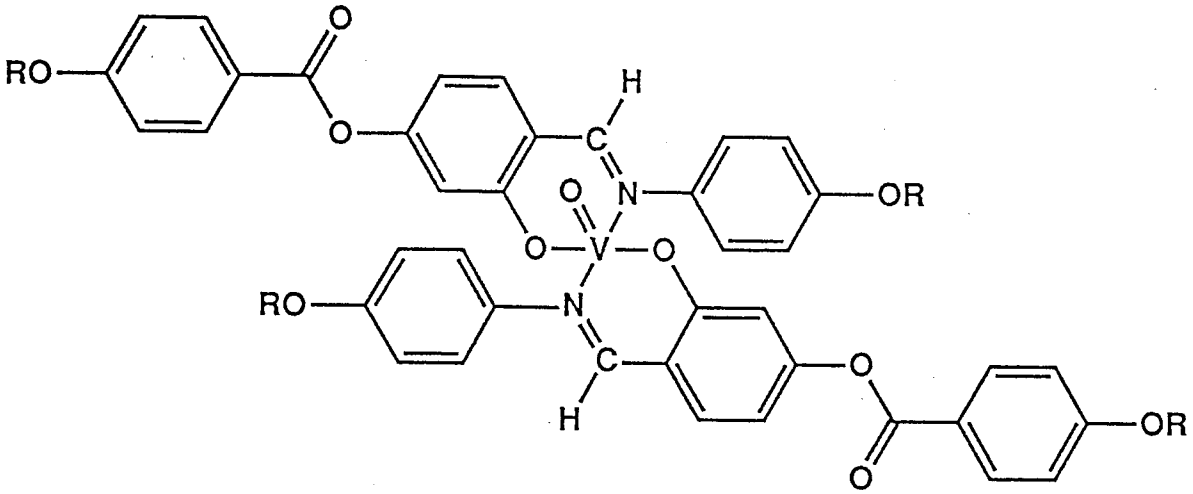
A number of metallomesogens, selected to illustrate the wide diversity of molecular structures capable of forming LC mesophases, are shown in Fig. 13

Fig. 13

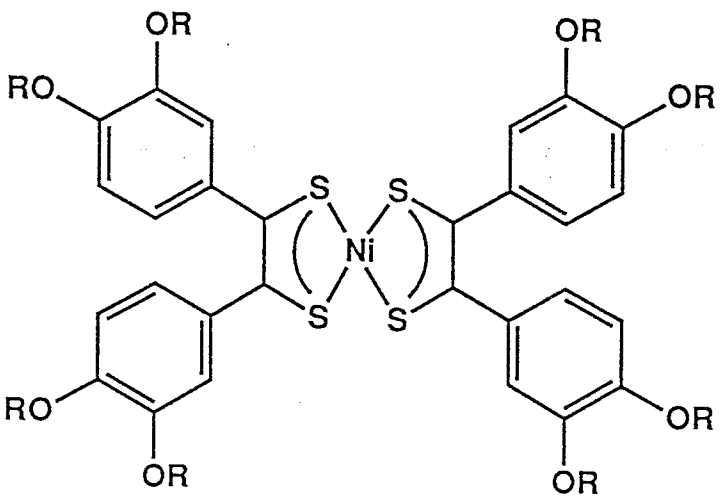
Some Representative Examples of Metallomesogens



[36] Silver(I) stilbazole[146] (R = n-C_8H_{17})

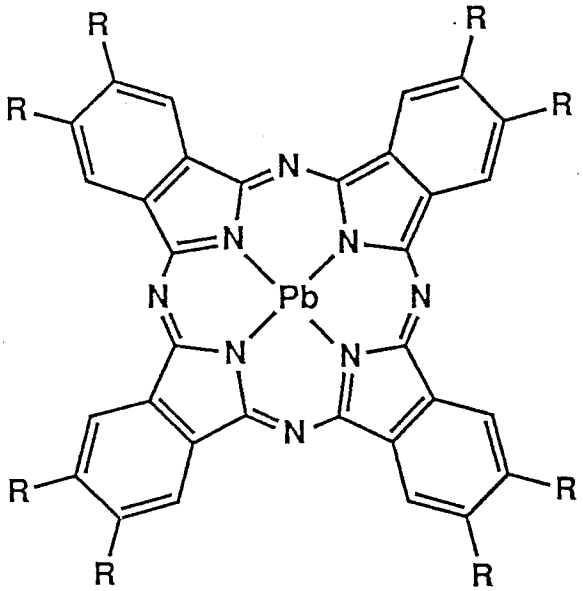


[37] Vanadium(IV) schiff base[153] (R = n-$C_{10}H_{21}$)

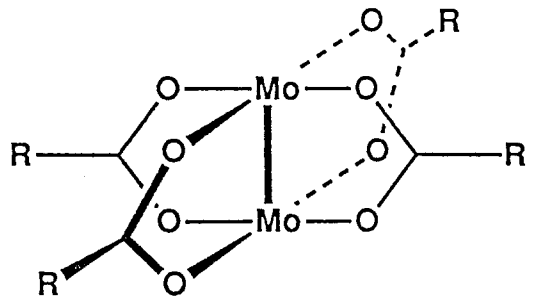


[38] Nickel(IV) dithiolene[166] (R = n-$C_{10}H_{21}$)

Fig. 13 (*Continued*)



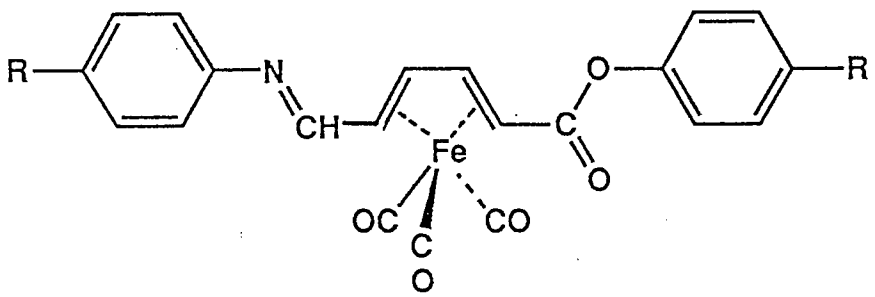
[39] Lead(II) phthalocyanine[154] (R = n-$C_8H_{17}OCH_2$)



[40]

Dimolybdenum(II) tetracarboxylate[164]

(R = n-C_5H_{11})



[41] Iron(0) butadiene complex[157(b)] (R = n-$C_7H_{15}O$)

As discussed earlier, certain molybdenum and tungsten mononitrosyl complexes have recently been found to exhibit interesting mixed-valence behaviour as well as photochemical quenching effects. They therefore seem to be versatile species with regards to molecular electronic properties, and investigation of their relevance to other interesting phenomena should produce further remarkable results. The chemistry and physical nature of these complexes will now be discussed in some detail.

I-7 MOLYBDENUM AND TUNGSTEN MONONITROSYL COMPLEXES

I-7.1 TRISPYRAZOLYLBORATE LIGANDS

These are uninegative chelating ligands of general formula $[RB(pz)_3]^-$ where pz = pyrazolyl (often substituted), and are members of the broader class of ligands known as polypyrazolylborates of general formula $[R_nB(pz)_{4-n}]^-$ where n=0, 1, or 2. First reported by Trofimenko in 1966,[167] they are synthesised by reaction of pyrazole or a substituted pyrazole[168] with either an unsubstituted or alkyl-substituted alkali metal borohydride, the extent of boron substitution being controlled by the temperature of the reaction.[169]

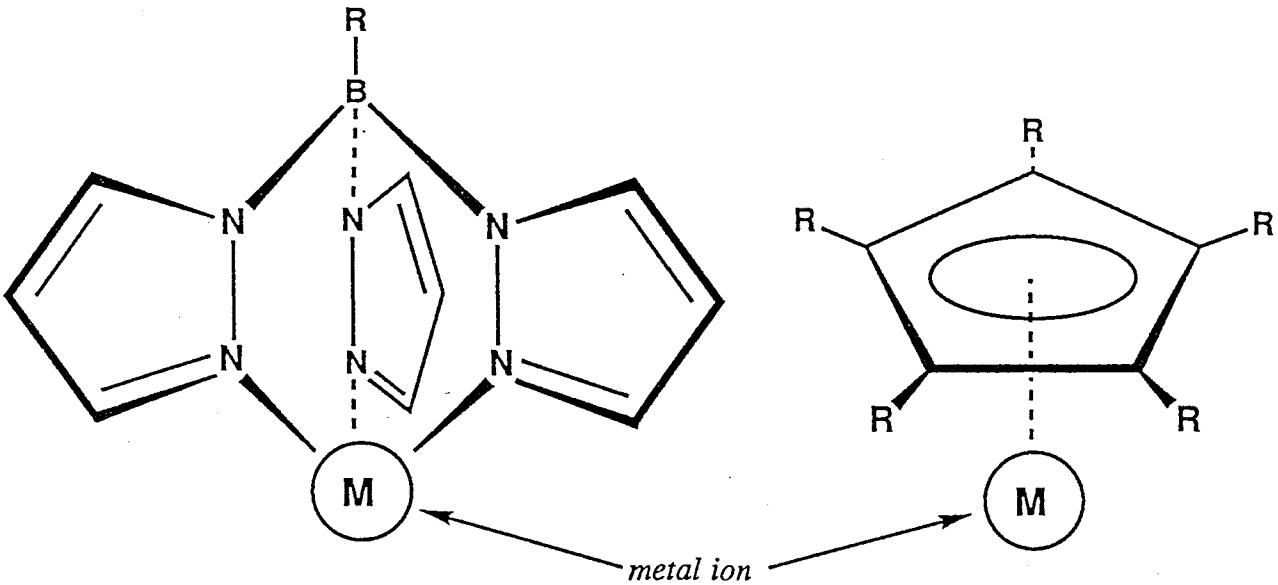
In all of these species the boron atom exists in a tetrahedral environment and chelating coordination to a metal can occur via the nitrogen atoms at the 2-position of each pyrazolyl ring. Bispyrazolylborates are therefore bidentate whilst trispyrazolylborates are tridentate and occupy three facial coordination sites of a complexed metal. Hence trispyrazolylborate ligands have some degree of similarity to the ubiquitous cyclopentadienide (Cp) species: both are uninegative, supply six electrons to the metal centre, and formally occupy three coordination sites (Fig. 14). Also, many trispyrazolylborate analogues of Cp complexes have been prepared including "sandwich", "half-sandwich", and "oyster" species.

However, this convenient analogy turns out on more detailed inspection to be somewhat tenuous; the two classes of ligand are in many respects extremely different. Firstly, in a rather obvious sense they are sterically highly dissimilar. Trispyrazolylborate has threefold symmetry whilst Cp has fivefold symmetry, and furthermore trispyrazolylborate has a substantially greater steric bulk.[170] The unusual shape of a trispyrazolylborate ligand serves to enclose a metal to some degree especially if the pyrazolyl rings possess substituents,[171,172] and this reduces the space available for the coordination of other ligands. Crystal packing

will also be strongly influenced by the presence of the bulky tripodal ligand.

Fig. 14

Trispyrazolylborate and Cyclopentadienyl Ligands



R = H: trispyrazolylhydroborate (L) R = H: η^5-cyclopentadienyl (Cp)

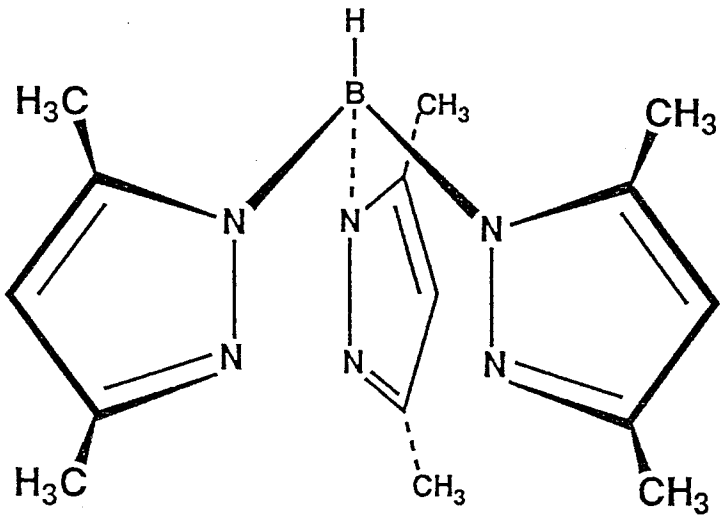
Also, but less obviously, the electronic binding properties of trispyrazolylborates are different to Cp. The latter binds a metal by carbon-metal π-donation from ring π-molecular orbitals and also by π-acceptance into ring orbitals. Trispyrazolylborate functions as a nitrogen-metal π-donor (using appropriate combinations of σ orbitals)[173] and a π-acceptor. There is evidence to show that trispyrazolylborate forms stronger bonds to metals than does Cp, and this along with the protection provided by steric effects, means that trispyrazolylborate complexes are generally more stable.[171] Hence, stable trispyrazolylborate complexes have become more abundant than their cyclopentadienide predecessors. The large range of known complexes includes transition metals of the first row (*e.g.* copper,[174] iron,[175] and vanadium[176]), second row (*e.g.* technetium[177] and zirconium[178]), and third row (*e.g.* rhenium[179] and iridium[180]) as well as alkaline earths (*e.g.* magnesium[181]), main group (*e.g.* aluminium[182] and tin[183]), lanthanides,[170] and even

actinides (*i.e.* uranium).[184] Very few of these contain organometallic ligands other than carbonyl, but recently other organometallic trispyrazolylborates of rhodium[185] containing ethene and other hydrocarbon ligands have been prepared and used in C-H bond activation studies.

This study has used exclusively the tris(3,5-dimethylpyrazol-1-yl)hydroborate ligand, denoted $HB(Me_2C_3N_2H)_3^-$ or L* (Fig. 15), which forms particularly stable transition metal complexes.

Fig. 15

The Tris(3,5-dimethylpyrazolyl)borate Ligand



I-7.2 MOLYBDENUM AND TUNGSTEN L* COMPLEXES

The precursor complexes used for this study are the previously described[186,187,188] series of mononitrosyl dihalides of general formula $[M(NO)L^*(X)_2]$ (M = Mo, X = F, Cl, Br, I; or M = W, X = Cl). These contain a linear nitric oxide ligand bonded to an octahedrally coordinated metal centre which is formally in a 2+ oxidation state and has a valence electron count of 16.[189] Hence they are coordinatively unsaturated but stabilised by the steric

and electronic properties of the L* ligand which prevent expansion of the coordination sphere. They are prepared according to the synthetic scheme shown in Fig. 16.

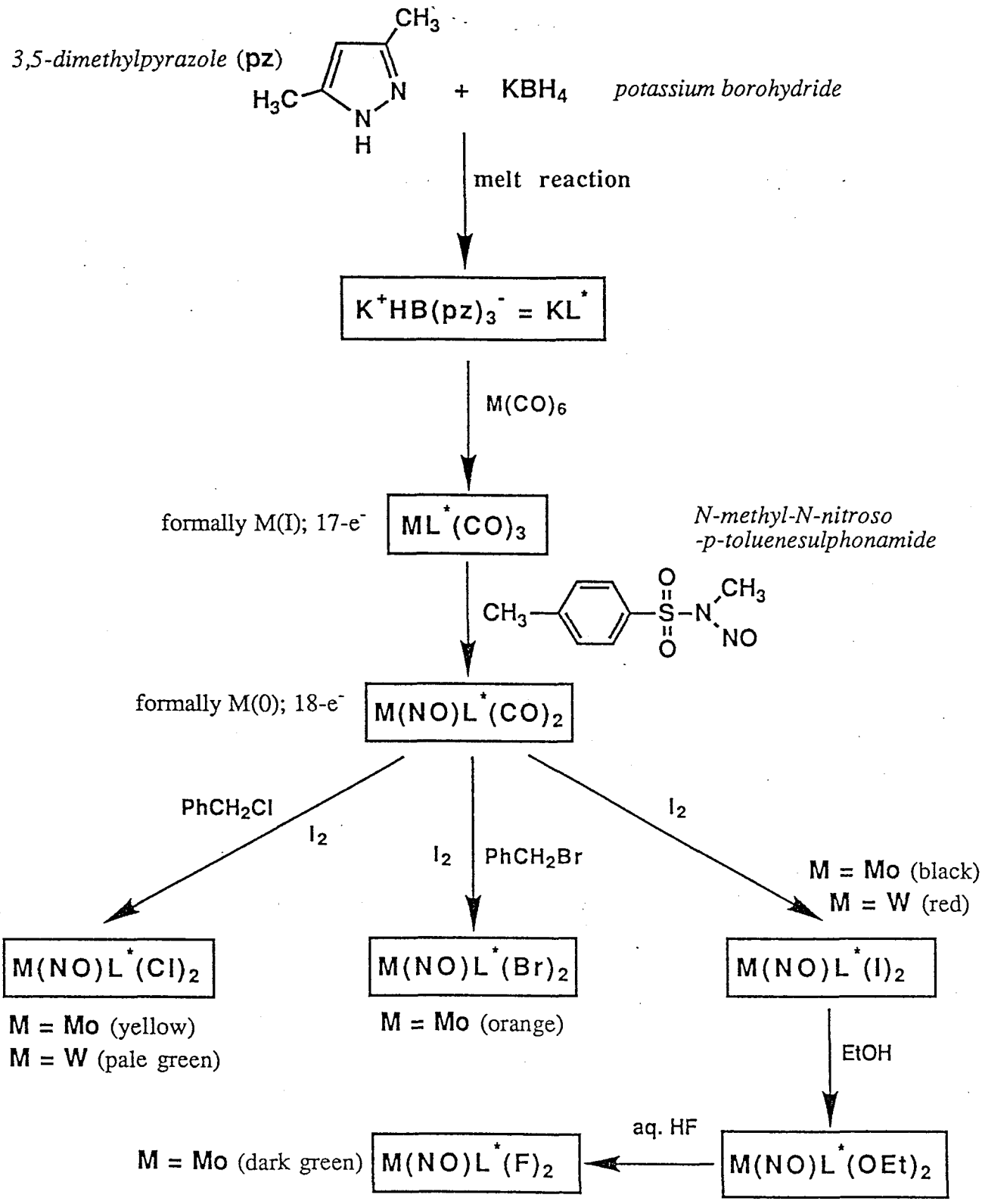
All of these dihalide complexes behave as simple monomeric species with the exception of the molybdenum difluoride which has some rather different characteristics.[188] They are all indefinitely air stable but react with water to varying degrees to give hydroxy and μ-oxo[190] bimetallic species.

Through facile replacement of one or both halides by oxygen, nitrogen, or sulphur donor ligands, many neutral complexes of general formula [M(NO)L*(X)(Y)] where X and Y are halogen, alkoxo,[191,192] aryloxo,[193] thiolato,[194] alkylamido,[195] arylamido,[196] and hydrazido[197] have been prepared and characterised over the last 20 years. More recently studied complexes have included carboxylate,[198] and thiocyanate and azide[199] species. All are air and moisture stable, containing an octahedral 16-electron metal centre in an $\{M(NO)\}^{3+}$ core. Complexes of the unsubstituted trispyrazolylborate ligand can expand their coordination spheres by dimerisation through halide bridging[191] or metal-metal bonding,[173] but this has not been observed in L* derivatives.

Difunctional ligands can give rise to homo- and hetero-bimetallic species containing two {M(NO)L*} centres,[200,201] but early attempts at chelate complex formation using diols[202] or amino-pyridine derivatives[203] proved unsuccessful. However, chelation has been achieved more recently using difunctional ferrocenyl ligands,[204] polyether alcohols,[205] and toluene-3,4-dithiol.[206] Reaction of $[Mo(NO)L^*(I)_2]$ with saturated heterocyclic amines such as piperidine can produce neutral 17-electron paramagnetic mono-amine[207] complexes as well as the usual 16-electron amides. The use of non-protic heterocyclic nitrogen donor ligands such as pyridines can produce neutral 17-electron (monosubstituted)[106] and 17-electron cationic (disubstituted)[208] octahedral complexes in which the ligand functions as a neutral 2-electron donor rather than the usual anionic 2-electron donors such as alkoxide.

Fig. 16

Synthetic Scheme for Mononitrosyl Dihalide Complexes



16-electron [M(NO)L*(X)(Y)] complexes will undergo one-electron reduction reactions to produce anionic 17-electron $\{M(NO)\}^{2+}$ complexes without expanding the metal coordination number, and the reduced dihalide salts $[Mo(NO)L^*(I)_2]^-(Et_2O)_2Li^+$ and $[Mo(NO)L^*(Cl)_2]^-Et_3N^+$ have been isolated and characterised.[189,106] The acceptance of an additional monodentate ligand to give an 18-electron, seven coordinate species has not yet been observed.

I-7.2(a) Physical Properties and Methods of Study

A number of properties make complexes of the {M(NO)L*} unit particularly ammenable to study by several physical techniques. The most important of the available techniques in the context of this work are infra-red and ^1H n.m.r. spectroscopy and electrochemistry. Each of these will now be given brief consideration.

I-7.2(a)(i) Infra-Red Spectroscopy

Nitrosyl stretching frequency

The stretching of the linearly bonded nitrosyl ligand gives rise to a single sharp intense absorption band usually occurring in the region 1710-1600 cm^{-1}. The precise frequency of this band is a very sensitive indicator of the electron density at the metal atom and therefore of the other ligands attached to it.[209] As the electron density at the metal increases so too does the extent of $d\pi$ to $p\pi^*$ back-donation from metal to nitrosyl. This filling of an antibonding nitrosyl orbital serves to weaken the N-O bond and hence results in a lowering of the nitrosyl stretching frequency. Some examples to illustrate this effect for molybdenum complexes are given in Table III.

The situation for tungsten is entirely analogous except that the higher electron density of tungsten gives frequencies which are between 20 and 60 cm^{-1} lower than those of the corresponding molybdenum complexes.[196,210]

TABLE III

Nitrosyl Stretching Frequencies of Molybdenum Mononitrosyl Complexes [Mo(NO)L*(X)(Y)]

X	Y	ν_{NO}/cm^{-1} (KBr disc)	
Cl	Cl	1702[209]	
Cl	OR	1675[209]	
Cl	HNR	1660[193]	frequency falls
OR	OR	1660[192]	as donor capacity
CO	CO	1655[209]	of co-ligands
HNPh	HNPh	1632[196]	increases
$HNPr^n$	$HNPr^n$	1618[153]	

Other i.r. Bands

The L* ligand also gives ν(B-H) at *ca* 2550 cm^{-1} and a set of four bands centred around 1400 cm^{-1} due to its carbon framework. These bands can be used to verify the presence of L* in a compound but not to indicate what other ligands are attached to the metal since their positions are not sensitive to its electronic environment.

I-7.2(a)(ii) ^1H n.m.r. Spectroscopy

The L* ligand has six methyl groups, three at the 3- and three at the 5-positions of the pyrazolyl rings, and three ring protons at the 4-positions. The number of signals which these give rise to in the ^1H n.m.r. spectrum is determined by the symmetry of the complex, and three general cases are possible:

(i) A complex of the type [ML*$(X)_3$] has C_{3v} symmetry (a C_3 axis and three σ_v planes) and should therefore give only one signal for the ring-protons (3 protons) and two distinct signals for the six methyls in the ratio 9:9.

(ii) A complex of the type [M(NO)L*$(X)_2$] such as one of the dihalides has only one σ_v plane and its symmetry is therefore C_s. In theory this should give two signals for the ring protons in the



ratio 2:1, and four methyl signals in the ratio 3:6:6:3.

(iii) An [M(NO)L*(X)(Y)] complex has three different substituents and therefore no symmetry at all which makes it chiral. Such a system should ideally give three discrete ring proton signals (1:1:1), and six methyl signals (3:3:3:3:3:3).

These three possibilities are illustrated in Fig. 17. Although some accidental coincidence of peaks (perhaps due to similarities between the different substituents) often occurs, the general arguments outlined above can still prove of considerable use. The observation of larger numbers of peaks than found in case *(iii)* is a clear indication of either discernable configurational isomers or of bimetallic species. Clearly, any co-ligand protons will also give signals which will prove useful in complex identification. The use of ^{13}C n.m.r. is perfectly feasible but takes longer and is rarely necessary if ^{1}H data is available.

I-7.2(a)(iii) Electrochemistry: Cyclic Voltammetry

Both [Mo(NO)L*(I)$_2$] and [Mo(NO)L*(Cl)$_2$] have been found to readily undergo reversible one-electron reductions. Under anhydrous conditions iodide dissociation from the reduced diiodide can occur,[211] but no chloride dissociation from the reduced dichloride has been observed.[200] The reduction potentials measured against the SCE in acetonitrile are +0.22 V and +0.09 V for the diiodide and dichloride respectively.

Further studies using cyclic voltammetry[212] have shown that nearly all [M(NO)L*(X)(Y)] complexes undergo reversible or quasi-reversible reduction with E_f strongly dependent on the nature of X and Y. In general the more electron-releasing X and Y groups give rise to a higher electron density at the metal and hence make reduction more difficult *i.e.* E_f becomes more cathodic. This is demonstrated by the examples shown in Table IV. The same trend is seen for E_f values as for ν_{NO} mentioned earlier, and some success has been achieved in correlating these two variables. The theory of cyclic voltammetry can be found elsewhere[213] and will not be discussed here.

Fig. 17

Theoretical ^1H n.m.r. Spectra for Mononitrosyl Complexes

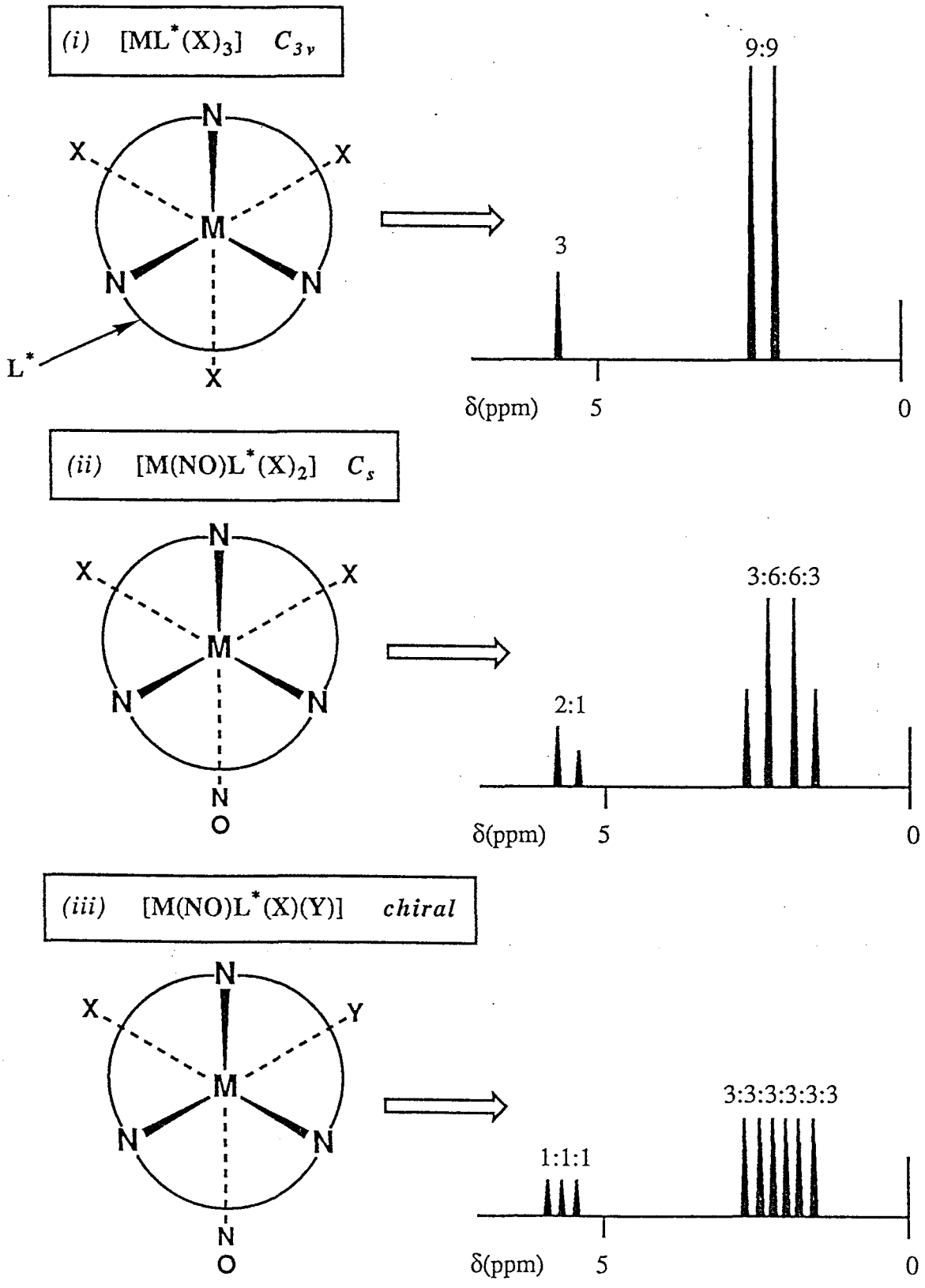


TABLE IV

Reduction Potentials of Mononitrosyl Complexes

[M(NO)L*(X)(Y)]

X	Y	M = Mo E_r/V vs. SCE	M = W E_r/V vs. SCE
Cl	Cl	+0.09	-0.42
Cl	SPh	-0.37	-0.83
Cl	OPh	-0.42	-0.86
SPh	SPh	-0.64	-1.04
OPh	OPh	-0.74	-1.20
Cl	HNPh	-0.85	-1.30[a]
HNPh	HNPh	-1.32	-

All of these results were obtained[210] using 0.2 M $[NBu_4][BF_4]$ in acetonitrile, or thf,[a] at a platinum bead electrode.

I-7.2(b) Molybdenum and Tungsten Mononitrosyl Complexes for Nonlinear Optics

The main reasons why {M(NO)L*} complexes seem likely to be good candidates for NLO properties can be summarised as follows:

(i) Electronic Properties

Previously referenced and other[214,215] electrochemical studies have indicated that the 16-electron {M(NO)L*(X)}$^+$ moiety in such complexes can act as an efficient acceptor of charge. Not only is the coordinatively unsaturated metal electron deficient, but NO is a powerful π-acceptor and attached ligands such as chloride are electronegative. Corroborating evidence for this behaviour has come from X-ray structural studies[191,194,195] revealing shortened bond lengths from metal to O, S, or N donor atoms which is thought to indicate some degree of pπ to dπ ligand to metal donation resulting from the electron accepting nature of the metal centre.[209] The inherently higher electron density of tungsten would

suggest that it should be a less effective electron acceptor centre than molybdenum. Furthermore, cyclic voltammetric studies have shown the reduced 17-electron {M(NO)L*(X)} moiety to function as an electron donating substituent, so {M(NO)L*} complexes containing metallic centres which function as powerful electron acceptors and/or electron donors may be prepared.

(ii) **Chirality**

The chirality of the octahedral metal centre in [M(NO)L*(X)(Y)] ($X \neq Y$) ensures a dissymmetric molecular structure. However, unless the complexes can be resolved, a centrosymmetric packing, which precludes bulk NLO effects, is highly likely.

(iii) **Synthetic Versatility**

It is synthetically easy to attach polarisable organic ligands to the metal using phenol, thiophenol or aniline derivatives. Provided that suitable ligands with donor moieties built in can be prepared then the complexes should generally prove readily accessible.

(iv) **Stability**

Complexes of type [M(NO)L*(X)(Y)] show good resistance to air and atmospheric moisture as well as high thermal stability. They also appear to be generally insensitive to photochemical degradation, but no information regarding their stability to high energy laser beams is yet available.

Following the previously outlined general criteria for the occurrence of a high molecular hyperpolarisability tensor β, mono-substituted complexes of the type [M(NO)L*(X){E-Ar-D}] (where M = Mo or W; X = halide; E = O, NH, or S; Ar = aromatic bridge; D = electron donor substituent) would seem to be better candidates for desirable effects than would bis-subsituted derivatives of the form [M(NO)L*{E-Ar-D}$_2$]. In the former a single metal electron acceptor centre is linked via a delocalised aromatic bridge to an electron donor group, whilst in the latter the acceptor "power" of the metal centre is shared between two donor functions in a "V-

shaped" geometry. Hence a mono-substituted complex would be expected to possess a larger molecular dipole and also hyperpolarisability. Furthermore, mono-subsituted derivatives have a chiral centre whereas the bis-substituted complexes have a molecular plane of symmetry. However, for the sake of completeness and out of chemical interest, bis-substituted derivatives of all ligands have been prepared and fully characterised wherever possible.

With these factors in mind, and following the precedent set by the observation of SHG from the molybdenum-TPP complex [31] mentioned earlier,[145] the preparation of a large number of "engineered" {M(NO)L*} complexes was embarked upon.

CHAPTER ONE

FERROCENYL LIGANDS AND PRECURSOR COMPOUNDS

II-1 DISCUSSION

The report by Green *et al.*[129] of efficient SHG from an acceptor-substituted aryl ferrocene compound suggested the use of the versatile ferrocenyl moiety as the donor group in molybdenum and tungsten complexes designed to possess NLO properties. In order to achieve this it was first necessary to prepare and fully characterise a number of ferrocenyl anilines and phenols for use as ligands.

II-1.1 SYNTHETIC METHODS

A total of nine ferrocenyl ligands were prepared and these are shown in Fig. 18.

Fig. 18
Ferrocenyl Ligands

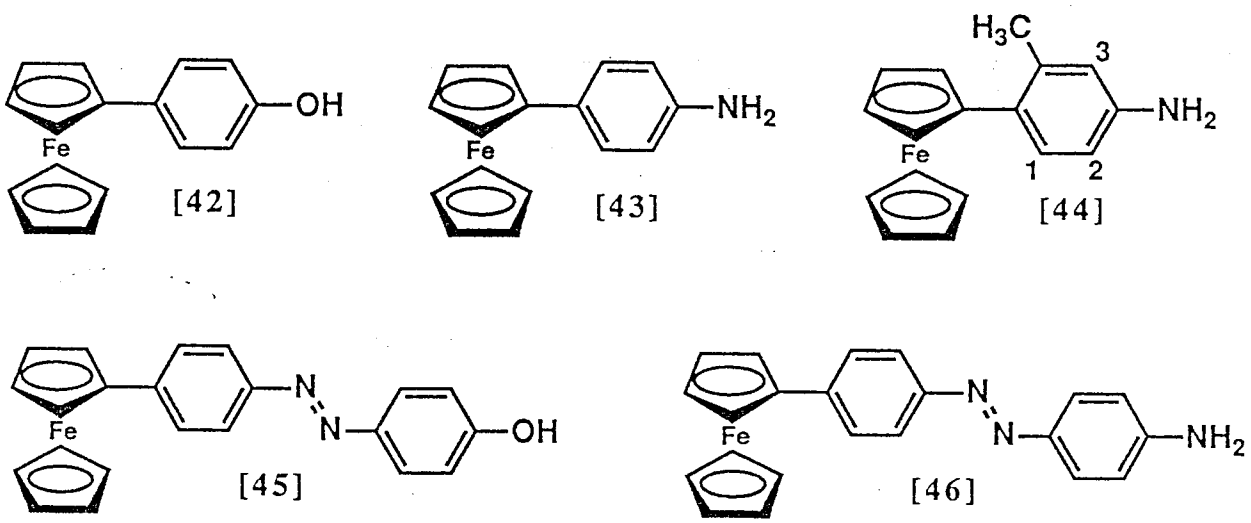
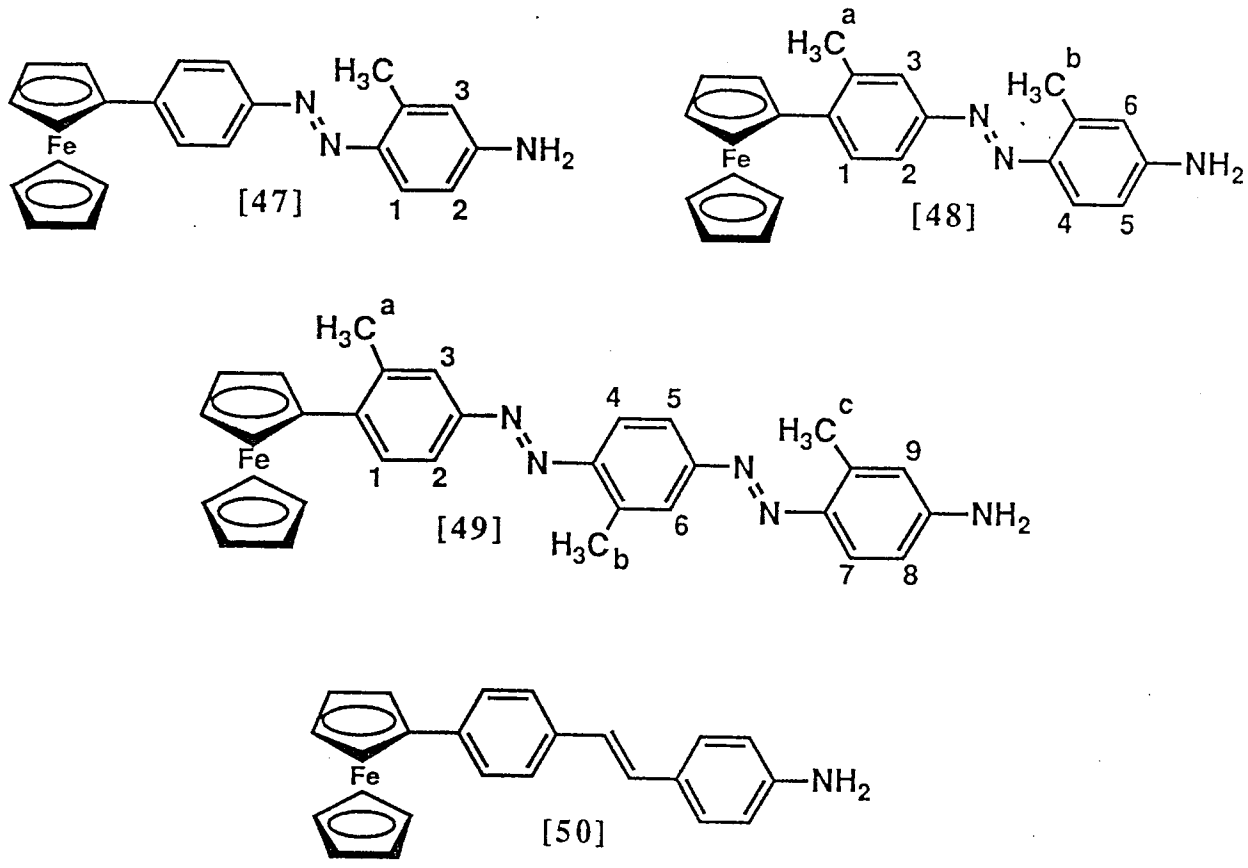


Fig. 18 (*Continued*)



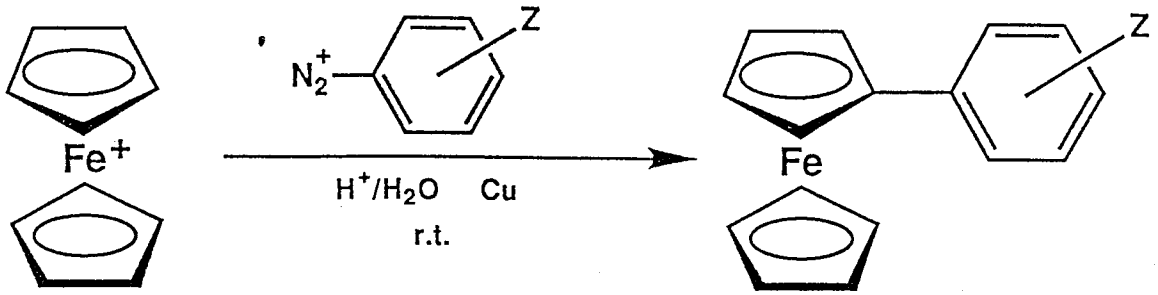
II-1.1(a) Mono-aryl Compounds

The mono-aryl ferrocenes [42], [43], and [44] were prepared using some slight modifications of previously published procedures[216,217] which involve the arylation of ferrocenium ion with a diazonium salt. A general illustration of this reaction, which is thought to proceed via a free radical mechanism,[218] is shown in Fig. 19. Good yields can be obtained with various different Z groups, but of the three ligands shown only 4-ferrocenylphenol [42] is prepared in a single step. The aniline ligands [43] and [44] are prepared via a straightforward tin-hydrochloric acid reduction of their precursor nitro derivatives [51] and [52] which are obtained in high yield from the diazonium reaction.

All of the ferrocenyl ligand precursors are shown in Fig. 20, along with organic reagents used in their syntheses and a number of other compounds to be discussed later in this chapter.

Fig. 19

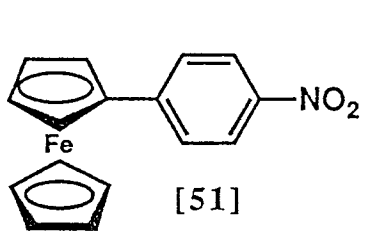
Arylation of Ferrocene by Diazonium Salts



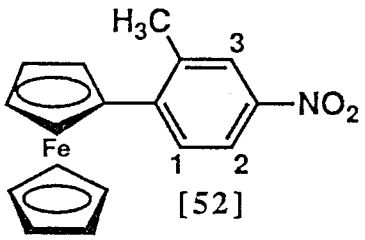
Z = NO_2, OH, CN, Hal, *etc.*

Fig. 20

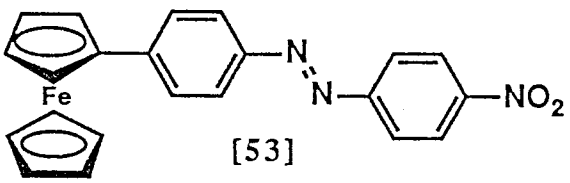
Ferrocenyl Ligand Precursors and Organic Reagents



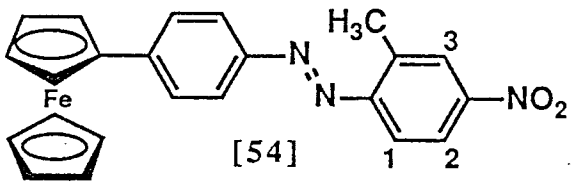
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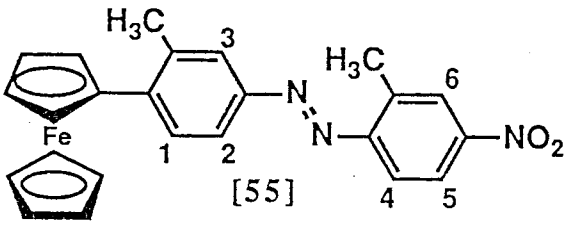
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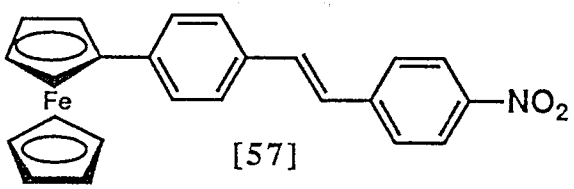
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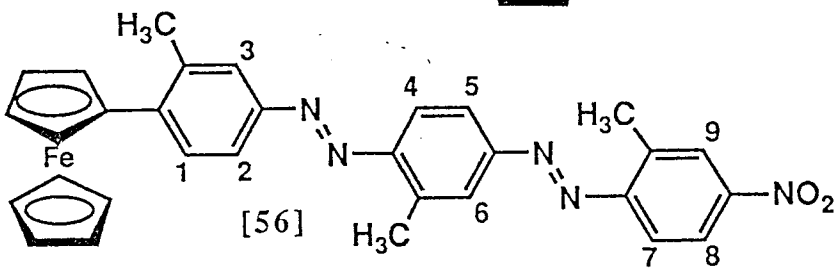
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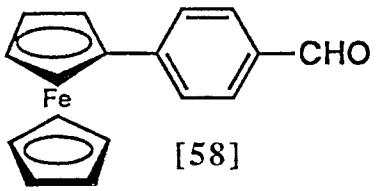


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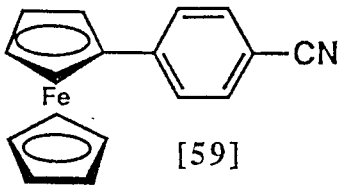


[56]

Fig. 20 (*Continued*)



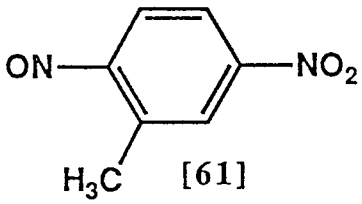
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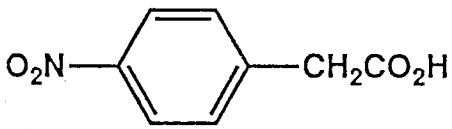
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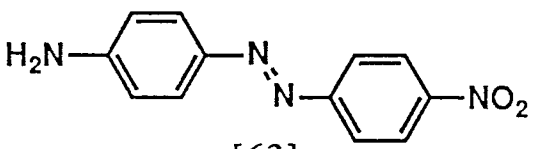
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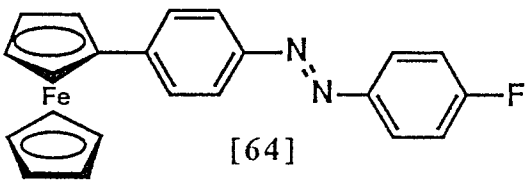
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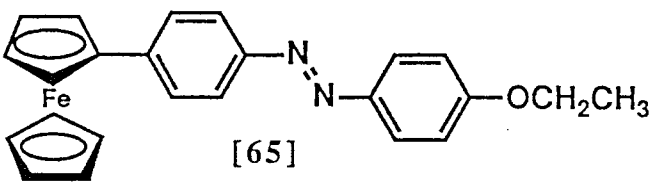
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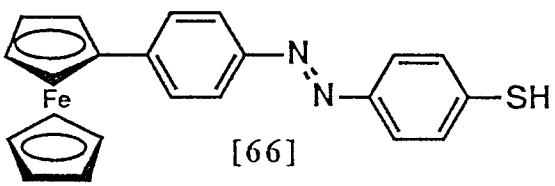
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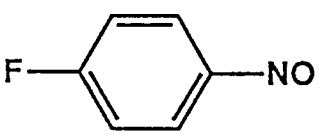
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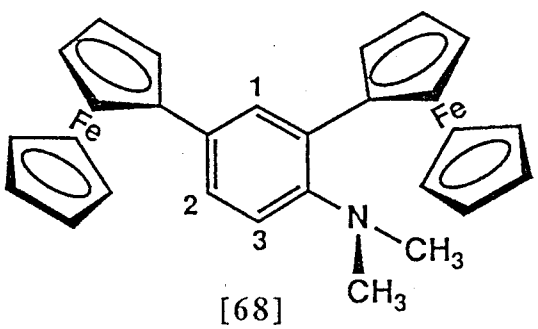
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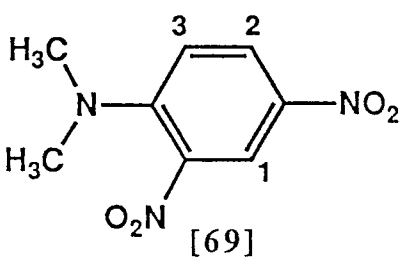
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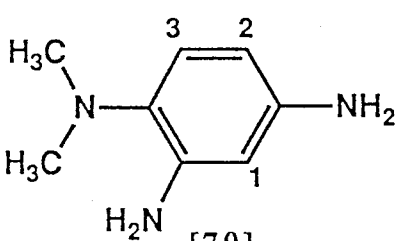
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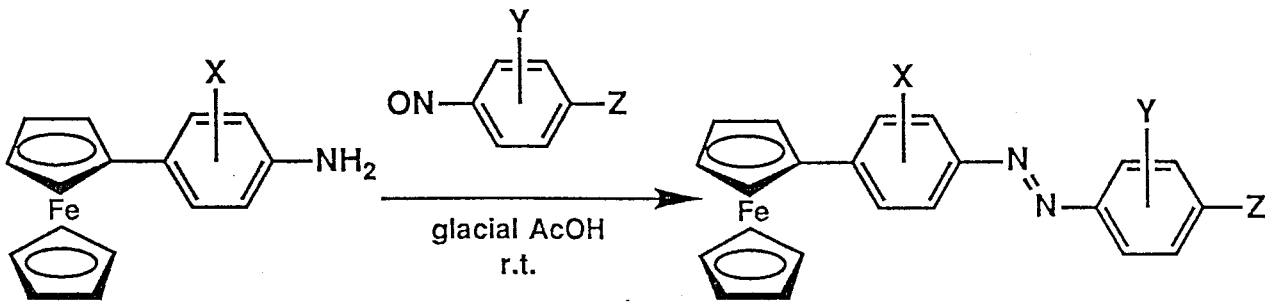


[70]

II-1.1(b) Azobenzene Compounds

The azobenzene (or diphenylazo) group was chosen as a linker between metal centres since it has been found to optimise the molecular β by efficient electron transmission[35] and is also readily synthetically accessible. The nitro precursor to the ligand [46] is 4-nitro-4'-ferrocenylazobenzene [53] and this was prepared via a diazonium reaction using the commercial dye Disperse Orange 3 (4-nitro-4'-aminoazobenzene; [63]). However, this reaction gave a very poor yield, and a much better method for obtaining such compounds is to use a condensation reaction known as the Mills Reaction, a general case of which is shown in Fig. 21.

Fig. 21
Preparation of Ferrocenylazobenzenes

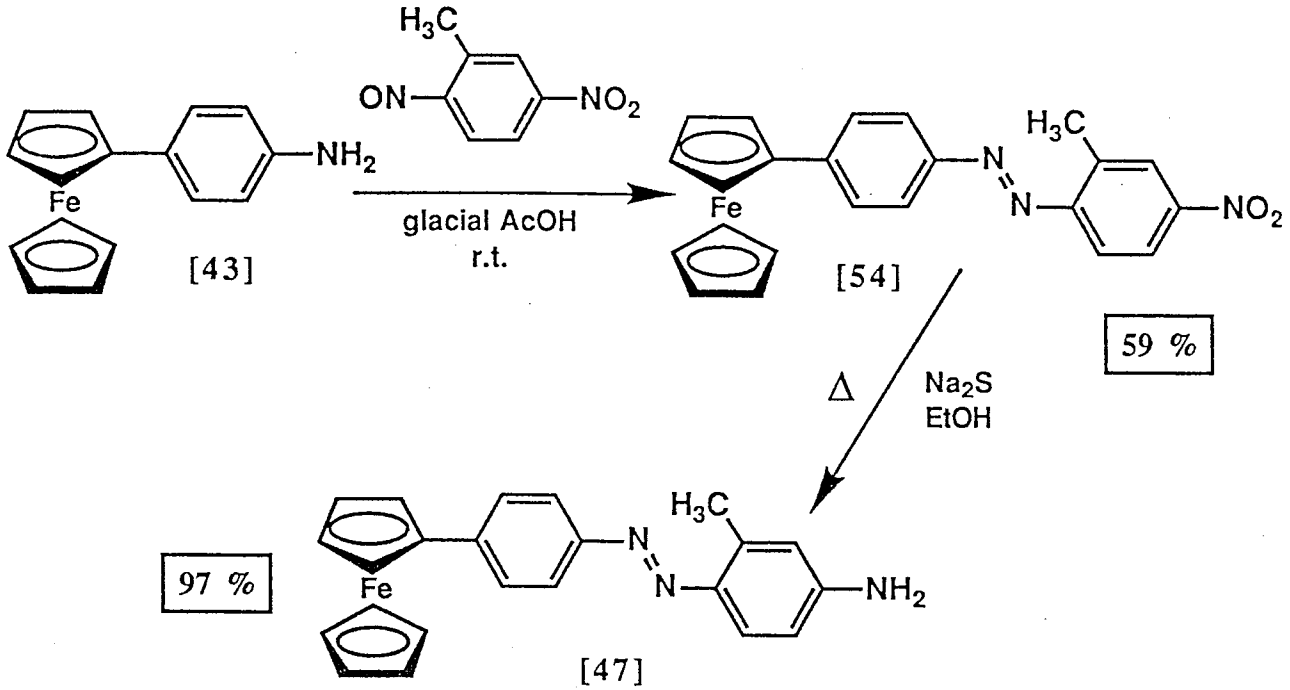


This approach has previously been used to prepare a number of ferrocenylazobenzenes,[219,220] including [53], but none of the ligands [45], [46], [47] or [48] have been previously reported. 4-Hydroxy-4'-ferrocenylazobenzene [45] was prepared in low yield via the condensation of 4-ferrocenylaniline [43] and the commercially available 4-nitrosophenol [60]. The nitro precursors [54] and [55] were prepared in fairly high yield by condensing 4-ferrocenyl-aniline or 4-ferrocenyl-3-methylaniline [44] with 2-nitroso-5-nitrotoluene [61]. The latter is not a commercial reagent but was prepared by the partial oxidation of 2-methyl-4-nitroaniline using Caro's acid.[221] The amino compounds [47] and [48] were obtained in very high yield using a sodium sulphide-ethanol reduction of their

nitro precursors. The overall scheme for the preparation of [47] is shown in Fig. 22.

Fig. 22

Preparation of 4-Amino-2-methyl-4'-ferrocenylazobenzene



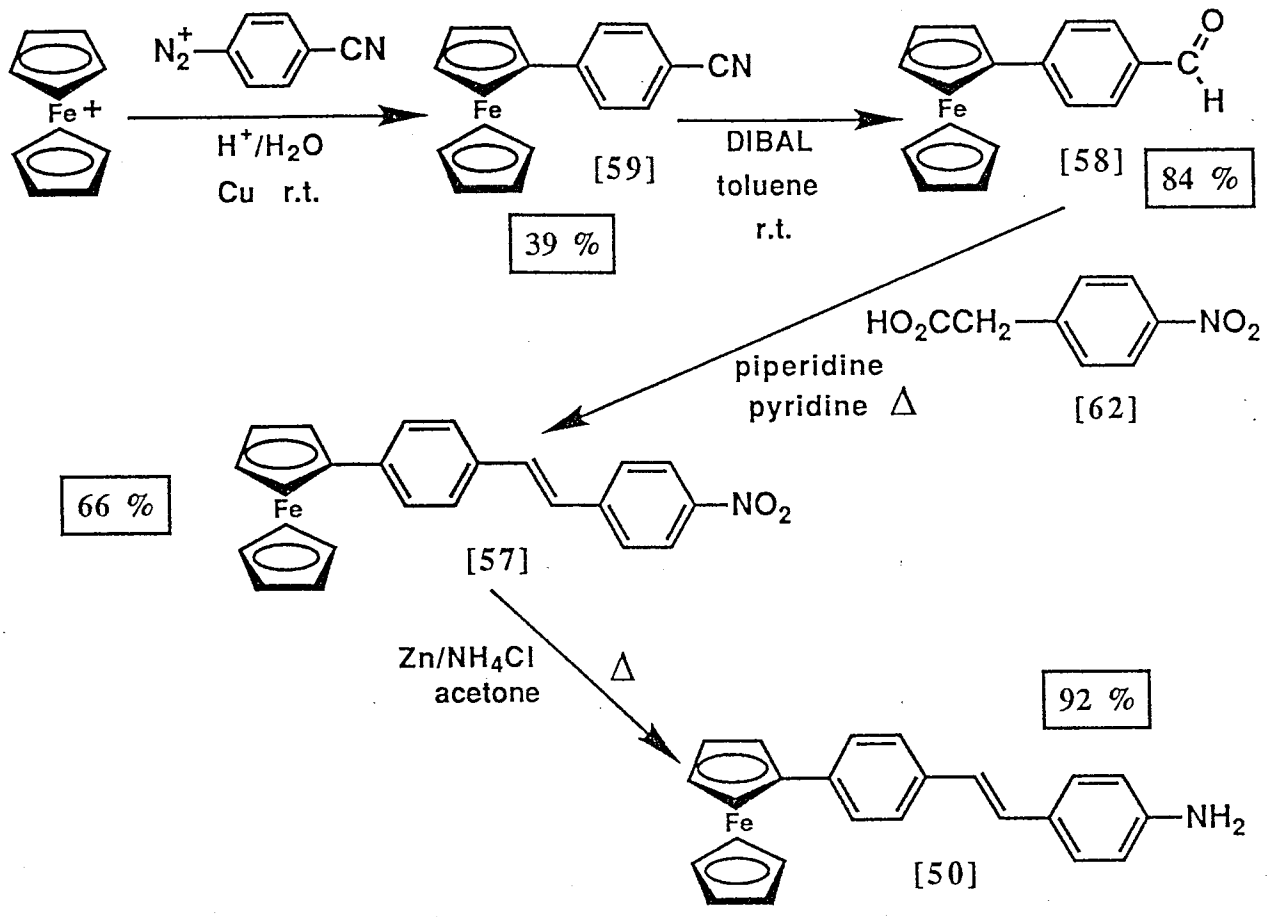
The bis-azo ligand [49] was prepared via a second Mills reaction of 2-nitroso-5-nitrotoluene with [48] to give the nitro compound [56] followed by sulphide reduction. This species was chosen with a view to producing complexes for third-order $\chi^{(3)}$ effects since the increased π-conjugation length in such structures has recently been shown to give enhanced THG in side-chain polymer materials.[222]

II-1.1(c) Stilbene Compounds

The new stilbene ligand 4-amino-4'-ferrocenyl-*trans*-stilbene [50] (*trans*-1-(4-aminophenyl)-2-(4-ferrocenylphenyl)ethylene) was prepared from the zinc-ammonium chloride reduction of 4-nitro-4'-ferrocenyl-*trans*-stilbene [57]. The latter was obtained using a classical base-catalysed condensation reaction between

4-ferrocenylbenzaldehyde [58] and 4-nitrophenylacetic acid [62]. [58] is a known compound, but its preparation via the DIBAL reduction of 4-ferrocenylbenzonitrile [59] (also known; from the standard diazonium reaction described earlier) has not been previously reported. The steps involved in the ferrocenylstilbene synthesis are shown in Fig. 23.

Fig. 23
Preparation of Ferrocenylstilbenes



II-1.1(d) Attempted Preparation of a Thiophenol Ligand

In an effort to extend the series of complexes to include sulphur linked species, some work was carried out on the attempted synthesis of the thiophenol ligand 4-mercapto-4'-ferrocenyl-azobenzene [66]. Thiophenols have been successfully prepared via nucleophilic aromatic substitution reactions where fluoride acts

as the leaving group,[223,224] and since the compounds 4-halo-4'-ferrocenylazobenzene (where halo = Cl, Br, or I) are known,[219] it was decided that 4-fluoro-4'-ferrocenylazobenzene [64] might serve as a precursor to the desired ligand. 4-Mercaptoazobenzenes have not been prepared in such a way before, but a fluorine *para* to an electron-withdrawing azo group could be expected to be relatively active towards nucleophilic displacement. The new compound [64] was synthesised in reasonable yield from the condensation between 4-ferrocenylaniline and the known compound 4-fluoronitrosobenzene [67]. The latter was obtained using established chemistry involving the reduction of 4-fluoronitrobenzene to its hydroxylamine derivative with zinc-aluminium chloride, followed by oxidation to the nitroso compound with ferric chloride.[225]

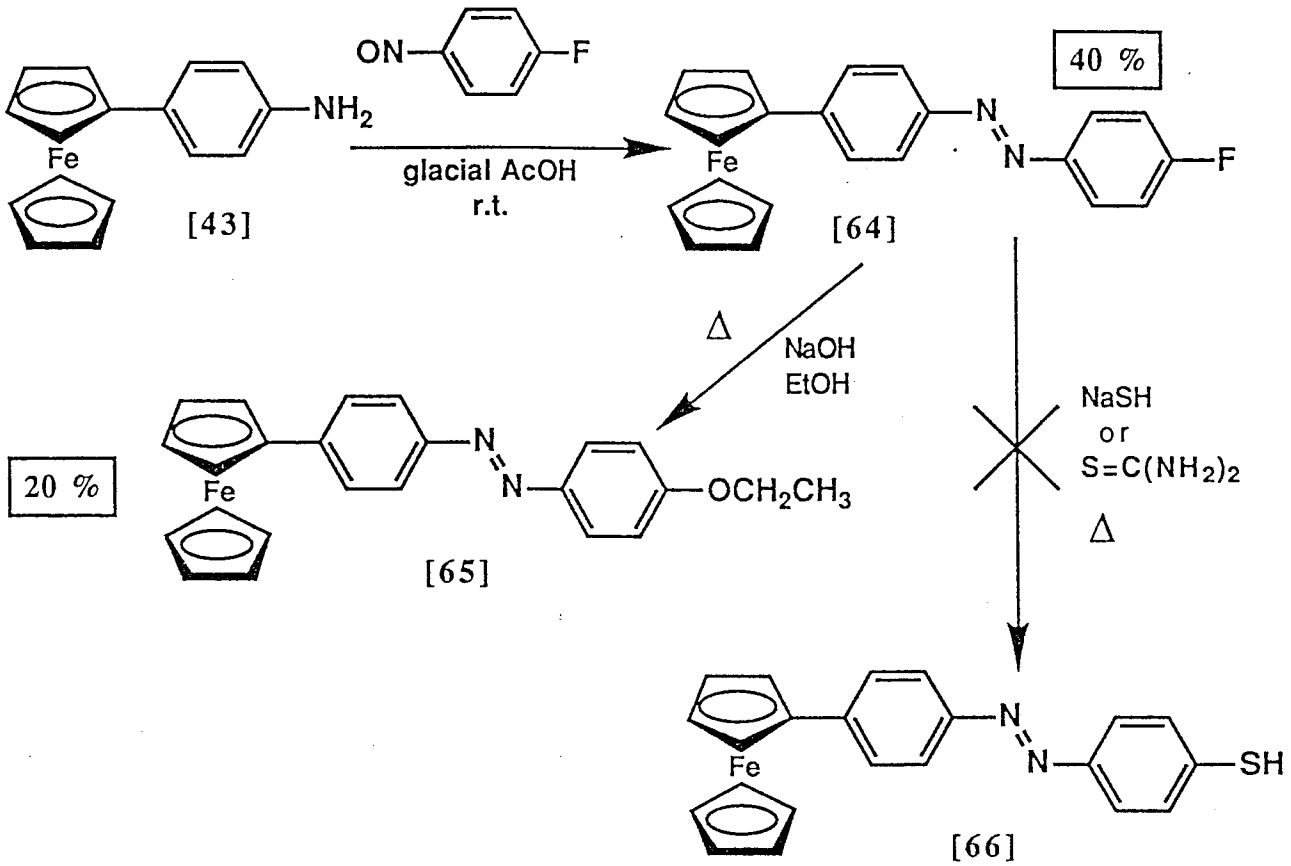
A successful displacement reaction on [64] using ethoxide ion in ethanol gave a high yield of the new compound 4-ethoxy-4'-ferrocenylazobenzene [65], thus proving that the fluorine is sufficiently activated towards nucleophilic displacement. Since sulphur species are generally held to be more nucleophilic than oxygen species, this seemed to suggest that the displacement of the fluorine by sulphur would be readily accomplished. However, a large number of attempts using hydrosulphide or thiourea in a variety of solvents both protic (ethanol) and non-protic (pyridine, acetonitrile, DMF, or DMSO) failed to produce even a trace of the desired product [66]. Sodium hydrosulphide was generated by the bubbling of hydrogen sulphide gas through a solution of sodium hydroxide in ethylene glycol, and thiourea was chosen as a possible alternative since it is a non-ionic species of similar nucleophilic strength to hydrosulphide.[226]

In all cases where reaction occurred the regeneration of 4-ferrocenylaniline was observed, implying that in the presence of sulphur compounds reductive cleavage of the azo linkage takes place before any fluoride displacement can occur. This is perhaps not too unexpected particularly as hydrosulphide solution inevitably contains dissolved hydrogen sulphide which is known to be a reducing agent. Further attempts at reaction using other sulphur nucleophiles such as disulphide might well prove fruitful, particularly as the azo linkage is known to survive sulphide ion

during the production of the earlier described amino-azo ligands. However, further investment of time and effort was deemed unwise in the context of this study and the preparation of [66] was abandoned in favour of other more productive ligand syntheses. The preparation of compounds [64] and [65] is shown in Fig. 24.

Fig. 24

Preparation and Reaction of 4-Fluoro-4'-ferrocenylazobenzene

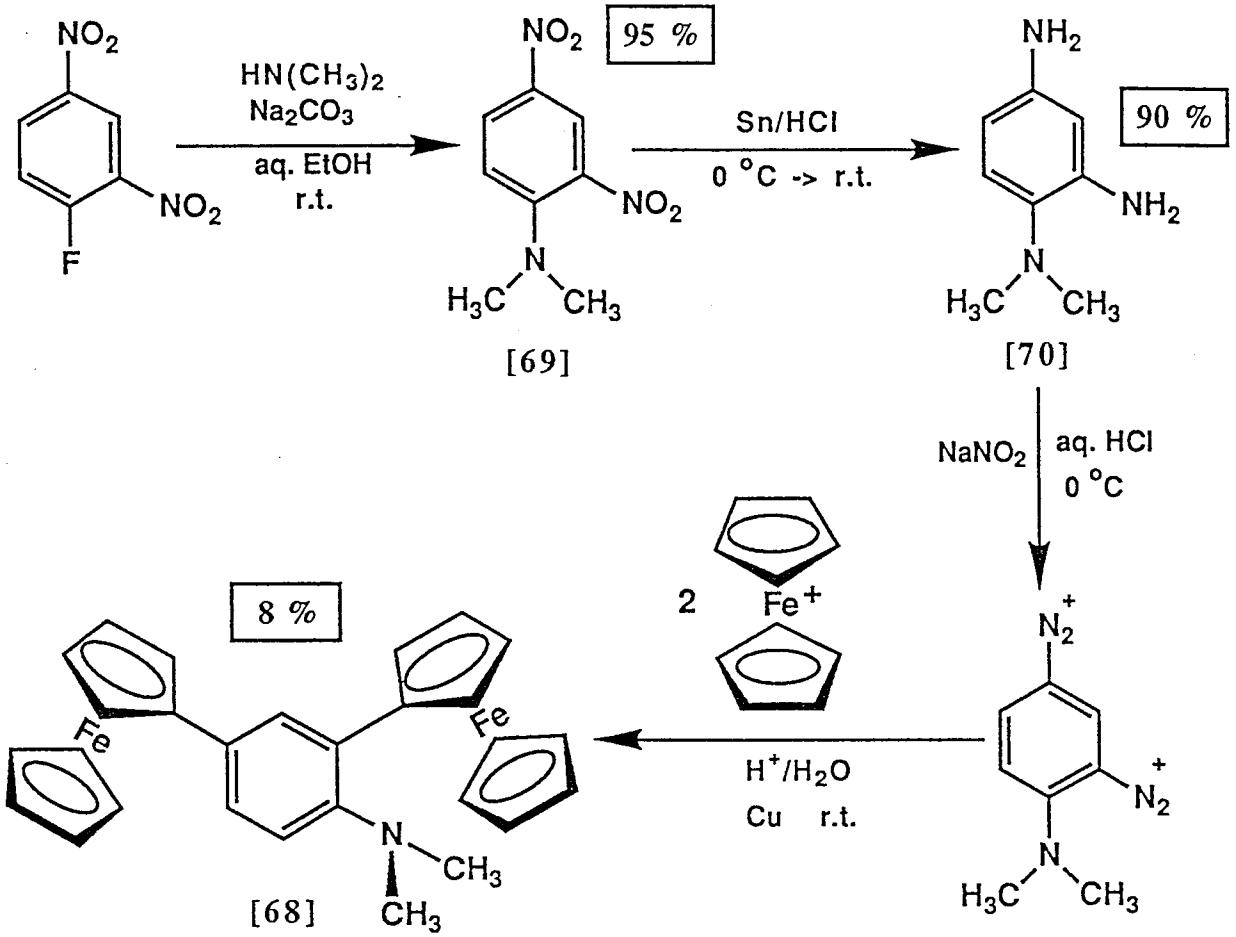


II-1.1(e) Attempted Preparation of a Bisferrocenyl Ligand

Another unsuccessful ferrocenyl ligand synthesis resulted in the preparation of the novel compound 2,4-bisferrocenyl-N,N-dimethylaniline [68]. The related compounds 1,4-bisferrocenyl-benzene and 1,3-bisferrocenylbenzene have been known for many years,[227] but [68] is a new derivative. This was prepared in low yield from the reaction of the diazonium salt of 2,4-diamino-N,N-dimethylaniline with ferrocenium ion, as shown in Fig. 25.

Fig. 25

Preparation of 2,4-Bisferrocenyl-N,N-dimethylaniline



The reactions used to prepare the known organic precursors [69] and [70] differ from the usual literature methods, and are hence reported in the experimental section II-2. The intention was to prepare a bisferrocenylaniline ligand by a simple demethylation of [68] using cyanogen bromide[228] in dry toluene, but no reaction was observed even under forcing conditions. This is likely to be due to some sort of steric hindrance effect exerted by the *ortho* ferrocenyl group, and a precedent for such behaviour in some dimethylamino biphenyl compounds has in fact been reported.[229] Other reagents such as phosgene[230] are available for the dealkylation of tertiary aromatic amines, but these reactions tend to involve rather severe conditions. Since this might destroy the ferrocenyl groups as well as achieving demethylation, this idea was not further investigated.

II-1.2 PHYSICAL CHARACTERISATION

All of the ferrocenyl precursors and ligands were characterised using i.r. and ^1H n.m.r. spectroscopy, EI mass spectrometry, elemental analyses, and melting point. These techniques all gave results in accord with the proposed molecular formulations (see experimental section II-2) and will be given only brief consideration here. Electrochemical and u.v.-visible solution absorption data were recorded for selected compounds, and the results of these studies are reported in more detail in sections II-1.2(e) and II-1.2(f) respectively.

II-1.2(a) Elemental Analyses

All compounds gave satisfactory analyses for C, H, (and N), except for the bis-azo compounds [49] and [56] which both retain a small amount of dichloromethane of crystallisation; the presence of the quoted amounts of solvent was also shown in ^1H n.m.r. spectra.

II-1.2(b) Infra-Red Spectroscopy

Aside from the usual aromatic absorptions around 1600 cm^{-1}, mono-arylferrocenes exhibit a medium intensity band at *ca.* 890 cm^{-1} which can be observed in the spectra of all the compounds discussed here. This band is quite characteristic of such substances, and may be associated with a C-H bending mode of the ferrocene ring.[231] Compounds which possess other functionalities also show the usual characteristic absorptions for NH_2, OH, CN, CHO, and NO_2.

II-1.2(c) ^1H n.m.r. Spectroscopy

All compounds showed signals associated with aryl protons with shifts greatly dependent upon the nature of close substituents as would be expected. In particular, reduction of nitro precursors to amino ligands can cause upfield shifts as large as 1.7 ppm (proton

9 in [56], [49]) due to the change from strongly deshielding nitro acceptor group to strongly shielding amino donor group. In the fluoro compound [64] ^1H-^{19}F coupling is observed along with ^1H-^1H aryl splittings, and coupling constants of $J(HF)_{ortho} \simeq 9.0$ Hz and $J(HF)_{meta} \simeq 5.2$ Hz have been derived. These values compare favourably with the usual couplings in fluoroaryl molecules. In the stilbene species, the ethylene bridge signals give a coupling constant of $\simeq$ 16 Hz which shows that the expected *trans* stereochemistry is present.

Ferrocenyl groups give rise to the expected patterns; the unsubstituted C_5H_5 ring giving a singlet at essentially the same position as ferrocene itself, and the monosubstituted C_5H_4 ring giving an unsymmetrical pair of triplets corresponding to the spectrum of an A_2B_2 case with J(adjacent) $\cong$ J(cross) and small compared to the chemical shift difference between $H_{2,5}$ and $H_{3,4}$.[232] These triplets appear to low field of the C_5H_5 singlet, showing that all four ring protons are deshielded by the aryl ring irrespective of whether the aryl ring bears donor or acceptor substituents. The exact positions of these triplets change to a small extent (up to *ca.* 0.25 ppm) with variation of aryl substituent, and both pairs of equivalent protons 2 and 5 and 3 and 4 seem to be affected similarly.

Hydroxy, amino and formyl functions give the expected singlet signals, and the azo compounds give OH and NH_2 signals which are at lower field by *ca.* 0.5 ppm compared to their mono-aryl counterparts, implying decreased H-bonding in the former. This is likely to be a result of electron-withdrawal by the azo function rendering the amino or hydroxy groups less electron-rich and therefore less able to form H-bonds.

II-1,2(d) Mass Spectrometry

All compounds show intense molecular ion peaks, and fragmentation patterns are as would be expected for simple aryl compounds; *e.g.* nitro compounds show loss of NO_2 (M - 46) and generally loss of NO (M - 30). Fragments containing iron show ion envelopes with peak intensities in accord with the isotopic

distribution of iron. In most cases only a few peaks of high intensity are observed, and other peaks of low intensity are not reported.

II-1,2(e) Cyclic Voltammetry

The electrochemical properties of all of the nitro ferrocenyl compounds and most of the other derivatives were investigated in dichloromethane solution using cyclic voltammetry and the results obtained are presented in Table V.

By comparison of ΔE_p values with that of the ferrocene standard it is clear that several of the compounds show reversible or quasi-reversible one-electron iron oxidation waves. In cases where ΔE_p is much above 100 mV, the oxidation process may be chemically reversible but electrochemically irreversible (*i.e.* slow electron-transfer occurs). The large range of E_f values demonstrates that the oxidation potential is highly sensitive to substitution on the aryl ring directly attached to ferrocene. The vast difference of some 220 mV between 4-aminophenylferrocene [43] and 4-nitrophenylferrocene [51] shows how much influence close substituents can have on the electron density at the iron centre. The electron donor amino group renders the iron more electron rich than in ferrocene itself, and an 80 mV cathodic shift is produced. On the other hand, the strongly electron withdrawing nitro group significantly depletes the electron density at the iron giving rise to a 140 mV anodic shift in redox potential. Comparison of [51] and [52] shows a 40 mV cathodic shift from 4-nitrophenylferrocene as an *ortho* methyl group is added to the benzene ring.

The results for compounds [45], [46] and [53] show that a small degree of electronic communication through the azo bridge can be detected, but the shifts are not particularly large. Comparison of [46] and [50] and [53] and [57] shows that moving from diphenylazo to stilbenyl produces a 50 mV cathodic shift which is in keeping with the superior electron withdrawing nature of the azo function as well as its greater electronic conduction ability. An additional irreversible wave at highly cathodic potential is observed in compounds with nitro groups, and a pair

of such waves are seen for the nitro-azo compounds. These may be attributed to purely organic reduction processes of such functionalities, but their study is outside the scope of this project.

TABLE V

Cyclic Voltammetry Data for Ferrocenyl Compounds

4-Fc-Z [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$]

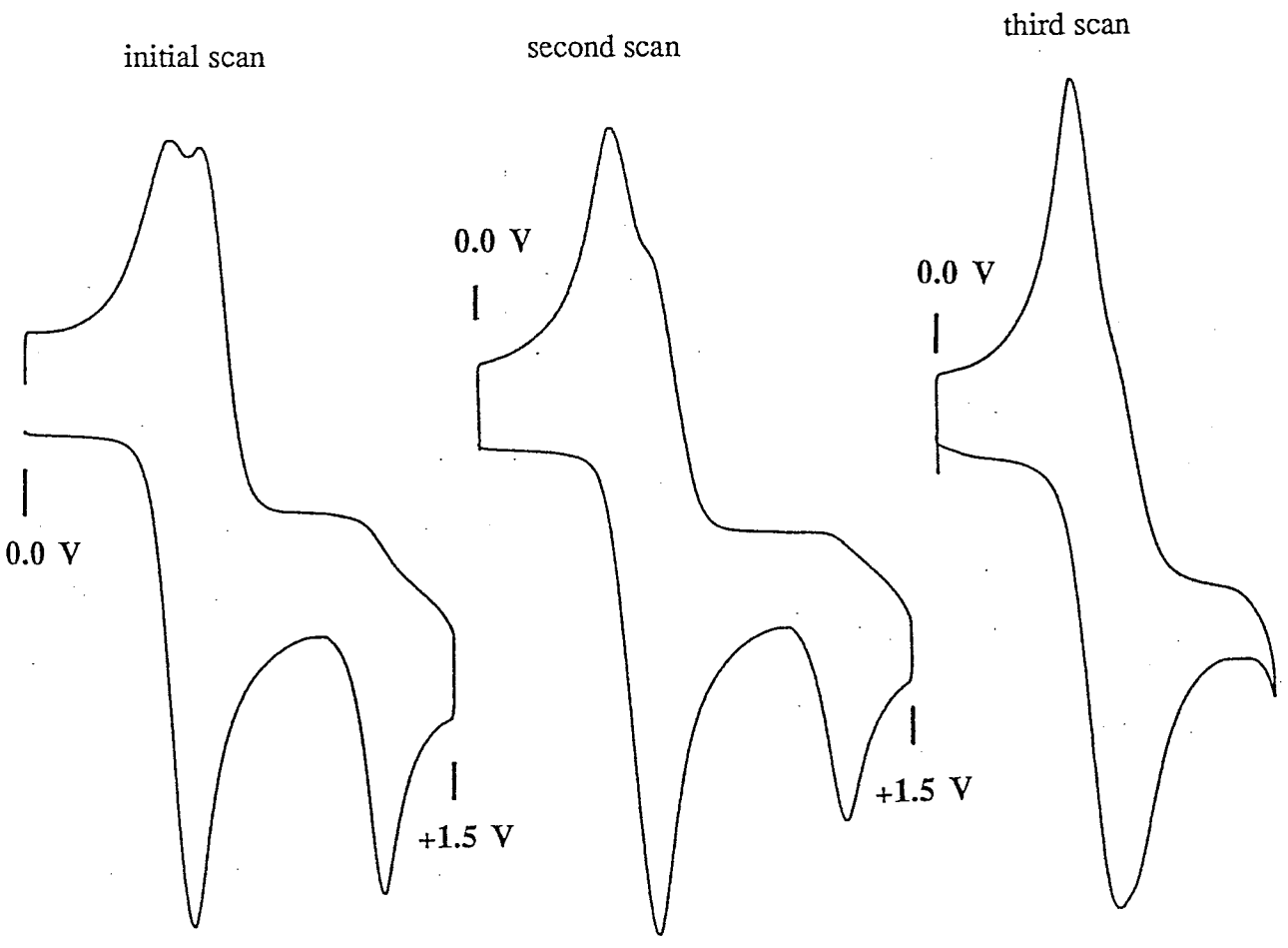
Z[a] (compound no.)	E_f [Fe]/V[b]	ΔE_p/mV	Other waves [E_f (ΔE_p)]
ΦNH_2 [43]	+0.49	420	
ΦOH [42]	+0.53	240	
$\Phi CH{=}CH\Phi NH_2$ [50]	+0.55	150	
H (ferrocene)	+0.57	70	
$\Phi N{=}N\Phi OH$ [45]	+0.59	70	
$\Phi N{=}N\emptyset NH_2$ [47]	+0.59	155	
$\Phi CH{=}CH\Phi NO_2$ [57]	+0.59	115	−0.93 (185)
$\Phi N{=}N\Phi NH_2$ [46]	+0.60	110	
$\emptyset N{=}N\emptyset NO_2$ [55]	+0.62	90	−0.77 (90)
			−1.03 (85)
$\emptyset N{=}N\emptyset N{=}N\emptyset NO_2$ [56]	+0.62	95	−0.70 (155)
			−1.79 (200)
$\Phi N{=}N\Phi NO_2$ [53]	+0.64	145	−0.73 (160)
			−1.02 (170)
$\Phi N{=}N\emptyset NO_2$ [54]	+0.64	185	−0.76 (195)
			−1.03 (170)
ΦCHO [58]	+0.65	130	
ΦCN [59]	+0.67	180	
$\emptyset NO_2$ [52]	+0.67	100	−1.04 (115)
ΦNO_2 [51]	+0.71	170	−0.98 (470)

[a] $\Phi = -C_6H_4-$, $\emptyset = -C_6H_3\text{-}2\text{-}CH_3-$. [b] All potentials measured relative to SCE in dry CH_2Cl_2 using a platinum-bead working electrode; 0.2 M $[NBu_4][BF_4]$ as supporting electrolyte; scan rate 200 mV s^{-1}.

Earlier work has contained reports of electrochemical studies on several of the compounds discussed here along with a number of other derivatives. These have involved the measurement of oxidation potentials using potentiometric titrations,[233] and also the study of chronopotentiometric[234] and polarographic[235] potentials. All have demonstrated that the electrochemical behaviour of mono-aryl ferrocenes is markedly dependant upon the electronic nature of substituent groups attached to the aryl ring, a trend which is reinforced by this c.v. study. Chronopotentiometric measurements on several 4'-substituted-4-ferrocenylazobenzenes, including [53], have shown that the quarter-wave potentials are not greatly influenced by the nature of the 4'-substituent which also agrees with the results reported here.

Fig. 26

Cyclic Voltammogram for 2,4-Bisferrocenyl-N,N-dimethylaniline



The electrochemistry of the bisferrocenyl compound [68] was also investigated (Fig. 26), but is clearly of a more complex nature than that observed for the monoferrocenyl derivatives. An initial scan to anodic potential reveals two close peaks at +0.50 and +0.63 V, and upon reverse scan an irreversible wave at +1.26 V is recorded along with a single peak at +0.59 V. However, repeated scanning between 0.0 and +1.0 V gives rise to a merging of the two close peaks to produce a single wave which appears quasi-reversible. It seems likely that the irreversible wave at +1.26 V may be associated with oxidation of the dimethylamino group; other dimethylamino-substituted aromatics, which are discussed in Chapter Three, have been found to give similar waves. Furthermore, either one or two waves can be observed for the oxidation of the two mutually *meta* ferrocenyl groups depending upon the point at which the scan is reversed. This suggests some sort of interaction occurring between the dimethylamino group and the ferrocenyl moiety *ortho* to it.

II-1.2(f) U.V.-Visible Absorption Spectra and Solvatochromism Studies

The study of electronic absorption spectra in solution is of considerable importance to the preparation of molecules for NLO for two reasons. Firstly, in order to understand how a compound will interact with laser light it is necessary to know at which wavelengths transparency can be expected and where the compound will absorb significant amounts of light. This has been discussed earlier, but is reiterated here because of its importance. Transparency at the fundamental frequency (usually 1,907 or 1,064 nm) is desirable, and any absorption at harmonic frequencies (usually 953 or 532 nm) will affect the amount of SHG observed from a solid sample. For the purposes of SHG into the visible, the onset of absorption closer to the u.v. is desirable, but this is not essential for other properties such as the linear electro-optic effect.

Another aspect of importance is the phenomenon of solvatochromism *i.e.* solvent-induced shifts in absorption spectra.

This arises from dipolar interactions between solvent and solute molecules, and hence the greatest changes in absorption spectra are observed between solvents of largely differing polarity (*e.g.* n-hexane and DMF). Previous reports have noted that the occurrence of significant solvatochromism is often an indicator of high molecular β,[41] and hence may imply bulk NLO properties. As regards metal-organic compounds, relationships between solvatochromism and MLCT excitations have been drawn,[236] and the compound (*cis*)-[1-ferrocenyl-2-(4-nitrophenyl)ethylene] [26] is an example of a species which displays marked solvatochromism and also high powder SHG.[129] However, despite some efforts to establish a direct correlation between solvatochromism and NLO properties,[237] none has been found.

The electronic absorption spectra of a number of the compounds described here have already been investigated in detail by other workers. Of the mono-aryl ferrocenes, 4-aminophenyl- and 4-hydroxyphenylferrocene exhibit two broad absorptions, one in the visible and one in the u.v. with the former having the greater extinction coefficient. 4-Nitrophenylferrocene shows three bands with two in the u.v. region. The visible band in particular shows marked bathochromic shifts as more electron-withdrawing aryl substituents are introduced, and is thought to be due to an MLCT excitation.[238] For the ferrocenylazobenzenes,[219] again two bands are present and similar shifts are observed implying large resonance interactions between 4-ferrocenyl and 4'-substituents occurring via the azobenzene bridge.

Spectra were recorded in dichloromethane for a number of the ferrocenyl compounds both new and previously reported, and results are presented in Table VI along with several useful reference compounds.

A solvatochromism study was carried out on the compound 4-nitro-2-methyl-4'-ferrocenylazobenzene [54] involving eight solvents of differing nature, but only modest shifts of up to 24 nm were observed. Results are presented in Table VII.

TABLE VI

U.V.-Visible Excitation Maxima for Ferrocenyl Compounds

4-Fc-Z [Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$]

Z[a] (compound no.)	λ_{max}/nm[b]	ε/mol^{-1} dm^3 cm^{-1}
ΦNH$_2$ [43]	287	16,800
	437	350
ΦOH [42]	282	11,100
	442	290
ΦNO$_2$ [51]	324	8,600
	396	2,600
	500	2,800
ΦN=NØNH$_2$ [47]	390	29,900
	470[c]	9,300[c]
ΦN=NΦOH [45]	356	29,000
	476	5,300
ΦN=NΦNO$_2$ [53]	372	26,500
	540	6,300
ΦN=NØNO$_2$ [54]	374	24,200
	536	5,900
ferrocene[d]	326	50
	440	87
azobenzene[a]	316	21,200
	441	519
4-ferrocenylazobenzene[a]	350	25,100
	488	4,640

[a] Φ = $-C_6H_4-$, Ø = $-C_6H_3\text{-}2\text{-}CH_3-$. [b] All spectra recorded in dichloromethane at ambient temperature; concentrations of *ca.* 10^{-5} M for u.v. spectra and *ca.* 10^{-4} M for visible spectra were used. [c] Estimated values; absorption appears as close shoulder on main peak. [d] In absolute ethanol.[239] [a] In absolute ethanol.[219]

TABLE VII

Solvatochromism Study for 4-Nitro-2-methyl-4'-ferrocenylazobenzene

Solvent	λ_{max} (vis.)[a]	λ_{max} (u.v.)[b]
n-pentane	518	368
ethyl acetate	526	371
methanol	528	370
acetone	529	370
ethanol	531	373
chloroform	536	372
dichloromethane	536	374
DMF	542	379

[a] Spectra recorded at ambient temperature using concentrations of *ca.* 10^{-4} M. [b] Spectra recorded at ambient temperature using concentrations of *ca.* 10^{-5} M.

II-1.3 KURTZ POWDER TESTS

Of the various ferrocenyl compounds synthesised, several appear to have molecular structures which could be expected to possess large β values. The actual ligands themselves all have a ferrocenyl donor group at one end and either an amino or hydroxy group at the other. Since these represent systems with a donor group at both ends of their π-systems, they would not appear to be good candidates for significant NLO properties. However, all of the seven nitro ligand precursors [51]-[57] have ferrocenyl donors along with powerful nitro acceptors, and these were tested for powder SHG using a 1,907 nm fundamental.

None of the compounds [51]-[56] gave any detectable SHG ([51], [53], and [54] were tested at GEC, and [52], [55], and [56] at Durham), but the stilbenyl nitro compound [57] did give significant SHG. This compound, tested at Durham University, gave a signal about 1.0 times urea (under the same conditions, DAN gave

5.0 times urea). The nitrile [59], aldehyde [58], and fluoro [64] derivatives could also be good candidates for NLO properties but these have not been powder tested.

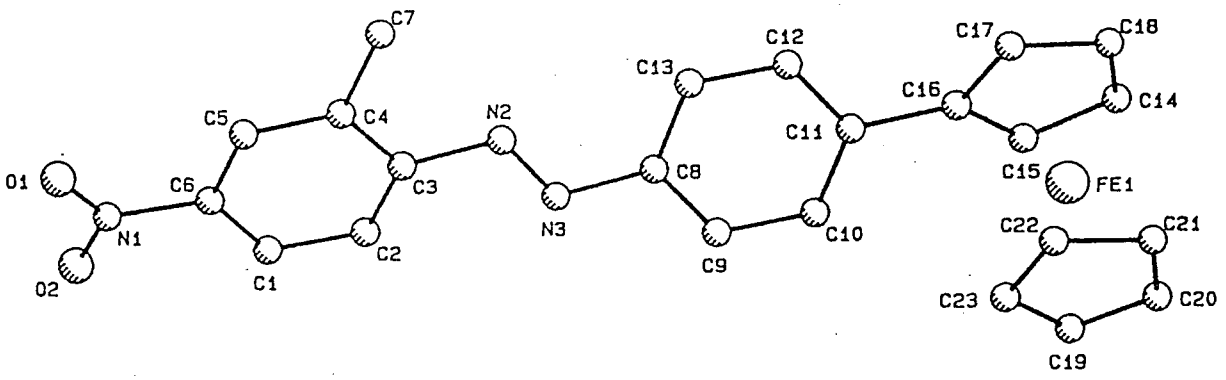
II-1.4 STRUCTURAL STUDIES

II-1.4(a) Single Crystal Structure of 4-Nitro-2-methyl-4'-ferrocenylazobenzene [54]

Compound [54], which exhibits no powder SHG despite its favourable molecular structure, readily forms large purple diamond-shaped crystals when allowed to crystallise from dichloromethane by slow evaporation at room temperature. In order to establish why this compound does not show bulk NLO effects, a single crystal X-ray diffraction study was carried out by J-D. Foulon and T. A. Hamor at the University of Birmingham.

Fig. 27

Molecular Structure of 4-Nitro-2-methyl-4'-ferrocenylazobenzene



The molecular structure (Fig. 27) is entirely as expected. The azobenzene residue has the *trans* configuration, with a C-N-N-C torsion angle of 177.2(7)°, and an N=N bond length of 1.238(6) Å. The cyclopentadienyl rings of the ferrocenyl moiety are eclipsed with Fe-C distances between 2.005(7) and 2.053(6) Å, mean 2.034(4) Å. The rings are inclined at 2.7(6)° to one another, and the C_5H_4 ring is rotated by 27.9(6)° relative to the plane of the attached

phenyl ring about the C-C linking bond. The distances between the Fe atom and the ring centroids are 1.643 and 1.647 Å, and the angle subtended at Fe by the ring centroids is 177.7°, so that the iron atom lies very close to the centroid of the ferrocenyl residue. Inspection of the bond lengths N-C (nitro-phenyl), C-N (phenyl-azo), and C-C (phenyl-cyclopentadienyl) indicates that there is no significant electronic delocalisation in the ground state of the molecule. The parameters for the phenylferrocene group are similar to those found previously in other compounds such as 4-biphenylferrocene,[240] and the *ortho*-, *meta*-, and *para*-nitrophenylferrocenes.[241]

It is the crystal packing diagram (Fig. 28) which is of rather more interest from the NLO viewpoint. The space group adopted is the monoclinic centrosymmetric $P2_1/c$. The unit cell parameters are; a = 15.020(9), b = 7.555(2), c = 18.134(15) Å, β = 112.22(6)°, V = 1905 Å^3. The unit cell contains 4 molecules, and it can be clearly seen how these align antiparallel to give the complete cancellation of dipoles which precludes any bulk NLO effects. It seems likely that similar centrosymmetric packing arrays may occur in the other ferrocenyl compounds which show no SHG activity. This packing is likely to be a result of the "L-shaped" nature of the arylferrocene units.

II-1-4(b) Powder Diffraction Studies

In fact, powder X-ray diffraction studies show that the two azo derivatives [53] and [54] adopt different crystal packing arrangements. This is perhaps surprising, because the structural effects of the methyl substituent might be expected to be minimal. However, since compound [53] exhibits no SHG, it must also adopt a centrosymmetric packing, albeit different from that adopted by [54]. Clearly, the SHG-active stilbene compound [57] must have a non-centrosymmetric crystal structure which is different from either of those found with the azo compounds. Again, this is perhaps a surprising result in view of the similarity to its azo-analogue [53]. Powder X-ray diffraction traces for [57] and [53] show that these two compounds do indeed adopt different packing

arrangements, but in the absence of a single crystal structure of [57] no more can be said about this result at present. Powder diffraction traces for [53], [54], and [57] are shown in Fig. 29.

Fig. 28
Crystal Packing Diagram for
4-Nitro-2-methyl-4'-ferrocenylazobenzene

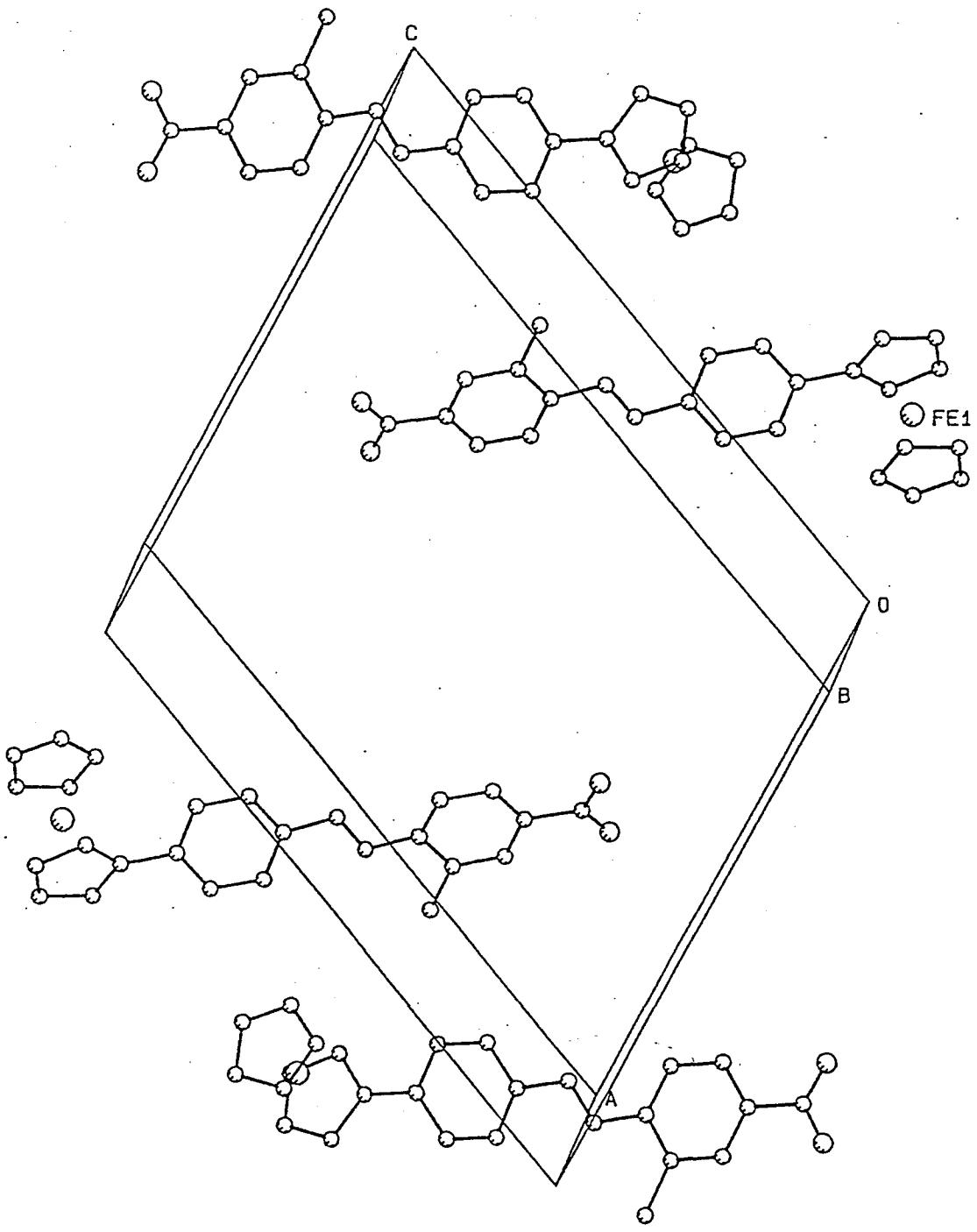
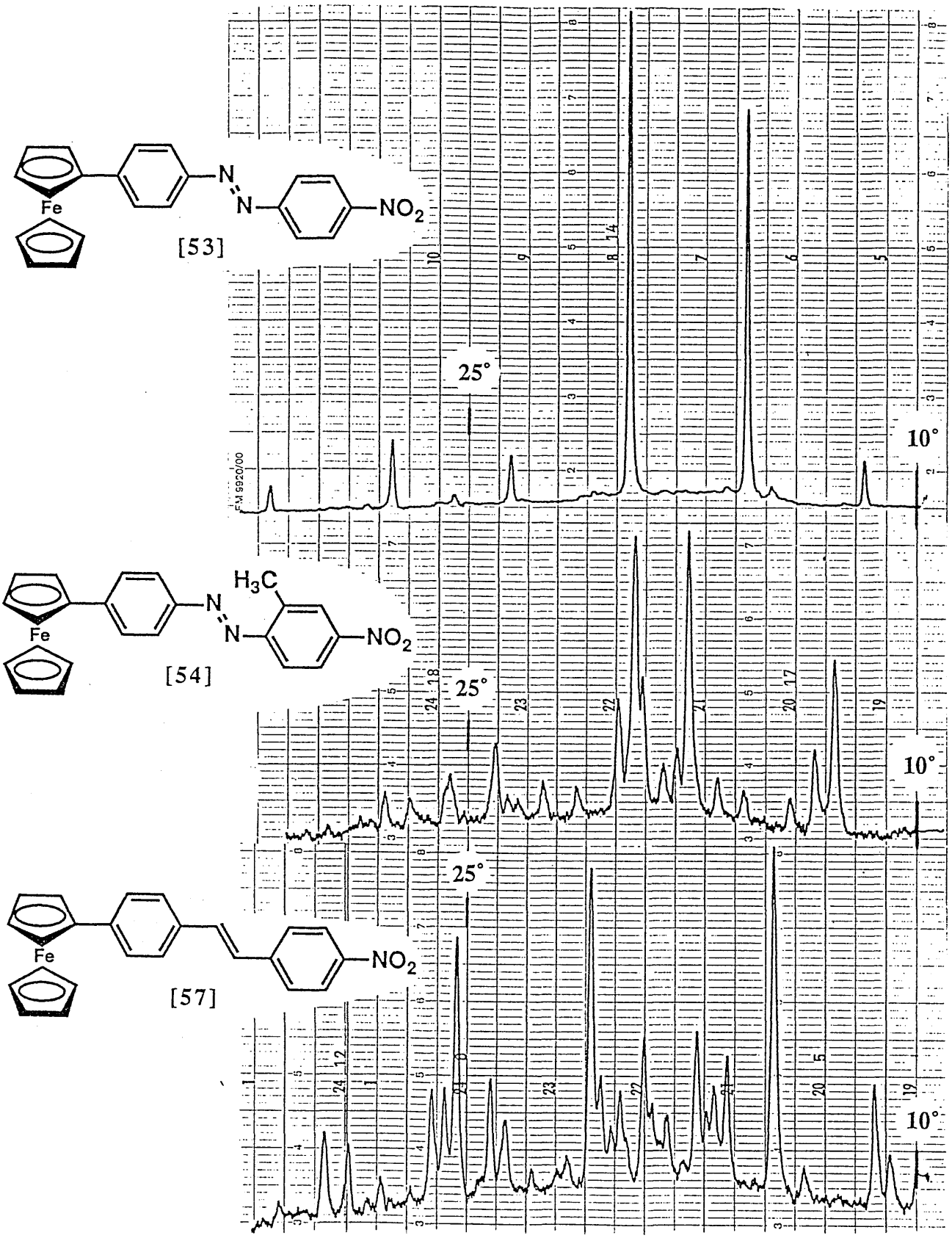


Fig. 29

Powder X-ray Diffraction Traces for Ferrocenyl Compounds



II-2 EXPERIMENTAL

All commercial reagents were used as supplied unless otherwise specified. Silica gel 60 (70-230 mesh) was used for all column chromatographic separations which were carried out on a column of dimensions 50 x 3.5 cm unless otherwise specified.

4-Nitrophenylferrocene [51]

Ferrocene (3.80 g, 20.4 mmol) was added to sulphuric acid (s.g. 1.84, 25 cm^3) and the resulting deep blue ferrocenium solution stirred at room temperature for 2 h. After this time the solution was poured into iced water (100 cm^3) and allowed to warm to room temperature. A solution of sodium nitrite (0.91 g, 13.2 mmol) in water (5 cm^3) at 0 °C was added dropwise to a stirred solution of 4-nitroaniline (1.66 g, 12.0 mmol) in 1:1 water/hydrochloric acid (s.g. 1.18) (10 cm^3) kept at 0 °C by an ice/water bath. This was stirred for 30 min to ensure full diazotisation. Copper powder (1.0 g) was added to the ferrocenium solution and the diazonium solution was added dropwise whilst the mixture was stirred vigorously by an overhead mechanical stirrer.

After stirring at room temperature for 24 h, effervescence due to liberated nitrogen had ceased and ascorbic acid (5 g) was added to the dark reaction mixture to reduce any remaining ferrocenium back to ferrocene. Dichloromethane (100 cm^3) was added and the organic layer separated using a separating funnel. The aqueous layer was extracted with further dichloromethane (4 x 50 cm^3), and the combined organic extracts were filtered through celite before removal of the solvent *in vacuo* to give a dark solid. This was separated into its components by column chromatography using gradient elution with an increasing proportion of dichloromethane in n-hexane. The first yellow fraction eluted in pure n-hexane yielded unreacted ferrocene, and the second eluted with 40% dichloromethane/n-hexane produced upon evaporation deep red-purple microcrystalline 4-nitrophenyl-ferrocene (1.33 g, 36%). A third deep purple fraction was also collected using 60% dichloromethane/n-hexane as eluent; t.l.c. on

alumina revealed that this contained a mixture of at least three compounds which were likely to be bis-arylated ferrocene derivatives. This fraction was not further investigated.

$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_4\text{-}4\text{-}NO_2$, m.p. 166-169 °C (lit.,[216] 169-170 °C) (Found: C, 62.4; H, 4.3; N, 4.5%; M^+, 307. $C_{16}H_{13}FeNO_2$ requires C, 62.6; H, 4.3; N, 4.6%; M, 307); $\nu_{max.}(NO_2)$ 1505s and 1340s cm^{-1}; $\delta_H(CDCl_3)$ 8.14 and 7.56 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4], 4.74 and 4.47 [2 H, d, J(HH) 1.8 Hz; 2 H, d, J(HH) 1.6 Hz, C_5H_4], 4.06 [5 H, s, C_5H_5]; *m/z* 307 (M^+), 261 (M - NO_2), 121 (M - $C_{11}H_8NO_2$).

4-Hydroxyphenylferrocene [42]

This compound was prepared in an identical manner to [51] using 4-aminophenol (1.31 g, 12.0 mmol) in place of 4-nitroaniline. Again column chromatography using gradient elution was used to separate the products. The first yellow fraction yielded ferrocene, and the second major fraction eluted in 100% dichloromethane yielded orange-yellow microcrystalline 4-hydroxyphenylferrocene (0.87 g, 26%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_4\text{-}4\text{-}OH$, m.p. 161-165 °C (lit.,[242] 165 °C) (Found: C, 69.0; H, 5.4%; M^+, 278. $C_{16}H_{14}FeO$ requires C, 69.1; H, 5.1%; M, 278); $\nu_{max.}(OH)$ 3520s cm^{-1}; $\delta_H(CDCl_3)$ 7.36 and 6.77 [2 H, d, J(HH) 8.2 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 4.61 [1 H, br s, OH], 4.56 and 4.26 [2 H, d, J(HH) 1.6 Hz; 2 H, d, J(HH) 1.6 Hz, C_5H_4], 4.03 [5 H, s, C_5H_5]; *m/z* 278 (M^+), 157 (M - C_5H_5Fe), 121 (M - $C_{11}H_9O$).

4-Cyanophenylferrocene [59]

This compound was prepared in an identical manner to [51] using 4-aminobenzonitrile (1.42 g, 12.0 mmol) in place of 4-nitroaniline. Again column chromatography using gradient elution was used to separate the products. The first yellow fraction yielded ferrocene, and the second major fraction eluted in 60% dichloromethane yielded orange-red microcrystalline 4-cyanophenylferrocene (1.34 g, 39%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_4\text{-}4\text{-}CN$, m.p. 139-142 °C (lit.,[234] 145-146 °C) (Found: C, 70.8; H, 4.7; N, 5.0%; M^+, 287. $C_{17}H_{13}FeN$ requires C,

71.1; H, 4.6; N, 4.9%; M, 287); $\nu_{max.}$(CN) 2220s cm^{-1}; $\delta_H(CDCl_3)$ 7.56 and 7.51 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4], 4.69 and 4.42 [2 H, t, J(HH) 1.8 Hz; 2 H, d, J(HH) 1.8 Hz, C_5H_4], 4.04 [5 H, s, C_5H_5]; *m/z* 287 (M^+), 222 (M - C_5H_5), 166 (M - C_5H_5Fe), 121 (M - $C_{12}H_8N$)

4-Nitro-2-methylphenylferrocene [52]

This compound was prepared in an identical manner to [51] using 2-methyl-4-nitroaniline (1.83 g, 12.0 mmol) in place of 4-nitroaniline. Again column chromatography using gradient elution was used to separate the products. The first yellow fraction yielded ferrocene, and the second major fraction eluted in 50% dichloromethane yielded deep red-purple microcrystalline 4-nitro-2-methylphenylferrocene (1.31 g, 34%).
$(\eta^5-C_5H_5)Fe(\eta^5C_5H_4)-C_6H_3-2-CH_3-4-NO_2$, m.p. 122-125 °C (lit.,[234] 127-129 °C) (Found: C, 63.6; H, 4.9; N, 4.1%; M^+, 321. $C_{17}H_{15}FeNO_2$ requires C, 63.6; H, 4.7; N, 4.4%; M, 321); $\nu_{max.}(NO_2)$ 1505s and 1340s cm^{-1}; $\delta_H(CDCl_3)$ 8.01 and 7.98 [1½ H, br s, C_6H_3(3 and 2); ½ H, s, C_6H_3(2)] 7.78 [1 H, d, J(12) 9.1 Hz, C_6H_3(1)], 4.58 and 4.42 [2 H, d, J(HH) 1.8 Hz; 2 H, d, J(HH) 1.6 Hz, C_5H_4], 4.13 [5 H, s, C_5H_5], 2.51 [3 H, s, CH_3]; *m/z* 321 (M^+), 291 (M - NO), 275 (M - NO_2), 121 (M - $C_{12}H_{10}NO_2$).

4-Nitro-4'-ferrocenylazobenzene [53]

This compound was prepared in an identical manner to [51] using 4-nitro-4'-aminoazobenzene [63] (2.91 g, 12.0 mmol) in place of 4-nitroaniline. [63] was obtained by an overnight Soxhlet extraction of the commercial dye Disperse Orange 3 using dichloromethane. Again column chromatography using gradient elution was used to separate the products. The first yellow fraction yielded ferrocene, and the second major purple-red fraction eluted in 100% dichloromethane yielded deep emerald green microcrystalline 4-nitro-4'-ferrocenylazobenzene (0.35 g, 7%).
$(\eta^5-C_5H_5)Fe(\eta^5C_5H_4)-C_6H_4N=NC_6H_4-4-NO_2$, m.p. 246-249 °C (lit.,[219] 260 °C dec.) (Found: C, 64.4; H, 4.3; N, 10.4%; M^+, 411. $C_{22}H_{17}FeN_3O_2$ requires C, 64.3; H, 4.2; N, 10.2%; M, 411); $\nu_{max.}(NO_2)$ 1520s and 1345s cm^{-1}; $\delta_H(CDCl_3)$ 8.39 and 8.03 [2 H, d, J(HH) 9.2 Hz; 2 H, d,

J(HH) 9.2 Hz, C_6H_4-NO_2] 7.91 and 7.63 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4-Fc], 4.77 and 4.45 [2 H, s; 2 H, s, C_5H_4], 4.08 [5 H, s, C_5H_5]; *m/z* 411 (M^+), 365 (M - NO_2), 261 (M - $N_2C_6H_4NO_2$).

2,4-Dinitro-N,N-dimethylaniline [69]

A solution of 2,4-dinitrofluorobenzene (10.0 g, 54 mmol) in ethanol (100 cm^3) was added dropwise to a stirred solution of dimethylamine (10 cm^3, 151 mmol) and sodium carbonate (5 g) in a 1:1 water/ethanol mixture (100 cm^3) at room temperature. Immediate formation of a bright yellow precipitate was observed. After addition was completed, the mixture was stirred for 1 h. Water (200 cm^3) was added and the bright yellow product filtered off under suction. This was washed with water (100 cm^3) and dried in air to yield bright yellow needles of 2,4-dinitro-N,N-dimethylaniline (10.83 g, 95%). m.p. 82-85 °C (lit.,[243] 87 °C) $\nu_{max.}$(NO_2) 1530 and 1330 cm^{-1}; δ_H($CDCl_3$) 8.70 [1 H, d, J(12) 2.8 Hz, C_6H_3(1)] 8.23 and 8.20 [½H, d; ½H, d, J(12) 2.8 Hz, J(23) 9.5 Hz, C_6H_3(2)] 7.02 [1 H, d, J(23) 9.5 Hz, C_6H_3(3)] 3.07 [6 H, s, N(CH_3)$_2$].

2,4-Diamino-N,N-dimethylaniline [70]

A solution of [69] (10.0 g, 47 mmol) in ethanol (100 cm^3) was added dropwise to a stirred mixture of granulated tin (5.0 g), hydrochloric acid (s.g. 1.18, 50 cm^3) and ethanol (100 cm^3) kept at 0 °C in an ice-water bath. After addition was completed, the mixture was stirred for 1 h and then allowed to warm slowly to room temperature and stirred for a further 1 h. The disappearance of the yellow colour showed that reduction was complete. Water (100 cm^3) was added and the mixture adjusted to pH 11 by the addition of 40% aq. sodium hydroxide solution. Dichloromethane (100 cm^3) was added, the mixture agitated, and the organic layer separated. The aqueous layer was extracted with further dichloromethane (3 x 50 cm^3), and the combined organic extracts evaporated to yield crude 2,4-diamino-N,N-dimethylaniline as a pale brown oil (6.40 g, 90%) m.p. lit.,[244] 44 °C. $\nu_{max.}$(NH_2) 3410m and 3340m cm^{-1} (liquid film); δ_H($CDCl_3$) 6.84 [1 H, d, J(23) 8.8 Hz,

C_6H_3(3)] 6.09, 6.09, 6.09, 6.07, 6.06 [2 H, C_6H_3(1 and 2)], 3.98 and 3,42 [2 H, br s, NH_2; 2 H, br s, NH_2], 2.58 [6 H, s, $N(CH_3)_2$].

2,4-Bisferrocenyl-N,N-dimethylaniline [68]

This compound was prepared in an identical manner to [51] using [70] (6.40 g, 42.0 mmol) in place of 4-nitroaniline. Quantities of other reagents were also changed as follows; ferrocene (30.0 g, 161 mmol), sulphuric acid (s.g. 1.84, 200 cm^3), iced water (600 cm^3), sodium nitrite (3.17 g, 46 mmol), 1:1 water/conc. hydrochloric acid (s.g. 1.18) (30 cm^3), copper powder (2.0 g), ascorbic acid (30 g). Due to the large amounts of black material produced, the crude reaction mixture with dichloromethane was filtered through a no. 2 sinter under suction prior to separation of the organic layer. Again column chromatography was used to separate the products. A 90% n-hexane/dichloromethane mixture was used as the eluent, the first yellow fraction yielding ferrocene, and the second yellow fraction yielding orange-yellow microcrystalline 2,4-bisferrocenyl-N.N-dimethylaniline (1.64 g, 8%).

2,4-{(η^5-C_5H_5)Fe($\eta^5C_5H_4$)-}$_2$-C_6H_3-$N(CH_3)_2$ m.p. 123-129 °C (Found: C, 68.6; H, 5.7; N, 2.8%; M^+, 489. $C_{28}H_{27}Fe_2N$ requires C, 68.7; H, 5.6; N, 2.9%; M, 489); $\delta_H(CDCl_3)$ 7.86 [1 H, d, J(12) 2.4 Hz, C_6H_3(1)], 7.27 and 7.24 [½ H, d, J(12) 2.4 Hz; ½ H, d, J(12) 2.4 Hz, J(23) 8.3 Hz, C_6H_3(2)], 6.86 [1 H, d, J(23) 8.2 Hz, C_6H_3(3)], 2.51 [6 H, s, $N(CH_3)_2$], 4.75 and 4.29 [2 H, t, J(HH) 2.0 Hz; 2 H, t, J(HH) 2.0 Hz, C_5H_4], 4.63 and 4.12 [2 H, t, J(HH) 1.8 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.12 [5 H, s, C_5H_5], 4.09 [5 H, s, C_5H_5], 2.51 [6 H, s, $N(CH_3)_2$]; *m/z* 489 (M^+), 376 , 325, 305.

4-Aminophenylferrocene [43]

A mixture of granulated tin (2.0g) and [51] (2.0 g, 6.5 mmol) in 1:1 hydrochloric acid (s.g. 1.18)/ethanol (50 cm^3) was stirred at reflux for 2 h. After this time the resulting orange solution was cooled to room temperature and neutralised with 40% aq. sodium hydroxide solution. Water (100 cm^3) and dichloromethane (100 cm^3) were added, and the mixture filtered through dichloromethane/silica gel to remove inorganic salts. The orange

organic layer was separated and the aqueous layer extracted with further dichloromethane (3 x 30 cm^3). The combined organic extracts were evaporated to dryness to yield 4-amino-phenylferrocene as an orange powder (1.71 g, 95%)
(η^5-C_5H_5)Fe($\eta^5C_5H_4$)-C_6H_4-4-NH_2, m.p. 157-159 °C (lit.,[217] 159-160.5 °C) (Found: C, 69.3; H, 5.7; N, 5.1%; M^+, 277. $C_{16}H_{15}FeN$ requires C, 69.3; H, 5.5; N, 5.1%; M, 277); $\nu_{max.}(NH_2)$ 3445m and 3355m cm^{-1}; $\delta_H(CDCl_3)$ 7.29 and 6.63 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 4.53 and 4.23 [2 H, t, J(HH) 1.9 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.03 [5 H, s, C_5H_5], 3.62 [1 H, br s, NH_2]; *m/z* 277 (M^+), 156 (M - C_5H_5Fe), 121 (M - $C_{11}H_{10}N$).

4-Amino-2-methylphenylferrocene [44]

This compound was prepared in an identical manner to [43] using [52] (1.89 g, 6.5 mmol) in place of [51]. This produced orange 4-amino-2-methylphenylferrocene (1.70 g, 90%).
(η^5-C_5H_5)Fe($\eta^5C_5H_4$)-C_6H_3-2-CH_3-4-NH_2, m.p. 87-91 °C (Found: C, 70.5; H, 6.2; N, 5.0%; M^+, 291. $C_{17}H_{17}FeN$ requires C, 70.1; H, 5.9; N, 4.8%; M, 291); $\nu_{max.}(NH_2)$ 3410m and 3340m cm^{-1}; $\delta_H(CDCl_3)$ 7.50 [1 H, d, J(12) 8.1 Hz, C_6H_3(1)], 6.55 and 6.52 [½ H, d, J(23) 2.6 Hz; ½ H, d, J(23) 2.4, J(12) 8.2 Hz, C_6H_3(2)], 6.48 [1 H, d, J(23) 1.8 Hz, C_6H_3(3)], 4.39 and 4.22 [2 H, t, J(HH) 1.8 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.11 [5 H, s, C_5H_5], 3.57 [2 H, br s, NH_2], 2.30 [3 H, s, CH_3]; *m/z* 291 (M^+), 121 (M - $C_{12}H_{12}N$).

4-Nitro-2-methyl-4'-ferrocenylazobenzene [54]

A mixture of 2-nitroso-5-nitrotoluene (3.6 g, 22 mmol) and [43] (5.0 g, 18 mmol) in glacial acetic acid (s.g. 1.05, 400 cm^3) was stirred at room temperature for 5 d. Water (1000 cm^3) and dichloromethane (100 cm^3) were added, the mixture shaken and the organic layer separated. The aqueous layer was extracted with further dichloromethane (3 x 50 cm^3), and the combined organic extracts were evaporated to dryness to yield the crude product. This was purified by column chromatography using gradient elution from 50% dichloromethane/n-hexane to 100% dichloromethane. The major purple band collected in 70% dichloromethane/n-hexane afforded upon evaporation deep purple microcrystalline 4-nitro-2-

methyl-4'-ferrocenylazobenzene (4.5 g, 59%)
$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_4N{=}NC_6H_3\text{-}2\text{-}CH_3\text{-}4\text{-}NO_2$, m.p. 156-160 °C (Found: C, 64.7; H, 4.8; N, 9.8%; M^+, 425. $C_{23}H_{19}FeN_3O_2$ requires C, 65.0; H, 4.5; N, 9.9%; M, 425); $\nu_{max.}(NO_2)$ 1520s and 1345s cm^{-1}; $\delta_H(CDCl_3)$ 8.23 [1 H, s, C_6H_3(3)], 8.14 [1 H, d, J(12) 8.6 Hz, C_6H_3(1)], 7.71 [1 H, d, J(12) 8.8 Hz, C_6H_3(2)], 7.91 and 7.63 [2 H, d, J(HH) 7.7 Hz; 2 H, d, J(HH) 7.9 Hz, C_6H_4-Fc], 4.77 and 4.45 [2 H, s; 2 H, s, C_5H_4], 4.08 [5 H, s, C_5H_5], 2.80 [3 H, s, CH_3]; *m/z* 425 (M^+), 261 (M - $N_2C_6H_4CH_3NO_2$).

4-Nitro-2-methyl-3'-methyl-4'-ferrocenylazobenzene [55]

This compound was prepared in an identical manner to [54] using [44] (5.24 g, 18 mmol) in place of [43]. The major purple fraction from the column yielded upon evaporation deep green-black microcrystalline 4-nitro-2-methyl-3'-methyl-4'-ferrocenylazobenzene (5.14 g, 65%)
$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_3\text{-}2\text{-}CH_3\text{-}4\text{-}N{=}NC_6H_3\text{-}2\text{-}CH_3\text{-}4\text{-}NO_2$, m.p. 142-145 °C (Found: C, 65.3; H, 4.9; N, 9.6%; M^+, 439. $C_{24}H_{21}FeN_3O_2$ requires C, 65.6; H, 4.8; N, 9.6%; M, 439); $\nu_{max.}(NO_2)$ 1520s and 1345s cm^{-1}; $\delta_H(CDCl_3)$ 8.23 [1 H, s, C_6H_3(6)], 8.15 and 8.12 [½ H, d, J(56) 1.8 Hz; ½ H, d, J(56) 2.0 Hz, J(45) 8.7 Hz, C_6H_3(5)], 7.84 [1 H, d, J(45) 8.8 Hz, C_6H_3(4)], 7.78, 7.77, 7.76, 7.76, 7.76, and 7.75 [2 H, C_6H_3(2 and 3)], 7.70 [1 H, d, J(12) 9.0 Hz, C_6H_3(1)], 4.62 and 4.41 [2 H, t, J(HH) 1.8 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.16 [5 H, s, C_5H_5], 2.80 [3 H, s, CH_3(b)], 2.55 [3 H, s, CH_3(a)]; *m/z* 439 (M^+), 271 (M - $N_2C_6H_3CH_3NO_2$).

4-Hydroxy-4'-ferrocenylazobenzene [45]

This compound was prepared in an identical manner to [54] using 4-nitrosophenol (2.71 g, 22 mmol) in place of 2-nitroso-5-nitrotoluene. Careful column chromatography using a long (60 x 3.5 cm) column followed by a shorter one (35 x 3.0 cm) with pure dichloromethane as eluent yielded a red fraction which was evaporated to give dark red 4-hydroxy-4'-ferrocenylazobenzene (0.34 g, 5%).
$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_4N{=}NC_6H_4\text{-}4\text{-}OH$, m.p. 166-170 °C (Found: C, 69.4; H, 4.9; N, 7.6%; M^+, 382. $C_{22}H_{18}FeN_2O$ requires C, 69.1; H, 4.8; N,

7.3%; M, 382); $\nu_{max.}$(OH) 3400m br cm^{-1}; $\delta_H(CDCl_3)$ 7.89 and 6.95 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4-OH], 7.81 and 7.57 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4-Fc], 5.15 [1 H, br s, OH], 4.76 and 4.42 [2 H, s; 2 H, s, C_5H_4], 4.09 [5 H, s, C_5H_5]; *m/z* 382 (M^+), 261 (M - $N_2C_6H_4OH$).

4-Amino-4'-ferrocenylazobenzene [46]

A solution of [53] (0.5 g, 1.22 mmol) and sodium sulphide hydrate (1.0 g) in ethanol (100 cm^3) was heated at reflux for 1 h during which time the solution colour changed from purple to red. The solvent was then removed *in vacuo* and the crude product purified by column chromatography in dichloromethane. The major red band afforded upon evaporation a deep burgundy powder which was crystallised from dichloromethane/n-pentane to give dark red needles of 4-amino-4'-ferrocenylazobenzene (0.44 g, 95%). (η^5-C_5H_5)Fe($\eta^5C_5H_4$)-C_6H_4N=NC_6H_4-4-NH_2, m.p. 180-185 °C (Found: C, 69.3; H, 4.7; N, 11.3%; M^+, 381. $C_{22}H_{19}FeN_3$ requires C, 69.3; H, 5.0; N, 11.0%; M, 381); $\nu_{max.}$(NH_2) 3455m and 3360m cm^{-1}; $\delta_H(CDCl_3)$ 7.82 and 7.57 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4-NH_2] 7.80 and 6.75 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-Fc], 4.71 and 4.37 [2 H, t, J(HH) 1.8, 2.0 Hz; 2 H, t, J(HH) 1.8, 2.0 Hz, C_5H_4], 4.05 [5 H, s, C_5H_5], 4.02 [2 H, s, NH_2]; *m/z* 381 (M^+), 261 (M - $N_2C_6H_4NH_2$).

4-Amino-2-methyl-4'-ferrocenylazobenzene [47]

This compound was prepared in an identical manner to [46] using [54] (0.52 g, 1.22 mmol) in place of [53]. This yielded deep burgundy 4-amino-2-methyl-4'-ferrocenylazobenzene (0.47 g, 97%). (η^5-C_5H_5)Fe($\eta^5C_5H_4$)-C_6H_4N=NC_6H_3-2-CH_3-4-NH_2, m.p. 143-146 °C (Found: C, 69.7; H, 5.1; N, 10.5%; M^+, 395. $C_{23}H_{21}FeN_3$ requires C, 69.9; H, 5.4; N, 10.6%; M, 395); $\nu_{max.}$(NH_2) 3455m and 3360m cm^{-1}; $\delta_H(CDCl_3)$ 7.80 and 7.56 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4-Fc], 7.67 [1 H, d, J(12) 8.6 Hz, C_6H_3(1)], 6.59 [1 H, d, J(23) 2.7 Hz, C_6H_3(3)], 6.56 and 6.53 [½ H, d, J(23) 2.7 Hz; ½ H, d, J(23) 2.6 Hz, J(12) 8.5 Hz, C_6H_3(2)], 4.71 and 4.37 [2 H, t, J(HH) 1.8 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.06 [5 H, s, C_5H_5], 3.94 [2 H, s, NH_2], 2.67 [3 H, s, CH_3]; *m/z* 395 (M^+), 261 (M - $N_2C_6H_3CH_3NH_2$).

4-Amino-2-methyl-3'-methyl-4'-ferrocenylazobenzene [48]

This compound was prepared in an identical manner to [46] using [55] (0.53 g, 1.22 mmol) in place of [53]. This yielded deep burgundy 4-amino-2-methyl-3'-methyl-4'-ferrocenylazobenzene (0.46 g, 94%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_3\text{-}2\text{-}CH_3\text{-}4\text{-}N{=}NC_6H_3\text{-}2\text{-}CH_3\text{-}4\text{-}NH_2$, m.p. 138-140 °C (Found: C, 70.7; H, 6.0; N, 10.2%; M^+, 409. $C_{24}H_{23}FeN_3$ requires C, 70.4; H, 5.7; N, 10.3%; M, 409); $\nu_{max.}(NH_2)$ 3455m and 3360m cm^{-1}; $\delta_H(CDCl_3)$ 7.77 [1 H, d, J(HH) 8.1 Hz, C_6H_3(1)], 7.68 and 7.64 [3 H, C_6H_3(2, 3, and 4)], 6.57 [1 H, d, J(56) 2.2 Hz, C_6H_3(6)], 6.54 and 6.50 [½ H, d, J(56) 2.6 Hz; ½ H, d, J(56) 2.6 Hz, J(45) 8.6 Hz, C_6H_3(5)], 4.56 and 4.33 [2 H, t, J(HH) 2.0, 1.8 Hz; 2 H, t, J(HH) 2.0, 1.8 Hz, C_5H_4], 4.13 [5 H, s, C_5H_5], 3.93 [2 H, s, NH_2], 2.67 [3 H, s, CH_3(b)], 2.49[3 H, s, CH_3(a)]; *m/z* 409 (M^+), 275 (M - $N_2C_6H_3CH_3NH_2$).

4-(4-Nitro-2-methylphenylazo)-2-methyl-3'-methyl-4'-ferrocenylazobenzene [56]

This compound was prepared in an identical manner to [54] using [48] (0.30 g, 0.73 mmol) in place of [43]. Quantities of other reagents were also changed as follows; 2-nitroso-5-nitrotoluene (0.25 g, 1.51 mmol), glacial acetic acid (s.g. 1.05, 50 cm^3), water (100 cm^3), and the reaction time was reduced to 24 h. The major dark brown fraction from the column yielded upon evaporation dark olive green microcrystalline 4-(4-Nitro-2-methyl phenylazo)-2-methyl-3'-methyl-4'-ferrocenylazobenzene (0.14 g, 35%)

$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_3\text{-}2\text{-}CH_3\text{-}4\text{-}N{=}NC_6H_3\text{-}2\text{-}CH_3\text{-}4\text{-}N{=}NC_6H_3\text{-}2\text{-}CH_3\text{-}4\text{-}NO_2$, m.p. 204-208 °C (Found: C, 66.0; H, 4.5; N, 12.3%; M^+, 557. $C_{31}H_{27}FeN_5O_2.0.1CH_2Cl_2$ requires C, 66.0; H, 4.8; N, 12.4%; M, 557); $\nu_{max.}(NO_2)$ 1530s and 1345s cm^{-1}; $\delta_H(CDCl_3)$ 8.24 [1 H, d, J(89) 2.0 Hz, C_6H_3(9)], 8.15 and 8.12 [½ H, d, J(89) 2.8 Hz; ½ H, d, J(89) 2.6 Hz, J(78) 8.7 Hz, C_6H_3(8)], 7.95, 7.89, 7.89, 7.85, 7.83, 7.82, 7.80, 7.78, 7.77, 7.76 [6 H, C_6H_3(7, 6, 5, 4, 3, and 2)], 7.73 [1 H, d, J(12) 9.0 Hz, C_6H_3(1)], 4.61 and 4.40 [2 H, t, J(HH) 1.8 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.16 [5 H, s, C_5H_5], 2.84 and 2.83 [3

H, s; 3 H, s, CH_3(b and c)], 2.55 [3 H, s; CH_3(a)]; *m/z* 557 (M^+), 527 (M - NO), 393 (M - $N_2C_6H_3NO_2$), 275 (M - $N_2C_6H_3CH_3N_2C_6H_3CH_3NO_2$).

4-(4-Amino-2-methylphenylazo)-2-methyl-3'-methyl-4'-ferrocenylazobenzene [49]

This compound was prepared in an identical manner to [46] using [56] (0.10 g, 0.18 mmol) in place of [53]. Quantities of other reagents were also changed as follows; sodium sulphide hydrate (0.5 g), ethanol (25 cm^3), and the reaction time was reduced to 5 min. Only a short reaction time was allowed because decomposition was expected. Column chromatography gave 7% recovery of [56] and deep red-orange 4-(4-Amino-2-methylphenylazo)-2-methyl-3'-methyl-4'-ferrocenylazobenzene (0.041 g, 43%).
$(\eta^5-C_5H_5)Fe(\eta^5C_5H_4)-C_6H_3-2-CH_3-4-N=NC_6H_3-2-CH_3-4-N=NC_6H_3-2-CH_3-4-NH_2$, m.p. 188-190 °C (Found: C, 69.0; H, 5.4; N, 13.1%; M^+, 527. $C_{31}H_{29}FeN_5.0.18CH_2Cl_2$ requires C, 69.0; H, 5.5; N, 12.9%; M, 527); $\nu_{max.}(NH_2)$ 3475m and 3380m cm^{-1}; $\delta_H(CDCl_3)$ 7.82, 7.82, 7.80, 7.79, 7.76, 7.73, 7.72, and 7.68 [7 H, C_6H_3(1, 2, 3, 4, 5, 6, and 7)], 6.57 [1 H, s, C_6H_3(9)], 6.54 and 6.51 [½ H, d, J(89) 2.4 Hz; ½ H, d, J(89) 2.6 Hz, J(78) 8.7 Hz, C_6H_3(8)], 4.59 and 4.36 [2 H, t, J(HH) 1.8 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.15 [5 H, s, C_5H_5], 3.99 [2 H, s, NH_2], 2.81 [3 H, s, CH_3(b)], 2.69 [3 H, s, CH_3(c)], 2.53 [3 H, s, CH_3(a)]; *m/z* 527 (M^+), 275 (M - $N_2C_6H_3CH_3N_2C_6H_3CH_3NH_2$).

4-Fluoro-4'-ferrocenylazobenzene [64]

This compound was prepared in an identical manner to [54] using 4-fluoronitrosobenzene (2.75 g, 22 mmol) in place of 2-nitroso-5-nitrotoluene. The major red band from column chromatography yielded deep red microcrystalline 4-fluoro-4'-ferrocenylazobenzene (2.77 g, 40%).
$(\eta^5-C_5H_5)Fe(\eta^5C_5H_4)-C_6H_4N=NC_6H_4-4-F$, m.p. 193-196 °C (Found: C, 68.6; H, 4.6; N, 7.0%; M^+, 384. $C_{22}H_{17}FFeN_2$ requires C, 68.8; H, 4.5; N, 7.3%; M, 384); $\delta_H(CDCl_3)$ 7.96 and 7.92 [1 H, d, J(HF) 5.3 Hz; 1 H, d, J(HF) 5.1 Hz, J(HH) 9.1 Hz, C_6H_4-F(1 and 4)], 7.84 and 7.59 [2 H, d, J(HH) 6.8 Hz; 2 H, d, J(HH) 6.8 Hz, C_6H_4-Fc], 7.21 and 7.18 [1 H, d, J(HF) 9.0 Hz; 1 H, d, J(HF) 8.4 Hz, J(HH) 8.7 Hz, C_6H_4-F(2

and 3)], 4.73 and 4.40 [2 H, t, J(HH) 1.8 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.06 [5 H, s, C_5H_5]; *m/z* 384 (M^+), 261 ($M - N_2C_6H_4F$).

4-Ethoxy-4'-ferrocenylazobenzene [65]

A solution of [64] (0.50 g, 1.30 mmol) and sodium hydroxide (0.5 g, 12.5 mmol) in ethanol (20 cm^3) was stirred at reflux for 4 h. The solution was cooled and water (20 cm^3) and dichloromethane (20 cm^3) were added. The organic layer was separated, the aqueous layer extracted with further dichloromethane (2 x 10 cm^3), and the combined organic extracts evaporated to give a red solid. This was separated into its components by column chromatography using a 50% dichloromethane/n-hexane solution as eluent. The first red fraction was unreacted [64] (0.40 g, 80% recovery), and the second major red-orange band yielded deep red-brown 4-ethoxy-4'-ferrocenylazobenzene (0.11 g, 20%).
$(\eta^5-C_5H_5)Fe(\eta^5C_5H_4)-C_6H_4N=NC_6H_4-4-OCH_2CH_3$, m.p. 164-168 °C (Found: C, 70.0; H, 5.4; N, 6.6%; M^+, 410. $C_{24}H_{22}FeN_2O$ requires C, 70.3; H, 5.4; N, 6.8%; M, 410); $\delta_H(CDCl_3)$ 7.91 and 7.00 [2 H, d, J(HH) 9.2 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-OCH_2CH_3] 7.82 and 7.58 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-Fc], 4.73 and 4.39 [2 H, t, J(HH) 2.0, 1.8 Hz; 2 H, t, J(HH) 2.0, 1.7 Hz, C_5H_4], 4.13 [2 H, q, J(HH) 7.1 Hz, OCH_2CH_3], 4.06 [5 H, s, C_5H_5], 1.46 [3 H, t, J(HH) 7.0 Hz, OCH_2CH_3]; *m/z* 410 (M^+), 261 ($M - N_2C_6H_4OCH_2CH_3$).

4-Formylphenylferrocene [58]

A solution of DIBAL (Diisobutylaluminiumhydride; 1.0 M in dry dichloromethane, 3.5 cm^3) was added dropwise to a stirred solution of [59] (1.0 g, 3.5 mmol) in dry toluene (20 cm^3) at room temperature under a dry nitrogen atmosphere. Addition was completed after 15 min during which time a 3 °C rise in temperature was detected. The solution was stirred for a further 2 h, then methanol (5 cm^3) was added to destroy any residual DIBAL. Aqueous sulphuric acid (sulphuric acid, s.g. 1.84, in water 1:3, 20 cm^3) was added to hydrolyse the intermediate imine complex and the solution was then extracted with dichloromethane (5 x 10cm^3). The organic extracts were combined and evaporated to yield the crude product. This was purified by column chromatography using an 80%

dichloromethane/n-hexane solution as eluent. The first major red-orange fraction was [59] (0.10 g, 10% recovery), and the second major orange fraction yielded 4-formylphenylferrocene (0.85 g, 84%).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_4\text{-}4\text{-}CHO$, m.p. 133–136 °C (lit.,[245] 136.5–137 °C) (Found: C, 70.1; H, 5.2%; M^+, 290. $C_{17}H_{14}FeO$ requires C, 70.4; H, 4.9%; M, 290); $\nu_{max.}$(OC–H) 2810w, 2790w, and 2730w, $\nu_{max.}$(CO) 1695s cm^{-1}; $\delta_H(CDCl_3)$ 9.97 [1 H, s, OC*H*], 7.79 and 7.59 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 4.74 and 4.43 [2 H, t, J(HH) 1.7, 2.0 Hz; 2 H, t, J(HH) 1.7, 2.0 Hz, C_5H_4], 4.04 [5 H, s, C_5H_5]; *m/z* 290 (M^+), 121 ($M - C_{11}H_8CHO$).

4-Nitro-4'-ferrocenylstilbene [57]

A solution of [58] (0.5 g, 1.72 mmol), 4-nitrophenylacetic acid (1.0 g, 5.52 mmol) and piperidine (1 cm^3) was stirred at reflux in pyridine (5 cm^3) under a nitrogen atmosphere for 13 h. The mixture was cooled and the solvent removed *in vacuo.* before purification by column chromatography using gradient elution starting from a 70% dichloromethane/n-hexane solution with increasing dichloromethane concentration. The first major red band yielded upon evaporation dark brick-red 4-nitro-4'-ferrocenylstilbene (0.47 g, 66%), and the second major orange fraction was unreacted [58] (0.12 g, 23% recovery).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_4CH{=}CHC_6H_4\text{-}4\text{-}NO_2$, m.p. 270 °C (dec.) (Found: C, 70.0; H, 4.7; N, 3.0%; M^+, 409. $C_{24}H_{19}FeNO_2$ requires C, 70.4; H, 4.7; N, 3.4%; M, 409); $\nu_{max.}(NO_2)$ 1510s and 1330s cm^{-1}; $\delta_H(CDCl_3)$ 8.22 and 7.64 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-NO_2], 7.48 [4 H, s, C_6H_4-Fc], 7.26 and 7.13 [1 H, d, $J(HH)_{trans}$ 16.1 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 4.69 and 4.37 [2 H, t, J(HH) 1.8, 2.0 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.05 [5 H, s, C_5H_5]; *m/z* 409 (M^+), 379 ($M - NO$), 362 (M -1- NO_2).

4-Amino-4'-ferrocenylstilbene [50]

A solution of [57] (0.5 g, 1.22 mmol) and ammonium chloride (0.5 g, 9.35 mmol) in acetone (50 cm^3) and water (10 cm^3) was heated to reflux. Zinc powder (0.5 g, 7.65 mmol) was added and the mixture stirred at reflux for 1 h. Further ammonium chloride (0.5

g) and zinc powder (0.5 g) were added and the mixture was stirred at reflux for a further 22 h. The colour of the solution changed from red to orange during this time. The reaction mixture was cooled and the zinc powder removed by filtration. The acetone was removed *in vacuo*. and water (20 cm^3) and dichloromethane (20 cm^3) were added. The orange organic layer was separated and the aqueous layer extracted with further dichloromethane (3 x 10 cm^3). The combined organic extracts were evaporated and the product purified by column chromatography using dichloromethane as eluent. The major orange band yielded upon evaporation 4-amino-4'-ferrocenylstilbene as a pale orange solid (0.43 g, 92%).
$(\eta^5\text{-}C_5H_5)Fe(\eta^5C_5H_4)\text{-}C_6H_4CH{=}CHC_6H_4\text{-}4\text{-}NH_2$, m.p. 245 °C (dec.) (Found: C, 75.6; H, 5.6; N, 3.4%; M^+, 379. $C_{24}H_{21}FeN$ requires C, 76.0; H, 5.6; N, 3.7%; M, 379); $\nu_{max.}(NH_2)$ 3445m and 3350m cm^{-1}; $\delta_H(CDCl_3)$ 7.44 and 7.39 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-Fc], 7.35 and 6.68 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4-NH_2], 7.03 and 6.90 [1 H, d, $J(HH)_{trans}$ 15.9 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 4.65 and 4.32 [2 H, t, J(HH) 1.8, 2.0; 2 H, t, J(HH) 1.8, C_5H_4], 4.04 [5 H, s, C_5H_5], 3.76 [2 H, br s, NH_2]; *m/z* 379 (M^+).

CHAPTER TWO

BIMETALLIC COMPLEXES CONTAINING FERROCENYL AND MOLYBDENUM OR TUNGSTEN MONONITROSYL REDOX CENTRES

III-1 DISCUSSION

III-1.1 DIHALIDE COMPLEXES

Although syntheses of the dihalide complexes $[Mo(NO)L^*(Cl)_2]$[186] and $[Mo(NO)L^*(Br)_2]$[188] have been previously reported, the standard halogenation methods used can give rise to experimental difficulties. In particular, the synthesis of $[Mo(NO)L^*(Cl)_2]$ via reaction of $[Mo(NO)L^*(CO)_2]$ with nitrosyl chloride (NOCl) often produces a side-product in which chlorination of one pyrazolyl ring has taken place to give the complex $[Mo(NO)\{HB(3,5\text{-}Me_2\text{-}pz)_2(4\text{-}Cl\text{-}3,5\text{-}Me_2\text{-}pz)\}(Cl)_2]$. Indeed, an alkoxide derivative containing the tri-chlorinated trispyrazolylborate ligand (*i.e.*, $\{HB(4\text{-}Cl\text{-}3,5\text{-}Me_2\text{-}pz)_3\}$) was characterised by single crystal X-ray diffraction some years ago.[191] The problem is generally a lack of control over the reaction; in some cases only pure $[Mo(NO)L^*(Cl)_2]$ is produced as desired, but often contamination by the chlorinated species is found. This creates difficulties in the purification of subsequent complex derivatives, and is clearly undesirable. The preparation of pure $[Mo(NO)\{HB(3,5\text{-}Me_2\text{-}pz)_2(4\text{-}Cl\text{-}3,5\text{-}Me_2\text{-}pz)\}(Cl)_2]$ is possible under certain conditions.[246]

Hence, an alternative route to the preparation of pure $[Mo(NO)L^*(Cl)_2]$ was sought. It seems likely that the displacement of the two neutral carbonyl ligands from $[Mo(NO)L^*(CO)_2]$ should involve halogen radicals rather than halide ions. Benzyl chloride was chosen as a chlorinating agent because the marked stability of the benzyl radical should render this compound a good source of chlorine radicals. It was found that the diiodide $[Mo(NO)L^*(I)_2]$

could be converted to the dichloride in high yield by reaction with benzyl chloride in dry toluene under reflux, but this represents a waste of laboratory time and resources because the initial preparation of the diiodide from the dicarbonyl takes several days.[187]

Subsequent experiments showed that the dichloride can be prepared almost quantitatively from the dicarbonyl by reaction with benzyl chloride in toluene in the presence of a stoichiometric amount of iodine. The use of less than stoichiometric iodine gives incomplete carbonyl displacement, as evidenced by i.r. spectroscopy, and if excess iodine is added a darkened product is isolated due to iodine contamination. The iodine used to "catalyse" the conversion is not recovered and benzyl iodide is a likely but unproven side-product. This reaction also works with benzyl bromide to yield pure $[Mo(NO)L^*(Br)_2]$, and details of these improved routes to the dichloride and dibromide complexes are given in the experimental section III-2.

III-1,2 FERROCENYL COMPLEXES

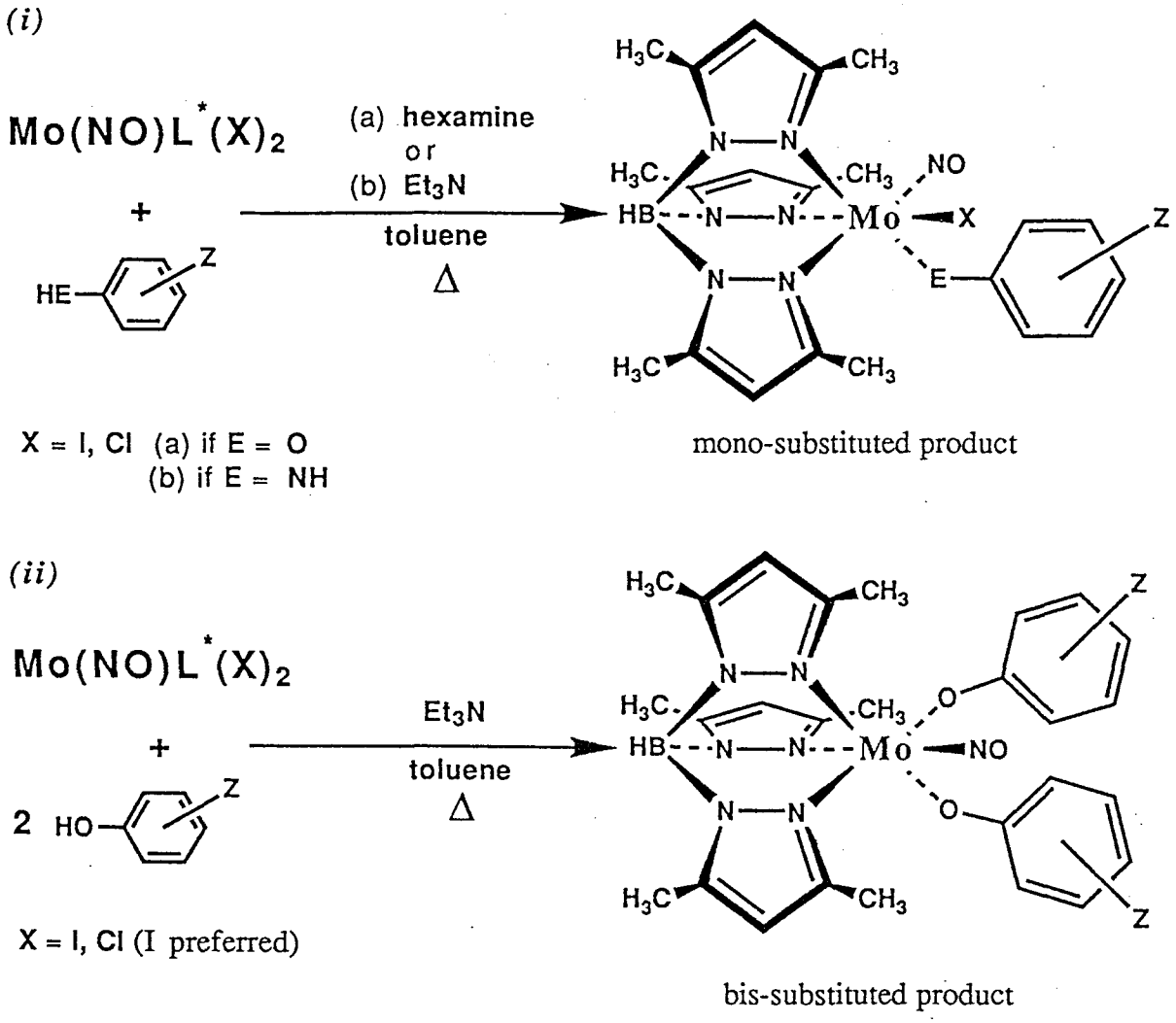
III-1,2(a) Molybdenum Complexes

Mono-substituted derivatives of the form $[Mo(NO)L^*(X)(ER)]$ (X = Cl, I; E = O, NH; R = arylferrocenyl group) were prepared in straightforward fashion by reaction of $[Mo(NO)L^*(X)_2]$ (X = Cl, I) with a slight excess of the appropriate ligand in toluene under reflux. The presence of a non-coordinating nitrogen base improves the yield of such reactions by removing the hydrogen halide liberated as a quaternary ammonium salt. It was found that the use of the mild base hexamine (hexamethylenetetramine) is preferable to encourage the formation of mono-phenoxide complexes from both dihalide precursors. Triethylamine was used in the preparation of mono-anilide complexes, but when used with phenolic ligands this relatively strong base was found to promote formation of bis-substituted complexes of the form $[Mo(NO)L^*(OR)_2]$ (R = arylferrocenyl group) even when the dihalide and ligand were

reacted in a 1:1 stoichiometry. However, the diiodide reacts faster when triethylamine is used, and is hence the preferred choice for the preparation of bis-phenoxide complexes (Fig. 30).

Fig. 30

Preparation of Mono- and Bis-substituted Aryl Molybdenum Complexes



An interesting and initially somewhat puzzling result was found in many of the reactions between [Mo(NO)L*(I)$_2$] and aniline ligands (both the ferrocenyl compounds and others discussed in Chapters 3, 4, and 5). T.l.c. study of the crude reactions using 30% n-hexane/dichloromethane revealed a second minor spot running closely behind the major mono-iodo product. These minor spots are of the same colour as the iodo products, and were thought at first

to serve as evidence of the unexpected formation of bis-anilide complexes. However, column chromatography was used to separate the major and minor products and i.r. study showed that the two have identical spectra, proving that bis-subsitution has not taken place. The minor product accounts for typically only 1-2% of the original diiodide, and ^{1}H n.m.r. spectroscopy revealed that what in fact was being produced is the mono-chloro derivative of the appropriate ligand. The origin of the mono-chloro products is unclear, particularly since the reactions were carried out in toluene, not dichloromethane (some exchange of iodide for chloride has previously been detected when mono-iodo complexes are refluxed for extended periods in dichloromethane).[247]

Whether the chlorides are formed during column chromatography in dichloromethane, or whether they are present in the crude reactions is a matter for investigation. It is interesting to note that no evidence for the production of chlorides was seen in reactions of $[Mo(NO)L^*(I)_2]$ with phenolic ligands, proving that $[Mo(NO)L^*(Cl)_2]$ is not present as a trace impurity in the $[Mo(NO)L^*(I)_2]$. One possibility is that some of the aniline ligands contain traces of hydrogen chloride (*i.e.* a small proportion of their molecules are present as quaternary ammonium salts), as an artifact of their preparation by the reduction of nitro compounds using tin-hydrochloric acid or zinc-ammonium chloride. Since the levels of chloride production are very low and separation from the desired iodide product is facile, this question was not addressed further.

The preparation of a bis-anilide complex of one of the ferrocenyl ligands was attempted in several reactions of $[Mo(NO)L^*(I)(HNC_6H_4\text{-}Fc)]$ (Fc = ferrocenyl) with further 4-aminophenylferrocene in the presence of sodium naphthalenide according to previously established principles.[196] However, none of the desired bis-anilide complex was isolated, and complete decomposition of the mono-anilide complex was found. A similar approach using silver acetate as a halide abstracter[192] gave an equally unsuccessful result. In all reactions unreacted 4-aminophenylferrocene was retrieved by column chromatography and no $\{Mo(NO)L^*\}$ complexes were isolated. This may be due to reduction of

the coordinated ferrocenyl moiety leading to complex decompostion. Further studies using other ferrocenyl amines were not attempted.

The complete molybdenum-halide series was prepared for one ligand, 4-amino-2-methyl-4'-ferrocenylazobenzene, using the previously reported but somewhat less exploited difluoride and dibromide complexes, [Mo(NO)L*(F)$_2$] and [Mo(NO)L*(Br)$_2$].[188] Although the difluoride is apparently insoluble in toluene, reaction occurred under reflux, albeit in low yield. Whether this involves a solution or heterogeneous process is unclear.

The replacement of the second iodide in the complex [Mo(NO)L*(I)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] by an alkoxide ligand to give mixed alkoxy-anilido complexes was also carried out. Several alcohol ligands were used including cyclohexanol, 1,1,1-trifluoroethanol, n-octanol, 3-butyn-1-ol, isopentanol (1,1-dimethylpropanol), and 2,4-dinitrophenol. Of these, the latter two failed to give any detectable alkoxy-anilide products. This is presumably due to steric effects for isopentanol, and because the high acidity of 2,4-dinitrophenol (pK_a = 4.1)[248] would render any Mo-O bond too weak to be stable. However, mixed complexes of the form [Mo(NO)L*(OR)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] (R = alkyl) were isolated for the first four alcohols.

III-1.2(b) Tungsten Complexes

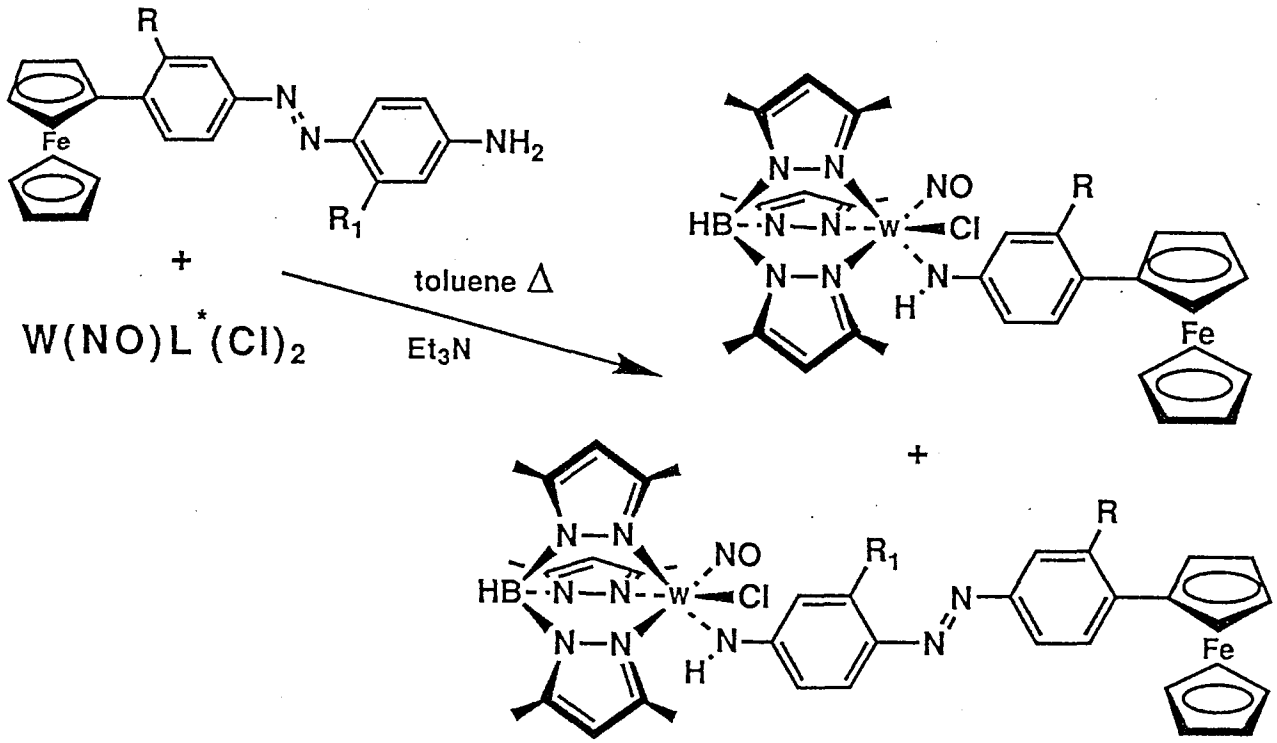
Triethylamine was used as base in the preparation of all tungsten mono-phenoxide and mono-anilide derivatives. [W(NO)L*(Cl)$_2$] is considerably less reactive than [Mo(NO)L*(Cl)$_2$] with both phenolic and aniline ligands, and gives markedly lower yields in all reactions, despite extended reaction times.

In all reactions between [W(NO)L*(Cl)$_2$] and azo-aniline ligands, not only were poor yields of azo-anilide complex isolated, but also some considerable degree of cleavage of the azo functionality was detected, giving rise to mono-aryl anilide complexes as shown in Fig. 31. This phenomenon was not observed in the corresponding reactions of [Mo(NO)L*(Cl)$_2$]. Whether reductive cleavage occurs on coordinated or uncoordinated ligands is unclear, but longer reaction times were found to give rise to

increasing proportions of the appropriate mono-aryl complexes (up to 50%) which were separated from the desired azo complexes by careful column chromatography.

Fig. 31

Cleavage of Azo Linkages in Reactions of [W(NO)L*(Cl)$_2$]



R = R_1 = H; R = H, R_1 = CH_3; R = R_1 = CH_3

Azobenzenes bearing strongly electron-donating substituents have previously been studied by various electrochemical techniques, and found to readily undergo four-electron reductions resulting in cleavage of the azo bond and formation of the corresponding amines.[249] By contrast, a two-electron reduction to give a hydrazobenzene is observed for azobenzenes substituted with groups which are not strongly electron-donating or electroactive. Since electrochemical studies have indicated that the {W(NO)L*(Cl)} centre acts as a poorer electron-acceptor than {Mo(NO)L*(Cl)}, the azo linkage in the tungsten azo-anilide complexes should be more electron-rich than in their molybdenum analogues, and hence more

susceptible to reductive cleavage. It may be the case that the metal plays a more direct role in the reduction, but detailed electrochemical data for both free ligands and complexes are required before any firm conclusions can be drawn.

The sole bis-phenoxide derivative of tungsten was prepared in reasonable yield using sodium hydride as a more powerful base to encourage substitution of the second chloride ligand.[210] Previous attempts to prepare tungsten bis-anilide complexes have been unsuccessful, although bis-alkylamides can be isolated.[210] Since the yields of mono-anilido complexes are in any case rather low, no effort was directed at the synthesis of bis-ferrocenylanilides of tungsten.

III-1.3 PHYSICAL CHARACTERISATION

All complexes were characterised using i.r. and ^{1}H n.m.r. spectroscopy, EI mass spectrometry, elemental analyses, and cyclic voltammetry. U.v.-visible absorption spectra were recorded for selected complexes, with particular attention being paid to any evidence of solvatochromism.

III-1.3(a) Elemental Analyses

Most of the complexes, except for several of the mixed alkoxy-anilide species, show satisfactory analyses for C, H, and N, but it has been found that many retain between 0.25 and 1.0 mole of dichloromethane of crystallisation which may also be detected by ^{1}H n.m.r. spectroscopy. Further evidence for this tendency to retain solvent is found in X-ray structural studies (see section III-1.5(a)). Samples were dried for extended periods under vacuum at *ca* 100 °C, but in most cases this was insufficient to remove solvent. Higher temperatures were not used for fear of decomposing the compounds.

Considering those compounds for which quoted C or N analyses deviate from the expected by ± 0.6-1.0% (4 out of 28 for C, and 3 out of 28 for N), the given values represent the best of two or

more results. In such cases, attempts at further improvement were deemed unnecessary in view of the large amount of other characteristic physical evidence (*i.e.* i.r. and ^{1}H n.m.r. spectra, EI mass spectra, cyclic voltammetry).

The single fluoride complex [89] gave a rather low N analysis (-1.0%), and the mixed alkoxy-anilido complexes [100], [101], and [102] all gave high C analyses (+1.1, +3.1, and +1.7% respectively). All of these complexes proved to be somewhat unstable, decomposing during column chromatography to give free amine ligand, and their unsatisfactory analyses are thought to be due to decomposition during drying at elevated temperatures. Again, for all of these compounds, confirmation of formulation is given by other characterisation techniques.

III-1.3(b) Infra-Red Spectroscopy

All of the new complexes exhibit $\nu_{max.}$(BH) at *ca* 2550 cm^{-1} as well as $\nu_{max.}$(NO) at frequencies in accord with their formulations. In addition, the arylamide derivatives exhibit $\nu_{max.}$(NH) at 3300-3260 cm^{-1} due to the amide moiety. The intensity of this absorption varies considerably.

The fluoride complex [89] has $\nu_{max.}$(NO) at 1645 cm^{-1} which is some 20 cm^{-1} lower than that of its chloride, bromide, and iodide counterparts. This value is close to the 1640 cm^{-1} reported for the methylamide complex.[188] This observation goes against expectations based upon halide electronegativity, but a lower frequency is in keeping with the observation that the difluoride precursor has $\nu_{max.}$(NO) at 1685 cm^{-1}, some 15 cm^{-1} lower than the other dihalide complexes. It has been postulated that this is a result of fluoride bridging interactions giving rise to a seven-coordinate species,[188] which is perhaps unlikely in view of the steric restrictions imposed upon the molybdenum by the bulky L* ligand, and structural or other confirmation of this has yet to be obtained. A more likely explanation for this lowered nitrosyl stretch is the strong pπ-dπ donation ability of fluoride. This renders its coordination behaviour more like that of oxygen than of the other halides which are weaker pπ-donors.

The mixed alkoxy-anilide complexes [91], [100], [101], and [102] all have $\nu_{max.}$(NO) at about 1640 cm^{-1} which is considerably lower than typical values of 1660 cm^{-1} for bis-alkoxides,[192] but slightly higher than typical values of 1630 cm^{-1} for bis-anilide complexes.[196] The mixed complex of 3-butyn-1-ol [102] also shows $\nu_{max.}$(≡CH) at 3290 cm^{-1} which overlays the weak NH absorption.

III-1.3(c) ^{1}H n.m.r. Spectroscopy

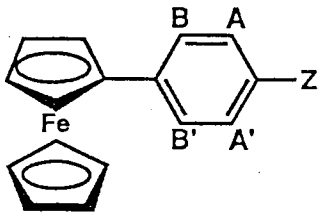
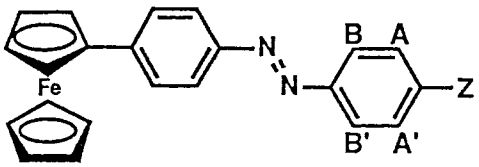
All complexes exhibit the expected signals attributable to the L* ligand which integrate for three pyrazolyl 4-protons and six pyrazolyl 3- and 5-methyls. In most cases the mono-substituted complexes give the usual three pyrazolyl 4-proton signals along with six discrete pyrazolyl 3,5-methyl signals, and the bis-substituted give two proton and four methyl signals due to the symmetry conditions described earlier in section I-7.3(b).

Aromatic signals are as expected and peaks have been assigned as far as possible with coupling constants calculated where necessary. Some consideration of aromatic proton shifts as evidence of shielding is worthwhile, and results for some of the molybdenum chloride complexes are summarised in Table VIII, along with shifts for the uncomplexed ferrocenyl ligands. Signal assignments are made on intuitive grounds.

Firstly, it can be seen that attachment of an {Mo(NO)L*(Cl)} moiety to an $-NH_2$ group produces downfield shifts which are large (0.77 ppm for 4-aminophenylferrocene, and 0.85 ppm for 4-amino-4'-ferrocenylazobenzene), and imply roughly half the extent of deshielding of that produced by a nitro group. Attachment of {Mo(NO)L*(Cl)} to an -OH group produces a downfield shift of 0.51 ppm for 4-hydroxyphenylferrocene, and 0.50 ppm for 4-hydroxy-4'-ferrocenylazobenzene, implying considerable deshielding in both cases. Also the $\Delta\delta$ values are roughly the same for 4-nitro-, 4-amino-, and 4-hydroxy-phenylferrocene, but become considerably smaller in the {Mo(NO)L*(Cl)} complexes. In the azo compounds $\Delta\delta$ also decreases markedly on complexation. Differences between aryl proton shifts for complexes of all three {Mo(NO)L*(Cl)}, {Mo(NO)L*(I)}, and {W(NO)L*(Cl)} centres are small.

TABLE VIII

Aryl Proton Shifts for Selected Molybdenum Ferrocenyl Complexes

	Z[a]	δ(A,A')[b]	δ(B,B')[c]	Δδ
	$-NO_2$	8.14	7.56	0.58
	$-NH\{Mo\}$	7.40	7.51	0.11
	$-NH_2$	6.63	7.29	0.66
	$-O\{Mo\}$	7.28	7.51	0.23
	$-OH$	6.77	7.36	0.59
	$-NO_2$	8.39	8.03	0.36
	$-NH\{Mo\}$	7.60	8.01	0.41
	$-NH_2$	6.75	7.80	1.05
	$-O\{Mo\}$	7.45	8.02	0.57
	$-OH$	6.95	7.89	0.94

[a] {Mo} = Mo(NO)L*(Cl). [b] Centre of doublet for protons A and A', ppm. [c] Centre of doublet for protons B and B', ppm.

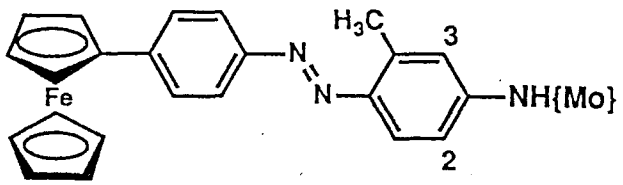
Considering the aryl protons 2 and 3 in the molybdenum halide series [Mo(NO)L*(X)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)], some comments concerning the effect of halide variation on shielding can be made. The shifts, shown in Table IX, reveal a steady trend of increasing deshielding moving down the group from F to I, which is the opposite of that which would be expected from electronegativity values for the halogen group. The total downfield shift from F to I is 0.35 ppm for proton (2) and 0.40 ppm for proton (3). This result is likely to be due to the considerable pπ-donor character of F, which is also thought to be the cause of the unusually low nitrosyl stretching frequency for the fluoride complex (see section III-1.3(b) earlier).

All of the ferrocenyl complexes show the usual three signals (ratio 2:2:5) attributable to the ferrocenyl moiety. Modest downfield shifts of about 0.1 ppm occur for the C$_5$H$_4$ ring triplets on complexation of the mono-aryl ligands, but corresponding shifts

for the azo ligands are only about 0.03 ppm, reflecting the reduced communication through the extended aromatic systems.

TABLE IX

Aryl Proton Shifts for Molybdenum-Halide Series

	X	δ(2)[a]	δ(3)[b]
	F	7.11	7.25
	Cl	7.30	7.51
	Br	7.37	7.57
	I	7.46	7.65

{Mo} = Mo(NO)L*X

[a] Centre of doublet for proton 2, ppm.

[b] Centre of doublet for proton 3, ppm.

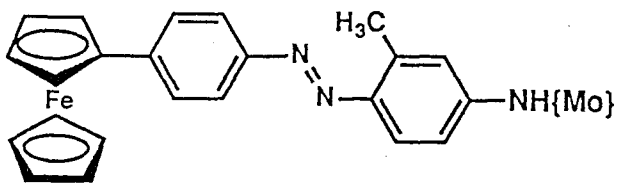
All of the anilide complexes show a sharp singlet attributable to the amide proton, the position of which is highly sensitive to the exact nature of the attached metal centre. Molybdenum iodide complexes have δ(NH) typically at about 13.0 ppm, molybdenum chlorides at 12.6 ppm, and tungsten chloride complexes at about 10.7 ppm. Values for the molybdenum halide and mixed alkoxy-anilide complexes are shown in Table X.

Once again, moving down the halide group from F to I shows increasing deshielding, with the fluoride complex having an NH shift which is markedly higher than those for the other three halides. No comparison of this value with the previously prepared mono-fluoro methylamide complex is possible because the latter was not characterised by ^1H n.m.r. owing to insolubility.[188] The total chemical shift difference between the F and I complexes is 2.79 ppm, whereas that between the Cl and I complexes is only 0.46 ppm. This is further evidence for fluoride pπ-donation to the molybdenum centre. For the alkoxides, the electron-withdrawing nature of the trifluoromethyl group in the trifluoroethoxide

complex leads to an NH shift which is 1.15 ppm downfield of that for the cyclohexanol complex.

TABLE X

Amide Proton Shifts for Molybdenum Complexes



{Mo} = Mo(NO)L*X

X	δ(NH)/ppm
OC_6H_{11}	9.42
OC_8H_{17}-n	9.56
$OC_2H_4C{\equiv}CH$	9.90
F	10.18
OCH_2CF_3	10.57
Cl	12.51
Br	12.74
I	12.97

III-1,3(d) Mass Spectrometry

Most complexes show molecular ion envelopes of relatively low intensity along with varying numbers of fragment envelopes. Owing to the presence of a large number of possible isotope combinations of the elements Mo, W, Fe, B, Cl, and I, ion envelopes have complex forms with the highest peak often not corresponding exactly to the fragmental mass calculated from relative atomic mass values. In most cases the highest peak and not the averaged fragment mass is quoted. Several unassigned ion envelopes of high intensity are also reported.

The only complexes which show no evidence of a molecular ion are the bis(azo-phenoxide) [84] (M = 1186), the mixed 3-butyn-1-ol-amide complex [102] (M = 887), the fluoro-amide [89] (M = 836), and the bis-azo complex [96] (M = 985). Indeed, the former two show no significant fragments except those corresponding to ligands; a clear indication of insufficient volatility. For the latter two a number of significant fragments have been assigned

and these correspond to the expected fragmentation patterns for such complexes.

III-1.3(e) Cyclic Voltammetry

Most of the phenoxide and arylamide complexes show reversible or quasi-reversible one-electron molybdenum or tungsten reduction waves at potentials which are in accord with expectations. In cases where ΔE_p is much above 100 mV, the reduction process may be chemically reversible but irreversible on the electrochemical timescale (*i.e.* slow electron-transfer). Also present are reversible or quasi-reversible waves for the one-electron oxidation of the ferrocenyl moiety. These results are summarised in Table XI.

TABLE XI

Cyclic Voltammetry Data for

Molybdenum and Tungsten Ferrocenyl Complexes [M(NO)L*(X)(Y)]

M	X[a]	Y[a]	E_f[M]/V[b]	ΔE_p/mV	E_f[Fe]/V[b]	ΔE_p/mV
Mo	Cl	OΦFc	−0.35	125	+0.57	100
Mo	I	OΦFc	−0.31	120	+0.58	100
Mo	OΦFc	OΦFc	−0.70	120	+0.53	120
W	Cl	OΦFc	−0.86	170	+0.56	100
W	OΦFc	OΦFc	−1.21	200	+0.53	110
Mo	Cl	HNΦFc	−0.82	120	+0.59	100
Mo	I	HNΦFc	−0.78	110	+0.59	100
W	Cl	HNΦFc	−1.23	110	+0.56	100
Mo	Cl	HNØFc	−0.84	90	+0.59	70
Mo	I	HNØFc	−0.80	110	+0.59	80
W	Cl	HNØFc	−1.25	215	+0.56	75

TABLE XI (*Continued*)

M	X[a]	Y[a]	E_f[M]/V[b]	ΔE_p/mV	E_f[Fe]/V[b]	ΔE_p/mV
Mo	Cl	OΦN=NΦFc	−0.21	100	+0.61	80
Mo	I	OΦN=NΦFc	−0.15	90	+0.60	80
Mo	OΦN=NΦFc	OΦN=NΦFc	−0.43	140	+0.60	80
Mo	Cl	HNΦN=NΦFc	−0.57	110	+0.63	90
W	Cl	HNΦN=NΦFc	−0.97	105	+0.60	100
Mo	F	HNØN=NΦFc	−0.99	180	+0.60	110
Mo	Cl	HNØN=NΦFc	−0.58	240	+0.62	80
Mo	Br	HNØN=NΦFc	−0.57	100	+0.62	70
Mo	I	HNØN=NΦFc	−0.54	80	+0.60	80
W	Cl	HNØN=NΦFc	−1.01	110	+0.62	90
Mo	OC_6H_{11}	HNØN=NΦFc	−1.09	60	+0.60	55
Mo	OC_8H_{17}-n	HNØN=NΦFc	−1.08	360	+0.60	75
Mo	OCH_2CF_3	HNØN=NΦFc	−0.88	265	+0.60	55
Mo	OC_2H_4CCH	HNØN=NΦFc	−1.01	430	+0.60	60
Mo	Cl	HNØN=NØFc	−0.59	135	+0.61	75
Mo	I	HNØN=NØFc	−0.55	125	+0.61	80
W	Cl	HNØN=NØFc	−1.00	145	+0.60	85
Mo	Cl	HNΦCH=CHΦFc	−0.74	100	+0.58	105
Mo	I	HNΦCH=CHΦFc	−0.70	85	+0.57	100
W	Cl	HNΦCH=CHΦFc	−1.16	220	+0.57	110
Mo	Cl	HNØN=NØN=NØFc	−0.52	630	+0.61	100

[a] Φ = $-C_6H_4-$, Ø = $-C_6H_3-3-CH_3-$, Fc = $-4-(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)$.

[b] All potentials measured relative to SCE in dry CH_2Cl_2 using a platinum-bead working electrode; 0.2 M $[NBu_4][BF_4]$ as supporting electrolyte; scan rate 200 mV s^{-1}.

Examination of this data reveals the usual range of potentials for molybdenum or tungsten reduction in the various classes of complex,[210] and in particular the tungsten compounds give potentials which are some 400-500 mV more cathodic than their molybdenum analogues.[212] As expected, substituents attached to aryl rings directly bound to the metal centre are found to exert a large influence on the reduction potential. Moving from a *para*-ferrocenyl to a *para*-azophenyl substituent produces anodic shifts of 140-160 mV for phenoxide and 250-260 mV for anilide complexes, reflecting the electron-withdrawing nature of the azo moiety. Comparison of the stilbenyl- and azo-anilide complexes shows an anodic shift of 170-190 mV due to the azo moiety, again demonstrating the electron-withdrawing properties of the latter. Addition of a second azoaryl function to give the bis-azo complex produces a further anodic shift of 70 mV. The addition of *meta*-methyl substituents to a ring adjacent to a metal centre produces very slight cathodic shifts of 10-20 mV.

This collection of electrochemical data contains the only complete set of reduction potentials for a full {Mo(NO)L*} halide series. In fact, no previous cyclic voltammetry data has been reported for fluoride derivatives, and their chemical and physical properties have been very little studied in any case. The fluoride complex [89] has already been found to exhibit a rather low nitrosyl stretching frequency, when compared to its other three halide analogues, and it has an accordingly cathodic reduction potential of -0.99 V. Only a small cathodic shift of 40 mV is found in moving from iodide to chloride, but the shift between chloride and fluoride is very large at 490 mV. This observation is further evidence for extensive pπ-donation from fluoride to molybdenum, which overrides expectations based upon electronegativity values for the halide series. The reduction potential for [89] is almost the same as that of the alkoxy-anilide complex [Mo(NO)L*(OC_2H_4CCH)(HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-Fc)], which supports the assertion made earlier that fluoride has a pπ-donor capacity similar to oxygen. Hence, there is good agreement between results from electrochemical, i.r. and ^1H n.m.r. studies for this unusual complex.

For the mixed alkoxy-anilide complexes, the molybdenum reduction is found to vary quite considerably according to the nature of the alcohol ligand. A large anodic shift of 210 mV is produced in going from cyclohexanol to 1,1,1-trifluoroethanol, due to the strongly electron-withdrawing nature of the trifluoromethyl group. This observation is in keeping with the trends found in the δ(NH) values from ^{1}H n.m.r. spectroscopy.

The oxidation potential of the ferrocenyl moiety is found to be relatively insensitive to complexation and to metal centre character. Attachment of the ligand 4-hydroxyphenylferrocene to a molybdenum centre produces anodic shifts of 40-50 mV and attachment to a tungsten centre gives a lower anodic shift of 30 mV. Anodic shifts are larger for 4-aminophenylferrocene; 100 mV for molybdenum and 70 mV for tungsten complexation. These results provide some slight evidence for the greater electron-acceptor power of {Mo(NO)L*(Cl)} over {W(NO)L*(Cl)}, but the differences are not large. Furthermore, the observation of larger shifts for the anilide complexes shows that interaction between {M(NO)L*(X)} and the ferrocenyl group is more significant in anilido than in analogous phenoxide complexes. Much smaller anodic shifts are found for azo ligands (0-30 mV), and also for stilbenyl complexes (20-30 mV), owing to greater distance between the two metal centres.

III-1.3(f) U.V.-Visible Absorption Spectra and Solvatochromism Studies

Electronic absorption spectra were measured for a number of the ferrocenyl complexes in dichloromethane, and other solvents were used for selected compounds to search for any evidence of solvatochromic behaviour. Results are shown in Tables XII and XIII.

Table XII shows that most of the complexes studied have one absorption in the visible and another in the u.v., with larger extinction coefficients for the u.v. bands. The mono-aryl anilide complexes have two visible bands and one in the u.v. The mono-aryl complexes all have strong visible and u.v. absorptions, with ε

values ranging from about 7,000 to 8,000 mol^{-1} dm^3 cm^{-1} for the visible and 13,000 to 24,000 mol^{-1} dm^3 cm^{-1} for the u.v. The azo complexes have stronger absorptions, and several bands, both u.v. and visible, have very high ε values in excess of 30,000 mol^{-1} dm^3 cm^{-1}. These high extinction coefficients are clear evidence for extensive charge-transfer interactions between ferrocenyl ligands and coordinated {M(NO)L*} centres, which are necessary for high molecular hyperpolarisability values. However, it is not possible to be more specific about the precise nature of the bands observed without further detailed physical data.

TABLE XII

U.V.-Visible Excitation Maxima for Selected Ferrocenyl Complexes

M	X[a]	Y[a]	λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})[b]		
Mo	Cl	OΦFc	502 (6,800)	286 (14,000)	
Mo	I	OΦFc	522 (7,500)	284 (13,000)	
Mo	OΦFc	OΦFc	430 (8,200)	288 (23,700)	
Mo	Cl	HNΦFc	588 (8,300)	462 (14,000)	287 (14,100)
Mo	I	HNΦFc	618 (8,000)	479 (13,400)	285 (12,400)
Mo	Cl	OΦN=NΦFc	500 (17,200)	359 (33,600)	
Mo	I	OΦN=NΦFc	482 (15,600)	360 (27,900)	
Mo	OΦN=NΦFc	OΦN=NΦFc	468 (17,600)	371 (34,700)	
Mo	F	HNØN=NΦFc	509 (29,900)	441 (31,300)	
Mo	Cl	HNØN=NΦFc	488 (19,600)	358 (13,500)	
Mo	I	HNØN=NΦFc	511 (21,300)	379 (18,600)	
W	Cl	HNØN=NΦFc	427 (39,800)		

[a] Φ = $-C_6H_4-$, Ø = $-C_6H_3-3-CH_3-$, Fc = $-4-(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)$.

[b] All spectra recorded in dichloromethane at ambient temperature, concentration *ca* 10^{-5} M.

TABLE XIII

Solvent Dependence of U.V.-Visible Excitation Maxima for Selected Ferrocenyl Complexes

M	X[a]	Y[a]	λ_{max}/nm[b] n-hexane	DCM	DMF	Δλ/nm[c]
Mo	Cl	OΦFc	485	502	502	17
			290	286	282	8
Mo	I	OΦFc	478	522	530	52
			290	284	286	6
Mo	OΦFc	OΦFc	420	430	433	13
			282	288	281	7
W	Cl	OΦFc	393	405	405	12
			273	279	279	6
W	OΦFc	OΦFc	352	360	360	8
Mo	Cl	HNΦFc	545	588	576	43
			485	462	458	27
			280	287	280	7
Mo	I	HNΦFc	572	618	608	36
			479	479	478	1
			292	285	286	7
W	Cl	HNΦFc	395	400	400	5
Mo	Cl	OΦN=NΦFc	508	500	495	13
			354	359	362	8
Mo	I	OΦN=NΦFc	540	482	dec.	58
			357	360		3
Mo	Cl	HNΦN=NΦFc	480	480	476	4
			351	355	358	7
W	Cl	HNΦN=NΦFc	416	422	426	10
Mo	F	HNØN=NΦFc	497	509	528	31
			437	441	445	8

TABLE XIII (*Continued*)

M	X[a]	Y[a]	λ_{max}/nm[b] n-hexane	DCM	DMF	Δλ/nm[c]
Mo	Cl	HNØN=NΦFc	496	488	480	16
			350	358	361	11
Mo	I	HNØN=NΦFc	520	511	497	23
			382	379	379	3
W	Cl	HNØN=NΦFc	413	427	432	19
Mo	Cl	HNΦCH=CHΦFc	498	519	516	21
			331	335	341	10
Mo	I	HNΦCH=CHΦFc	514	536	536	22
			332	340	346	14
W	Cl	HNΦCH=CHΦFc	415	430	431	16
			350	325	333	25

[a] Φ = $-C_6H_4-$, Ø = $-C_6H_3-3-CH_3-$, Fc = $-4-(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)$.
[b] All spectra recorded at ambient temperature, concentrations *ca* 10^{-5} M. [c] Difference between highest and lowest λ_{max} values.

The extensive solvent studies recorded in Table XIII show that some shifts in absorption bands do occur, but differences are generally small. The number of bands and overall absorption profile of the u.v.–visible spectrum does not change with solvent for any of the complexes studied.

Spectra for all of the complexes were recorded from the near i.r. (1,000 nm) into the visible, and it was found that most absorb only very little above the visible–i.r. boundary of 700 nm. Approximate absorption "cut-off wavelengths" above which absorption is less than 1% of that of the visible peak are shown in Table XIV. These values are of interest when considering possible SHG into the visible or near i.r.

TABLE XIV

Absorption Edges for Selected Ferrocenyl Complexes

M	X[a]	Y[a]	λ/nm[b]
Mo	Cl	OΦFc	1,000
Mo	I	OΦFc	1,020
Mo	OΦFc	OΦFc	860
W	Cl	OΦFc	740
W	OΦFc	OΦFc	660
Mo	Cl	HNΦFc	800
Mo	I	HNΦFc	820
W	Cl	HNΦFc	650
Mo	Cl	OΦN=NΦFc	880
Mo	I	OΦN=NΦFc	800
Mo	OΦN=NΦFc	OΦN=NΦFc	780
Mo	Cl	HNΦN=NΦFc	760
W	Cl	HNΦN=NΦFc	680
Mo	F	HNØN=NΦFc	700
Mo	Cl	HNØN=NΦFc	770
Mo	I	HNØN=NΦFc	800
W	Cl	HNØN=NΦFc	680
Mo	Cl	HNΦCH=CHΦFc	740
Mo	I	HNΦCH=CHΦFc	760
W	Cl	HNΦCH=CHΦFc	660

[a] Φ = $-C_6H_4-$, Ø = $-C_6H_3-3-CH_3-$, Fc = $-4-(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)$.

[b] All spectra recorded at ambient temperature in dichloromethane, concentrations *ca* 10^{-5} M.

All of the complexes absorb very strongly around 530 nm, making SHG of a 1,064 nm laser fundamental impractical because of extensive absorption leading to thermal damage. However, doubling of the 1,907 nm laser wavelength produces a harmonic at 953 nm, and Table XIV shows that most of the complexes show negligible absorption at wavelengths well below this value. Several spectra were recorded from further into the i.r. (2,500 nm) and these showed no absorptions in the 1,000-2,500 nm range.

Some general trends which emerge from the data in Table XIV are that all of the tungsten complexes show considerably lower wavelength cut-offs than their molybdenum counterparts; differences range from 80 to 260 nm. Also, the phenoxide complexes of both molybdenum and tungsten have cut-offs which are higher than their anilide analogues by 90-200 nm. Addition of a methyl substituent or changing azo for stilbene have negligible effects on cut-off wavelengths.

III-1.4 KURTZ POWDER TESTS

Almost all of the complexes described in this Chapter were tested for SHG using modifications of the standard Kurtz powder test on unsized powdered samples. Samples were contained in small wells of dimensions 2 x 5 mm formed by fixing a metal washer between a glass microscope slide and glass cover-slip using araldite glue.

Tests were carried out over a period of years at two separate locations using slightly differing techniques, and results are presented in Table XV. Although these reveal that a number of the complexes give SHG signals which are considerably greater than that from a similarly mounted urea powder reference sample, there clearly exist large discrepencies between the two sets of figures. This is not due to sample decomposition with time nor is it a result of any other factors pertaining to sample nature, but arises from physical differences between the two sets of apparatus used to record the SHG signals. Some effort will now be made to explain these inconsistencies, and also to make some observations concerning the general trends evident in Table XV.

TABLE XV

Powder SHG Data for Ferrocenyl Complexes

No.	M	X[a]	Y[a]	SHG[b]	SHG[c]
[71]	Mo	Cl	OΦFc	n.d.	
[72]	Mo	I	OΦFc	0.009	
[73]	Mo	OΦFc	OΦFc	v.w.	
[74]	W	Cl	OΦFc	n.d.	
[75]	W	OΦFc	OΦFc	n.d.	
[76]	Mo	Cl	HNΦFc	0.01	
[77]	Mo	I	HNΦFc	1.15	0.4
[78]	W	Cl	HNΦFc	n.d.	
[79]	Mo	Cl	HNØFc		n.d.
[80]	Mo	I	HNØFc		n.d.
[81]	W	Cl	HNØFc		n.d.
[82]	Mo	Cl	OΦN=NΦFc	v.w.	
[83]	Mo	I	OΦN=NΦFc	0.06	n.d.
[85]	Mo	Cl	HNΦN=NΦFc	59	5.5
[86]	W	Cl	HNΦN=NΦFc		3.4
[89]	Mo	F	HNØN=NΦFc		n.d.
[87]	Mo	Cl	HNØN=NΦFc	123	5.4
[90]	Mo	Br	HNØN=NΦFc		3.8
[88]	Mo	I	HNØN=NΦFc	0.12	0.9
[92]	W	Cl	HNØN=NΦFc	53	2.5
[93]	Mo	Cl	HNØN=NØFc		0.7
[94]	Mo	I	HNØN=NØFc		n.d.
[95]	W	Cl	HNØN=NØFc		n.d.

TABLE XV (*Continued*)

No.	M	X[a]	Y[a]	SHG[b]	SHG[c]
[97]	Mo	Cl	HNΦCH=CHΦFc		6.0
[98]	Mo	I	HNΦCH=CHΦFc		7.5
[99]	W	Cl	HNΦCH=CHΦFc		2.4
[96]	Mo	Cl	HNØN=NØN=NØFc		n.d.

[a] Φ = $-C_6H_4-$, Ø = $-C_6H_3-3-CH_3-$, Fc = $-4-(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)$.
[b] Relative harmonic intensity for second harmonic generation measured with a 1,907 nm laser wavelength using a urea powder standard; measurement made at GEC Marconi Research Centre.
[c] Relative harmonic intensity for second harmonic generation measured with a 1,907 nm laser wavelength using a urea powder standard; measurement made at Durham University. n.d. = no SHG detected. v.w. = very weak signal.

(i) **GEC Marconi Research Centre, London.**

Tests were carried out by P. V. Kolinsky and R. J. Jones between June 1988 and June 1989. The 1,064 nm fundamental output of a Nd:YAG laser was passed through a specially built high pressure hydrogen cell to give a Raman-shifted output at 1,907 nm. There is no reason to question the reliability of the results obtained from these tests.

(ii) **Department of Applied Physics, Durham University.**

Tests were carried out by the author in February 1991, using the apparatus shown schematically in section I-2.5(a). Unfortunately, this set-up differs in several aspects from that used to make the initial measurements at GEC, and as a result it is not possible to make any detailed comparisons between the two sets of SHG efficiencies. The problem seems to be that the hydrogen cell used at Durham is considerably shorter than that used at GEC, and this leads to power outputs at 1,907 nm which are

reduced by a factor of about 40. It is necessary to defocus the laser beam incident upon the sample to record meaningful SHG signals because this ensures that the beam is spread over a sufficient number of randomly orientated crystallites. However, with such a low initial output from the Raman cell, this cannot be achieved without loss of incident power to a level which is insufficient to record SHG signals.

Because of the factors outlined above, the Durham experiments yielded SHG values for the complexes which are much lower than those obtained at GEC; *e.g.* a reduction by a factor of 23 for [87], and by a factor of 21 for [92]. However, the highly NLO-active organic compound DAN [6] was found to give a signal 5.0 Ξ (Ξ = SHG efficiency of urea at 1,907 nm, taken as unity) which also represents a reduction by a factor of 23 from the literature value of 115 Ξ for this compound.[16] Hence there is at least some consistency in the relative SHG values, if not in their actual magnitudes.

Another unfortunate result of the low power used in the Durham experiments is that the signal-to-noise ratio was found to be extremely low, thus rendering the detection of harmonic signals smaller than about 0.3 Ξ impossible. In the GEC tests a much smoother background (*i.e.* high signal-to-noise ratio) meant that SHG intensities as low as 0.001 Ξ could be detected. Therefore complexes which showed no detectable signal at Durham cannot be described as definitely inactive, but merely as not active enough to measure. It should be noted that the quoted SHG values for the Durham experiments are averaged results taken from a total of five readings for each sample recorded at different times. This gives more accurate data from readings which showed considerable fluctuations of as much as ± 50% with time.

Trends in SHG Activity

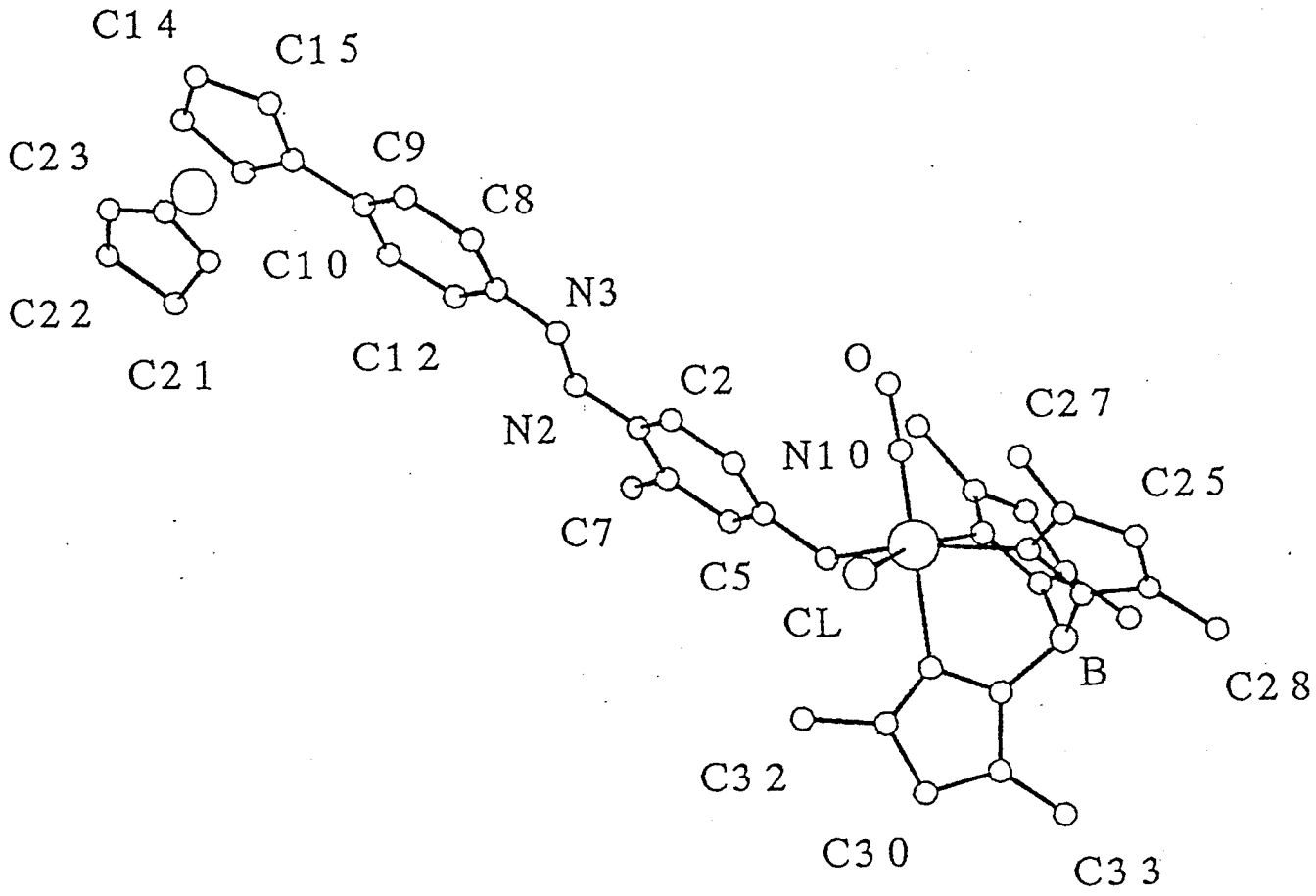
The first and most obvious conclusion to be drawn from Table XV is that none of the complexes of mono-arylferrocenyl ligands show significant SHG, with the exception of [77] which is about as active as urea. Many of the ferrocenylazobenzene complexes show

[Mo(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] [87]

This complex was crystallised by slow evaporation from dichloromethane, and the structure solved by M. B. Hursthouse and M. Harman. The molecular structure, shown in Fig. 32, does not display any unusual features. As in the nitro-ferrocenyl ligand precursor, the azobenzene residue has the *trans* configuration, and the two ferrocenyl cyclopentadienyl rings are essentially eclipsed. Bond lengths and angles for this ligand are as expected.

Fig. 32

Molecular Structure of [Mo(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)]



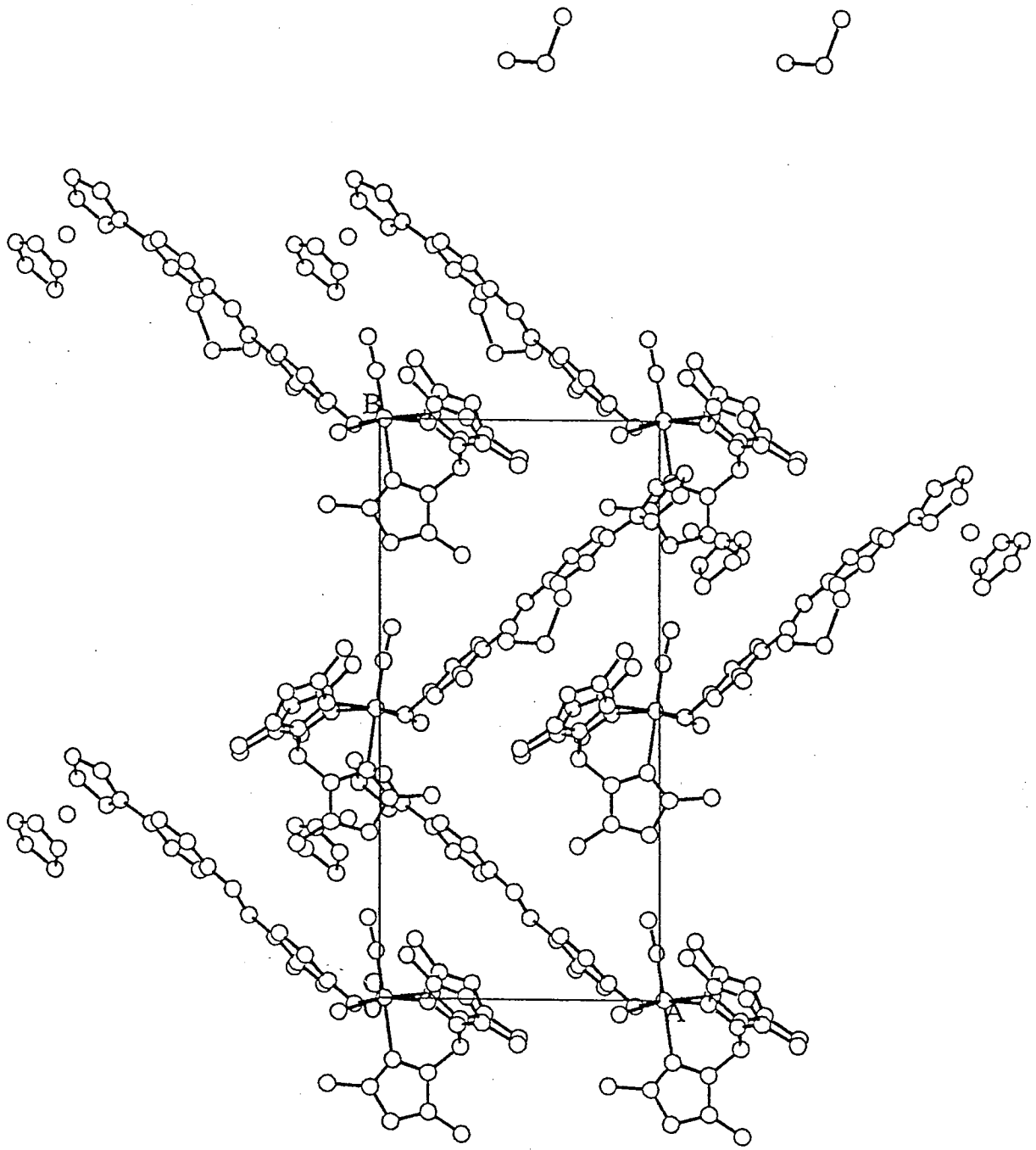
Some important dimensions for the molecular structure are as follows. The Mo-Cl bond length of 2.392(7) Å is relatively short for a pure σ-bond, thus implying some degree of chlorine to molybdenum π-donation. The nitrosyl has an N-O bond length of 1.262(26) Å and is almost linearly coordinated with an Mo-N-O

angle of 172.0(15)°. The Mo-NO bond length of 1.729(20) Å is the shortest of all the five Mo-N bonds, the average of the three Mo-N(pyrazolyl) bonds being 2.201 Å. Other values are discussed later with comparisons drawn between the Mo and W structures.

Fig. 33

Crystal Packing Diagram for

[Mo(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)]



The molecules of [87] pack in the monoclinic non-centrosymmetric space group $P2_1$ with 2 molecules in the unit cell and unit cell parameters a = 10.0954(2), b = 20.6345(5), c = 10.3965(5) Å, and β = 91.9109(3)°. A packing diagram, depicted in Fig. 33, shows how the molecules align in a "herring-bone" array with one uncoordinated molecule of dichloromethane included in the lattice. The presence of this solvent is also shown by elemental analyses and ^{1}H n.m.r. spectroscopy. An alternative view of the crystal packing is shown in Fig. 34. The crystal contains only one single enantiomer of the possible *R* and *S* configurations at molybdenum, but precisely which absolute configuration about the metal is present cannot be decided without further physical data.

Since it is known that there are certain optimum angular relations between the molecular dipolar axis and the crystallographic axes to give maximum phase-matched SHG (PMSHG), some simple calculations have been carried out to assess the effectiveness of the molecular, and hence dipolar, orientation within this packing array. The complicated shape of the polarisation chain between the iron and molybdenum centres precludes a totally accurate identification of the true dipolar axis, but estimates can be used with reasonable confidence. The angle between the N(3)-C(16) vector, which was taken as a good approximation to the dipolar axis, and the crystallographic b axis is 56.88°. Also, that between the Mo-C(16) vector, an alternative polarisation axis, and the b axis is 58.39°. Both of these values are very close to the optimum value of θ_m = 54.74° for PMSHG in the $P2_1$ space group,[66] so it would seem that the packing of this molecule is close to the ideal for maximum SHG.

A very similar angle of alignment is found in the organic compound NPP [7] which also crystallises in the $P2_1$ space group,[23] has θ = 58.6° and exhibits a powder SHG of 150 x urea. The crystal structure of this organic is influenced not only by the chirality of the L-prolinol group, but also by intermolecular hydrogen-bonds between the hydroxyl of one molecule and the nitro group of the next. These serve to hold the molecules in the head-to-tail fashion which gives rise to effective dipolar orientation for near-optimal SHG. By contrast, no H-bonds are present in the

crystal structure of the molybdenum complex, and it is the overall shape of the molecule, dominated by the chiral molybdenum centre and the bulky ferrocenyl moiety, which gives rise to the favourable packing arrangement. A crystal packing diagram of NPP is shown in Fig. 35 for comparison with that of the complex.

Fig. 34

Alternative Crystal Packing Diagram for

[Mo(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)]

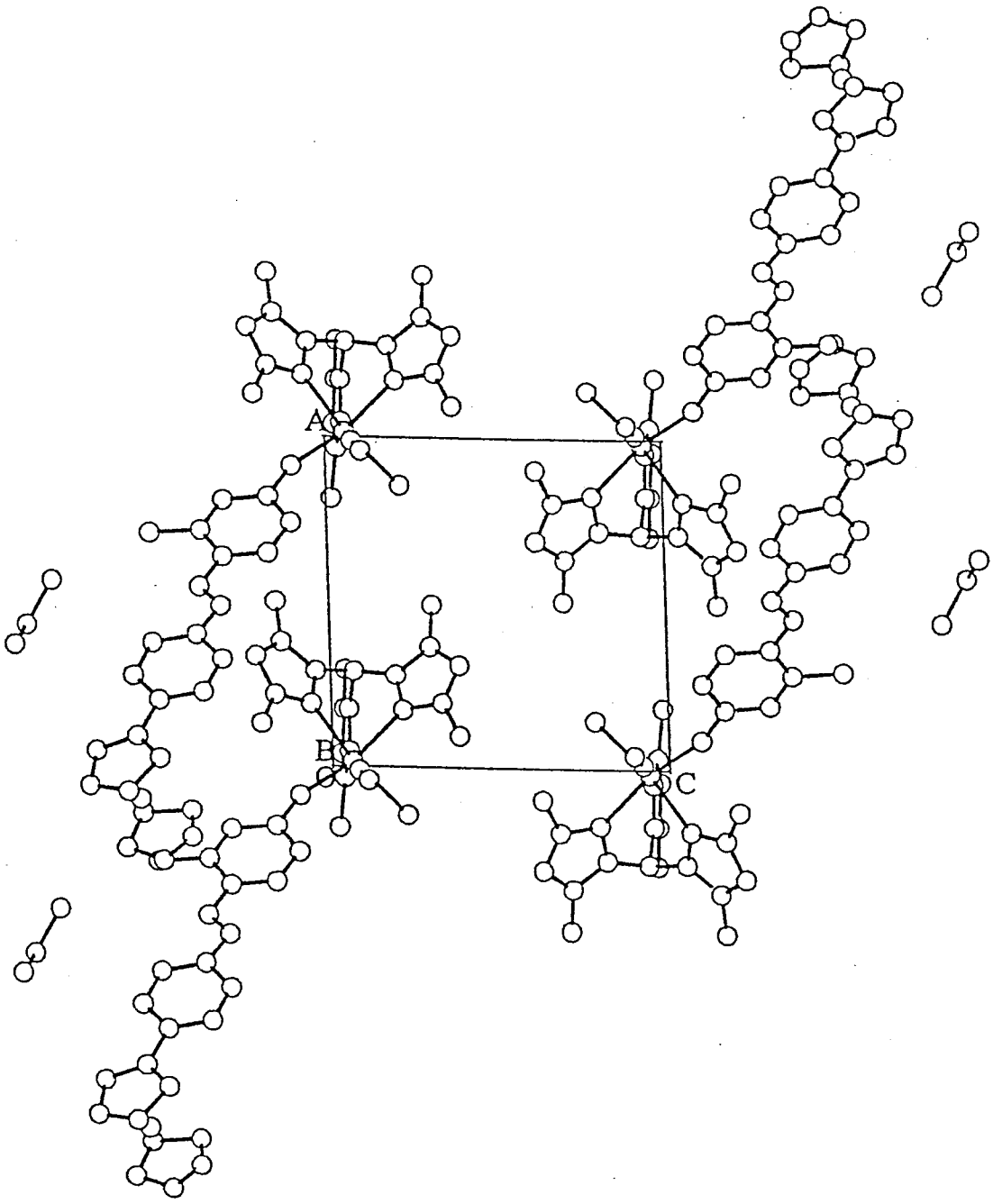
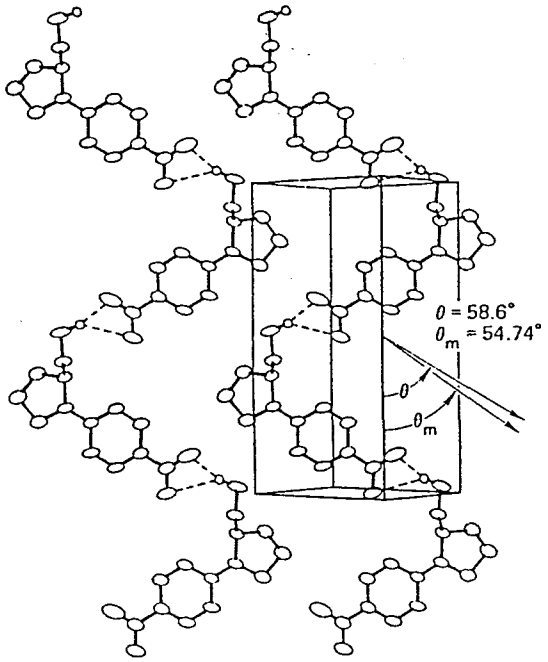


Fig. 35

Crystal Packing Diagram for N-(4-Nitrophenyl)-(L)-prolinol (NPP)



[W(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] [92]

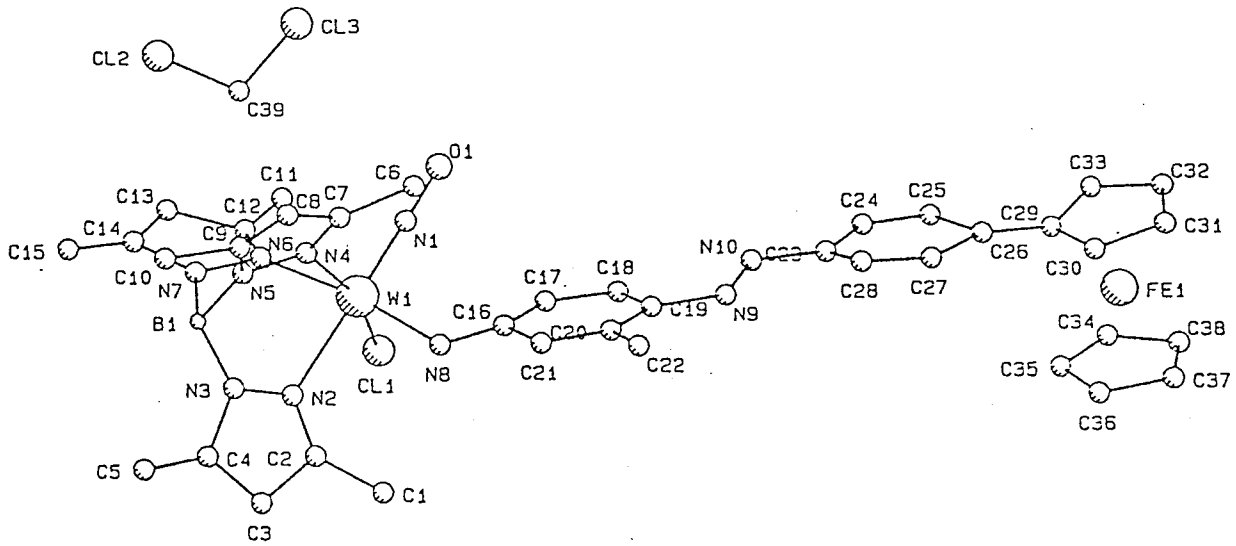
This complex was crystallised by slow evaporation from a mixture of dichloromethane and absolute ethanol, and the structure solved by J-D. Foulon and T. A. Hamor. [92] adopts isostructural molecular and crystal packing arrangements to its molybdenum analogue [87], which might be expected since the two metals have similar covalent radii and the coordination geometry is unchanged. In the only previous case for which both tungsten and molybdenum (M(NO)L*) crystal structures have been solved, the bis-amido pyridine complexes [M(NO)L*(2-NH-C$_5$H$_4$N)$_2$] (M = Mo, W), it was also found that changing the metal atom has no significant effects on the solid state structure.[203]

Some important dimensions for the molecular structure (Fig. 36) are as follows. The W-Cl bond length of 2.373(15) Å is relatively short for a pure σ-bond, implying some degree of chlorine to tungsten π-donation. This is also observed in the molybdenum complex. The nitrosyl has an N-O bond length of

1.248(44) Å and shows more nearly linear coordination than in the Mo analogue with a W-N-O angle of 178.2(31)°. The W-NO bond length of 1.730(27) Å is the shortest of all the five W-N bonds, the average of the three W-N(pyrazolyl) bonds being 2.215 Å. The W-N(amido) bond length of 2.056(32) Å is short for a pure single bond, and hence some degree of pπ-dπ ligand to metal donation may be present. The large W-N(8)-C(16) angle of 133.1(32)° is consistent with this assertion. The corresponding bond in the molybdenum analogue is significantly shorter at 1.932(14) Å, with a slightly larger Mo-N(1)-C(6) angle of 134.8°. This may be an indication of an increased degree of pπ-dπ donation in the molybdenum complex resulting from the greater electron acceptor strength of the metal centre. Furthermore, the short bond length N-C_6H_4 of 1.294(45) Å indicates some delocalisation between phenyl ring and amido nitrogen. Such a competitive delocalisation does not appear to occur in the molybdenum analogue where the corresponding C-N bond length is 1.425(17) Å.

Fig. 36

Molecular Structure of [W(NO)L*(Cl)(HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-Fc)]



Again, bond lengths and angles for the azobenzene ligand residue are much as would be expected, with a *trans* configuration and an eclipsed ferrocenyl moiety attached. The tilt angle between

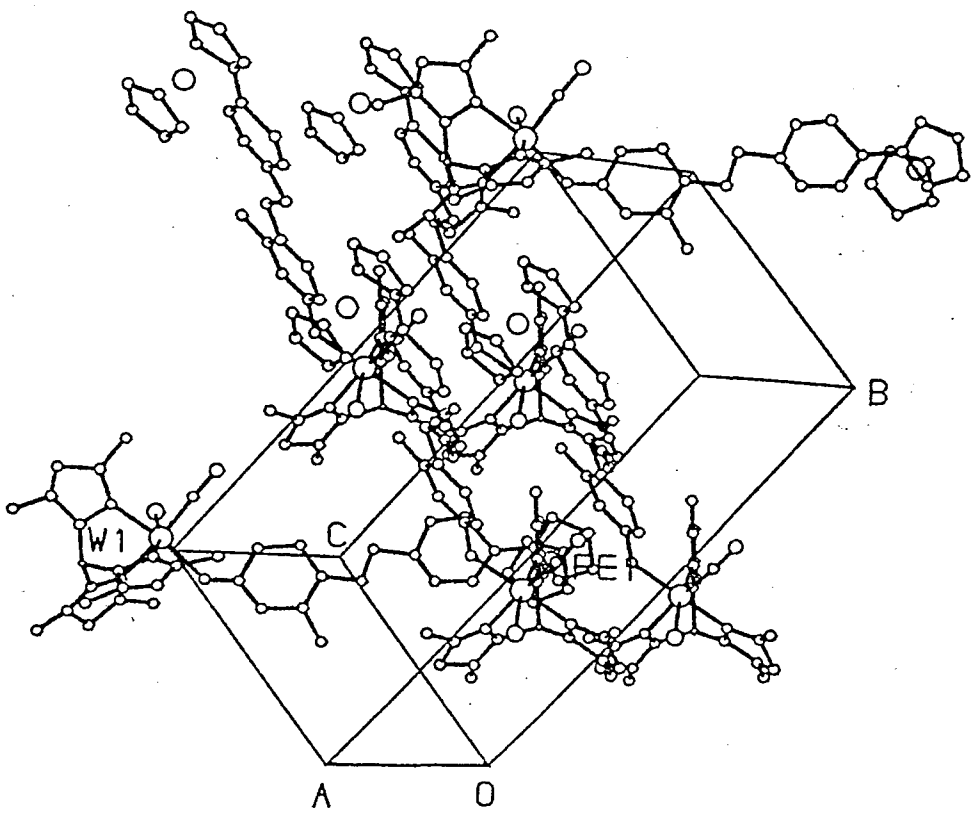
the C_5H_4 cyclopentadienyl ring and the attached phenyl ring is 13.5° which is almost half of the rotation about the C(29)-C(30) bond observed in the ligand precursor 4-nitro-2-methyl-4'-ferrocenylazobenzene discussed earlier in II-1.4.

As with the molybdenum analogue, the molecules of [92] pack in the monoclinic non-centrosymmetric space group $P2_1$ with unit cell parameters a = 10.150(7), b = 20.455(7), c = 10.367(3) Å, and β = 91.79(3)°. A packing diagram (Fig. 37) shows, once again, the distinctive "herring-bone" packing with one molecule of dichloromethane included in the lattice. The crystal contains only one single enantiomer, and the absolute configuration about the metal is the same as for the molybdenum analogue. The angle between the W-C(29) vector and the b axis is 59.5°, which is close to that found in the molybdenum structure, and the angle between the N(10)-C(29) vector and the b axis is 58.7°.

Fig. 37

Crystal Packing Diagram for

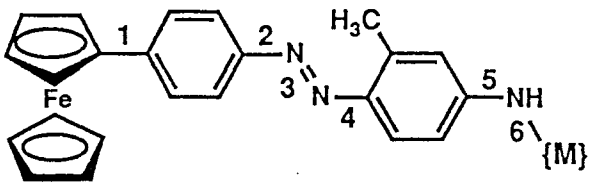
[W(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)]



Bond length values for the proposed ferrocenyl to {M(NO)L*} delocalisation path are shown in Table XVI.

TABLE XVI

Bond Lengths* for the Polarisable Bridge



{M} = M(NO)L*Cl; M = Mo, W

Bond	M = Mo	M = W
(1)	1.528(22)	1.323(33)
(2)	1.391(19)	1.450(49)
(3)	1.271(20)	1.230(39)
(4)	1.412(18)	1.432(52)
(5)	1.425(17)	1.294(45)
(6)	1.932(14)	2.056(32)

* In Å with e.s.d.'s in parentheses.

Crystals of several of the other SHG-active ferrocenyl complexes have been grown, but unfortunately these were in every case unsuitable for structural determination. However, some data for the molybdenum bromide complex [90] was collected at QMC which revealed that this has the same space group as the analogous Mo and W complexes described above, *i.e.* $P2_1$.[250] This is unsurprising because replacement of chloride by bromide would not be expected to cause any significant structural changes.

III-1.5(b) Powder Diffraction Studies

In order to gain some further information concerning the solid state structures of these complexes and in the absence of any suitable single crystals, powder X-ray diffraction traces were recorded for a number of derivatives.

The complexes [Mo(NO)L*(I)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] [88] and [W(NO)L*(Cl)(HNC$_6$H$_4$-4-N=NC$_6$H$_4$-4-Fc)] [86] gave no peaks at all, but traces for those which did give a diffraction pattern are shown in Fig. 38. From these patterns the following general

observations can be made:

(i) [Mo(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] [87] and its tungsten analogue [92] have the same structure, a result confirmed by single crystal studies. The low SHG of the iodo analogue of [87], [88], is likely to be due to poor sample crystallinity since no powder X-ray diffraction trace could be obtained for this compound.

(ii) Removal of a methyl group from the ligand in [87] to give [Mo(NO)L*(Cl)(HNC$_6$H$_4$-4-N=NC$_6$H$_4$-4-Fc)] [85] does not substantially alter the crystal packing. Bearing in mind the overall shape and size of the molecule, this is not a surprising result.

(iii) Addition of a second methyl substituent to [87] to give [Mo(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_3$-3-CH$_3$-4-Fc)] [93] does not substantially alter the structure. However, the iodo analogue of [93], [Mo(NO)L*(I)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_3$-3-CH$_3$-4-Fc)] [94] has a different structure.

(iv) Changing the nitrogen donor atom in [85] for oxygen to give [Mo(NO)L*(Cl)(OC$_6$H$_4$-4-N=NC$_6$H$_4$-4-Fc)] [82] gives rise to a different structure, and [Mo(NO)L*(I)(OC$_6$H$_4$-4-N=NC$_6$H$_4$-4-Fc)] [83] has a different structure again. These observations are perhaps surprising since neither the donor atom nor the halide is expected to be structurally influential. However, the fact that neither of the phenoxide complexes shows any powder SHG whilst [85] is highly active makes this result more acceptable.

(v) Subtle alteration of the polarisable bridge by replacing the azo linkage in [85] with ethylene to give the stilbenyl complex [Mo(NO)L*(Cl)(HNC$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-Fc)] [97] does not alter the crystal structure substantially. This is expected since CH=CH and N=N are isoelectronic functions and both adopt a *trans* geometry.

(vi) Substituting W for Mo in the stilbenyl complex [97] to give [W(NO)L*(Cl)(HNC$_6$H$_4$-4-N=NC$_6$H$_4$-4-Fc)] [99] does not alter the structure. This agrees with observation *(i)*.

(vii) Replacement of chloride ligand by iodide in [97] to give [Mo(NO)L*(Cl)(HNC$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-Fc)] [98] is also an isostructural change.

(viii) Replacement of chloride ligand by fluoride in [87] to

give [Mo(NO)L*(F)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] [89] produces a different structure.

Summary

ISOSTRUCTURAL CHANGES include: changing Mo for W; sometimes changing Cl ligand for I (or Br, from single crystal data); changing N=N for CH=CH; attaching a methyl group to a phenyl ring.

NON-ISOSTRUCTURAL CHANGES include: changing donor atom N for O; changing Cl ligand for F, or sometimes for I.

It should be noted that these conclusions can only be applied to the ferrocenyl complexes discussed, and may not necessarily be true for other ligand systems.

III-1.6 CONCLUSIONS

The inconsistencies in the powder SHG data (Table XV) coupled with the crude nature of the powder diffraction studies described in III-1.5(b) make it impossible to draw many firm conclusions concerning structure-activity relationships for these molybdenum and tungsten ferrocenyl complexes. However, reasonable conclusions which can be made are as follows:

(a) As expected, the tungsten analogues of the molybdenum complexes are isostructural, but show significantly lower NLO-activity due to the poorer electron-accepting nature of the more electron-rich W atom.

(b) Changing the halide ligand in {Mo(NO)L*(X)} (X = F, Cl, Br, or I) complexes may or may not alter the crystal structure. In cases where the structure is unaltered, SHG differences are probably not significant.

(c) None of the phenoxide complexes shows any NLO-activity, but this appears to be due to structural rather than electronic effects.

(d) Stilbenyl and azobenzene complexes are isostructural and display roughly eqivalent NLO-activity.

(e) Derivatisation of the azobenzene unit with methyl groups

does not alter the crystal structure, nor does it alter NLO-activity. This is because the crystal packing is decided by the overall shape of the complex which is dominated by the chiral {M(NO)L*} centre and the bulky ferrocenyl moiety.

(f) Complexes with a mono-aryl linkage between {M(NO)L*} and ferrocenyl groups show little or no NLO-activity. This is likely to be because the shorter molecules pack together in a centrosymmetric fashion, but this cannot be proven without single crystal structural data. The complex with a very long tris-aryl linkage shows no NLO-activity, and structural effects are again likely to be decisive.

Fig. 38

Powder X-Ray Diffraction Traces for Ferrocenyl Complexes

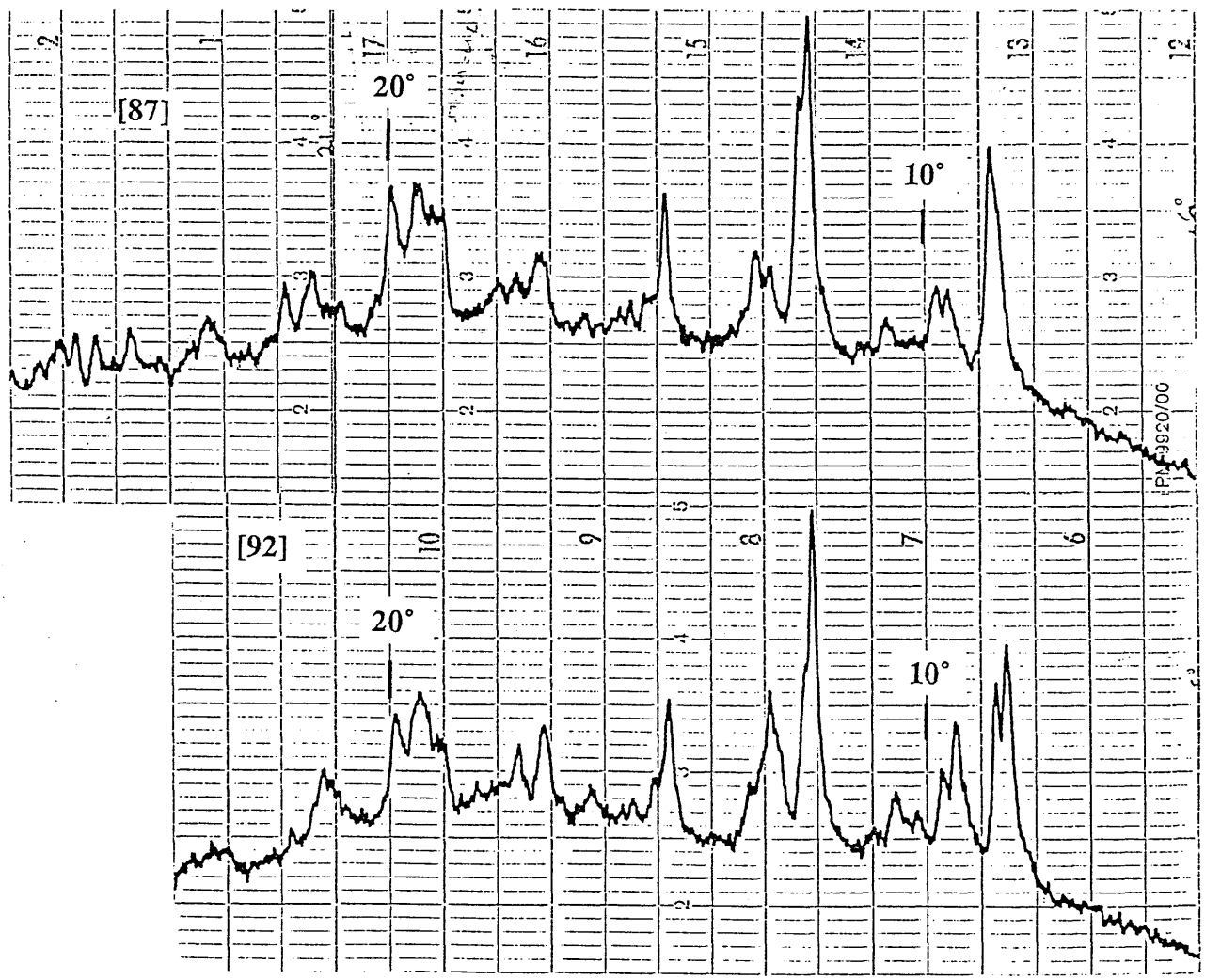


Fig. 38 (*Continued*)

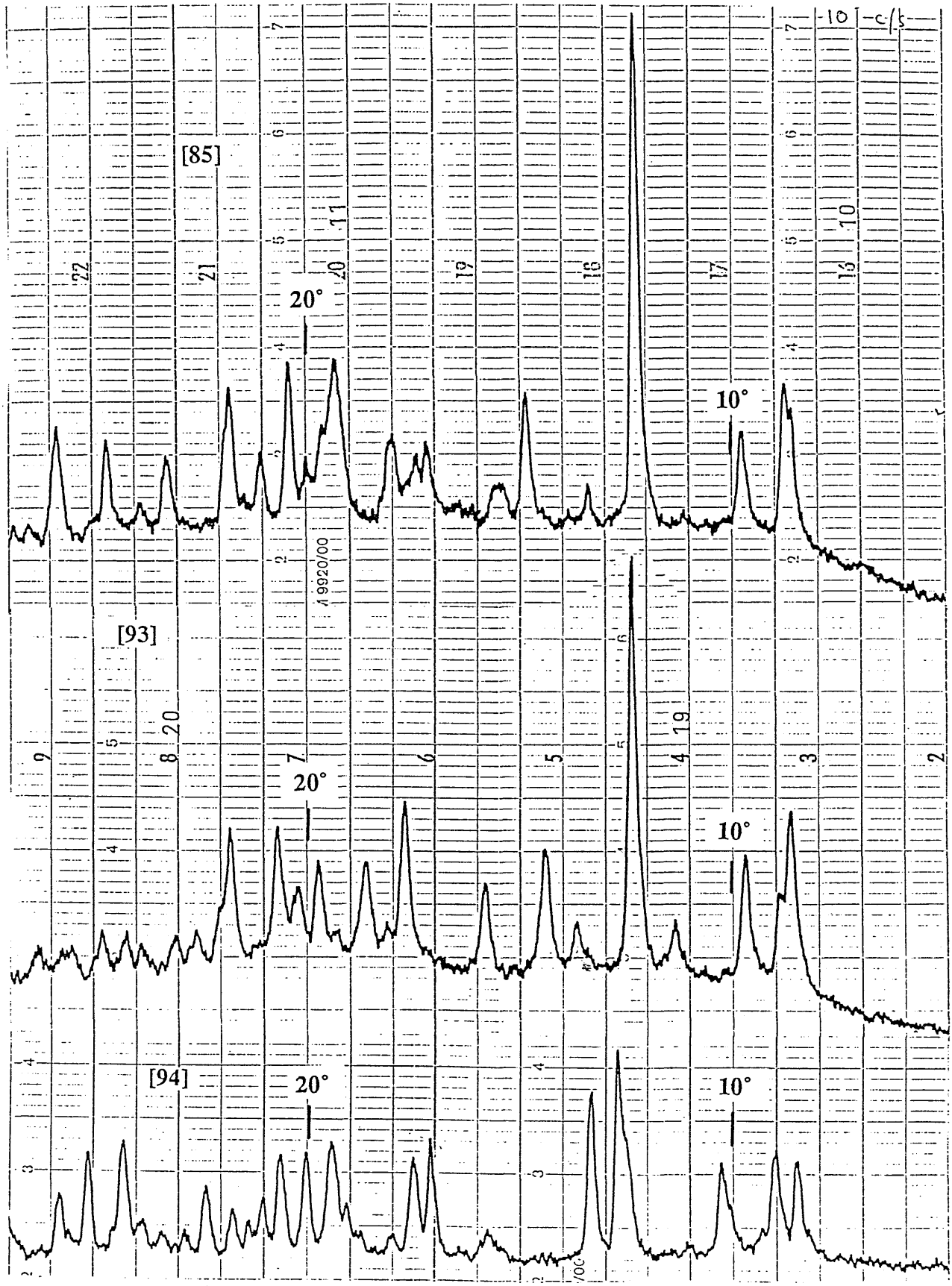


Fig. 38 (*Continued*)

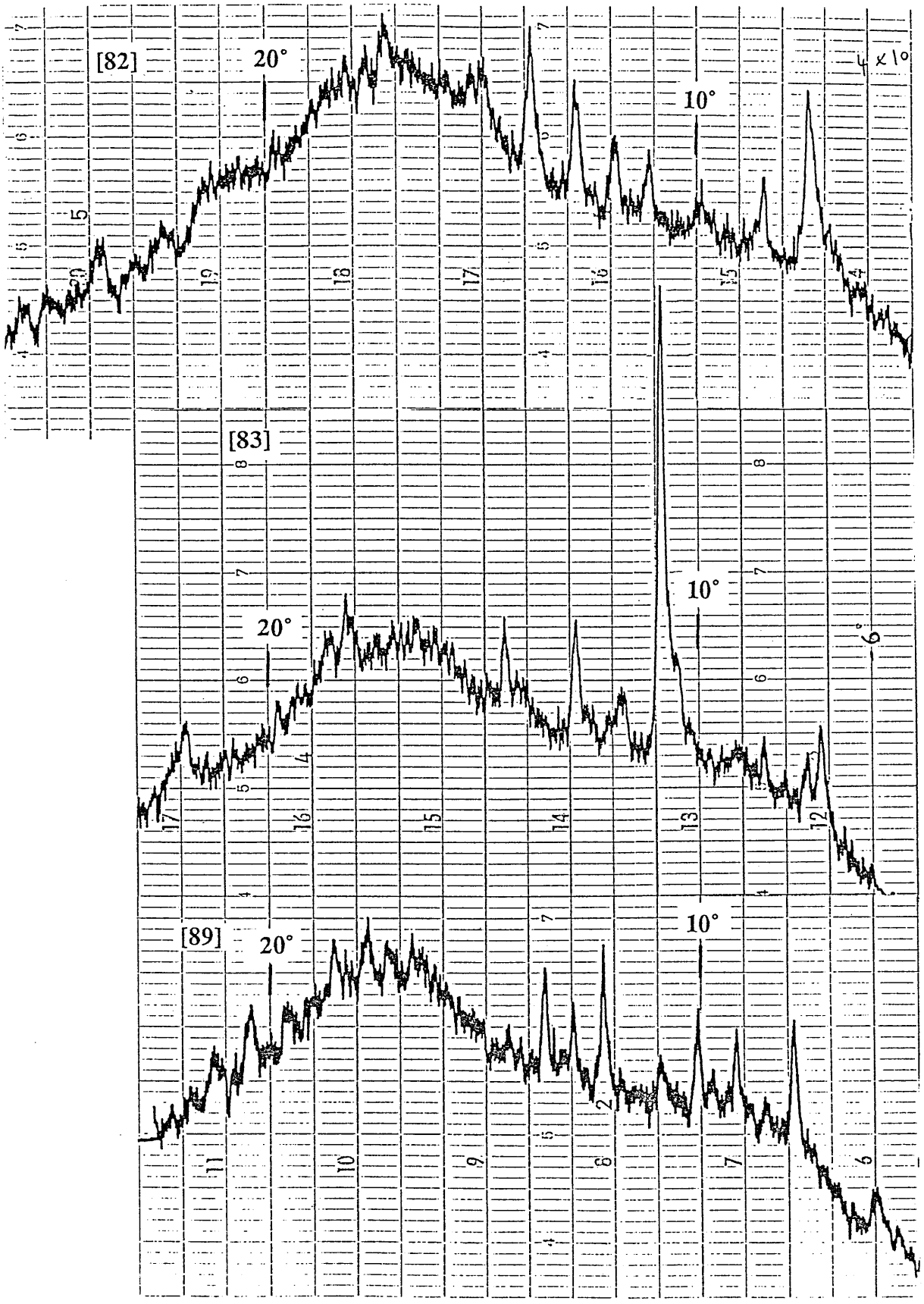
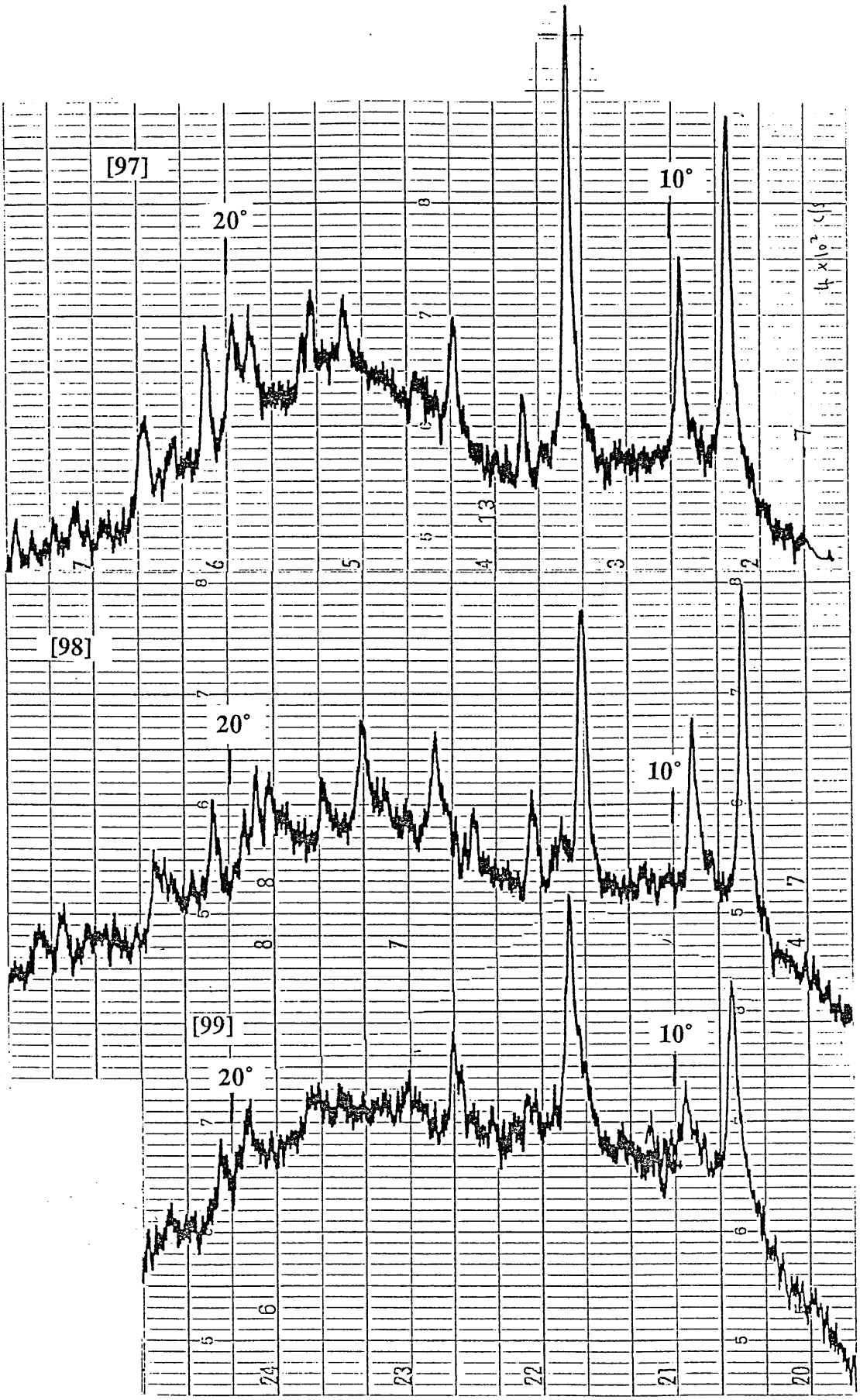


Fig. 38 (*Continued*)



III-2 EXPERIMENTAL

The complexes [Mo(NO)L*(I)$_2$], [Mo(NO)L*(F)$_2$], and [W(NO)L*(Cl)$_2$] were prepared by previously described methods.[187,188,191] [Mo(NO)L*(Cl)$_2$] and [Mo(NO)L*(Br)$_2$] were prepared by previously described methods,[186,188] and also using the new techniques described below. Since the diiodide is actually isolated as its mono toluene solvate [Mo(NO)L*(I)$_2$].C_7H_8, all yields are calculated taking this into account. Benzyl chloride and benzyl bromide were dried over magnesium sulphate and stored over molecular sieve type 4A prior to use. Triethylamine was dried over sodium and stored over activated alumina, and hexamine was recrystallised from absolute ethanol and dried under vacuum. Other reagents were used as supplied, and all reaction solvents were redistilled from drying agents according to standard methods prior to use. All reactions were performed under an atmosphere of dry nitrogen but the reaction products were handled in air. Column chromatography was carried out using silica gel 60 (70-230 mesh) or alumina 90 (70-230 mesh), and column dimensions of 40 x 2 cm unless otherwise specified.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}(Cl)$_2$]

A solution of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}(CO)$_2$] (1.00 g, 2.09 mmol), iodine (0.53 g, 2.09 mmol) and benzyl chloride (5 cm^3, 43.4 mmol) was stirred under reflux in toluene (55 cm^3) for 21 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure, and n-hexane (75 cm^3) added. The resulting yellow solid was removed by filtration, washed with n-hexane, and dried under vacuum to yield yellow [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}(Cl)$_2$] (1.00 g, 97%). $\nu_{max.}$(NO) 1700s cm^{-1}; δ_H($CDCl_3$) 5.98 and 5.80 [2 H, s; 1 H, s, ($Me_2C_3N_2$*H*)$_3$], 2.41, 2.39, and 2.38 [12 H, s; 3 H, s; 3 H, s, (*Me*$_2C_3N_2H)_3$].

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}(Br)$_2$]

A solution of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}(CO)$_2$] (1.00 g, 2.09 mmol), iodine (0.53 g, 2.09 mmol) and benzyl bromide (5 cm^3, 42.0

mmol) was stirred under reflux in toluene (55 cm^3) for 21 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure, and n-hexane (75 cm^3) added. The resulting dark solid was removed by filtration, washed with n-hexane, and dried under vacuum to yield red-orange [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Br)_2$] (1.16 g, 95%). $\nu_{max.}$(NO) 1700s cm^{-1}; δ_H($CDCl_3$) 5.95 and 5.90 [2 H, s; 1 H, s, ($Me_2C_3N_2$*H*)$_3$], 2.51, 2.44, 2.37, and 2.33 [3 H, s; 3 H, s; 6 H, s; 6 H, s, (*Me*$_2C_3N_2$H)$_3$].

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [71]

A solution of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.30 g, 0.61 mmol), 4-hydroxyphenylferrocene (0.21 g, 0.76 mmol) and hexamine (0.05 g, 0.36 mmol) was stirred under reflux in toluene (20 cm^3) for 3 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The resulting deep purple solid was purified by column chromatography on silica using 30% n-hexane/dichloromethane as the eluent. The major purple band was collected and crystallised from a dichloromethane/n-hexane mixture to afford the deep purple product (0.45 g, 95%). m.p. *ca* 240 °C (Found: C, 51.2; H, 4.9; N, 12.8%; M^+, 737. $C_{31}H_{35}BClFeMoN_7O_2$ requires C, 50.6; H, 4.8; N, 13.3%; M, 736); $\nu_{max.}$(NO) 1680s cm^{-1}; δ_H($CDCl_3$) 7.51 and 7.28 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4], 5.93, 5.88, and 5.78 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2$*H*)$_3$], 4.66 and 4.33 [2 H, d, J(HH) 4 Hz; 2 H, s, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.60, 2.41, 2.40, 2.24, and 2.06 [3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, (*Me*$_2C_3N_2$H)$_3$]; *m/z* 737 (M^+), 460 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 430 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 278 (HOC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [72]

This compound was prepared in an identical manner to [71] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(I)_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 4-hydroxyphenylferrocene (0.19 g, 0.68 mmol). A deep purple solid was obtained (0.41 g, 95%). m.p. *ca* 180 °C (Found: C, 43.7; H, 4.2; N, 10.7%; M^+, 829. $C_{31}H_{35}BFeIMoN_7O_2$.0.5CH_2Cl_2 requires C, 43.5; H, 4.2; N, 11.3%; M, 827); $\nu_{max.}$(NO) 1675s cm^{-1}; δ_H($CDCl_3$) 7.47 and 7.40 [2 H,

d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4], 5.91, 5.85, and 5.83 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.67 and 4.35 [2 H, d, J(HH) 4 Hz; 2 H, s, C_5H_4], 4.08 [5 H, s, C_5H_5], 2.60, 2.45, 2.40, 2.38, 2.35, and 1.99 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 829 (M^+), 700 (M - I), 552 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 519 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 278 (HOC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}$_2$] [73]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$.C_7H_8 (0.40 g, 0.52 mmol) and 4-hydroxyphenylferrocene (0.36 g, 1.29 mmol) using the procedure described for [71] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A black solid was obtained (0.46 g, 91%). m.p. *ca* 180 °C (Found: C, 57.7; H, 5.3; N, 10.3%; M^+, 979. $C_{47}H_{48}BFe_2MoN_7O_3$ requires C, 57.8; H, 5.0; N, 10.0%; M, 977); $\nu_{max.}$(NO) 1660s cm^{-1}; δ_H($CDCl_3$) 7.44 and 7.14 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.6 Hz, 2 x C_6H_4], 5.84, and 5.78 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.62 and 4.28 [4 H, s; 4 H, t, J(HH) 1.8 Hz, 2 x C_6H_4], 4.06 [10 H, s, 2 x C_5H_5], 2.43, 2.41, 2.24, and 2.19 [3 H, s; 6 H, s; 6 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 979 (M^+), 737 (M - 2 x Fe(η^5-C_5H_5)), 720 (M - 2 x Fe(η^5-C_5H_5) - NO), 702 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 424 (M - 2 x OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 278 (HOC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [74]

This compound was prepared in an identical manner to [71] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$], 4-hydroxyphenylferrocene (0.22 g, 0.79 mmol), and triethylamine (0.5 cm^3, 3.7 mmol). A dark brown solid was obtained (0.43 g, 76%). m.p. 265 °C (Found: C, 45.9; H, 4.0; N, 11.6%; M^+, 823. $C_{31}H_{35}BClFeN_7O_2W$ requires C, 45.2; H, 4.3; N, 11.9%; M, 824); $\nu_{max.}$(NO) 1640s cm^{-1}; δ_H($CDCl_3$) 7.50 and 7.21 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 5.93, 5.90, and 5.84 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.62 and 4.29 [2 H, t, J(HH) 1.8 Hz; 2 H, s, C_5H_4], 4.06 [5 H, s, C_5H_5], 2.68, 2.39, 2.32, and 2.19 [3 H, s; 9 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 823 (M^+), 792 (M - NO), 516 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 480 (M -

OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO - Cl), 278 (HOC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}$_2$] [75]

A solution of [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.50 g, 0.86 mmol) and 4-hydroxyphenylferrocene (0.50 g, 1.80 mmol) was stirred under reflux with sodium hydride (0.2 g) in toluene (40 cm^3) for 24 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The resulting dark brown solid was purified by column chromatography on silica using dichloromethane as the eluent. The major brown band was collected and crystallised from a dichloromethane/n-hexane mixture to afford the dark brown product (0.29 g, 32%). m.p. *ca* 215 °C (Found: C, 52.7; H, 4.3; N, 9.4%; M$^+$, 1065. $C_{47}H_{46}BFe_2N_7O_3W$ requires C, 53.0; H, 4.5; N, 9.2%; M, 1065); $\nu_{max.}$(NO) 1620s cm^{-1}; δ_H($CDCl_3$) 7.46 and 7.19 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.6 Hz, 2 x C_6H_4], 5.85 [3 H, s, ($Me_2C_3N_2H$)$_3$], 4.60 and 4.26 [4 H, s; 4 H, t, J(HH) 1.8 Hz, 2 x C_5H_4], 4.05 [10 H, s, 2 x C_5H_5], 2.43, 2.39, 2.33, and 2.28 [3 H, s; 6 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 1065 (M$^+$), 879 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5)), 790 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 757 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 513 (M - 2 x OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 278 (HOC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [76]

This compound was prepared in similar manner to [71] using 4-aminophenylferrocene (0.21 g, 0.76 mmol) in place of 4-hydroxyphenylferrocene and triethylamine (0.5 cm^3, 3.7 mmol) in place of hexamine, with a reaction time of 8 h. Column chromatography followed by recrystallisation yielded a dark brown solid (0.40 g, 90%) m.p. *ca* 275 °C (Found: C, 50.7; H, 5.1; N, 15.3%; M$^+$, 736. $C_{31}H_{36}BClFeMoN_6O$ requires C, 50.7; H, 5.0; N, 15.3%; M, 735); $\nu_{max.}$(NH) 3290w, $\nu_{max.}$(NO) 1660s cm^{-1}; δ_H($CDCl_3$) 12.64 [1 H, s, N*H*], 7.51 and 7.40 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 5.89, 5.87, and 5.79 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.68 and 4.37 [2 H, d, J(HH) 6.4 Hz; 2 H, s, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.70, 2.42, 2.38, 2.37, 2.18, and 2.04 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 736 (M$^+$), 706 (M - NO),

700 (M - Cl), 668 (M - C_5H_5), 640 (M - 96), 610 (M - 96 - NO), 460 (M - HNC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 430 (M - HNC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 277 ($H_2NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{HNC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [77]

This compound was prepared in an identical manner to [76] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-aminophenylferrocene (0.19 g, 0.69 mmol). A black solid was obtained (0.38 g, 88%). m.p. *ca* 275 °C (Found: C, 45.1; H, 4.7; N, 13.5%; M^+, 828. $C_{31}H_{36}BFeIMoN_8O$ requires C, 45.1; H, 4.4; N, 13.6%; M, 826); $\nu_{max.}$(NH) 3275w, $\nu_{max.}$(NO) 1655s cm^{-1}; δ_H($CDCl_3$) 13.09 [1 H, s, N*H*], 7.54 and 7.46 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4], 5.94, 5.86, and 5.76 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.69 and 4.38 [2 H, d, J(HH) 4.4 Hz; 2 H, s, C_5H_4], 4.08 [5 H, s, C_5H_5], 2.73, 2.52, 2.47, 2.37, and 2.00 [3 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 828 (M^+), 732 (M - 96), 699 (M - I), 603 (M - 223), 491 (M - HNC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - C_5H_5), 424 (M - HNC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - I), 277 ($H_2NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [78]

This compound was prepared in an identical manner to [76] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-aminophenylferrocene (0.22 g, 0.79 mmol), with a reaction time of 8 h. A red-brown solid was obtained (0.27 g, 48%) m.p. *ca* 290 °C (Found: C, 46.2; H, 4.4; N, 13.5%; M^+, 822. $C_{31}H_{36}BClFeN_8OW$ requires C, 45.3; H, 4.4; N, 13.6%; M, 823); $\nu_{max.}$(NH) 3290w, $\nu_{max.}$(NO) 1625s cm^{-1}; δ_H($CDCl_3$) 10.79 [1 H, s, N*H*], 7.50 and 7.33 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 5.95, 5.89, and 5.82 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.64 and 4.32 [2 H, s; 2 H, s, C_5H_4], 4.06 [5 H, s, C_5H_5], 2.74, 2.49, 2.43, 2.37, 2.36, and 2.16 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 822 (M^+), 726 (M - 96), 696 (M - 96 - NO), 277 ($H_2NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_3-2-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [79]

This compound was prepared in an identical manner to [76] using 4-amino-2-methylphenylferrocene (0.22 g, 0.76 mmol) in place of 4-aminophenylferrocene. A black-green solid was obtained (0.34 g, 74%). (Found: C, 50.2; H, 5.1; N, 14.7%; M^+, 750. $C_{32}H_{38}BClFeMoN_8O.0.25CH_2Cl_2$ requires C, 50.3; H, 5.0; N, 14.6%; M, 749); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1650s cm^{-1}; δ_H($CDCl_3$) 12.64 [1 H, s, N*H*], 7.72 and 7.34 [1 H, d, J(12) 8.2 Hz; 1 H, d, J(12) 8.2 Hz, C_6H_3(1 and 2)], 7.23 [1 H, s, C_6H_3(3)], 5.87, and 5.80 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.55 and 4.34 [2 H, d, J(HH) 2 Hz; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.71, 2.45, 2.42, 2.41, 2.38, 2.37, and 2.07 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$ and C_6H_3-CH_3]; *m/z* 750 (M^+), 713 (M - Cl), 654 (M - 96), 624 (M - 96 - NO), 291 ($H_2NC_6H_4$-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{HNC_6H_3-2-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [80]

This compound was prepared in an identical manner to [79] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-amino-2-methylphenylferrocene (0.20 g, 0.69 mmol). A black solid was obtained (0.29 g, 66%) (Found: C, 45.5; H, 4.7; N, 13.5%; M^+, 842. $C_{32}H_{38}BFeIMoN_8O$ requires C, 45.7; H, 4.6; N, 13.3%; M, 840); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1655s cm^{-1}; δ_H($CDCl_3$) 13.09 [1 H, s, N*H*], 7.68 and 7.50 [1 H, d, J(12) 8.4 Hz; 1 H, d, J(12) 8.4 Hz, C_6H_3(1 and 2)], 7.35 [1 H, s, C_6H_3(3)], 5.93, 5.86, and 5.77 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.56 and 4.35 [2 H, d, J(HH) 2 Hz; 2 H, t, J(HH) 1.7 Hz, C_5H_4], 4.15 [5 H, s, C_5H_5], 2.73, 2.50, 2.49, 2.46, 2.37, and 2.03 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$ and C_6H_3-CH_3]; *m/z* 842 (M^+), 746 (M - 96), 713 (M - I), 291 ($H_2NC_6H_4$-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_3-2-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [81]

This compound was prepared in an identical manner to [79] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-amino-2-methylphenylferrocene (0.23 g, 0.79 mmol), with a reaction time of 10 h. A red-brown solid was obtained (0.11 g, 19%) (Found: C, 44.2; H, 4.6; N,

13.0%; M^+, 836. $C_{32}H_{38}BClFeN_8OW.0.5CH_2Cl_2$ requires C, 44.4; H, 4.5; N, 12.8%; M, 837); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1620s cm^{-1}; $\delta_H(CDCl_3)$ 10.77 [1 H, s, NH], 7.72 [1 H, d, J(12) 8.2 Hz, $C_6H_3(1)$], 7.28 [1 H, dd, J(12) 8.2 Hz, J(23) 2.5 Hz, $C_6H_3(2)$], 7.13 [1 H, d, J(23) 2.5 Hz, $C_6H_3(3)$], 5.94, 5.88, and 5.83 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.50 and 4.30 [2 H, s; 2 H, t, J(HH) 1.8 Hz, C_5H_4], 4.14 [5 H, s, C_5H_5], 2.74, 2.47, 2.42, 2.42, 2.38, 2.36, and 2.34 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$ and $C_6H_3-CH_3$]; *m/z* 836 (M^+), 740 (M - 96), 710 (M - 96 - NO), 577 (M - C_6H_4-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 547 (M - C_6H_4-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 291 ($H_2NC_6H_4$-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{OC_6H_4N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [82]

This compound was prepared in identical manner to [71] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.10 g, 0.20 mmol) and 4-hydroxy-4'-ferrocenylazobenzene (0.085 g, 0.22 mmol) in place of 4-hydroxyphenylferrocene, in toluene (15 cm^3) with a reaction time of 3½ h. Column chromatography yielded the deep red-purple product (0.080 g, 48%). m.p. *ca* 255 °C (Found: C, 52.9; H, 4.5; N, 14.9%; M^+, 841. $C_{37}H_{39}BClFeMoN_9O_2$ requires C, 52.9; H, 4.7; N, 15.0%; M, 840); $\nu_{max.}$(NO) 1680s cm^{-1}; $\delta_H(CDCl_3)$ 8.02 and 7.45 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4], 7.85 and 7.58 [2 H, d, J(HH) 8.2 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 5.94, 5.92, and 5.78 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.77 and 4.42 [2 H, s; 2 H, s, C_5H_4], 4.09 [5 H, s, C_5H_5], 2.59, 2.43, 2.42, 2.40, 2.22, and 2.09 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$]; *m/z* 841 (M^+), 734 (M - 107), 460 (M - OC_6H_4N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 430 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 382 (HOC_6H_4N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{OC_6H_4N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [83]

This compound was prepared in an identical manner to [82] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.20 g, 0.26 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-hydroxy-4'-ferrocenylazobenzene (0.12 g, 0.31 mmol). A deep purple solid was obtained (0.18 g, 75%). m.p. *ca* 255 °C (Found: C, 48.0; H, 4.3; N, 13.3%; M^+, 933. $C_{37}H_{39}BFeIMoN_9O_2$ requires C, 47.7; H, 4.2; N, 13.5%;

M, 931); $\nu_{max.}$(NO) 1680s cm^{-1}; $\delta_H(CDCl_3)$ 7.97 and 7.58 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4], 7.86 and 7.60 [2 H, d, J(HH) 8.2 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 5.92 and 5.86 [1 H, s; 2 H, s, $(Me_2C_3N_2H)_3$], 4.74 and 4.40 [2 H, s; 2 H, s, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.57, 2.46, 2.41, 2.38, 2.32, and 2.01 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 933 (M^+), 826 (M - 107), 552 (M - $OC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 522 (M - OC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 382 ($HOC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{$OC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}$_2$] [84]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$.C_7H_8 (0.10 g, 0.13 mmol) and 4-hydroxy-4'-ferrocenylazobenzene (0.10 g, 0.26 mmol) using the procedure described for [71] except that triethylamine (0.2 cm^3, 1.5 mmol) was used in place of hexamine. A dark red-brown solid was obtained (0.046 g, 30%). (Found: C, 59.8; H, 4.9; N, 12.7%. $C_{59}H_{56}BFe_2MoN_{11}O_3$ requires C, 59.8; H, 4.8; N, 13.0%; M, 1186); $\nu_{max.}$(NO) 1665s cm^{-1}; $\delta_H(CDCl_3)$ 7.95 and 7.20 [4 H, d, J(HH) 9.2 Hz; 4 H, d, J(HH) 8.6 Hz, 2 x C_6H_4], 7.83 and 7.59 [4 H, d, J(HH) 8.4 Hz; 4 H, d, J(HH) 8.2 Hz, 2 x C_6H_4], 5.90 and 5.75 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.73 and 4.39 [4 H, s; 4 H, s, 2 x C_5H_4], 4.07 [10 H, s, 2 x C_5H_5], 2.44, 2.28, and 2.07 [9 H, s; 6 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 382 ($HOC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$HNC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [85]

This compound was prepared in similar manner to [71] using 4-amino-4'-ferrocenylazobenzene (0.20 g, 0.52 mmol) in place of 4-hydroxyphenylferrocene, [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.25 g, 0.51 mmol) and triethylamine (0.5 cm^3, 3.7 mmol) in place of hexamine, with a reaction time of 5 h. Column chromatography yielded the deep red-purple product (0.31 g, 73%). m.p. *ca* 235 °C (Found: C, 53.0; H, 4.9; N, 16.7%; M^+, 840. $C_{37}H_{40}BClFeMoN_{10}O$ requires C, 53.0; H, 4.8; N, 16.7%; M, 839); $\nu_{max.}$(NH) 3260m, $\nu_{max.}$(NO) 1660s cm^{-1}; $\delta_H(CDCl_3)$ 12.51 [1 H, s, N*H*], 8.01 and 7.60 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 7.86 and 7.60 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 5.89, 5.88, and

5.81 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.74 and 4.40 [2 H, t, J(HH) 1.7 Hz; 2 H, t, J(HH) 2.0, 1.7 Hz, C_5H_4], 4.06 [5 H, s, C_5H_5], 2.70, 2.43, 2.40, 2.38, 2.37, and 2.04 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 840 (M^+), 733 (M - 107), 460 (M - $H_2NC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 430 (M - $H_2NC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 381 ($H_2NC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$HNC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [86]

This compound was prepared in an identical manner to [85] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.10 g, 0.17 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 4-amino-4'-ferrocenylazobenzene (0.08 g, 0.21 mmol), with a reaction time of 24 h. A dark brown solid was obtained (0.040 g, 25%). (Found: C, 47.0; H, 5.0; N, 14.8%; M^+, 926. $C_{37}H_{40}BClFeN_{10}OW.0.3CH_2Cl_2$ requires C, 47.0; H, 4.3; N, 14.7%; M, 927); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1630s cm^{-1}; $\delta_H(CDCl_3)$ 10.69 [1 H, s, N*H*], 8.00 and 7.60 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.85 and 7.51 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 5.95, 5.89, and 5.84 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.74 and 4.40 [2 H, d, J(HH) 1.7 Hz; 2 H, d, J(HH) 1.7 Hz, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.74, 2.47, 2.43, 2.38, 2.36, and 2.16 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 926 (M^+), 548 (M - $H_2NC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 518 (M - $H_2NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 381 ($H_2NC_6H_4N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_3-3-CH_3-4-$N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [87]

This compound was prepared in similar manner to [71] using 4-amino-2-methyl-4'-ferrocenylazobenzene (0.25 g, 0.63 mmol) in place of 4-hydroxyphenylferrocene, [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.30 g, 0.61 mmol) and triethylamine (0.5 cm^3, 3.7 mmol) in place of hexamine, with a reaction time of 5 h. Column chromatography yielded the deep purple product (0.39 g, 75%). m.p. *ca* 280 °C (Found: C, 52.6; H, 5.1; N, 16.3%; M^+, 854. $C_{38}H_{42}BClFeMoN_{10}O.0.2CH_2Cl_2$ requires C, 52.7; H, 4.9; N, 16.1%; M, 853); $\nu_{max.}$(NH) 3260m, $\nu_{max.}$(NO) 1665s cm^{-1}; $\delta_H(CDCl_3)$ 12.51 [1 H, s, N*H*], 7.87 and 7.60 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 7.78 [1 H,

d, J(12) 8.9 Hz, C_6H_3(1)], 7.51 [1 H, s, C_6H_3(3)], 7.30 [1 H, d, J(12) 8.9 Hz, C_6H_3(2)], 5.89 and 5.81 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.74 and 4.41 [2 H, t, J(HH) 1.7 Hz; 2 H, t, J(HH) 1.7 Hz, C_5H_4], 4.08 [5 H, s, C_5H_5], 2.80, 2.70, 2.43, 2.41, 2.39, 2.38, and 2.05 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, C_6H_3-CH_3 and $(Me_2C_3N_2H)_3$]; *m/z* 854 (M^+), 757 (M - 96), 727 (M - 96 - NO), 460 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 430 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 395 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5))

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I{HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [88]

This compound was prepared in an identical manner to [87] using [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(I)_2$].C_7H_8 (0.30 g, 0.39 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] and 4-amino-2-methyl-4'-ferrocenylazobenzene (0.16 g, 0.41 mmol). Column chromatography yielded the deep purple product (0.29 g, 79%). m.p. *ca* 280 °C (Found: C, 48.4; H, 4.4; N, 14.5%; M^+, 946. $C_{36}H_{42}BFeIMoN_{10}O$ requires C, 48.3; H, 4.5; N, 14.8%; M, 944); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1665s cm^{-1}; $\delta_H(CDCl_3)$ 12.97 [1 H, s, N*H*], 7.88 and 7.59 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.73 [1 H, d, J(12) 8.6 Hz, C_6H_3(1)], 7.65 [1 H, s, C_6H_3(3)], 7.46 [1 H, d, J(12) 8.9 Hz, C_6H_3(2)], 5.95, 5.87 and 5.79 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.75 and 4.41 [2 H, t, J(HH) 2.0, 1.7 Hz; 2 H, t, J(HH) 1.7 Hz, C_5H_4], 4.08 [5 H, s, C_5H_5], 2.83, 2.72, 2.51, 2.47, 2.39, 2.38, and 2.01 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, C_6H_3-CH_3 and $(Me_2C_3N_2H)_3$]; *m/z* 946 (M^+), 826 (M - Fe(η^5-C_5H_5)), 817 (M - I), 550 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 530 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 395 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}F{HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [89]

This compound was prepared in an identical manner to [87] using [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(F)_2$] (0.12 g, 0.26 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] and 4-amino-2-methyl-4'-ferrocenylazobenzene (0.12 g, 0.30 mmol). Column chromatography on silica

using 1% thf/dichloromethane as eluent yielded the deep crimson product (0.065 g, 30%). (Found: C, 52.6; H, 5.0; N, 14.9%. $C_{38}H_{42}BFFeMoN_{10}O.0.5CH_2Cl_2$ requires C, 52.6; H, 4.9; N, 15.9%; M, 836); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1645s cm^{-1}; $\delta_H(CDCl_3)$ 10.18 [1 H, s, N*H*], 7.84 and 7.58 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 7.76 [1 H, d, J(12) 8.7 Hz, $C_6H_3(1)$], 7.25 [1 H, s, $C_6H_3(3)$], 7.11 [1 H, d, J(12) 8.7 Hz, $C_6H_3(2)$], 5.87, 5.82 and 5.78 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.72 and 4.38 [2 H, t, J(HH) 1.7, 2.0 Hz; 2 H, t, J(HH) 1.7 Hz, C_5H_4], 4.06 [5 H, s, C_5H_5], 2.75, 2.62, 2.40, 2.39, 2.36, 2.33, and 2.13 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $C_6H_3-CH_3$ and $(Me_2C_3N_2H)_3$]; *m/z* 650 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5)), 577 (M - C_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 563 (M - NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 549 (M - N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 424 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - F), 395 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5))

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Br{HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [90]

This compound was prepared in an identical manner to [87] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Br)$_2$] (0.10 g, 0.17 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-amino-2-methyl-4'-ferrocenylazobenzene (0.08 g, 0.20 mmol). Column chromatography yielded the deep purple product (0.11 g, 72%). (Found: C, 49.4; H, 4.8; N, 14.9%; M^+, 898. $C_{38}H_{42}BBrFeMoN_{10}O.0.5CH_2Cl_2$ requires C, 49.2; H, 4.6; N, 14.9%; M, 897); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1660s cm^{-1}; $\delta_H(CDCl_3)$ 12.74 [1 H, s, N*H*], 7.88 and 7.59 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.78 [1 H, d, J(12) 8.7 Hz, $C_6H_3(1)$], 7.57 [1 H, s, $C_6H_3(3)$], 7.37 [1 H, d, J(12) 8.7 Hz, $C_6H_3(2)$], 5.90, 5.87 and 5.80 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.74 and 4.40 [2 H, s; 2 H, s, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.81, 2.71, 2.44, 2.38, 2.37, and 2.03 [3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, $C_6H_3-CH_3$ and $(Me_2C_3N_2H)_3$]; *m/z* 898 (M^+), 802 (M - 96), 776 (M - Fe(η^5-C_5H_5)), 504 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 574 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 395 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(OC_6H_{11}){HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [91]

A solution of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [88] (0.10 g, 0.11 mmol), cyclohexanol (0.5 cm^3) and triethylamine (0.5 cm^3) was stirred under reflux in toluene (10 cm^3) for 2 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The resulting deep crimson solid was purified by column chromatography on alumina using 60% n-hexane/dichloromethane as the eluent. Unreacted [88] was removed as a second purple band, and the first major crimson band was collected and evaporated to afford the deep crimson product (0.064 g, 66%). (Found: C, 58.0; H, 6.1; N, 14.8%; M^+, 918. $C_{44}H_{53}BFeMoN_{10}O_2$ requires C, 57.7; H, 5.8; N, 15.3%; M, 917); $\nu_{max.}$(NH) 3300w, $\nu_{max.}$(NO) 1635s cm^{-1}; δ_H($CDCl_3$) 9.42 [1 H, s, N*H*], 7.82 and 7.57 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.88 [1 H, d, J(12) 8.7 Hz, C_6H_3(1)], 7.25 [1 H, d, J(12) 8.7 Hz, C_6H_3(2)], 7.11 [1 H, br s, C_6H_3(3)], 5.85, 5.83 and 5.70 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 5.59 [1 H, qn, OC*H*], 4.72 and 4.37 [2 H, t, J(HH) 1.7 Hz; 2 H, t, J(HH) 1.7 Hz, C_5H_4], 4.06 [5 H, s, C_5H_5], 2.71, 2.63, 2.40, 2.33, and 2.12 [3 H, s; 3 H, s; 3 H, s; 9 H, s; 3 H, s, C_6H_3-CH_3 and ($Me_2C_3N_2H$)$_3$], 1.80-1.20 [10 H, c m, C_5H_{10}]; *m/z* 918 (M^+), 818 (M - OC_6H_{11}), 705 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5) - C_2H_4), 677 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5) - C_4H_8), 650 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5) - C_6H_{11}), 522 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 422 (M - OC_6H_{11} - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 395 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 98 ($C_6H_{11}O$).

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [92]

This compound was prepared in an identical manner to [87] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.30 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-amino-2-methyl-4'-ferrocenyl-azobenzene (0.22 g, 0.56 mmol), with a reaction time of 24 h. A dark red-brown solid was obtained (0.18 g, 37%). (Found: C, 48.4; H, 4.2; N, 14.8%; M^+, 940. $C_{38}H_{42}BClFeN_{10}OW$ requires C, 48.5; H, 4.5; N, 14.9%; M, 941); $\nu_{max.}$(NH) 3275m, $\nu_{max.}$(NO) 1630s cm^{-1}; δ_H($CDCl_3$) 10.67 [1 H, s, N*H*], 7.85 and 7.59 [2 H, d, J(HH) 8.4 Hz; 2 H, d,

J(HH) 8.4 Hz, C_6H_4], 7.78 [1 H, d, J(12) 8.6 Hz, C_6H_3(1)], 7.43 [1 H, s, C_6H_3(3)], 7.22 [1 H, d, J(12) 8.9 Hz, C_6H_3(2)], 5.95, 5.89 and 5.84 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.73 and 4.39 [2 H, t, J(HH) 2.0, 1.7 Hz; 2 H, t, J(HH) 1.7 Hz, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.78, 2.74, 2.47, 2.42, 2.37, 2.36, and 2.17 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $C_6H_3-CH_3$ and $(Me_2C_3N_2H)_3$]; *m/z* 940 (M^+), 822 (M - Fe(η^5-C_5H_5)), 756 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5)), 726 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 698 (M - 242), 548 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 518 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 395 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl{HNC_6H_3-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [93]

This compound was prepared in similar manner to [71] using 4-amino-2-methyl-3'-methyl-4'-ferrocenylazobenzene (0.26 g, 0.64 mmol) in place of 4-hydroxyphenylferrocene, [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] (0.30 g, 0.61 mmol) and triethylamine (0.5 cm^3, 3.7 mmol) in place of hexamine, with a reaction time of 5 h. Column chromatography yielded the deep pink-purple product (0.39 g, 74%). (Found: C, 50.5; H, 5.2; N, 15.3%; M^+, 868. $C_{39}H_{44}BClFeMoN_{10}O.1.0CH_2Cl_2$ requires C, 50.5; H, 4.9; N, 14.7%; M, 867); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1655s cm^{-1}; $\delta_H(CDCl_3)$ 12.51 [1 H, s, N*H*], 7.77 and 7.75 [1 H, d, J(HH) 8.7 Hz; 1 H, d, J(HH) 8.2 Hz, C_6H_3(1 and 4)], 7.71 and 7.51 [1 H, s; 1 H, s, C_6H_3(3 and 6)], 7.31 and 7.17 [1 H, dd; 1 H, dd, C_6H_3(2 and 5)], 5.88 and 5.81 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.60 and 4.38 [2 H, s; 2 H, s, C_5H_4], 4.16 [5 H, s, C_5H_5], 2.80, 2.70, 2.52, 2.42, 2.40, 2.38, 2.37, and 2.05 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 2 x $C_6H_3-CH_3$ and $(Me_2C_3N_2H)_3$]; *m/z* 868 (M^+), 772 (M - 96), 742 (M - 96 - NO), 460 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 430 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 409 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I{HNC_6H_3-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [94]

This compound was prepared in an identical manner to [93]

using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.30 g, 0.39 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-amino-2-methyl-3'-methyl-4'-ferrocenylazobenzene (0.17 g, 0.42 mmol). Column chromatography yielded the deep purple product (0.23 g, 62%). (Found: C, 49.2; H, 4.8; N, 13.9%; M^+, 960. $C_{39}H_{44}BFeIMoN_{10}O$ requires C, 48.9; H, 4.6; N, 14.6%; M, 958); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1655s cm^{-1}; δ_H($CDCl_3$) 12.97 [1 H, s, N*H*], 7.77 and 7.72 [1 H, d, J(HH) 9.1 Hz; 1 H, d, J(HH) 8.7 Hz, C_6H_3(1 and 4)], 7.73 and 7.65 [1 H, s; 1 H, s, C_6H_3(3 and 6)], 7.46 and 7.17 [1 H, dd; 1 H, dd, C_6H_3(2 and 5)], 5.94, 5.87 and 5.79 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.59 and 4.37 [2 H, s; 2 H, s, C_5H_4], 4.15 [5 H, s, C_5H_5], 2.83, 2.72, 2.53, 2.50, 2.47, 2.38, 2.37, and 2.01 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 2 x C_6H_3-CH_3 and ($Me_2C_3N_2H$)$_3$]; *m/z* 960 (M^+), 838 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5)), 832 (M - I), 550 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 530 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 409 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_3-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [95]

This compound was prepared in an identical manner to [93] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.30 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-amino-2-methyl-3'-methyl-4'-ferrocenylazobenzene (0.22 g, 0.56 mmol), with a reaction time of 24 h. A dark red-brown solid was obtained (0.10 g, 20%). (Found: C, 48.4; H, 4.8; N, 14.6%; M^+, 954. $C_{39}H_{42}BClFeN_{10}OW.0.2CH_2Cl_2$ requires C, 48.4; H, 4.6; N, 14.4%; M, 955); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1630s cm^{-1}; δ_H($CDCl_3$) 10.67 [1 H, s, N*H*], 7.82, 7.78, 7.75, 7.73 and 7.70 [3 H, C_6H_3(1, 4, and 3)], 7.43 [1 H, s, C_6H_3(6)], 7.30-7.10 [2 H, C_6H_3(2 and 5)], 5.95, 5.89 and 5.84 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.58 and 4.36 [2 H, s; 2 H, s, C_5H_4], 4.15 [5 H, s, C_5H_5], 2.78, 2.74, 2.52, 2.47, 2.43, 2.37, 2.36, and 2.18 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, C_6H_3-CH_3 and ($Me_2C_3N_2H$)$_3$]; *m/z* 954 (M^+) 832 (M - Fe(η^5-C_5H_5)), 770 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5)), 740 (M - (η^5-C_5H_4)Fe(η^5-C_6H_5) - NO), 712 (M - 243), 548 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_6H_5)),

518 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 409 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_3-3-CH_3-4-N=NC_6H_3-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [96]

This compound was prepared in similar manner to [71] using 4-(4-amino-2-methylphenylazo)-2-methyl-3'-methyl-4'-ferrocenylazobenzene (0.032 g, 0.061 mmol) in place of 4-hydroxyphenylferrocene, [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.037 g, 0.075 mmol) and triethylamine (0.5 cm^3, 3.7 mmol) in place of hexamine, in toluene (10 cm^3) with a reaction time of 5 h. Column chromatography on silica using dichloromethane as eluent yielded the deep purple product (0.041 g, 69%). (Found: C, 55.0; H, 5.1; N, 16.7%. $C_{46}H_{50}BClFeMoN_{12}O.0.3CH_2Cl_2$ requires C, 55.0; H, 5.1; N, 16.6%; M, 985); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1660s cm^{-1}; δ_H($CDCl_3$) 12.48 [1 H, s, N*H*], 7.91, 7.85, 7.82, 7.82, 7.80, 7.77 and 7.76 [7 H, C_6H_3(1-7)], 7.53 [1 H, s, C_6H_3(9)], 7.33 [1 H, d, J(78) 9.1 Hz, C_6H_3(8)], 5.89 and 5.82 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.62 and 4.40 [2 H, s; 2 H, s, C_5H_4], 4.17 [5 H, s, C_5H_5], 2.84, 2.83, 2.70, 2.54, 2.43, 2.41, 2.39, 2.38, and 2.05 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 3 x C_6H_3-CH_3 and ($Me_2C_3N_2H$)$_3$]; *m/z* 933(M - 52), 460 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 430 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 527 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_3-3-CH_3-4-N=NC_6H_3-3-CH_3-4-(η^5-C_5H_4)Fe(η^5-C_5H_5).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_4CH=CHC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [97]

This compound was prepared in similar manner to [71] using 4-amino-4'-ferrocenylstilbene (0.24 g, 0.63 mmol) in place of 4-hydroxyphenylferrocene, [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.30 g, 0.61 mmol) and triethylamine (0.5 cm^3, 3.7 mmol) in place of hexamine, with a reaction time of 3 h. Column chromatography yielded the deep violet product (0.33 g, 65%). (Found: C, 54.9; H, 5.3; N, 13.2%; M^+, 838. $C_{39}H_{42}BClFeMoN_8O.0.25CH_2Cl_2$ requires C, 54.9; H, 5.0; N, 13.1%; M, 837); $\nu_{max.}$(NH) 3240m, $\nu_{max.}$(NO) 1650s cm^{-1}; δ_H($CDCl_3$) 12.59 [1 H, s, N*H*], 7.58, [2 H, d, J(HH) 8.7 Hz, C_6H_4],

7.49, 7.46 and 7.46 [4 H, C_6H_4], 7.12 [2 H, s, *CH=CH*], 5.87 and 5.80 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.67 and 4.34 [2 H, t, J(HH) 1.7 Hz; 2 H, t, J(HH) 1.7 Hz, C_5H_4], 4.05 [5 H, s, C_5H_5], 2.70, 2.42, 2.39, 2.38, 2.37, and 2.04 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 838 (M^+), 742 (M - 96), 712 (M - 96 - NO), 460 (M - $H_2NC_6H_4CH=CHC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 430 (M - $H_2NC_6H_4CH=CHC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 379 ($H_2NC_6H_4CH=CHC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{$HNC_6H_4CH=CHC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [98]

This compound was prepared in an identical manner to [97] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(I)_2$].C_7H_8 (0.30 g, 0.39 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 4-amino-4'-ferrocenylstilbene (0.16 g, 0.42 mmol). Column chromatography yielded the deep purple product (0.32 g, 88%). (Found: C, 50.1; H, 4.6; N, 12.2%; M^+, 930. $C_{39}H_{42}BFeIMoN_8O$ requires C, 50.5; H, 4.6; N, 12.1%; M, 928); $\nu_{max.}$(NH) 3240m, $\nu_{max.}$(NO) 1650s cm^{-1}; $\delta_H(CDCl_3)$ 13.03 [1 H, s, *NH*], 7.63 and 7.53 [2 H, d, J(HH) 8.7 Hz; 2 H, d, 8.7 Hz, C_6H_4], 7.46 [4 H, C_6H_4], 7.19 and 7.08 [1 H, d, $J(HH)_{trans}$ 16.1 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, *CH=CH*], 5.93, 5.86 and 5.78 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.68 and 4.35 [2 H, s; 2 H, s, C_5H_4], 4.06 [5 H, s, C_5H_5], 2.72, 2.49, 2.46, 2.38, 2.37, and 2.01 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 930 (M^+), 834 (M - 96), 804 (M - 96 - NO), 801 (M - I), 550 (M - $H_2NC_6H_4CH=CHC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 520 (M - $H_2NC_6H_4CH=CHC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 379 ($H_2NC_6H_4CH=CHC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$HNC_6H_4CH=CHC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [99]

This compound was prepared in an identical manner to [97] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.30 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 4-amino-4'-ferrocenylstilbene (0.22 g, 0.58 mmol), with a reaction time of 9 h. A dark orange-brown solid was obtained (0.25 g, 52%). (Found: C, 50.9; H, 4.6; N, 11.9%; M^+, 924. $C_{39}H_{42}BClFeN_8OW$ requires C, 50.7; H, 4.6; N,

12.1%; M, 925); $\nu_{max.}$(NH) 3260w, $\nu_{max.}$(NO) 1625s cm^{-1}; $\delta_H(CDCl_3)$ 10.75 [1 H, s, N*H*], 7.56 and 7.39 [2 H, d, J(HH) 8.7 Hz; 2 H, d, 8.4 Hz, C_6H_4], 7.47 and 7.42 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4], 7.14 and 7.03 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.1 Hz, C*H*=C*H*], 5.94, 5.88 and 5.83 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.66 and 4.33 [2 H, s; 2 H, s, C_5H_4], 4.05 [5 H, s, C_5H_5], 2.74, 2.46, 2.42, 2.37, 2.36, and 2.16 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 924 (M^+), 379 ($H_2NC_6H_4CH=CHC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(OC_8H_{17}-n){HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [100]

This compound was prepared in an identical manner to [91] using n-octanol (0.5 cm^3) instead of cyclohexanol. Column chromatography afforded the product as a deep crimson solid (0.070 g, 67%). (Found: C, 59.5; H, 6.4; N, 15.2%; M^+, 948. $C_{46}H_{59}BFeMoN_{10}O_2$ requires C, 58.4; H, 6.3; N, 14.8%; M, 947); $\nu_{max.}$(NH) 3300w, $\nu_{max.}$(NO) 1640s cm^{-1}; $\delta_H(CDCl_3)$ 9.56 [1 H, s, N*H*], 7.83 and 7.58 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.78 [1 H, d, J(12) 8.9 Hz, C_6H_3(1)], 7.19 [2 H, br s, C_6H_3(2 and 3)], 5.85, 5.84, and 5.73 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 5.62 and 5.25 [1 H, c m; 1 H, c m, OCH_2], 4.72 and 4.38 [2 H, t, J(HH) 2.0, 1.7 Hz; 2 H, t, J(HH) 1.7, 2.0 Hz, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.74, 2.67, 2.39, 2.34, 2.33, 2.33, and 2.13 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, C_6H_3-CH_3 and $(Me_2C_3N_2H)_3$], 1.70 [2 H, qn, OCH_2-CH_2], 1.45-1.15 [10 H, c m, C_5H_{10}], 0.82 [3 H, t, J(HH) 6.5 Hz, CH_3]; *m/z* 948 (M^+), 818 (M - OC_8H_{17}), 828 (M - Fe(η^5-C_5H_5)), 704 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5) - C_4H_9), 676 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5) - C_6H_{13}), 554 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 424 (M - OC_8H_{17} - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 395 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 130 ($C_8H_{17}OH$).

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(OCH_2CF_3){HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [101]

This compound was prepared in an identical manner to [91] using 1,1,1-trifluoroethanol (0.5 cm^3) instead of cyclohexanol.

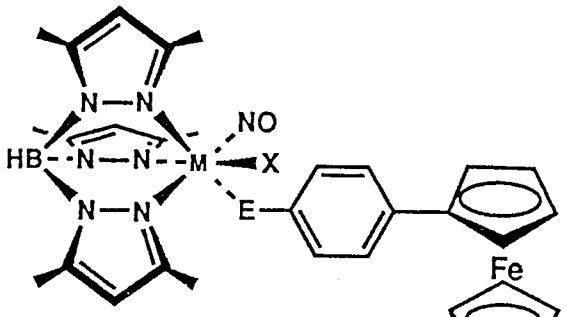
Column chromatography afforded the product as a deep crimson solid (0.043 g, 43%). (Found: C, 55.5; H, 5.3; N, 15.1%; M^+, 918. $C_{40}H_{44}BF_3FeMoN_{10}O_2$ requires C, 52.4; H, 4.8; N, 15.3%; M, 916); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1640s cm^{-1}; $\delta_H(CDCl_3)$ 10.57 [1 H, s, NH], 7.85 and 7.59 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.82 [1 H, d, J(12) 8.7 Hz, C_6H_3(1)], 7.31 [1 H, d, J(12) 8.7 Hz, C_6H_3(2)], 7.19 [1 H, br s, C_6H_3(3)], 5.87 and 5.74 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 5.45 [2 H, c m, OCH_2], 4.73 and 4.39 [2 H, t, J(HH) 2.0 Hz; 2 H, t, J(HH) 1.7 Hz, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.74, 2.63, 2.40, 2.35, 2.34, 2.32, and 2.08 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, C_6H_3-CH_3 and $(Me_2C_3N_2H)_3$]; *m/z* 918 (M^+), 818 (M - OCH_2CF_3), 788 (M - OCH_2CF_3 - NO), 648 (M - (η^5-C_5H_4)Fe(η^5-C_5H_5) - CH_2CF_3), 522 (M - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 424 (M - OCH_2CF_3 - $H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 395 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 98 (CF_3CH_2O).

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}($OCH_2CH_2C{\equiv}CH$){HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [102]

This compound was prepared in an identical manner to [91] using 3-butyn-1-ol (0.5 cm^3) instead of cyclohexanol. Column chromatography afforded the product as a deep crimson solid (0.045 g, 46%). (Found: C, 58.6; H, 5.5; N, 16.1%; $C_{42}H_{47}BFeMoN_{10}O_2$ requires C, 56.9; H, 5.3; N, 15.8%; M, 887); $\nu_{max.}$(≡CH, NH) 3290m, $\nu_{max.}$(NO) 1640s cm^{-1}; $\delta_H(CDCl_3)$ 9.90 [1 H, s, NH], 7.84 and 7.58 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.80 [1 H, d, J(12) 8.7 Hz, C_6H_3(1)], 7.25 [1 H, d, J(12) 8.7 Hz, C_6H_3(2)], 7.18 [1 H, br s, C_6H_3(3)], 5.85 and 5.74 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 5.65 and 5.37 [1 H, c m; 1 H, c m, OCH_2], 4.72 and 4.38 [2 H, t, J(HH) 2.0, 1.7 Hz; 2 H, t, J(HH) 1.7, 2.0 Hz, C_5H_4], 4.07 [5 H, s, C_5H_5], 2.75, 2.66, 2.39, 2.35, 2.33, and 2.12 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s, C_6H_3-CH_3 and $(Me_2C_3N_2H)_3$], 2.54 [2 H, t, J(HH) 6.3 Hz, OCH_2-CH_2], 1.89 [1 H, t, J(HH) 2.6 Hz, ≡CH]; *m/z* 395 ($H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 58 ($HC{\equiv}CH_2CH_2OH$).

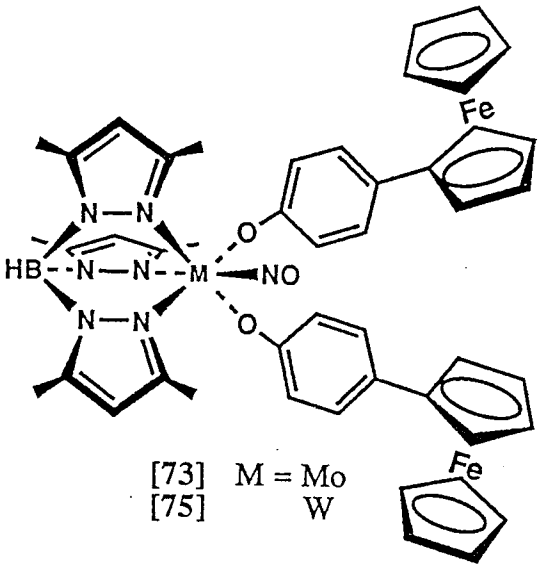
Fig. 39

Complexes Prepared in Chapter Two

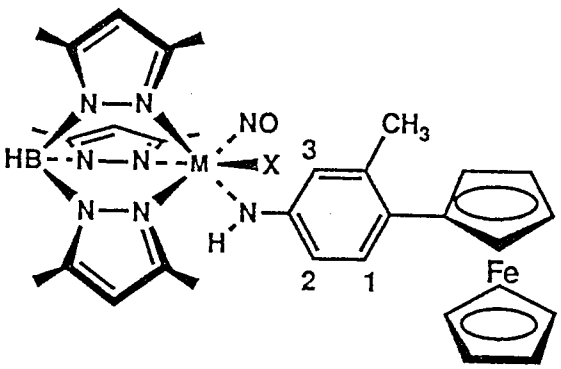


E = O { [71] M = Mo X = Cl; [72] I; [74] W Cl

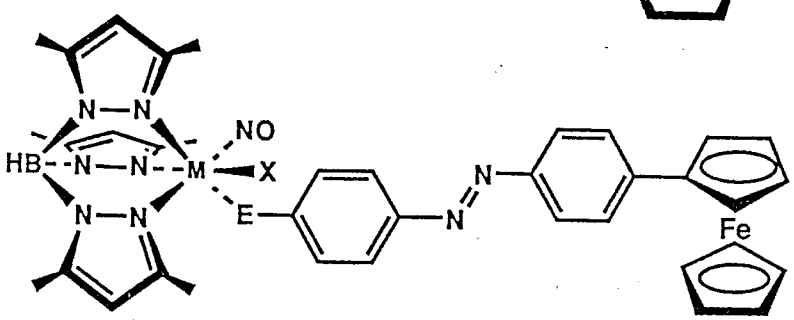
E = NH { [76] M = Mo Cl; [77] I; [78] W Cl



[73] M = Mo
[75] W

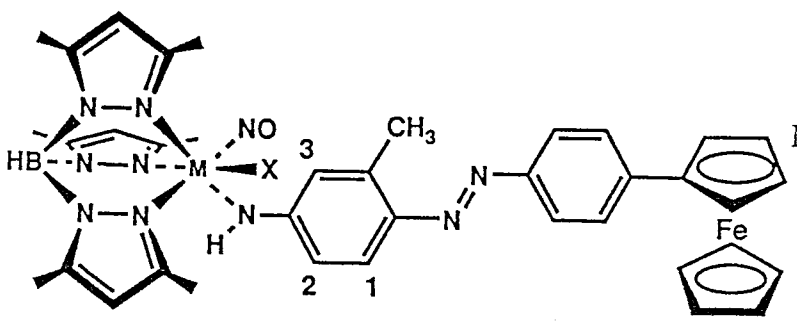


[79] M = Mo X = Cl
[80] I
[81] W Cl



E = O { [82] M = Mo X = Cl; [83] I

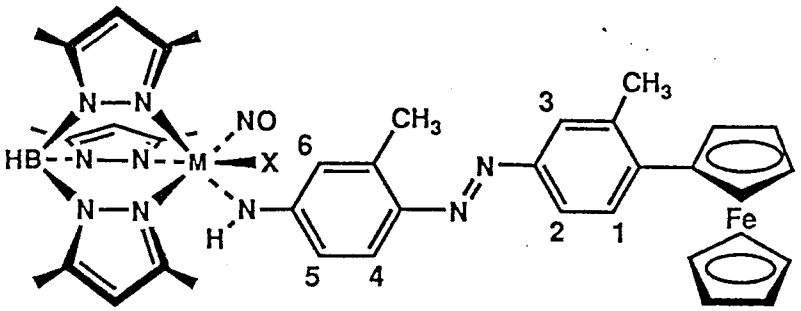
E = NH { [85] Mo Cl; [86] W Cl



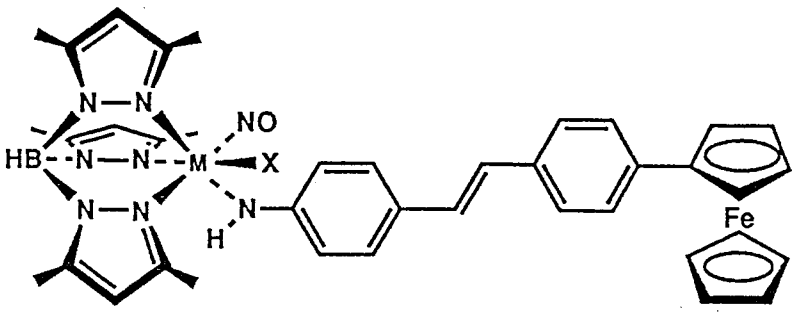
M = Mo { [87] X = Cl; [88] I; [89] F; [90] Br; [91] OC_6H_{11}; [100] OC_8H_{17}-n; [101] OCH_2CF_3; [102] OC_2H_4CCH

[92] M = W X = Cl

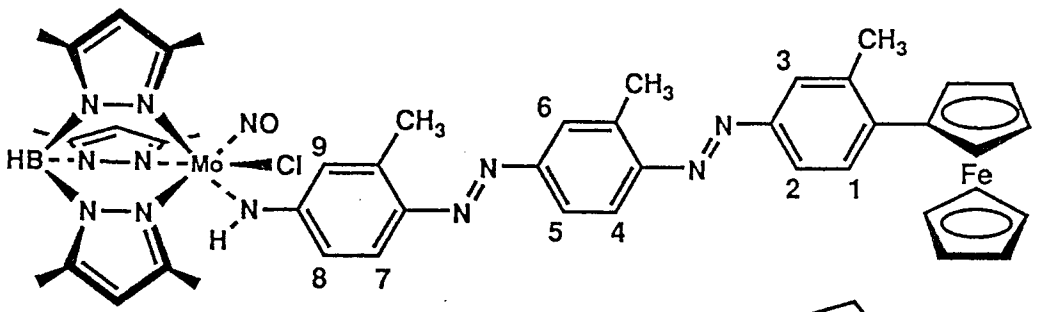
Fig. 39 (*Continued*)



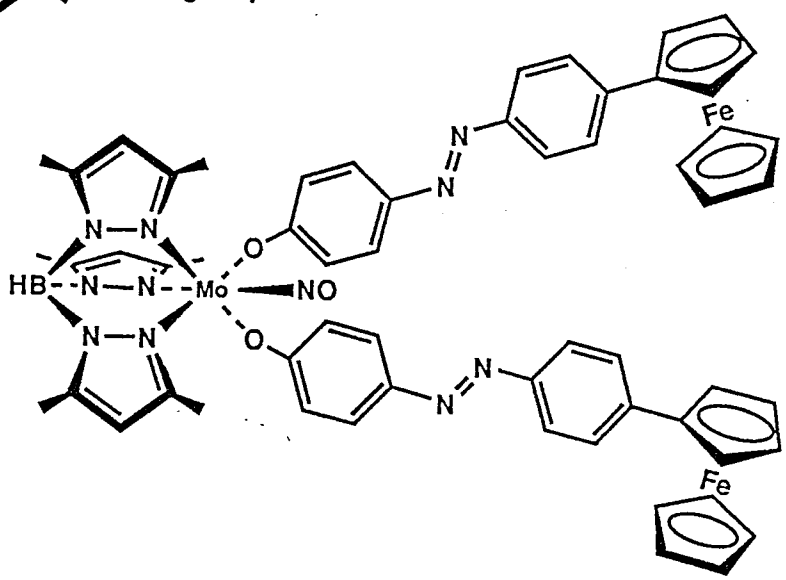
[93] M = Mo X = Cl
[94] I
[95] W Cl



[97] M = Mo X = Cl
[98] I
[99] W Cl



[96]



[84]

CHAPTER THREE

MOLYBDENUM AND TUNGSTEN MONONITROSYL COMPLEXES OF DONOR-SUBSTITUTED DIPHENYLAZO OR STILBENYL LIGANDS

IV-1 DISCUSSION

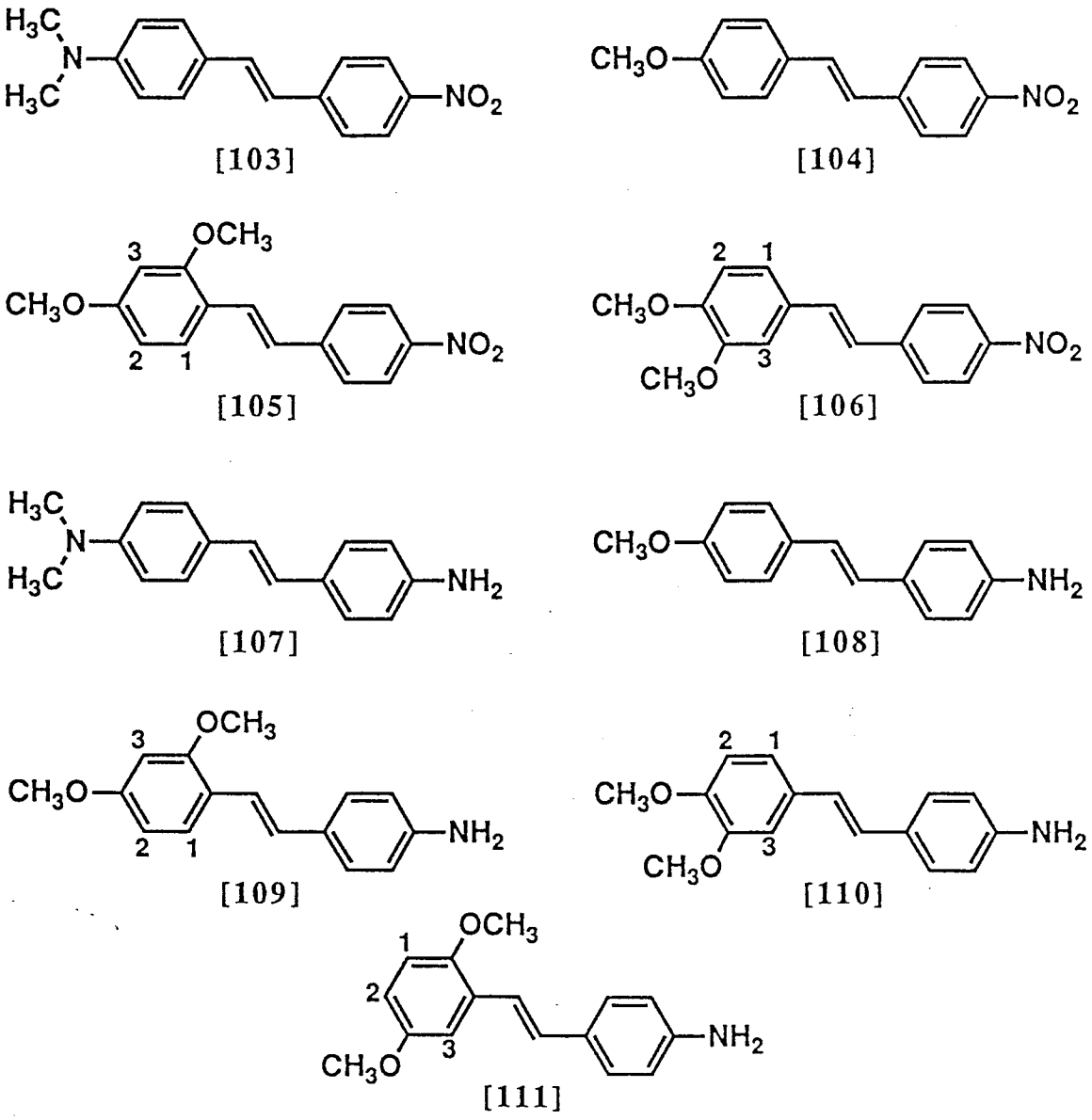
As has already been mentioned, the diphenylazo and stilbenyl organic moieties have been found to provide effective linkages between electron-donor and acceptor groups in many molecules which display high hyperpolarisability values and in many cases significant bulk NLO properties. In order to investigate the potential of molybdenum and tungsten mononitrosyl complexes containing purely organic donor functions for exhibiting NLO properties, a number of stilbene ligands have been synthesised. These, along with several commercially obtained diphenylazo and stilbene reagents, have been used to prepare a large number of complexes of subtly differing molecular structure. All have been fully characterised by the usual physical techniques as well as being subjected to SHG investigation using the Kurtz powder test.

IV-1.1 LIGANDS AND LIGAND PRECURSORS

Two basic synthetic approaches have been employed to prepare stilbene ligands. Amino-stilbenes were readily prepared via zinc-ammonium chloride reduction of their nitro precursors. These nitro compounds were synthesised by the condensation of 4-nitrophenyl-acetic acid with substituted benzaldehydes according to well established organic chemistry procedures. The benzaldehydes used were N,N-dimethylaminobenzaldehyde for 4-(N,N-dimethylamino)-4'-nitrostilbene [103],[251] 4-methoxybenzaldehyde for 4-methoxy-4'-

nitrostilbene [104],[252] 2,4-dimethoxybenzaldehyde for 2,4-dimethoxy-4'-nitrostilbene [105],[253] and 3,4-dimethoxybenzaldehyde for 3,4-dimethoxy-4'-nitrostilbene [106].[253] All of the reductions gave high yields of the amino compounds which were characterised by elemental analyses, ^1H n.m.r. spectroscopy and melting point. The structures of the four amino ligands, along with those of their nitro precursors, and 4-amino-2',5'-dimethoxystilbene (2',5'-dimethoxy-4-stilbenamine) [111], which was obtained commercially, are shown in Fig. 40.

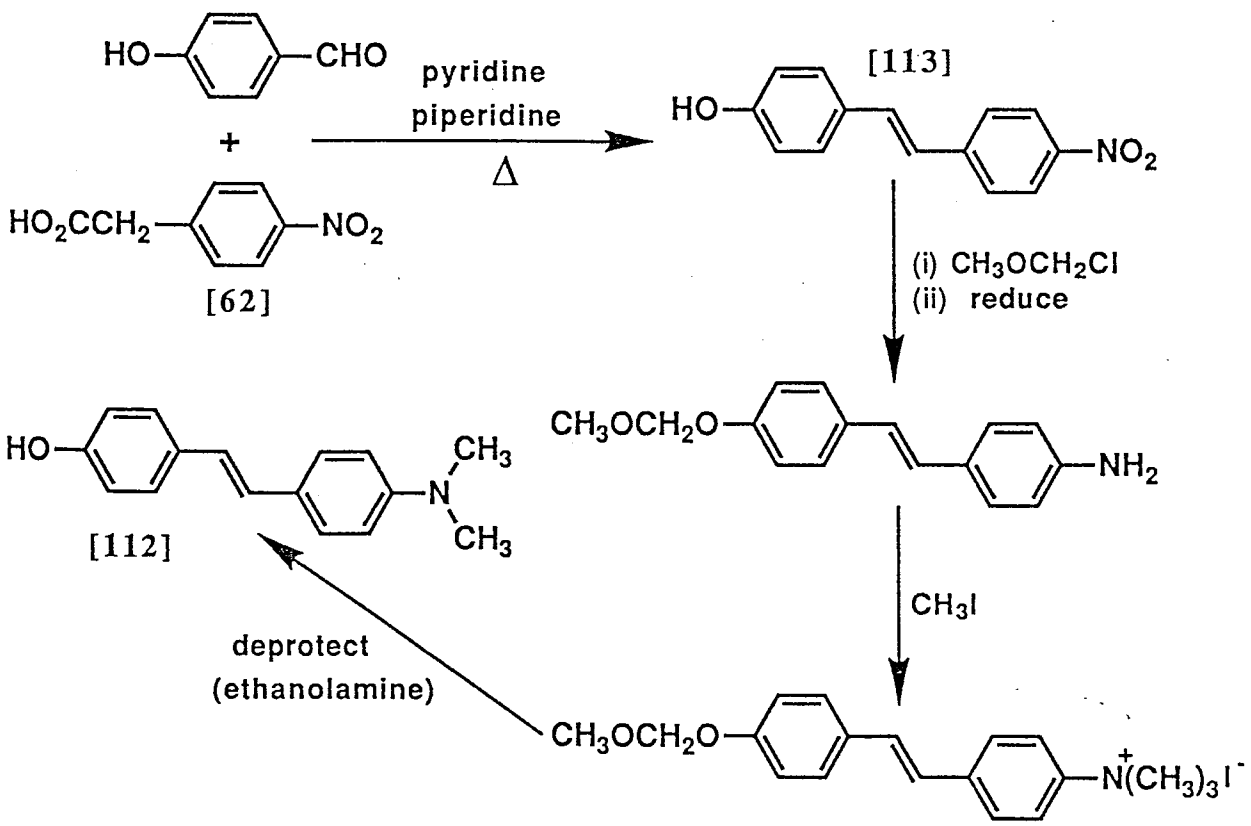
Fig. 40
Amino-stilbene Ligands and Nitro Precursors



The compound 4-amino-4'-(N,N-dimethylamino)stilbene [107] has been prepared previously using a tin chloride/acetic acid reduction of its nitro precursor.[254] 4-Amino-4'-methoxystilbene [108] was similarly prepared using a tin chloride/HCl reduction.[255] The use of zinc and ammonium chloride in this study has been found to give slightly improved yields of amine products. Although [111] is a known compound, prepared by the Raney-nickel/hydrogen reduction of its nitro precursor,[256] the two other isomers [109] and [110] are new products. These three isomeric dimethoxystilbene ligands were chosen with a view to increasing the molecular asymmetry of their complexes in order to encourage a noncentrosymmetric crystal packing from which bulk NLO effects might be observed. Such an approach represents a common strategy in the design of purely organic materials for NLO.[16-18]

Fig. 41

Literature Synthesis of 4-(N,N-Dimethylamino)-4'-hydroxystilbene

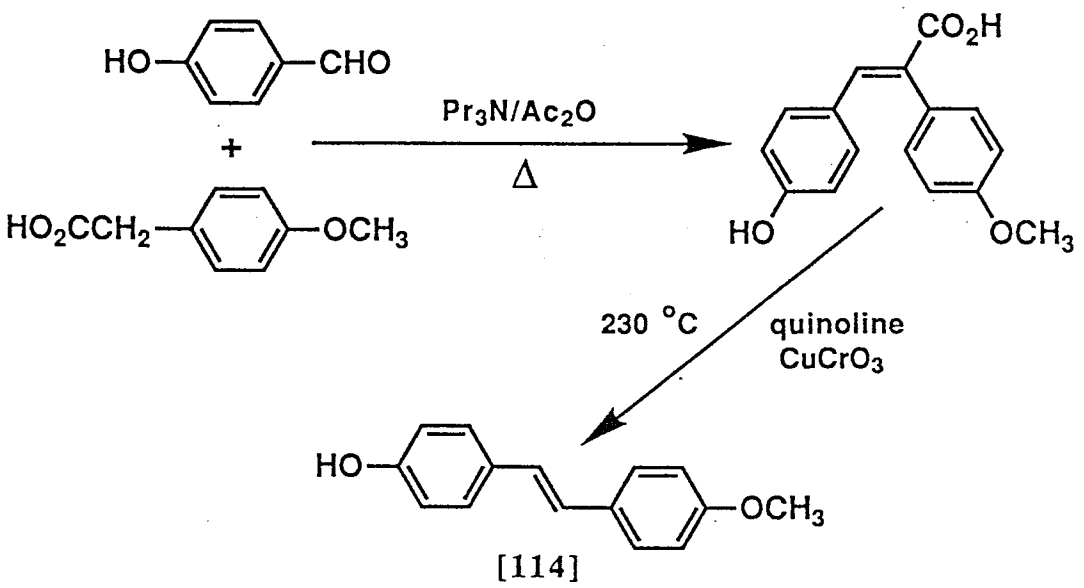


The hydroxy-stilbenes used in this study are also known compounds. 4-(N,N-dimethylamino)-4'-hydroxystilbene [112] has previously been prepared using a rather lengthy five step scheme (Fig. 41).[257] In this the first step consists of making the compound 4-hydroxy-4'-nitrostilbene [113] via the usual condensation of 4-nitrophenylacetic acid with 4-hydroxybenzaldehyde. The free hydroxyl group is then protected by reaction with α-chlorodimethylether, and the nitro group reduced without complications. Methylation of the product amine with methyl iodide gives the quaternary ammonium salt which is converted to the desired product by simultaneous deprotection of the hydroxyl and loss of methyl iodide in the presence of ethanolamine.

4-Hydroxy-4'-methoxystilbene [114] has been synthesised somewhat more simply by condensation of 4-methoxyphenylacetic acid with 4-hydroxybenzaldehyde. This is followed by decarboxylation of the resulting α-phenyl cinnamic acid (which has *cis*-phenyl groups) with quinoline and copper chromite ($CuCrO_3$) at high temperature to give the *trans*-stilbene product (Fig. 42).[258]

Fig. 42

Literature Synthesis of 4-Hydroxy-4'-methoxystilbene



[114]

In this study the hydroxy-stilbenes were prepared in a single step using a chemically simpler McMurry-type reaction between 4-hydroxybenzaldehyde and either 4-N,N-dimethylaminobenzaldehyde for 4-(N,N-dimethylamino)-4'-hydroxystilbene [112] or 4-methoxy-benzaldehyde for 4-hydroxy-4'-methoxystilbene [114]. In general terms, the McMurry reaction[259] involves the coupling of two carbonyl functions with deoxygenation to produce a *trans*-ethylene linkage. This heterogeneous process is thought to occur on the surface of Ti(0) particles which are produced by the zinc reduction of Ti(IV), but the precise nature of the Ti reagent is not clear, as is the case for various related reactions which involve low-valent titanium species. The McMurry reaction has been widely used to synthesise polyaromatic molecules which are of interest in pharmaceutical applications, starting from benzophenone and related compounds.[260] The exact mechanism of the reaction is a matter of some controversy, with both pinacolic (*i.e.* 1,2-diol)[261] and carbene[262] intermediates having been proposed, and it seems likely that the actual mechanism may depend upon the nature of the carbonyl reactants.

However, very low yields of hydroxy-stilbenes were produced, and it seems likely that the presence of the hydroxyl functionality may hinder the coupling. Certainly, the fact that both benzaldehyde reagents bear strongly electron-donating substituents in the 4-position would be expected to render the carbonyl groups more electron-rich and hence less reactive. In the coupling of 4-(N,N-dimethylamino)benzaldehyde with 4-hydroxy-benzaldehyde, a small amount of 4,4'-di(N,N-dimethylamino)-stilbene was isolated after column chromatography. The fact that the yield of the desired product was some four times the yield of this other side product supports the general assertion that cross-coupling is favoured in the reactions of aryl aldehydes.[260]

A schematic representation of the synthetic approach used to make the two hydroxy-stilbene ligands, which were characterised by elemental analyses, ^{1}H n.m.r. spectroscopy and melting point, is shown in Fig. 43.

The unsubstituted ligand 4-hydroxystilbene was obtained commercially.

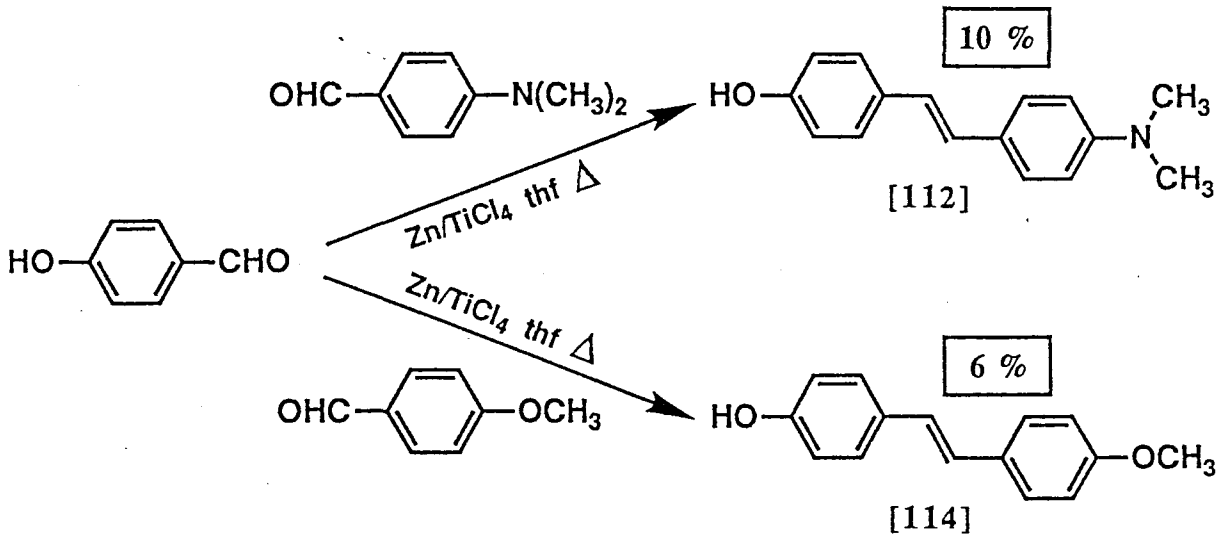
In this study the hydroxy-stilbenes were prepared in a single step using a chemically simpler McMurry-type reaction between 4-hydroxybenzaldehyde and either 4-N,N-dimethylaminobenzaldehyde for 4-(N,N-dimethylamino)-4'-hydroxystilbene [112] or 4-methoxybenzaldehyde for 4-hydroxy-4'-methoxystilbene [114]. In general terms, the McMurry reaction[259] involves the coupling of two carbonyl functions with deoxygenation to produce a *trans*-ethylene linkage. This heterogeneous process is thought to occur on the surface of Ti(0) particles which are produced by the zinc reduction of Ti(IV), but the precise nature of the Ti reagent is not clear, as is the case for various related reactions which involve low-valent titanium species. The McMurry reaction has been widely used to synthesise polyaromatic molecules which are of interest in pharmaceutical applications, starting from benzophenone and related compounds.[260] The exact mechanism of the reaction is a matter of some controversy, with both pinacolic (*i.e.* 1,2-diol)[261] and carbene[262] intermediates having been proposed, and it seems likely that the actual mechanism may depend upon the nature of the carbonyl reactants.

However, very low yields of hydroxy-stilbenes were produced, and it seems likely that the presence of the hydroxyl functionality may hinder the coupling. Certainly, the fact that both benzaldehyde reagents bear strongly electron-donating substituents in the 4-position would be expected to render the carbonyl groups more electron-rich and hence less reactive. In the coupling of 4-(N,N-dimethylamino)benzaldehyde with 4-hydroxybenzaldehyde, a small amount of 4,4'-di(N,N-dimethylamino)-stilbene was isolated after column chromatography. The fact that the yield of the desired product was some four times the yield of this other side product supports the general assertion that cross-coupling is favoured in the reactions of aryl aldehydes.[260]

A schematic representation of the synthetic approach used to make the two hydroxy-stilbene ligands, which were characterised by elemental analyses, ^{1}H n.m.r. spectroscopy and melting point, is shown in Fig. 43.

Fig. 43

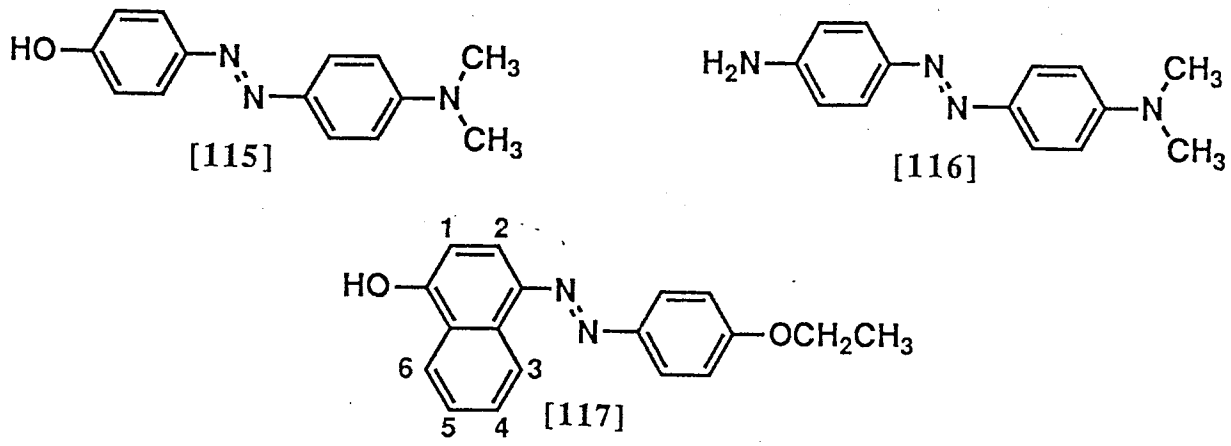
Synthesis of Hydroxy-stilbene Ligands using a McMurry Reaction



The donor-substituted diphenylazo compounds used as ligands were 4-(N,N-dimethylamino)-4'-hydroxyazobenzene [115], 4-amino-4'-(N,N-dimethylamino)azobenzene [116], and 4'-ethoxyphenylazo-1-naphthol (dye Fat Brown B) [117]. These were all obtained commercially and are shown in Fig. 44. The naphthol compound was chosen because the asymmetric shape of the naphthalene moiety appears attractive as a means of introducing greater molecular asymmetry into its complexes.

Fig. 44

Donor-substituted Diphenylazo Ligands

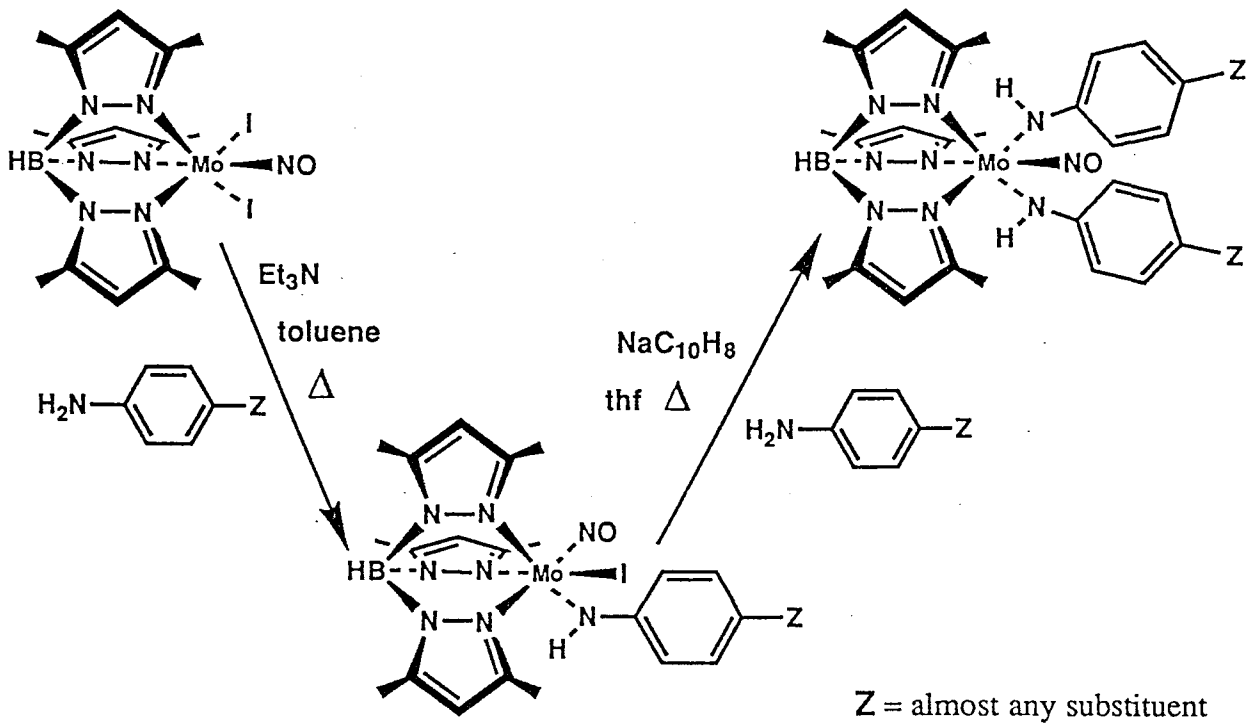


IV-1.2 COMPLEXES

Mono-substituted molybdenum derivatives were prepared by the usual methods involving reaction of either [Mo(NO)L*(Cl)$_2$] or [Mo(NO)L*(I)$_2$] with a slight excess of the appropriate ligand in refluxing toluene. As mentioned in Chapter Two, the mild base hexamine (hexamethylenetetramine) favours the formation of mono-phenoxide complexes from both dihalide precursors. Triethylamine was used in the preparation of mono-anilido molybdenum complexes and all tungsten complexes derived from [W(NO)L*(Cl)$_2$]. Again, in most reactions of [Mo(NO)L*(I)$_2$] with aniline ligands, traces of the mono-chloro derivatives were also detected. Molybdenum bis-phenoxide derivatives were prepared by reaction of [Mo(NO)L*(I)$_2$] with a little over two molar eqivalents of ligand in the presence of triethylamine.

Fig. 45

Preparation of Molybdenum Bis-anilide Complexes



Molybdenum bis-anilide derivatives were prepared under more forcing conditions by reaction of a mono-iodo anilide complex with

further ligand in the presence of the reducing agent sodium naphthalenide (Fig. 45). Displacement of the second iodide occurs readily at room temperature in the coordinating solvent thf, but heating under reflux has been found to give increased yields. The mechanism of this reaction is thought to involve an initial one-electron reduction of the mono-anilido complex followed by iodide displacement by a thf molecule.[196] Relatively low yields of these bis-anilide complexes were obtained which is thought to be due, in part at least, to decomposition during column chromatography on silica gel. In all cases, pale pink trails which may indicate the formation of the bis-hydroxide derivative $[Mo(NO)L^*(OH)_2]$, were observed behind the dark green bands of the complex.

Because it was feared that the use of sodium hydride would lead to reductive cleavage of ethenyl or azo linkages, the preparation of tungsten bis-phenoxide complexes of the stilbene or diphenylazo ligands was not attempted. As mentioned in Chapter Two, the preparation of bis-anilide complexes of tungsten has not yet been achieved, and was hence not pursued here.

IV-1.3 PHYSICAL CHARACTERISATION OF COMPLEXES

All of the new complexes were characterised using i.r. and ^1H n.m.r. spectroscopy, EI mass spectrometry, elemental analyses, and cyclic voltammetry. U.V.-visible absorption spectra were recorded for selected complexes, with particular attention being paid to any evidence of solvatochromism.

IV-1.3(a) Elemental Analyses

All of the complexes show satisfactory analyses for C, H, and N, but it has been found that some of the azo complexes retain between 0.30 and 1.0 mole of dichloromethane of crystallisation which may also be detected by ^1H n.m.r. spectroscopy. Samples were dried for extended periods under vacuum at *ca* 100 °C. In some cases this was clearly insufficient to completely remove the solvent,

but higher temperatures were not used in case this led to sample decomposition.

IV-1.3(b) Infra-Red Spectroscopy

All of the new complexes exhibit $\nu_{max.}$(BH) at *ca* 2550 cm^{-1} as well as $\nu_{max.}$(NO) at frequencies in accord with their formulations. In addition, the arylamide derivatives exhibit $\nu_{max.}$(NH) at 3300-3260 cm^{-1} due to the amide moiety. The intensity of this absorption varies considerably.

IV-1.3(c) ^{1}H n.m.r. Spectroscopy

All of the complexes exhibit signals attributable to the L* ligand which integrate for three pyrazolyl 4-protons and six pyrazolyl 3- and 5-methyl groups. In most cases the mono-substituted complexes give the usual three pyrazolyl 4-proton signals along with six discrete pyrazolyl 3,5-methyl signals, and the bis-substituted give two proton and four methyl signals due to the symmetry conditions described earlier in section I-7.3(b). Aromatic, ethenyl, methyl and ethyl signals due to the stilbene or diphenylazo ligands are as expected and peaks have been assigned as far as possible with coupling constants calculated where appropriate.

IV-1.3(d) Mass Spectrometry

All of the complexes show molecular ion envelopes of variable intensity along with varying numbers of fragment envelopes. Owing to the presence of a large number of possible isotope combinations of the elements Mo, W, B, Cl, and I, ion envelopes have complex forms with the highest peak often not corresponding to exactly the fragmental mass calculated from relative atomic mass values. In most cases the highest peak and not the averaged fragment mass is quoted. Several unidentified ion envelopes of high intensity are also reported.

IV-1.3(e) Cyclic Voltammetry

All of the complexes show reversible, quasi-reversible, or irreversible one-electron molybdenum or tungsten reduction waves at potentials which are in accord with expectations. The effects of changing the donor group on the metal reduction potential are small. For example, a cathodic shift of only 20 mV is observed moving from [Mo(NO)L*(Cl)($OC_6H_4CH=CHC_6H_5$] to [Mo(NO)L*(Cl)($OC_6H_4CH=CHC_6H_4$-4-OCH_3)], and a further cathodic shift of 20 mV occurs on moving to [Mo(NO)L*(Cl){$OC_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$}]. Also observed in most cases are one, two, or three completely irreversible oxidation waves in the region +0.5–1.5 V which are not quoted in the experimental section. These may be assigned to either metal centred oxidations or oxidations of the organic ligands.

IV-1.3(f) U.V.-Visible Absorption Spectra and Solvatochromism Studies

TABLE XVII

U.V.-Visible Excitation Maxima for Selected Molybdenum Chloride Complexes [Mo(NO)L*(Cl)(Y)]

Y[a]	λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1})[b]		
OΦCH=CHΦOCH_3	564 (9,600)	322 (28,700)	
OΦCH=CHΦ$N(CH_3)_2$	610 (8,300)	350 (25,500)	
OΦN=NΦ$N(CH_3)_2$	572 (13,600)	406 (26,100)	311 (11,200)
HNΦN=NΦ$N(CH_3)_2$	544 (23,700)	411 (13,900)	280 (8,200)
HNΦCH=CHΦOCH_3	509 (12,800)	323 (14,000)	
HNΦCH=CHΦ$N(CH_3)_2$	560 (18,100)	354 (17,700)	

[a] Φ = $-C_6H_4-$. [b] All spectra recorded in dichloromethane at ambient temperature, concentration *ca* 10^{-5} M.

Electronic absorption spectra were measured for several of the

complexes in dichloromethane, and spectra for the dimethoxystilbenamide chloride complexes were measured in n-hexane and in DMF in order to search for any evidence of solvatochromic behaviour. The results are shown in Tables XVII and XVIII.

TABLE XVIII

Solvent Dependence of U.V.-Visible Excitation Maxima for Dimethoxystilbenamide Chloride Complexes [M(NO)L*(Cl)(Y)]

M	Y[a]	λ_{max}/nm[b] n-hexane	DMF	Δλ/nm
Mo	HNΦCH=CHØ-2,4-$(OCH_3)_2$	328	336	8
		498	517	19
Mo	HNΦCH=CHØ-3,4-$(OCH_3)_2$	317	328	11
		492	509	17
Mo	HNΦCH=CHØ-2,5-$(OCH_3)_2$	299	309	10
		487	498	11
W	HNΦCH=CHØ-2,4-$(OCH_3)_2$	293	296	3
		318	321	3
		431	439	8
W	HNΦCH=CHØ-3,4-$(OCH_3)_2$	298	302	4
		311	320	9
		426	438	12
W	HNΦCH=CHØ-2,5-$(OCH_3)_2$	288	295	7
		326	338	12
		421	433	12

[a] Φ = $-C_6H_4-$, Ø = $-C_6H_3-$.

[b] All spectra recorded at ambient temperature, concentrations *ca* 10^{-5} M.

Table XVII shows that most of the complexes studied have absorption spectra which are similar in both form and intensity to those of the ferrocenyl complexes described in Chapter Two. Some

bands have very high extinction coefficients, and absorption generally becomes insignificant above about 700 nm. The limited studies of solvent effects shown in Table XVIII demonstrate that only rather small shifts occur between the strongly polar DMF and non-polar n-hexane, but it should be emphasised that this observation does not preclude NLO activity.

IV-1.4 KURTZ POWDER TESTS

All of the complexes described in this Chapter were tested for powder SHG at 1,907 nm. The stilbene complexes were tested at GEC, and the azo complexes at Durham University. None of the samples gave any detectable SHG.

IV-1.5 STRUCTURAL STUDIES AND CONCLUSIONS

All of these complexes have strongly polarisable dipolar molecular structures, and could reasonably be expected to possess large molecular β values owing to the strongly electron-donating nature of their organic substituent groups. In particular, the *para*-dimethylamino function should act as a considerably more powerful donor than the organometallic ferrocenyl moiety. Complexes of the ligand 4-amino-2',4'-dimethoxystilbene should also have enhanced hyperpolarisability due to the additive donation effects of the *ortho*- and *para*-methoxy groups. Furthermore, the inherent asymmetry of this ligand, and also of its 3',4'- and 2',5'-isomers, might be expected to encourage the adoption of a noncentrosymmetric crystal packing.

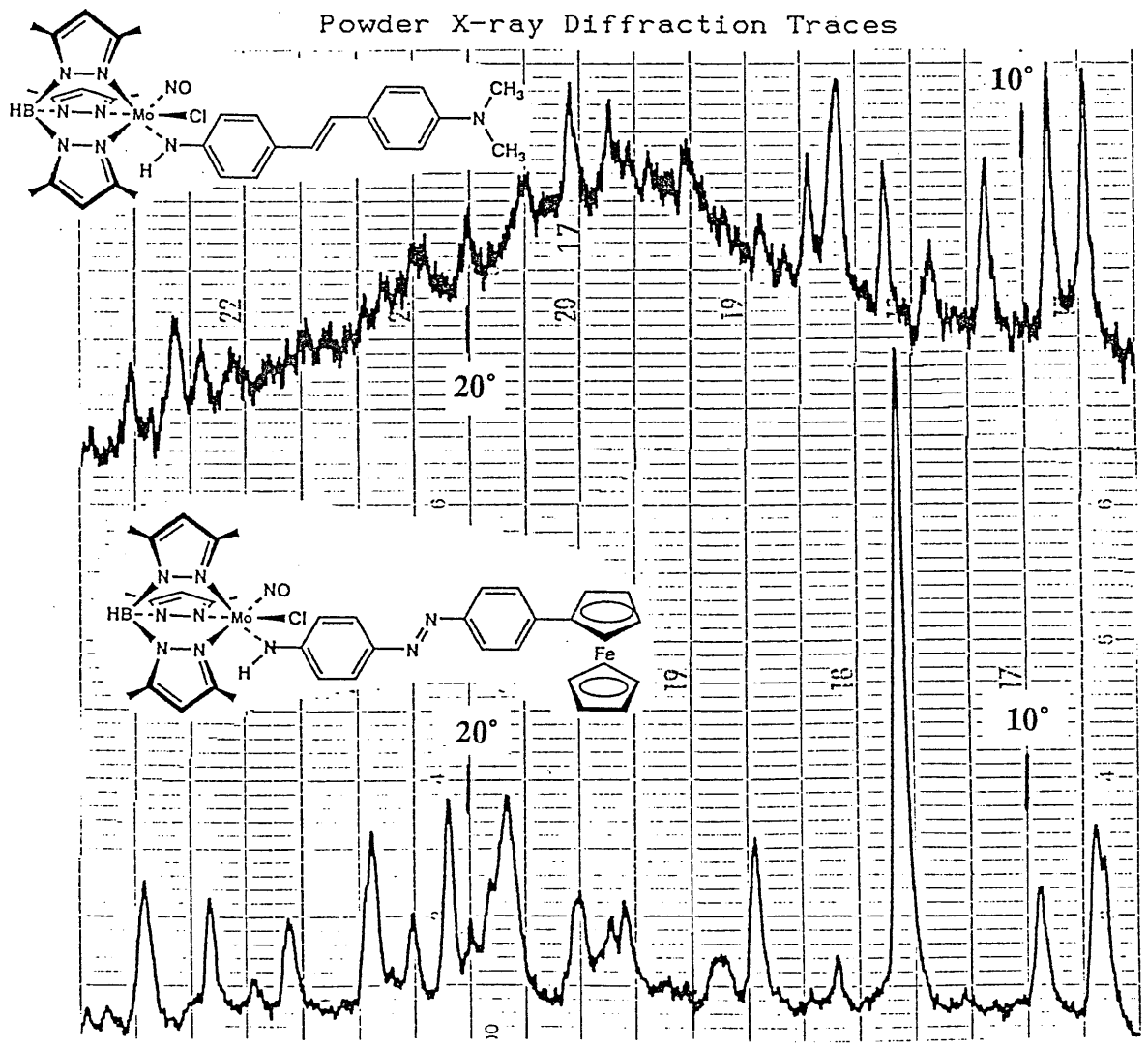
However, the absence of any powder SHG is a strong indication that all of the complexes adopt centrosymmetric packing structures in which complete cancellation of dipoles leads to vanishing $\chi^{(2)}$ values. In order to investigate the structural aspects of these complexes, a number of attempts at crystallisation for single crystal X-ray diffraction studies have been undertaken, but all have proved unsuccessful. Crystals can be grown for some of the

complexes, but they are not of suitable quality for data collection.

Powder X-ray diffraction traces were recorded for the complexes [Mo(NO)L*(Cl)(HNC$_6$H$_4$CH=CHC$_6$H$_4$-4-OCH$_3$)], [Mo(NO)L*(Cl)(HNC$_6$H$_4$CH=CHC$_6$H$_3$-2,4-(OCH$_3$)$_2$)], and [Mo(NO)L*(Cl)(HNC$_6$H$_4$CH=CHC$_6$H$_4$-4-N(CH$_3$)$_2$)], but no useful results were obtained. Such difficulty in obtaining even powder diffraction traces for these complexes shows that they tend to form poorly crystalline solids, which is clearly undesirable for the observation of bulk NLO effects. This factor has already been mentioned in Chapter Two, but seems to be more of a problem with the complexes of organic donor ligands than with the ferrocenyl complexes. However, [Mo(NO)L*(Cl)(HNC$_6$H$_4$N=NC$_6$H$_4$-4-N(CH$_3$)$_2$)] did give a weak powder diffraction pattern. This is shown in Fig. 46, along with that for the SHG-active [Mo(NO)L*(Cl)(HNC$_6$H$_4$N=NC$_6$H$_4$-4-Fc)] for comparison purposes.

Fig. 46

Powder X-ray Diffraction Traces



Unsurprisingly, these two compounds have different crystal structures. This shows how replacement of the bulky ferrocenyl group with a smaller dimethylamino function may conceivably improve the molecular hyperpolarisability, but certainly alters the crystal packing so that no bulk NLO effects can be observed. This observation underlines the fact that the ferrocenyl group has a crucial steric as well as electronic role to play in the creation of NLO-active molybdenum and tungsten complexes. The results from the studies with the ferrocenyl complexes show that further substitution of the azobenzene residue by methyl groups does not significantly alter the bulk properties. Therefore, the attachment of an *ortho*-methoxy or dimethylamino group to give a complex of formulation $[Mo(NO)L^*(Cl)\{HNC_6H_4N{=}NC_6H_3\text{-}2\text{-}D\text{-}4\text{-}Fc\}]$ (where D = $-OCH_3$ or $-N(CH_3)_2$) might prove to be a way of enhancing the molecular hyperpolarisability whilst retaining the favourable noncentrosymmetric packing arrangement for SHG. Such an approach is limited largely by the feasibility of the organic syntheses required to make the necessary ligand molecules.

IV-2 EXPERIMENTAL

$[Mo(NO)L^*(I)_2]$, and $[W(NO)L^*(Cl)_2]$ were prepared by previously described methods.[187,191] $[Mo(NO)L^*(Cl)_2]$ was prepared by a previously described method,[186] and also using the new technique described in Chapter Two. The diiodide is considered as its mono toluene solvate $[Mo(NO)L^*(I)_2].C_7H_8$ when calculating yields. Triethylamine was dried over sodium and stored over activated alumina, and hexamine was recrystallised from absolute ethanol and dried under vacuum. Other reagents were used as supplied, and all reaction solvents were redistilled from drying agents according to standard methods prior to use. All complexation reactions were performed under an atmosphere of dry nitrogen but the reaction products were handled in air. All column chromatography was carried out using silica gel 60 (70-230 mesh) and column dimensions of 40 x 2 cm unless otherwise specified.

IV-2.1 LIGANDS AND LIGAND PRECURSORS

4-Amino-4'-(N,N-dimethylamino)stilbene [107]

A solution of 4-(N,N-dimethylamino)-4'-nitrostilbene (1.0 g, 3.73 mmol) and ammonium chloride (1.0 g, 18.70 mmol) in acetone (50 cm^3) and water (10 cm^3) was heated to reflux. Zinc powder (0.5 g, 7.65 mmol) was added and the mixture stirred under reflux for 30 min. Further ammonium chloride (0.5 g) and zinc powder (0.5 g) were added, and the mixture was stirred at reflux for a further 30 min. The colour of the solution changed from dark red to yellow-orange during this time. The reaction mixture was cooled and the zinc powder removed by filtration. The acetone was removed *in vacuo*. and water (20 cm^3) and dichloromethane (20 cm^3) were added. The orange organic layer was separated and the aqueous layer extracted with further dichloromethane (3 x 10 cm^3). The combined organic extracts were evaporated and the product purified by recrystallisation from dichloromethane to yield a beige solid (0.75 g, 84%).

$(CH_3)_2N-C_6H_4CH=CHC_6H_4-4-NH_2$, m.p. 170-173 °C (lit.,[254] 172-173 °C) (Found: C, 80.8; H, 7.4; N, 12.0%. $C_{16}H_{18}N_2$ requires C, 80.6; H, 7.6; N, 11.8%); $\nu_{max.}(NH_2)$ 3400m and 3330m cm^{-1}; $\delta_H(CDCl_3)$ 7.37 and 6.79 [2 H, d, J(HH) 8.2 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 7.30 and 6.66 [2 H, d, J(HH) 8.1 Hz; 2 H, d, J(HH) 7.7 Hz, C_6H_4], 6.85 [2 H, s, C*H*=C*H*], 3.78 [2 H, v br s, NH_2], 2.97 [6 H, s, $-N(CH_3)_2$].

4-Amino-4'-methoxystilbene [108]

This compound was prepared in an identical manner to [107] using 4-methoxy-4'-nitromethoxystilbene (0.95 g, 3.72 mmol) in place of 4-(N,N-dimethylamino)-4'-nitrostilbene, and with a reaction time of 8 h. The product was obtained as a beige solid (0.65 g, 78%).

$CH_3O-C_6H_4CH=CHC_6H_4-4-NH_2$, m.p. 171-174 °C (lit.,[255] 172-173 °C) (Found: C, 80.2; H, 6.8; N, 6.3%. $C_{15}H_{15}NO$ requires C, 80.0; H, 6.7; N, 6.2%); $\nu_{max.}(NH_2)$ 3455m and 3360s cm^{-1}; $\delta_H(CDCl_3)$ 7.41 and 6.88 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4], 7.31 and 6.67 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 6.88 [2 H, s, C*H*=C*H*], 3.82 [3 H, s, $-OCH_3$], 3.71 [2 H, br s, NH_2].

4-Amino-2',4'-dimethoxystilbene [109]

This compound was prepared in an identical manner to [107] using 2,4-dimethoxy-4'-nitrostilbene (1.06 g, 3.72 mmol) in place of 4-(N,N-dimethylamino)-4'-nitrostilbene, and with a reaction time of 5 h. This yielded the product as a beige solid which was purified by recrystallisation from ethanol (0.90 g, 95%).
$2,4\text{-}(CH_3O)_2\text{-}C_6H_3CH{=}CHC_6H_4\text{-}4\text{-}NH_2$, m.p. 96.5-98 °C (Found: C, 75.3; H, 6.9; N, 5.3%. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); $\nu_{max.}(NH_2)$ 3460m and 3380m cm^{-1}; $\delta_H(CDCl_3)$ 7.47 [1 H, d, J(HH) 8.4 Hz, $C_6H_3(1)$], 7.32 and 6.64 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 7.20 and 6.90 [1 H, d, $J(HH)_{trans}$ 16.5 Hz; 1 H, d, $J(HH)_{trans}$ 16.5 Hz, $CH{=}CH$], 6.49 [1 H, dd, J(12) 8.4 Hz, J(23) 2.4 Hz, $C_6H_3(2)$], 6.45 [1 H, d, J(23) 2.4 Hz, $C_6H_3(3)$], 3.84 and 3.81 [3 H, s; 3 H, s, 2 x $-OCH_3$], 3.67 [2 H, br s, NH_2].

4-Amino-3',4'-dimethoxystilbene [110]

This compound was prepared in an identical manner to [107] using 3,4-dimethoxy-4'-nitrostilbene (1.06 g, 3.72 mmol) in place of 4-(N,N-dimethylamino)-4'-nitrostilbene, and with a reaction time of 5 h. This yielded the product as a beige solid which was purified by recrystallisation from ethanol (0.89 g, 94%).
$3,4\text{-}(CH_3O)_2\text{-}C_6H_3CH{=}CHC_6H_4\text{-}4\text{-}NH_2$, m.p. 158-160 °C (Found: C, 75.0; H, 6.5; N, 5.2%. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); $\nu_{max.}(NH_2)$ 3460m and 3380m cm^{-1}; $\delta_H(CDCl_3)$ 7.32 and 6.67 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 7.03 [1 H, d, J(13) 1.8 Hz, $C_6H_3(3)$], 7.00 [1 H, dd, J(12) 8.2 Hz, J(13) 2.0 Hz, $C_6H_3(1)$], 6.84 [1 H, d, J(12) 8.1 Hz, $C_6H_3(2)$], 6.88 [2 H, s, $CH{=}CH$], 3.93 and 3.89 [3 H, s; 3 H, s, 2 x $-OCH_3$], 3.72 [2 H, br s, NH_2].

4-(N,N-Dimethylamino)-4'-hydroxystilbene [112]

Titanium tetrachloride (4 cm^3, 36.5 mmol) was added dropwise to a stirred suspension of zinc dust (4.77 g, 73 mmol) in dry thf (50 cm^3) at -10 °C (ice/salt/water bath) under a dry nitrogen atmosphere. Addition was carried out over 10 min, and thick yellow fumes were evolved. After fuming had ceased, the mixture was allowed to warm to r.t. and then stirred at reflux for 1 h to produce a dark brown-black solution. This was cooled to r.t. and a

solution of 4-(N,N-dimethylamino)benzaldehyde (1.79 g, 12 mmol) and 4-hydroxybenzaldehyde (1.47 g, 12 mmol) in dry thf (30 cm^3) was added dropwise via a syringe. The reaction mixture was stirred at reflux for 2 h under a dry nitrogen atmosphere. After this time, the reaction mixture was cooled to r.t. and poured into a stirred solution of potassium carbonate (15 g) in water (150 cm^3), producing a dark blue neutral (pH = 7) mixture.

Diethyl ether (75 cm^3) was added and the yellow organic layer separated. The aqueous layer was extracted with ether (3 x 75 cm^3), and the combined ether extracts evaporated to yield a pale green solid. Dichloromethane was added to the crude product mixture and the resulting dark green solution filtered and evaporated once again. The green solid was dissolved in a minimum of dichloromethane and the products separated by column chromatography on silica using dichloromethane as eluent. Fractions were analysed by t.l.c. using a u.v. lamp to visualise the organic products. The first fraction was pale blue in solution and evaporated to a lime green solid, identified by i.r. and ^1H n.m.r. spectroscopy as 4,4'-di(N,N-dimethylamino)stilbene (0.082 g, 2.6%). The second fraction was pale yellow in solution and evaporated to a pale blue-green solid; 4-(N,N-dimethylamino)-4'-hydroxystilbene (0.273 g, 9.5%).

$(CH_3)_2N-C_6H_4CH=CHC_6H_4-4-OH$, m.p. 185-186 °C (lit.,[257] 184 °C) (Found: C, 80.6; H, 7.2; N, 5.8%. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.2; N, 5.9%); $\nu_{max.}$(OH) 3330m cm^{-1}; $\delta_H(CDCl_3)$ 7.38 and 6.80 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 7.36 and 6.72 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 6.92 and 6.84 [1 H, d, $J(HH)_{trans}$ 16.2 Hz; 1 H, d, $J(HH)_{trans}$ 16.2 Hz, $CH=CH$], 4.75 [1 H, s, OH], 2.99 [6 H, s, $-N(CH_3)_2$].

4-Hydroxy-4'-methoxystilbene [114]

This compound was prepared in an identical manner to [112] using 4-methoxybenzaldehyde (1.63 g, 12 mmol) in place of 4-(N,N-dimethylamino)benzaldehyde. Careful column chromatography yielded the product as a pink solid which was further purified by recrystallisation from n-pentane/thf (0.163 g, 6%).

$CH_3O-C_6H_4CH=CHC_6H_4-4-OH$, m.p. 197-200 °C (lit.,[258] 203-205 °C) (Found:

C, 79.3; H, 5.9%. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%); $\nu_{max.}$(OH) 3430m cm^{-1}; $\delta_H(CDCl_3)$ 7.42 and 6.89 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4], 7.39 and 6.82 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 6.92 [2 H, s, CH=CH], 4.75 [1 H, s, OH], 3.83 [3 H, s, $-OCH_3$].

IV-2.2 COMPLEXES

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{OC_6H_4CH=CHC_6H_5}] [118]

A solution of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.30 g, 0.61 mmol), 4-hydroxystilbene (0.14 g, 0.71 mmol) and hexamine (0.05 g, 0.36 mmol) was stirred under reflux in toluene (20 cm^3) for 3 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The resulting deep purple solid was purified by column chromatography on silica using 50% n-hexane/dichloromethane as the eluent. The major purple band was collected and crystallised from a dichloromethane/n-hexane mixture to afford the deep purple product (0.34 g, 85%). (Found: C, 53.5; H, 5.3; N, 14.8%; M^+, 655. $C_{29}H_{33}BClMoN_7O_2$ requires C, 53.3; H, 5.1; N, 15.0%; M, 654); $\nu_{max.}$(NO) 1675s cm^{-1}; $\delta_H(CDCl_3)$ 7.58 and 7.34 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 7.55-7.20 [5 H, c m, C_6H_5], 7.17 and 7.08 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, CH=CH], 5.93, 5.90, and 5.77 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 2.59, 2.42, 2.42, 2.39, 2.20, and 2.07 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 655 (M^+), 625 (M - NO), 460 (M - OC_6H_4CH=CHC_6H_5), 430 (M - OC_6H_4CH=CHC_6H_5 - NO), 196 (HOC_6H_4CH=CHC_6H_5). E_f = -0.29 V, ΔE_p = 100 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{OC_6H_4CH=CHC_6H_5}] [119]

This compound was prepared in an identical manner to [118] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-hydroxystilbene (0.12 g, 0.61 mmol). A deep purple solid was obtained (0.29 g, 76%). (Found: C, 46.5; H, 4.6; N, 13.3%; M^+, 747. $C_{29}H_{33}BIMoN_7O_2$ requires C, 46.7; H, 4.5; N, 13.2%; M, 745); $\nu_{max.}$(NO) 1675s cm^{-1}; $\delta_H(CDCl_3)$ 7.60-7.20 [9 H, c m, C_6H_4 and C_6H_5], 7.13 [2 H, s, CH=CH],

5.91 and 5.85 [1 H, s; 2 H, s, $(Me_2C_3N_2H)_3$], 2.58, 2.45, 2.40, 2.38, 2.31, and 2.07 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 747 (M^+), 620 (M - I), 552 (M - $OC_6H_4CH{=}CHC_6H_5$), 522 (M - $OC_6H_4CH{=}CHC_6H_5$ - NO), 196 ($HOC_6H_4CH{=}CHC_6H_5$). E_f = -0.26 V, ΔE_p = 100 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{$OC_6H_4CH{=}CHC_6H_5$}$_2$] [120]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$.C_7H_8 (0.40 g, 0.52 mmol) and 4-hydroxystilbene (0.25 g, 1.27 mmol) using the procedure described for [118] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A purple-brown solid was obtained (0.23 g, 55%). (Found: C, 63.2; H, 5.8; N, 12.3%; M^+, 815. $C_{43}H_{44}BMoN_7O_3$ requires C, 63.5; H, 5.5; N, 12.1%; M, 814); $\nu_{max.}$(NO) 1660s cm^{-1}; $\delta_H(CDCl_3)$ 7.55-7.10 [18 H, c m, 2 x C_6H_4 and 2 x C_6H_5], 7.12 and 7.02 [2 H, d, $J(HH)_{trans}$ 16.3 Hz; 2 H, d, $J(HH)_{trans}$ 16.3 Hz, 2 x C*H*=C*H*], 5.85 and 5.76 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.41, 2.25, and 2.11 [9 H, s; 6 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 815 (M^+), 620 (M - $OC_6H_4CH{=}CHC_6H_5$), 590 (M - $OC_6H_4CH{=}CHC_6H_5$ - NO), 424 (M - 2 x $OC_6H_4CH{=}CHC_6H_5$), 196 ($HOC_6H_4CH{=}CHC_6H_5$). E_f = -0.62 V, ΔE_p = 150 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$OC_6H_4CH{=}CHC_6H_4$-4-$N(CH_3)_2$}] [121]

This compound was prepared in identical manner to [118] using 4-(N,N-dimethylamino)-4'-hydroxystilbene (0.17 g, 0.71 mmol) in place of 4-hydroxystilbene. Column chromatography on silica using dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane yielded the deep indigo product (0.38 g, 89%). (Found: C, 53.9; H, 5.5; N, 16.4%; M^+, 698. $C_{31}H_{38}BClMoN_8O_2$ requires C, 53.4; H, 5.5; N, 16.1%; M, 697); $\nu_{max.}$(NO) 1690s cm^{-1}; $\delta_H(CDCl_3)$ 7.53 and 7.32 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4-$N(CH_3)_2$], 7.42 and 6.72 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-OMo], 7.05 and 6.95 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.1 Hz, C*H*=C*H*], 5.92, 5.88, and 5.76 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.99 [6 H, s, $N(CH_3)_2$], 2.60, 2.41, 2.39, 2.20, and 2.06 [3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 698 (M^+), 668 (M - NO), 460 (M - $OC_6H_4CH{=}CHC_6H_4$-

$N(CH_3)_2$), 430 (M - $OC_6H_4CH=CHC_6H_4-N(CH_3)_2$ - NO), 239 ($HOC_6H_4CH=CHC_6H_4-N(CH_3)_2$). E_f = -0.33 V, ΔE_p = 100 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{$OC_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$}] [122]

This compound was prepared in an identical manner to [121] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-(N,N-dimethylamino)-4'-hydroxystilbene (0.15 g, 0.63 mmol). A deep emerald green solid was obtained (0.33 g, 81%). (Found: C, 47.7; H, 4.6; N, 14.3%; M^+, 790. $C_{31}H_{38}BIMoN_8O_2$ requires C, 47.2; H, 4.9; N, 14.2%; M, 788); $\nu_{max.}$(NO) 1680s cm^{-1}; $\delta_H(CDCl_3)$ 7.50 and 7.45 [2 H, d, J(HH) 9.2 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-$N(CH_3)_2$], 7.43 and 6.72 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-OMo], 7.09 and 6.92 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 15.9 Hz, C*H*=C*H*], 5.90, 5.84, and 5.83 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 2.99 [6 H, s, $N(CH_3)_2$], 2.59, 2.44, 2.39, 2.38, 2.31, and 1.99 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 790 (M^+), 663 (M - I), 550 (M - $OC_6H_4CH=CHC_6H_4-N(CH_3)_2$), 520 (M - $OC_6H_4CH=CHC_6H_4-N(CH_3)_2$ - NO), 424 (M - $OC_6H_4CH=CHC_6H_4-N(CH_3)_2$ - I), 239 ($HOC_6H_4CH=CHC_6H_4-N(CH_3)_2$). E_f = -0.28 V, ΔE_p = 100 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{$OC_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$}$_2$] [123]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) and 4-(N,N-dimethylamino)-4'-hydroxystilbene (0.30 g, 1.25 mmol) using the procedure described for [118] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A deep purple solid was obtained (0.29 g, 62%). (Found: C, 62.4; H, 6.1; N, 14.3%; M^+, 901. $C_{47}H_{54}BMoN_9O_3$ requires C, 62.7; H, 6.1; N, 14.0%; M, 900); $\nu_{max.}$(NO) 1655s cm^{-1}; $\delta_H(CDCl_3)$ 7.45 and 7.16 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.6 Hz, 2 x C_6H_4-$N(CH_3)_2$], 7.40 and 6.72 [4 H, d, J(HH) 9.0 Hz; 4 H, d, J(HH) 8.8 Hz, 2 x C_6H_4-OMo], 6.98 and 6.91 [2 H, d, $J(HH)_{trans}$ 16.3 Hz; 2 H, d, $J(HH)_{trans}$ 15.9 Hz, 2 x C*H*=C*H*], 5.84 and 5.76 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 2.98 [12 H, s, 2 x $N(CH_3)_2$], 2.41, 2.40, 2.25, and 2.12 [3 H, s; 6 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 901 (M^+), 782 (M - C_6H_4-$N(CH_3)_2$), 752 (M - C_6H_4-

$N(CH_3)_2$ - NO), 663 (M - $OC_6H_4CH=CHC_6H_4-N(CH_3)_2$), 424 (M - 2 x $OC_6H_4CH=CHC_6H_4-N(CH_3)_2$), 239 ($HOC_6H_4CH=CHC_6H_4-N(CH_3)_2$). E_f = -0.63 V, ΔE_p = 100 mV, ΔE_p(Fc) = 90 mV.

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$OC_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$}] [124]

This compound was prepared in an identical manner to [121] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$], 4-(N,N-dimethylamino)-4'-hydroxystilbene (0.18 g, 0.75 mmol), and triethylamine (0.5 cm^3, 3.7 mmol), with a reaction time of 5 h. A deep pink-purple solid was obtained (0.46 g, 85%). (Found: C, 47.7; H, 4.7; N, 14.2%; M^+, 784. $C_{31}H_{38}BClN_8O_2W$ requires C, 47.4; H, 4.9; N, 14.3%; M, 785); $\nu_{max.}$(NO) 1640s cm^{-1}; $\delta_H(CDCl_3)$ 7.51 and 7.25 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-$N(CH_3)_2$], 7.41 and 6.72 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4-OW], 6.99 and 6.93 [1 H, d, $J(HH)_{trans}$ 16.6 Hz; 1 H, d, $J(HH)_{trans}$ 16.6 Hz, C*H*=C*H*], 5.93, 5.90, and 5.83 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 2.98 [6 H, s, $N(CH_3)_2$], 2.67, 2.40, 2.39, 2.29, and 2.19 [3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 784 (M^+), 546 (M - $OC_6H_4CH=CHC_6H_4-N(CH_3)_2$), 516 (M - $OC_6H_4CH=CHC_6H_4-N(CH_3)_2$ - NO), 239 ($HOC_6H_4CH=CHC_6H_4-N(CH_3)_2$). E_f = -0.84 V, ΔE_p = 130 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$OC_6H_4CH=CHC_6H_4$-4-OCH_3}] [125]

This compound was prepared in identical manner to [118] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.11 g, 0.22 mmol) and 4-hydroxy-4'-methoxystilbene (0.052 g, 0.23 mmol) in place of 4-hydroxystilbene. Column chromatography on silica using dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane yielded the deep indigo product (0.13 g, 83%). (Found: C, 53.0; H, 5.1; N, 14.2%; M^+, 685. $C_{30}H_{35}BClMoN_7O_3$ requires C, 52.7; H, 5.2; N, 14.3%; M, 684); $\nu_{max.}$(NO) 1690s cm^{-1}; $\delta_H(CDCl_3)$ 7.55 and 7.33 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4-OCH_3], 7.46 and 6.91 [2 H, d J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-OMo], 7.07 and 7.00 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 5.93, 5.89, and 5.77 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 3.83 [3 H, s, OCH_3], 2.59, 2.42, 2.39, 2.20, and 2.07 [3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 685

(M^+), 655 (M - NO), 460 (M - $OC_6H_4CH=CHC_6H_4-OCH_3$), 430 (M - $OC_6H_4CH=CHC_6H_4-OCH_3$ - NO), 226 ($HOC_6H_4CH=CHC_6H_4-OCH_3$). E_f = -0.31 V, ΔE_p = 110 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{$OC_6H_4CH=CHC_6H_4$-4-OCH_3}] [126]

This compound was prepared in an identical manner to [125] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.16 g, 0.21 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-hydroxy-4'-methoxystilbene (0.059 g, 0.26 mmol). A deep blue-black solid was obtained (0.135 g, 83%). (Found: C, 46.8; H, 4.3; N, 12.4%; M^+, 777. $C_{30}H_{35}BIMoN_7O_3$ requires C, 46.5; H, 4.6; N, 12.7%; M, 775); $\nu_{max.}$(NO) 1680s cm^{-1}; δ_H($CDCl_3$) 7.53-7.43 and 6.91 [6 H, c m; 2 H, d, J(HH) 8.8 Hz, $C_6H_4CH=CHC_6H_4$], 7.10 and 6.98 [1 H, d, J(HH)$_{trans}$ 16.3 Hz; 1 H, d, J(HH)$_{trans}$ 16.3 Hz, $CH=CH$], 5.91, 5.85, and 5.84 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 3.83 [3 H, s, OCH_3], 2.58, 2.45, 2.40, 2.38, 2.31, and 1.99 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 777 (M^+), 650 (M - I), 620 (M - I - NO), 552 (M - $OC_6H_4CH=CHC_6H_4-OCH_3$), 522 (M - $OC_6H_4CH=CHC_6H_4-OCH_3$ - NO), 424 (M - $OC_6H_4CH=CHC_6H_4-OCH_3$ - I), 226 ($HOC_6H_4CH=CHC_6H_4-OCH_3$). E_f = -0.26 V, ΔE_p = 90 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{$OC_6H_4CH=CHC_6H_4$-4-OCH_3}$_2$] [127]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.10 g, 0.13 mmol) and 4-hydroxy-4'-methoxystilbene (0.062 g, 0.27 mmol) using the procedure described for [118] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A deep pink-purple solid was obtained (0.051 g, 45%). (Found: C, 60.4; H, 5.2; N, 10.8%; M^+, 875. $C_{45}H_{48}BMoN_7O_5.0.33CH_2Cl_2$ requires C, 60.4; H, 5.4; N, 10.9%; M, 874); $\nu_{max.}$(NO) 1660s cm^{-1}; δ_H($CDCl_3$) 7.47 and 7.16 [4 H, d, J(HH) 9.0 Hz; 4 H, d, J(HH) 8.8 Hz, 2 x C_6H_4-OCH_3], 7.42 and 6.89 [4 H, d, J(HH) 9.0 Hz; 4 H, d, J(HH) 8.8 Hz, 2 x C_6H_4-OMo], 6.98 [4 H, s, 2 x $CH=CH$], 5.84 and 5.76 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 3.81 [6 H, s, 2 x OCH_3], 2.41, 2.40, 2.25 and 2.12 [3 H, s; 6 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 875 (M^+), 650 (M - $OC_6H_4CH=CHC_6H_4-OCH_3$), 620 (M - $OC_6H_4CH=CHC_6H_4-OCH_3$ - NO), 424 (M - 2 x $OC_6H_4CH=CHC_6H_4-OCH_3$), 226 ($HOC_6H_4CH=CHC_6H_4-OCH_3$). E_f = -0.62 V, ΔE_p = 110 mV, ΔE_p(Fc) = 90 mV.

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{OC_6H_4CH=CHC_6H_4-4-OCH_3}] [128]

This compound was prepared in an identical manner to [125] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.13 g, 0.22 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$], 4-hydroxy-4'-methoxystilbene (0.058 g, 0.26 mmol), and triethylamine (0.5 cm^3, 3.7 mmol), with a reaction time of 5 h. A dark orange-brown solid was obtained (0.12 g, 71%). (Found: C, 47.0; H, 4.6; N, 12.6%; M$^+$, 771. $C_{30}H_{35}BClN_7O_3W$ requires C, 46.7; H, 4.6; N, 12.7%; M, 772); $\nu_{max.}$(NO) 1630s cm^{-1}; δ_H($CDCl_3$) 7.52 and 7.26 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4-OCH_3], 7.45 and 6.90 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-OW], 7.00 [2 H, s, C*H*=C*H*], 5.93, 5.90, and 5.84 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 3.83 [3 H, s, OCH_3], 2.67, 2.40, 2.39, 2.29, and 2.19 [3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 771 (M$^+$), 741 (M - NO), 546 (M - OC_6H_4CH=CHC_6H_4-OCH_3), 516 (M - OC_6H_4CH=CHC_6H_4-OCH_3 - NO), 226 (HOC_6H_4CH=CHC_6H_4-OCH_3). E_f = -0.82 V, ΔE_p = 110 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl(HNC_6H_4CH=CHC_6H_4-4-$N(CH_3)_2$)] [129]

This compound was prepared in similar manner to [118] using 4-amino-4'-(N,N-dimethylamino)stilbene (0.15 g, 0.63 mmol) in place of 4-hydroxystilbene and triethylamine (0.5 cm^3) in place of hexamine. Column chromatography using dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.35 g, 84%). m.p. *ca* 280 °C (Found: C, 53.8; H, 5.5; N, 18.1%; M$^+$, 697. $C_{31}H_{39}BClMoN_9O$ requires C, 53.5; H, 5.7; N, 18.1%; M, 696); $\nu_{max.}$(NH) 3290w, $\nu_{max.}$(NO) 1655s cm^{-1}; δ_H($CDCl_3$) 12.61 [1 H, s, N*H*], 7.55-7.40 and 6.72 [6 H, c m; 2 H, d, J(HH) 8.7 Hz, C_6H_4CH=CHC_6H_4], 7.08 and 6.93 [1 H, d, J(HH)$_{trans}$ 16.3 Hz; 1 H, d, J(HH)$_{trans}$ 16.3 Hz, C*H*=C*H*], 5.86 and 5.79 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 2.99 [6 H, s, -(NCH_3)$_2$], 2.70, 2.42, 2.39, 2.37, 2.36, and 2.03 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 697 (M$^+$), 667 (M - NO), 661 (M - Cl), 631 (M - NO - Cl), 601 (M - 96), 571 (M - 96 - NO), 460 (M - HNC_6H_4CH=CHC_6H_4-4-$N(CH_3)_2$), 430 (M - HNC_6H_4CH=CHC_6H_4-4-$N(CH_3)_2$ - NO), 238 ($H_2NC_6H_4CH$=CHC_6H_4-4-$N(CH_3)_2$). E_f = -0.78 V, ΔE_p = 90 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I(HNC$_6$H$_4$CH=CHC$_6$H$_4$-4-N(CH$_3$)$_2$)] [130]

This compound was prepared in identical manner to [129] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-amino-4'-(N,N-dimethylamino)-stilbene (0.15 g, 0.63 mmol). A deep blue solid was obtained (0.31 g, 76%). m.p. *ca* 295 °C (Found: C, 47.6; H, 5.0; N, 15.9%; M$^+$, 789. $C_{31}H_{39}BIMoN_9O$ requires C, 47.3; H, 5.0; N, 16.0%; M, 787); $\nu_{max.}$(NH) 3290w, $\nu_{max.}$(NO) 1660s cm^{-1}; δ_H($CDCl_3$) 13.06 [1 H, s, N*H*], 7.62-7.40 and 6.72 [6 H, c m; 2 H, d, J(HH) 8.7 Hz, C$_6$*H*$_4$CH=CHC$_6$*H*$_4$], 7.14 and 6.89 [1 H, d, J(HH)$_{trans}$ 16.3 Hz; 1 H, d, J(HH)$_{trans}$ 16.3 Hz, C*H*=C*H*], 5.93, 5.86, and 5.77 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 2.99 [6 H, s, -(NC*H*$_3$)$_2$], 2.72, 2.48, 2.46, 2.37, 2.37, and 2.00 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, (*Me*$_2$C$_3$N$_2$H)$_3$]; *m/z* 789 (M$^+$), 660 (M - I), 630 (M - NO - I), 566 (M - C$_6$H$_4$CH=CHC$_6$H$_4$-4-N(CH$_3$)$_2$), 550 (M - HNC$_6$H$_4$CH=CHC$_6$H$_4$-4-N(CH$_3$)$_2$), 536 (M - C$_6$H$_4$CH=CHC$_6$H$_4$-4-N(CH$_3$)$_2$ - NO), 520 (M - HNC$_6$H$_4$CH=CHC$_6$H$_4$-4-N(CH$_3$)$_2$ - NO), 238 (H$_2$NC$_6$H$_4$CH=CHC$_6$H$_4$-4-N(CH$_3$)$_2$). E_f = -0.73 V, ΔE_p = 90 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{HNC$_6$H$_4$CH=CHC$_6$H$_4$-4-N(CH$_3$)$_2$}$_2$] [131]

Sodium (0.1 g, 4.35 mmol) was heated under reflux in dry thf (35 cm^3) for 30 min. Naphthalene (0.1 g, 0.78 mmol) was then added and the mixture stirred for 1 h under reflux during which time the solution became dark green. The mixture was then filtered under nitrogen, to remove excess sodium, and 4-amino-4'-(N,N-dimethylamino)stilbene (0.08 g, 0.34 mmol) was added to the filtrate. After stirring the resulting solution for 30 min at room temperature, [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{HNC$_6$H$_4$CH=CHC$_6$H$_4$-4-N(CH$_3$)$_2$}] (0.15 g, 0.19 mmol) was added and the mixture stirred under reflux for a further 2.5 h. The final dark green mixture was filtered in air to give a dark green filtrate from which the solvent was removed *in vacuo*. The product was purified by column chromatography on silica using dichloromethane as eluent, the major green fraction being collected. Further purification was effected by recrystallisation from n-hexane/dichloromethane to yield a deep emerald green solid (0.10 g, 58%) (Found: C, 63.7; H, 6.2; N, 17.3%; M$^+$, 899. $C_{47}H_{56}BMoN_{11}O$ requires C, 62.9; H, 6.3; N,

17.2%; M, 898); $\nu_{max.}$(NH) 3320w, $\nu_{max.}$(NO) 1635s cm^{-1}; $\delta_H(CDCl_3)$ 8.88 [2 H, s, 2 x N*H*], 7.40-7.20 and 6.71 [12 H, c m; 4 H, d, J(HH) 8.8 Hz, 2 x $C_6H_4CH=CHC_6H_4$], 6.94 and 6.87 [2 H, d, $J(HH)_{trans}$ 16.1 Hz; 2 H, d, $J(HH)_{trans}$ 16.1 Hz, 2 x C*H*=C*H*], 5.96 and 5.74 [1 H, s; 2 H, s, $(Me_2C_3N_2H)_3$], 2.96 [12 H, s, 2 x $-N(CH_3)_2$], 2.47, 2.35, and 2.27 [3 H, s; 9 H, s; 6 H, s, $(MeC_3N_2H)_3$]; *m/z* 899 (M^+), 662 (M - $C_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$), 238 ($H_2NC_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$). E_f = -1.22 V, ΔE_p = 130 mV, ΔE_p(Fc) = 95 mV.

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$HNC_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$}] [132]

This compound was prepared in an identical manner to [129] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 4-amino-4'-(N,N-dimethylamino)-stilbene (0.19 g, 0.78 mmol), with a reaction time of 8 h. A deep red-brown solid was obtained (0.13 g, 24%). (Found: C, 47.8; H, 4.9; N, 15.8%; M^+, 783. $C_{31}H_{39}BClN_9OW$ requires C, 47.5; H, 5.0; N, 16.1%; M, 784); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1620s cm^{-1}; $\delta_H(CDCl_3)$ 10.77 [1 H, s, N*H*], 7.51 and 7.36 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-$N(CH_3)_2$], 7.41 and 6.72 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4-NHW], 7.01 and 6.93 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 5.94, 5.88, and 5.82 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.99 [6 H, s, $-(NCH_3)_2$], 2.73, 2.46, 2.42, 2.37, 2.36, and 2.16 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$]; *m/z* 783 (M^+), 768 (M - CH_3), 753 (M - NO), 747 (M - Cl), 717 (M - NO - Cl), 687 (M - 96), 657 (M - 96 - NO), 546 (M - $HNC_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$), 516 (M - $HNC_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$ - NO), 238 ($H_2NC_6H_4CH=CHC_6H_4$-4-$N(CH_3)_2$). E_f = -1.19 V, ΔE_p = 130 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl($HNC_6H_4CH=CHC_6H_4$-4-OCH_3)] [133]

This compound was prepared in similar manner to [118] using 4-amino-4'-methoxystilbene (0.14 g, 0.63 mmol) in place of 4-hydroxystilbene and triethylamine (0.5 cm^3) in place of hexamine. Column chromatography using dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane yielded a deep pink-purple solid (0.33 g, 79%). m.p. *ca* 270 °C (Found: C, 53.0; H, 5.0; N, 16.2%; M^+, 684. $C_{30}H_{36}BClMoN_8O_2$ requires C, 52.8; H, 5.3; N,

16.4%; M, 683); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1660s cm^{-1}; $\delta_H(CDCl_3)$ 12.60 [1 H, s, N*H*], 7.56-7.45 and 6.91 [6 H, c m; 2 H, d, J(HH) 8.6 Hz, $C_6H_4CH{=}CHC_6H_4$], 7.09 and 6.99 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 5.87 and 5.79 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.83 [3 H, s, $-OCH_3$], 2.70, 2.42, 2.39, 2.38, 2.37, and 2.03 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$]; *m/z* 684 (M^+), 654 (M - NO), 648 (M - Cl), 618 (M - NO - Cl), 588 (M - 96), 558 (M - 96 - NO), 460 (M - $HNC_6H_4CH{=}CHC_6H_4$-4-OCH_3), 430 (M - $HNC_6H_4CH{=}CHC_6H_4$-4-OCH_3 - NO), 225 ($H_2NC_6H_4CH{=}CHC_6H_4$-4-OCH_3). E_f = -0.77 V, ΔE_p = 120 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I(HN$C_6H_4CH{=}CHC_6H_4$-4-OCH_3)] [134]

This compound was prepared in identical manner to [133] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-amino-4'-methoxystilbene (0.14 g, 0.63 mmol). A deep purple solid was obtained (0.33 g, 82%). m.p. *ca* 260 °C (Found: C, 46.7; H, 4.4; N, 14.5%; M^+, 776. $C_{30}H_{36}BIMoN_8O_2$ requires C, 46.5; H, 4.7; N, 14.5%; M, 774); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1660s cm^{-1}; $\delta_H(CDCl_3)$ 13.06 [1 H, s, N*H*], 7.61 and 7.50 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-OCH_3], 7.48 and 6.90 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4-NHMo], 7.15 and 6.95 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 5.93, 5.86, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.83 [3 H, s, $-OCH_3$], 2.72, 2.48, 2.46, 2.38, 2.37, and 2.00 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$]; *m/z* 776 (M^+), 746 (M - NO), 680 (M - 96), 649 (M - I), 619 (M - NO - I), 552 (M - $HNC_6H_4CH{=}CHC_6H_4$-4-OCH_3), 522 (M - $HNC_6H_4CH{=}CHC_6H_4$-4-OCH_3 - NO), 424 (M - $HNC_6H_4CH{=}CHC_6H_4$-4-OCH_3 - I), 225 ($H_2NC_6H_4CH{=}CHC_6H_4$-4-OCH_3). E_f = -0.73 V, ΔE_p = 100 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(HN$C_6H_4CH{=}CHC_6H_4$-4-OCH_3)$_2$] [135]

This compound was prepared in identical manner to [131] using [134] (0.15 g, 0.19 mmol) instead of [130] and 4-amino-4'-methoxystilbene (0.077 g, 0.34 mmol) instead of 4-amino-4'-(N,N-dimethylamino)stilbene. Column chromatography followed by recrystallisation afforded the product as a dark emerald green solid (0.062 g, 37%) (Found: C, 62.3; H, 5.2; N, 14.2%; M^+, 873.

$C_{45}H_{50}BMoN_9O_3$ requires C, 62.0; H, 5.3; N, 14.5%; M, 872); $\nu_{max.}$(NH) 3320w, $\nu_{max.}$(NO) 1635s cm^{-1}; δ_H($CDCl_3$) 8.91 [2 H, s, 2 x N*H*], 7.42 and 7.27 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.6 Hz, 2 x C_6H_4-OCH_3], 7.41 and 6.88 [4 H, d, J(HH) 8.8 Hz; 4 H, d, J(HH) 8.8 Hz, 2 x C_6H_4-NHMo], 6.94 [4 H, s, 2 x C*H*=C*H*], 5.96 and 5.75 [1 H, s; 2 H, s, $(Me_2C_3N_2H)_3$], 3.82 [6 H, s, 2 x -OCH_3], 2.47, 2.35, and 2.27 [3 H, s; 9 H, s; 6 H, s, $(MeC_3N_2H)_3$]; *m/z* 873 (M^+), 648 (M - C_6H_4CH=CHC_6H_4-4-OCH_3), 424 (M - 2 x C_6H_4CH=CHC_6H_4-4-OCH_3), 225 ($H_2NC_6H_4CH$=CHC_6H_4-4-OCH_3). E_f = -1.18 V, ΔE_p = 160 mV, ΔE_p(Fc) = 95 mV.

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_4CH=CHC_6H_4-4-OCH_3}] [136]

This compound was prepared in an identical manner to [133] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 4-amino-4'-methoxystilbene (0.18 g, 0.78 mmol), with a reaction time of 8 h. A deep red-brown solid was obtained (0.11 g, 21%). (Found: C, 46.4; H, 4.7; N, 14.2%; M^+, 770. $C_{30}H_{36}BClN_8O_2W$ requires C, 46.8; H, 4.7; N, 14.5%; M, 771); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1620s cm^{-1}; δ_H($CDCl_3$) 10.76 [1 H, s, N*H*], 7.53 and 7.38 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4-OCH_3], 7.45 and 6.90 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-NHW], 7.01 [2 H, s, C*H*=C*H*], 5.94, 5.88, and 5.82 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.83 [3 H, s, -OCH_3], 2.73, 2.45, 2.42, 2.37, 2.36, and 2.15 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$]; *m/z* 770 (M^+), 740 (M - NO), 734 (M - Cl), 704 (M - NO - Cl), 674 (M - 96), 644 (M - 96 - NO), 563 (M - C_6H_4CH=CHC_6H_4-4-OCH_3), 546 (M - HNC_6H_4CH=CHC_6H_4-4-OCH_3), 516 (M - HNC_6H_4CH=CHC_6H_4-4-OCH_3 - NO), 225 ($H_2NC_6H_4CH$=CHC_6H_4-4-OCH_3). E_f = -1.18 V, ΔE_p = 150 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_4CH=CHC_6H_3-3,4-$(OCH_3)_2$}] [137]

This compound was prepared in similar manner to [118] using 3',4'-dimethoxystilbenamine (0.16 g, 0.63 mmol) in place of 4-hydroxystilbene and triethylamine (0.5 cm^3) in place of hexamine. Column chromatography using dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.32 g, 74%). (Found: C, 52.3; H, 5.3; N, 15.9%; M^+,

714. $C_{31}H_{38}BClMoN_6O_3$ requires C, 52.2; H, 5.4; N, 15.7%; M, 713); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1650s cm^{-1}; $\delta_H(CDCl_3)$ 12.60 [1 H, s, N*H*], 7.55 and 7.46 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.08 and 7.06 [2 H, s, s, C_6H_3(1 and 3)], 7.09 and 6.99 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 6.87 [1 H, d, J(12) 8.2 Hz, C_6H_3(2)], 5.87 and 5.80 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.96 and 3.91 [3 H, s; 3 H, s, 2 x $-OCH_3$], 2.70, 2.42, 2.39, 2.38, 2.37, and 2.03 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$]; *m/z* 714 (M^+), 684 (M - NO), 678 (M - Cl), 648 (M - NO - Cl), 618 (M - 96), 588 (M - 96 - NO), 459 (M - $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$), 429 (M - $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$ - NO), 255 ($H_2NC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$). E_f = -0.76 V, ΔE_p = 130 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I{$HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$}] [138]

This compound was prepared in identical manner to [137] using [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(I)_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] and 3',4'-dimethoxystilbenamine (0.15 g, 0.59 mmol). A deep violet solid was obtained (0.37 g, 88%). (Found: C, 46.4; H, 4.5; N, 14.0%; M^+, 806. $C_{31}H_{38}BIMoN_6O_3$ requires C, 46.3; H, 4.8; N, 13.9%; M, 804); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1650s cm^{-1}; $\delta_H(CDCl_3)$ 13.06 [1 H, s, N*H*], 7.62 and 7.50 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.10 and 7.08 [2 H, d, d, C_6H_3(1 and 3)], 7.15 and 6.95 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 6.87 [1 H, d, J(12) 8.9 Hz, C_6H_3(2)], 5.93, 5.86, and 5.78 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.96 and 3.91 [3 H, s; 3 H, s, 2 x $-OCH_3$], 2.72, 2.49, 2.47, 2.38, 2.37, and 2.00 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$]; *m/z* 806 (M^+), 679 (M - I), 648 (M - NO - I), 583 (M - 223), 552 (M - $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$), 522 (M - $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$ - NO), 424 (M - $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$ - I), 255 ($H_2NC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$). E_f = -0.71 V, ΔE_p = 100 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}{$HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2)_2$] [139]

This compound was prepared in identical manner to [131] using [138] (0.15 g, 0.19 mmol) instead of [130] and 3',4'-dimethoxy-

stilbenamine (0.10 g, 0.39 mmol) instead of 4-amino-4'-(N,N-dimethylamino)stilbene. Column chromatography using 5% thf/dichloromethane as eluent followed by recrystallisation from n-hexane/dichloromethane afforded the product as a dark emerald green solid (0.058 g, 33%) (Found: C, 60.8; H, 5.7; N, 13.5%; M^+, 933. $C_{47}H_{54}BMoN_9O_5$ requires C, 60.6; H, 5.4; N, 13.5%; M, 932); $\nu_{max.}$(NH) 3300w, $\nu_{max.}$(NO) 1630s cm^{-1}; $\delta_H(CDCl_3)$ 8.92 [2 H, s, 2 x N*H*], 7.42 and 7.28 [4 H, d, J(HH) 8.4 Hz; 4 H, d, J(HH) 8.4 Hz, 2 x C_6H_4], 7.04 and 7.00 [4 H, d, d, 2 x C_6H_3(1 and 3)], 6.94 [4 H, s, 2 x C*H*=C*H*], 6.84 [2 H, d, J(12) 8.2 Hz, 2 x C_6H_3(2)], 5.96 and 5.75 [1 H, s; 2 H, s, $(Me_2C_3N_2H)_3$], 3.94 and 3.88 [6 H, s; 6 H, s, 4 x -OCH_3], 2.47, 2.35, and 2.28 [3 H, s; 9 H, s; 6 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 933 (M^+), 676 (M - $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$), 646 (M - $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$ - NO), 424 (M - 2 x $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$), 255 ($H_2NC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$). E_f = -1.19 V, ΔE_p = 180 mV, ΔE_p(Fc) = 95 mV.

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$}] [140]

This compound was prepared in an identical manner to [137] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 3',4'-dimethoxystilbenamine (0.20 g, 0.78 mmol), with a reaction time of 8 h. A dark orange-brown solid was obtained (0.10 g, 18%). (Found: C, 46.8; H, 4.8; N, 13.7%; M^+, 800. $C_{31}H_{38}BClN_8O_3W$ requires C, 46.5; H, 4.8; N, 14.0%; M, 801); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1620s cm^{-1}; $\delta_H(CDCl_3)$ 10.76 [1 H, s, N*H*], 7.53 and 7.38 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.07 and 7.04 [2 H, s, d, C_6H_3(1 and 3)], 7.00 [2 H, s, C*H*=C*H*], 6.86 [1 H, d, J(12) 8.2 Hz, C_6H_3(2)], 5.94, 5.88, and 5.83 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.96 and 3.90 [3 H, s; 3 H, s, 2 x -OCH_3], 2.73, 2.46, 2.42, 2.37, 2.35, and 2.16 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 800 (M^+), 770 (M - NO), 764 (M - Cl), 734 (M - NO - Cl), 704 (M - 96), 674 (M - 96 - NO), 546 (M - $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$), 516 (M - $HNC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$ - NO), 255 ($H_2NC_6H_4CH=CHC_6H_3$-3,4-$(OCH_3)_2$). E_f = -1.17 V, ΔE_p = 110 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl{$HNC_6H_4CH=CHC_6H_3$-2,4-$(OCH_3)_2$}] [141]

This compound was prepared in similar manner to [118] using 2',4'-dimethoxystilbenamine (0.16 g, 0.63 mmol) in place of 4-hydroxystilbene and triethylamine (0.5 cm^3) in place of hexamine. Column chromatography using dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.31 g, 72%). (Found: C, 52.2; H, 5.4; N, 15.9%; M^+, 714. $C_{31}H_{38}BClMoN_8O_3$ requires C, 52.2; H, 5.4; N, 15.7%; M, 713); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1645s cm^{-1}; δ_H($CDCl_3$) 12.62 [1 H, s, N*H*], 7.58-7.40 [6 H, c m, C_6H_3(1), =C*H*, and C_6H_4], 7.03 [1 H, d, J(HH)$_{trans}$ 16.6 Hz, =C*H*], 6.54 and 6.51 [½ H, d, J(23) 2.5 Hz; ½ H, d, J(23) 2.2 Hz, J(12) 8.5 Hz, C_6H_3(2)], 6.48 [1 H, d, J(23) 2.5 Hz, C_6H_3(3)], 5 87, 5.87, and 5.79 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H)_3$], 3.88 and 3.84 [3 H, s; 3 H, s, 2 x -OCH_3], 2.70, 2.42, 2.39, 2.38, 2.37, and 2.03 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H)_3$]; *m/z* 714 (M^+), 684 (M - NO), 678 (M - Cl), 648 (M - NO - Cl), 618 (M - 96), 588 (M - 96 - NO), 459 (M - $HNC_6H_4CH=CHC_6H_3$-2,4-$(OCH_3)_2$), 429 (M - $HNC_6H_4CH=CHC_6H_3$-2,4-$(OCH_3)_2$ - NO), 255 ($H_2NC_6H_4CH=CHC_6H_3$-2,4-$(OCH_3)_2$). E_f = -0.76 V, ΔE_p = 100 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I{$HNC_6H_4CH=CHC_6H_3$-2,4-$(OCH_3)_2$}] [142]

This compound was prepared in identical manner to [141] using [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(I)_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] and 2',4'-dimethoxystilbenamine (0.15 g, 0.59 mmol). A deep violet solid was obtained (0.35 g, 84%). (Found: C, 46.6; H, 4.9; N, 14.1%; M^+, 806. $C_{31}H_{38}BIMoN_8O_3$ requires C, 46.3; H, 4.8; N, 13.9%; M, 804); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1645s cm^{-1}; δ_H($CDCl_3$) 13.07 [1 H, s, N*H*], 7.62-7.46 [6 H, c m, C_6H_3(1), =C*H*, and C_6H_4], 7.03 [1 H, d, J(HH)$_{trans}$ 16.6 Hz, =C*H*], 6.54 and 6.51 [½ H, d, J(23) 2.5 Hz; ½ H, d, J(23) 2.5 Hz, J(12) 8.7 Hz, C_6H_3(2)], 6.48 [1 H, d, J(23) 2.2 Hz, C_6H_3(3)], 5.93, 5.86, and 5.77 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H)_3$], 3.87 and 3.84 [3 H, s; 3 H, s, 2 x -OCH_3], 2.72, 2.49, 2.46, 2.37, 2.37, and 2.00 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H)_3$]; *m/z* 806 (M^+), 679 (M - I), 648 (M - NO - I), 583 (M - 223), 552 (M - $HNC_6H_4CH=CHC_6H_3$-2,4-$(OCH_3)_2$), 522 (M - $HNC_6H_4CH=CHC_6H_3$-2,4-$(OCH_3)_2$ -

NO), 424 (M - $HNC_6H_4CH{=}CHC_6H_3$-3,4-$(OCH_3)_2$ - I), 255 ($H_2NC_6H_4CH{=}CHC_6H_3$-2,4-$(OCH_3)_2$). E_f = -0.73 V, ΔE_p = 90 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{$HNC_6H_4CH{=}CHC_6H_3$-2,4-$(OCH_3)_2$}$_2$] [143]

This compound was prepared in identical manner to [131] using [142] (0.15 g, 0.19 mmol) instead of [130] and 2',4'-dimethoxystilbenamine (0.10 g, 0.39 mmol) instead of 4-amino-4'-(N,N-dimethylamino)stilbene. Column chromatography using 5% thf/dichloromethane as eluent followed by recrystallisation from n-hexane/dichloromethane afforded the product as a dark emerald green solid (0.063 g, 36%) (Found: C, 60.6; H, 5.7; N, 13.4%; M^+, 933. $C_{47}H_{54}BMoN_9O_5$ requires C, 60.6; H, 5.4; N, 13.5%; M, 932); $\nu_{max.}$(NH) 3300w, $\nu_{max.}$(NO) 1630s cm^{-1}; δ_H($CDCl_3$) 8.90 [2 H, s, 2 x N*H*], 7.51-7.22 [12 H, c m, 2 x C_6H_3(1), 2 x =C*H*, and 2 x C_6H_4], 6.96 [2 H, d, J(HH)$_{trans}$ 16.3 Hz, 2 x =C*H*], 6.52 and 6.49 [1 H, d, J(23) 2.2 Hz; 1 H, d, J(23) 2.2 Hz, J(12) 8.6 Hz, 2 x C_6H_3(2)], 6.45 [2 H, d, J(23) 2.2 Hz, 2 x C_6H_3(3)], 5.95 and 5.73 [1 H, s; 2 H, s, ($Me_2C_3N_2H$)$_3$], 3.85 and 3.81 [6 H, s; 6 H, s, 4 x -OCH_3], 2.46, 2.34, and 2.26 [3 H, s; 9 H, s; 6 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 933 (M^+), 676 (M - $HNC_6H_4CH{=}CHC_6H_3$-2,4-$(OCH_3)_2$), 646 (M - $HNC_6H_4CH{=}CHC_6H_3$-2,4-$(OCH_3)_2$ - NO), 424 (M - 2 x $HNC_6H_4CH{=}CHC_6H_3$-2,4-$(OCH_3)_2$), 255 ($H_2NC_6H_4CH{=}CHC_6H_3$-2,4-$(OCH_3)_2$). E_f = -1.19 V, ΔE_p = 180 mV, ΔE_p(Fc) = 95 mV.

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$HNC_6H_4CH{=}CHC_6H_3$-2,4-$(OCH_3)_2$}] [144]

This compound was prepared in an identical manner to [141] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 2',4'-dimethoxystilbenamine (0.20 g, 0.78 mmol), with a reaction time of 8 h. A dark orange-brown solid was obtained (0.13 g, 23%). (Found: C, 46.7; H, 4.6; N, 14.2%; M^+, 800. $C_{31}H_{38}BClN_8O_3W$ requires C, 46.5; H, 4.8; N, 14.0%; M, 801); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1620s cm^{-1}; δ_H($CDCl_3$) 10.78 [1 H, s, N*H*], 7.56-7.32 [6 H, c m, C_6H_3(1), =C*H*, and C_6H_4], 7.02 [1 H, d, J(HH)$_{trans}$ 16.3 Hz, =C*H*], 6.54 and 6.51 [½ H, d, J(23) 2.5 Hz; ½ H, d, J(23) 2.2 Hz, J(12) 8.6 Hz, C_6H_3(2)], 6.47 [1 H, d, J(23) 2.2 Hz, C_6H_3(3)], 5.94, 5.88, and 5.82 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 3.87 and 3.84 [3 H, s; 3 H, s, 2 x -OCH_3], 2.73, 2.46, 2.42, 2.36, 2.35, and 2.15 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H,

s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 800 (M^+), 770 (M - NO), 764 (M - Cl), 734 (M - NO - Cl), 704 (M - 96), 674 (M - 96 - NO), 546 (M - $HNC_6H_4CH{=}CHC_6H_3$-2,4-(OCH_3)$_2$), 516 (M - $HNC_6H_4CH{=}CHC_6H_3$-2,4-(OCH_3)$_2$ - NO), 255 ($H_2NC_6H_4CH{=}CHC_6H_3$-2,4-(OCH_3)$_2$). E_f = -1.18 V, ΔE_p = 110 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$HNC_6H_4CH{=}CHC_6H_3$-2,5-(OCH_3)$_2$}] [145]

This compound was prepared in similar manner to [118] using 2',5'-dimethoxystilbenamine (0.16 g, 0.63 mmol) in place of 4-hydroxystilbene and triethylamine (0.5 cm^3) in place of hexamine. Column chromatography using dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.32 g, 74%). (Found: C, 52.3; H, 5.3; N, 15.8%; M^+, 714. $C_{31}H_{38}BClMoN_8O_3$ requires C, 52.2; H, 5.4; N, 15.7%; M, 713); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1655s cm^{-1}; δ_H($CDCl_3$) 12.60 [1 H, s, N*H*], 7.59 and 7.47 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 7.49 and 7.11 [1 H, d, $J(HH)_{trans}$ 16.5 Hz; 1 H, d, $J(HH)_{trans}$ 16.8 Hz, C*H*=C*H*], 7.16 [1 H, d, J(23) 2.7 Hz, C_6H_3(3)], 6.86-6.77 [2 H, c m, C_6H_3(1 and 2)], 5.87 and 5.79 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 3.85 and 3.83 [3 H, s; 3 H, s, 2 x -OCH_3], 2.69, 2.42, 2.39, 2.38, 2.37, and 2.03 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$]; *m/z* 714 (M^+), 684 (M - NO), 678 (M - Cl), 648 (M - NO - Cl), 618 (M - 96), 588 (M - 96 - NO), 459 (M - $HNC_6H_4CH{=}CHC_6H_3$-2,5-(OCH_3)$_2$), 429 (M - $HNC_6H_4CH{=}CHC_6H_3$-2,5-(OCH_3)$_2$ - NO), 255 ($H_2NC_6H_4CH{=}CHC_6H_3$-2,5-(OCH_3)$_2$). E_f = -0.76 V, ΔE_p = 110 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{$HNC_6H_4CH{=}CHC_6H_3$-2,5-(OCH_3)$_2$}] [146]

This compound was prepared in identical manner to [145] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 2',5'-dimethoxystilbenamine (0.15 g, 0.59 mmol). A deep violet solid was obtained (0.32 g, 75%). (Found: C, 46.6; H, 4.9; N, 14.0%; M^+, 806. $C_{31}H_{38}BIMoN_8O_3$ requires C, 46.3; H, 4.8; N, 13.9%; M, 804); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1655s cm^{-1}; δ_H($CDCl_3$) 13.06 [1 H, s, N*H*], 7.62 and 7.55 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4], 7.55 and 7.07 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 7.17 [1

H, d, J(23) 2.3 Hz, C_6H_3(3)], 6.83 [2 H, d, C_6H_3(1 and 2)], 5.93, 5.86, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.85 and 3.83 [3 H, s; 3 H, s, 2 x $-OCH_3$], 2.72, 2.49, 2.46, 2.38, 2.37, and 2.00 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 806 (M^+), 679 (M - I), 648 (M - NO - I), 583 (M - 223), 552 (M - $HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$), 522 (M - $HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$ - NO), 424 (M - $HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$ - I), 255 ($H_2NC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$). E_f = -0.71 V, ΔE_p = 90 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{$HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$}$_2$] [147]

This compound was prepared in identical manner to [131] using [146] (0.15 g, 0.19 mmol) instead of [130] and 2',5'-dimethoxystilbenamine (0.10 g, 0.39 mmol) instead of 4-amino-4'-(N,N-dimethylamino)stilbene. Column chromatography using 5% thf/dichloromethane as eluent followed by recrystallisation from n-hexane/dichloromethane afforded the product as a dark emerald green solid (0.032 g, 18%) (Found: C, 60.5; H, 5.7; N, 13.1%; M^+, 933. $C_{47}H_{54}BMoN_9O_5$ requires C, 60.6; H, 5.4; N, 13.5%; M, 932); $\nu_{max.}$(NH) 3300w, $\nu_{max.}$(NO) 1630s cm^{-1}; $\delta_H(CDCl_3)$ 8.92 [2 H, s, 2 x N*H*], 7.46 and 7.27 [4 H, d, J(HH) 8.2 Hz; 4 H, d, J(HH) 8.4 Hz, 2 x C_6H_4], 7.34 and 7.05 [2 H, d, $J(HH)_{trans}$ 16.5 Hz; 2 H, d, $J(HH)_{trans}$ 16.7 Hz, 2 x C*H*=C*H*], 7.15 [2 H, d, J(23) 2.8 Hz, 2 x C_6H_3(3)], 6.82 [2 H, d, J(12) 9.0 Hz, 2 x C_6H_3(1)], 6.75 and 6.72 [1 H, d, J(23) 2.8 Hz; 1 H, d, J(23) 2.9 Hz; 2 x C_6H_3(2)], 5.96 and 5.75 [1 H, s; 2 H, s, $(Me_2C_3N_2H)_3$], 3.83 and 3.81 [6 H, s; 6 H, s, 4 x $-OCH_3$], 2.47, 2.35, and 2.27 [3 H, s; 9 H, s; 6 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 933 (M^+), 676 (M - $HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$), 646 (M - $HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$ - NO), 424 (M - 2 x $HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$), 255 ($H_2NC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$). E_f = -1.16 V, ΔE_p = 220 mV, ΔE_p(Fc) = 95 mV.

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$}] [148]

This compound was prepared in an identical manner to [145] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 2',5'-dimethoxystilbenamine (0.20 g, 0.78 mmol), with a reaction time of 8 h. A dark orange-brown solid was obtained (0.16 g, 29%). (Found: C, 46.2; H, 4.8;

N, 14.2%; M^+, 800. $C_{31}H_{38}BClN_8O_3W$ requires C, 46.5; H, 4.8; N, 14.0%; M, 801); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1620s cm^{-1}; $\delta_H(CDCl_3)$ 10.76 [1 H, s, N*H*], 7.58 and 7.38 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 7.41 and 7.11 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 7.15 [1 H, d, J(23) 2.3 Hz, C_6H_3(3)], 6.84 [1 H, d, J(12) 8.9 Hz, C_6H_3(1)], 6.79 and 6.76 [½ H, d, J(23) 2.7 Hz; ½ H, d, J(23) 2.7 Hz, J(12) 9.1 Hz, C_6H_3(2)], 5.94, 5.88 and 5.83 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.85 and 3.83 [3 H, s; 3 H, s, 2 x $-OCH_3$], 2.73, 2.46, 2.42, 2.37, 2.36, and 2.15 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$]; *m/z* 800 (M^+), 770 (M - NO), 764 (M - Cl), 734 (M - NO - Cl), 704 (M - 96), 674 (M - 96 - NO), 546 (M - $HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$), 516 (M - $HNC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$ - NO), 255 ($H_2NC_6H_4CH=CHC_6H_3$-2,5-$(OCH_3)_2$). E_f = -1.16 V, ΔE_p = 100 mV, ΔE_p(Fc) = 90 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl{$OC_6H_4N=NC_6H_4$-4-$N(CH_3)_2$}] [149]

This compound was prepared in identical manner to [118] using 4-(N,N-dimethylamino)-4'-hydroxyazobenzene (0.17 g, 0.70 mmol) in place of 4-hydroxystilbene. Column chromatography on silica using dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane yielded the product as a dark green-black solid (0.34 g, 79%). (Found: C, 47.9; H, 5.0; N, 18.7%; M^+, 700. $C_{29}H_{36}BClMoN_{10}O_2.0.5CH_2Cl_2$ requires C, 47.8; H, 5.0; N, 18.9%; M, 699); $\nu_{max.}$(NO) 1680s cm^{-1}; $\delta_H(CDCl_3)$ 7.93 and 7.42 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-$N(CH_3)_2$], 7.88 and 6.77 [2 H, d J(HH) 9.2 Hz; 2 H, d, J(HH) 9.3 Hz, C_6H_4-OMo], 5.93, 5.90, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.09 [6 H, s, $N(CH_3)_2$], 2.59, 2.42, 2.41, 2.39, 2.22, and 2.06 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$]; *m/z* 700 (M^+), 670 (M - NO), 460 (M - $OC_6H_4N=NC_6H_4$-$N(CH_3)_2$), 430 (M - $OC_6H_4N=NC_6H_4$-$N(CH_3)_2$ - NO), 241 ($HOC_6H_4N=NC_6H_4$-$N(CH_3)_2$). E_f = -0.26 V, ΔE_p = 70 mV, ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I{$OC_6H_4N=NC_6H_4$-4-$N(CH_3)_2$}] [150]

This compound was prepared in an identical manner to [149] using [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(I)_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] and 4-(N,N-dimethylamino)-4'-hydroxyazobenzene (0.15 g, 0.62 mmol). A dark

green-black solid was obtained (0.28 g, 67%). (Found: C, 43.1; H, 4.4; N, 17.4%; M^+, 792. $C_{29}H_{36}BIMoN_{10}O_2.0.3CH_2Cl_2$ requires C, 43.1; H, 4.5; N, 17.2%; M, 790); $\nu_{max.}$(NO) 1685s cm^{-1}; $\delta_H(CDCl_3)$ 7.89 and 7.55 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-N$(CH_3)_2$], 7.89 and 6.77 [2 H, d J(HH) 9.0 Hz; 2 H, d, J(HH) 9.2 Hz, C_6H_4-OMo], 5.91, 5.85, and 5.84 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.09 [6 H, s, N$(CH_3)_2$], 2.57, 2.45, 2.40, 2.38, 2.32, and 1.99 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 792 (M^+), 665 (M - I), 635 (M - I - NO), 552 (M - $OC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$), 522 (M - $OC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$ - NO), 241 ($HOC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$). E_f = -0.21 V, ΔE_p = 70 mV, ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{$OC_6H_4N{=}NC_6H_4$-4-N$(CH_3)_2$}$_2$] [151]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$.C_7H_8 (0.40 g, 0.52 mmol) and 4-(N,N-dimethylamino)-4'-hydroxyazobenzene (0.30 g, 1.24 mmol) using the procedure described for [118] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. Column chromatography using 10% thf/dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane afforded a dark brown solid (0.12 g, 26%). (Found: C, 54.6; H, 5.7; N, 19.1%; M^+, 905. $C_{43}H_{50}BMoN_{13}O_3.0.7CH_2Cl_2$ requires C, 54.5; H, 5.4; N, 18.9%; M, 904); $\nu_{max.}$(NO) 1650s cm^{-1}; $\delta_H(CDCl_3)$ 7.88 and 7.21 [4 H, d, J(HH) 9.0 Hz; 4 H, d, J(HH) 9.0 Hz, 2 x C_6H_4-N$(CH_3)_2$], 7.85 and 6.75 [4 H, d, J(HH) 9.0 Hz; 4 H, d, J(HH) 9.2 Hz, 2 x C_6H_4-OMo], 5.86, and 5.74 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.04 [12 H, s, 2 x N$(CH_3)_2$], 2.40, 2.25, and 2.09 [9 H, s; 6 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 905 (M^+), 784 (M - C_6H_4-N$(CH_3)_2$), 771 (M - NC_6H_4-N$(CH_3)_2$), 757 (M - N=NC_6H_4-N$(CH_3)_2$), 666 (M - $OC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$), 636 (M - $OC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$ - NO), 424 (M - 2 x $OC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$), 241 ($HOC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$). E_f = -0.52 V, ΔE_p = 70 mV, ΔE_p(Fc) = 70 mV.

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$OC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$}] [152]

This compound was prepared in an identical manner to [149] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$], 4-(N,N-dimethylamino)-4'-hydroxyazobenzene (0.18 g, 0.75 mmol), and triethylamine (0.5 cm^3, 3.7

mmol), with a reaction time of 5 h. A dark red-brown solid was obtained (0.38 g, 78%). (Found: C, 43.3; H, 4.8; N, 17.1%; M^+, 786. $C_{29}H_{36}BClN_{10}O_2W.0.3CH_2Cl_2$ requires C, 43.3; H, 4.5; N, 17.2%; M, 787); $\nu_{max.}$(NO) 1640s cm^{-1}; $\delta_H(CDCl_3)$ 7.92 and 7.55 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-N$(CH_3)_2$], 7.87 and 6.77 [2 H, d J(HH) 9.2 Hz; 2 H, d, J(HH) 9.2 Hz, C_6H_4-OW], 5.94, 5.91, and 5.84 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.08 [6 H, s, N$(CH_3)_2$], 2.66, 2.40, 2.39, 2.30, and 2.19 [3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 786 (M^+), 756 (M - NO), 546 (M - $OC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$), 516 (M - $OC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$ - NO), 241 ($HOC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$). E_f = -0.78 V, ΔE_p = 90 mV, ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl{$HNC_6H_4N{=}NC_6H_4$-4-N$(CH_3)_2$}] [153]

This compound was prepared in similar manner to [118] using 4-amino-4'-(N,N-dimethylamino)azobenzene (0.17 g, 0.70 mmol) in place of 4-hydroxystilbene and triethylamine (0.5 cm^3, 3.7 mmol) in place of hexamine. Column chromatography on silica using dichloromethane as eluent followed by recrystallisation from dichloromethane/n-hexane yielded the product as a deep purple solid (0.29 g, 68%). (Found: C, 49.7; H, 5.3; N, 21.8%; M^+, 699. $C_{29}H_{37}BClMoN_{11}O$ requires C, 49.9; H, 5.3; N, 22.1%; M, 698); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1655s cm^{-1}; $\delta_H(CDCl_3)$ 12.58 [1 H, s, NH], 7.92 and 7.56 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-N$(CH_3)_2$], 7.88 and 6.76 [2 H, d, J(HH) 9.1 Hz; 2 H, d, J(HH) 9.1 Hz, C_6H_4-NHMo], 5.88, 5.87, and 5.80 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.10 [6 H, s, N$(CH_3)_2$], 2.70, 2.42, 2.41, 2.38, 2.37, and 2.02 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 699 (M^+), 663 (M - Cl), 603 (M - 96), 573 (M - 96 - NO), 460 (M - $HNC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$), 430 (M - $HNC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$ - NO), 240 ($H_2NC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$). E_f = -0.65 V, ΔE_p = 70 mV, ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I{$HNC_6H_4N{=}NC_6H_4$-4-N$(CH_3)_2$}] [154]

This compound was prepared in an identical manner to [153] using [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(I)_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] and 4-amino-4'-(N,N-dimethylamino)azobenzene (0.15 g, 0.62 mmol). A deep blue-purple solid was obtained (0.30 g, 74%) (Found: C, 43.8; H, 4.7; N,

19.8%; M^+, 791. $C_{29}H_{37}BIMoN_{11}O$ requires C, 44.1; H, 4.7; N, 19.5%; M, 789); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1655s cm^{-1}; $\delta_H(CDCl_3)$ 13.04 [1 H, s, N*H*], 7.90 and 6.76 [2 H, d, J(HH) 9.2 Hz; 2 H, d, J(HH) 9.2 Hz, C_6H_4-N$(CH_3)_2$], 7.87 and 7.70 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4-NHMo], 5.94, 5.86, and 5.78 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.09 [6 H, s, N$(CH_3)_2$], 2.71, 2.50, 2.47, 2.38, 2.37, and 1.99 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 791 (M^+), 695 (M - 96), 665 (M - 96 - NO), 663 (M - I), 633 (M - I - NO), 568 (M - $C_6H_4N{=}NC_6H_4$-N$(CH_3)_2$), 553 (M - $HNC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$), 424 (M - $HNC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$ - I), 240 ($H_2NC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$). E_f = -0.61 V, ΔE_p = 70 mV, ΔE_p(Fc) = 70 mV.

[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$HNC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$}] [155]

This compound was prepared in an identical manner to [153] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 4-amino-4'-(N,N-dimethylamino)-azobenzene (0.18 g, 0.75 mmol), with a reaction time of 8 h. A dark red-brown solid was obtained (0.065 g, 12%) (Found: C, 43.5; H, 4.8; N, 19.2%; M^+, 785. $C_{29}H_{37}BClN_{11}OW.0.3CH_2Cl_2$ requires C, 43.4; H, 4.7; N, 19.0%; M, 786); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1625s cm^{-1}; $\delta_H(CDCl_3)$ 10.74 [1 H, s, N*H*], 7.91 and 7.48 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4-N$(CH_3)_2$], 7.86 and 6.75 [2 H, d, J(HH) 9.1 Hz; 2 H, d, J(HH) 9.1 Hz, C_6H_4-NHW], 5.94, 5.88, and 5.82 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.08 [6 H, s, N$(CH_3)_2$], 2.73, 2.46, 2.42, 2.36, 2.35, and 2.14 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 785 (M^+), 755 (M - NO), 749 (M - Cl), 660 (M - 125), 546 (M - $HNC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$), 516 (M - $HNC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$ - NO), 240 ($H_2NC_6H_4N{=}NC_6H_4$-N$(CH_3)_2$). E_f = -1.06 V, ΔE_p = 80 mV, ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$OC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3}] [156]

This compound was prepared in identical manner to [118] using Fat Brown B (4-(4'-ethoxyphenylazo)-1-naphthol) (0.20 g, 0.68 mmol) in place of 4-hydroxystilbene. The product was isolated by column chromatography on silica using dichloromethane as eluent, collecting the major green band which afforded on evaporation a deep emerald green solid (0.067 g, 15%). (Found: C, 52.6; H, 5.3;

N, 16.9%; M^+, 751. $C_{33}H_{37}BClMoN_9O_3$ requires C, 52.9; H, 5.0; N, 16.8%; M, 750); $\nu_{max.}$(NO) 1680s cm^{-1}; $\delta_H(CDCl_3)$ 8.94 [1 H, d, J(34) 8.2 Hz, $C_{10}H_6$(3)], 8.04 and 7.05 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-OC_2H_5], 8.07 [1 H, d, J(56) 8.4 Hz, $C_{10}H_6$(6)], 7.86 [1 H, d, J(12) 8.4 Hz, $C_{10}H_6$(2)], 7.67-7.57 [2 H, c m, $C_{10}H_6$(1 and 4)], 7.37 [1 H, t, $C_{10}H_6$(5)], 5.96, 5.83, and 5.78 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.15 [2 H, q, J(HH) 7.0 Hz, OCH_2-CH_3], 2.61, 2.46, 2.44, 2.16, and 1.77 [3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 1.48 [3 H, t, J(HH) 7.0 Hz, OCH_2-CH_3]; *m/z* 751 (M^+), 721 (M - NO), 715 (M - Cl), 460 (M - $OC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3), 430 (M - $OC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3 - NO), 292 ($HOC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3). E_f = -0.21 V, ΔE_p = 95 mV, ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{$OC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3}] [157]

This compound was prepared in an identical manner to [156] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and Fat Brown B (0.19 g, 0.65 mmol). A dark emerald green solid was obtained (0.23 g, 53%). (Found: C, 45.1; H, 4.8; N, 14.4%; M^+, 843. $C_{33}H_{37}BIMoN_9O_3$.0.6CH_2Cl_2 requires C, 45.2; H, 4.3; N, 14.1%; M, 841); $\nu_{max.}$(NO) 1680s cm^{-1}; $\delta_H(CDCl_3)$ 8.94 [1 H, d, J(34) 8.4 Hz, $C_{10}H_6$(3)], 8.17 [1 H, d, J(56) 8.4 Hz, $C_{10}H_6$(6)], 8.05 and 7.05 [2 H, d, J(HH) 9.2 Hz; 2 H, d, J(HH) 9.2 Hz, C_6H_4-OC_2H_5], 8.01 [1 H, d, J(12) 8.4 Hz, $C_{10}H_6$(2)], 7.61-7.55 [2 H, c m, $C_{10}H_6$(1 and 4)], 7.38 [1 H, t, $C_{10}H_6$(5)], 5.94, 5.87, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.15 [2 H, q, J(HH) 7.0 Hz, OCH_2-CH_3], 2.59, 2.51, 2.44, 2.41, 2.25, and 1.71 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 1.56 [3 H, t, J(HH) 6.2 Hz, OCH_2-CH_3]; *m/z* 843 (M^+), 716 (M - I), 686 (M - I - NO), 552 (M - $OC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3), 522 (M - $OC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3 - NO), 292 ($HOC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3). E_f = -0.16 V, ΔE_p = 75 mV, ΔE_p(Fc) = 70 mV.

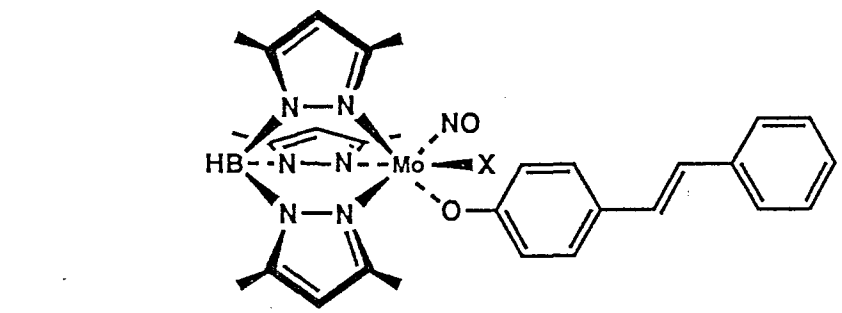
[W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$OC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3}] [158]

This compound was prepared in an identical manner to [156] using [W(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.40 g, 0.69 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$], Fat Brown B (0.22 g, 0.75 mmol), and triethylamine (0.5 cm^3, 3.7 mmol), with a reaction time of 5 h.

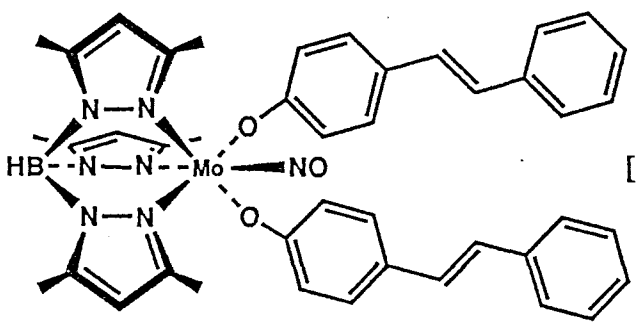
A dark red-brown solid was obtained (0.26 g, 45%) (Found: C, 44.7; H, 4.6; N, 13.9%; M^+, 837. $C_{33}H_{37}BClN_9O_3W.0.85CH_2Cl_2$ requires C, 44.7; H, 4.3; N, 13.9%; M, 838); $\nu_{max.}$(NO) 1640s cm^{-1}; $\delta_H(CDCl_3)$ 8.94 [1 H, d, J(34) 8.6 Hz, $C_{10}H_6$(3)], 8.06 [1 H, d, J(56) 8.2 Hz, $C_{10}H_6$(6)], 8.03 and 7.04 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-OC_2H_5], 7.76 [1 H, d, J(12) 8.4 Hz, $C_{10}H_6$(2)], 7.64-7.55 [2 H, c m, $C_{10}H_6$(1 and 4)], 7.34 [1 H, t, $C_{10}H_6$(5)], 5.97, 5.86, and 5.84 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.15 [2 H, q, J(HH) 7.0 Hz, OCH_2-CH_3], 2.69, 2.44, 2.42, 2.25, and 1.89 [3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 1.48 [3 H, t, J(HH) 7.0 Hz, OCH_2-CH_3]; *m/z* 837 (M^+), 807 (M - NO), 546 (M - $OC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3), 516 (M - $OC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3 - NO), 292 ($HOC_{10}H_6$-4-N=NC_6H_4-4-OCH_2CH_3). E_f = -0.73 V, ΔE_p = 100 mV, ΔE_p(Fc) = 70 mV.

Fig. 47

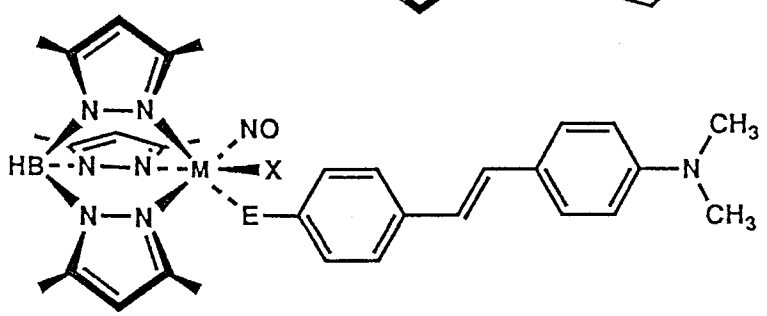
Complexes Prepared in Chapter Three



[118] X = Cl
[119] I



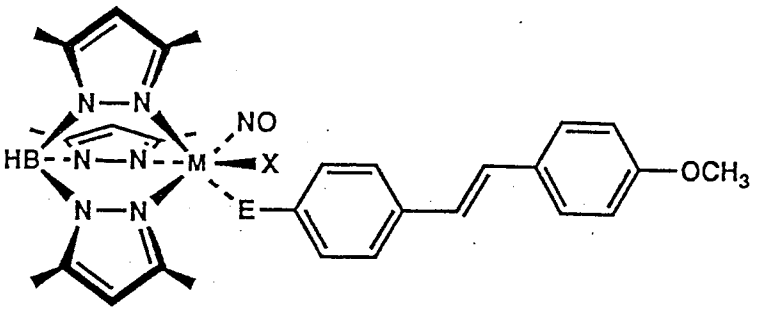
[120]



E = O { [121] M = Mo X = Cl; [122] X = I; [124] W Cl }

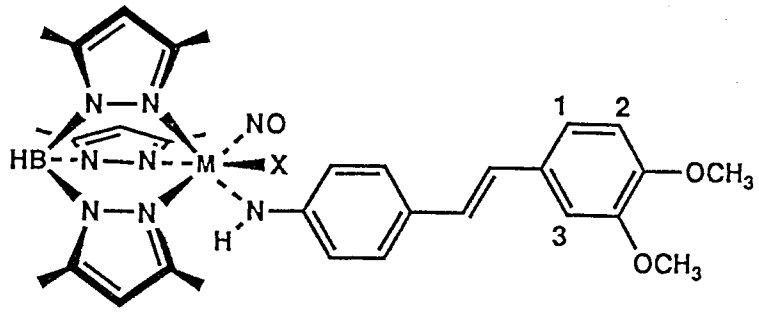
E = NH { [129] M = Mo X = Cl; [130] X = I; [132] W Cl }

Fig. 47 (*Continued*)

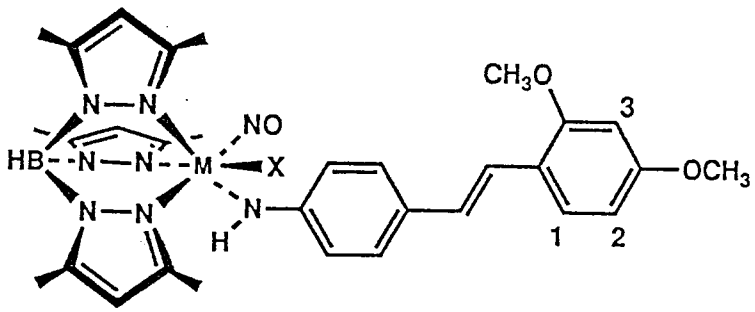


E = O { [125] M = Mo X = Cl; [126] X = I; [128] M = W X = Cl

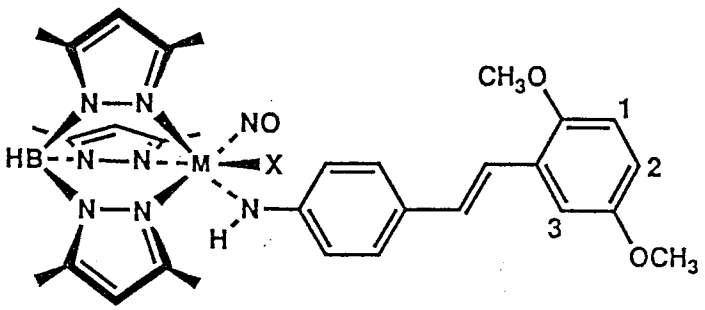
E = NH { [133] M = Mo X = Cl; [134] X = I; [136] M = W X = Cl



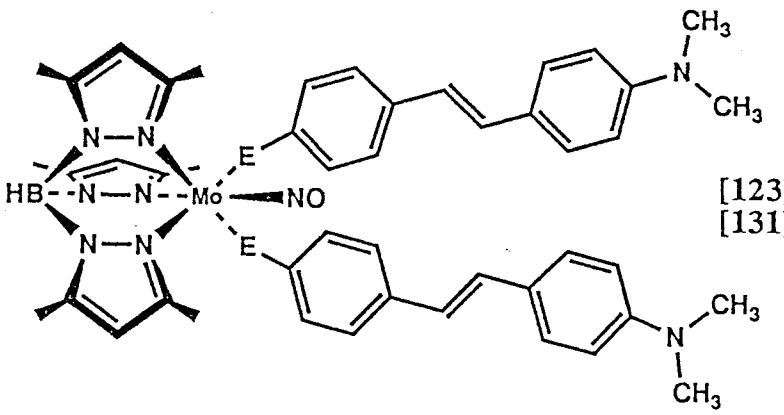
[137] M = Mo X = Cl
[138] X = I
[140] M = W X = Cl



[141] M = Mo X = Cl
[142] X = I
[144] M = W X = Cl

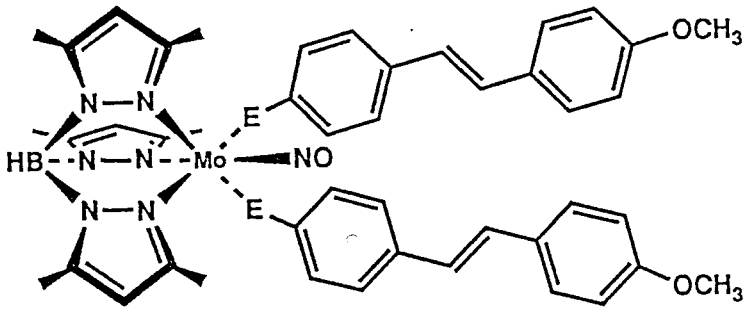


[145] M = Mo X = Cl
[146] X = I
[148] M = W X = Cl

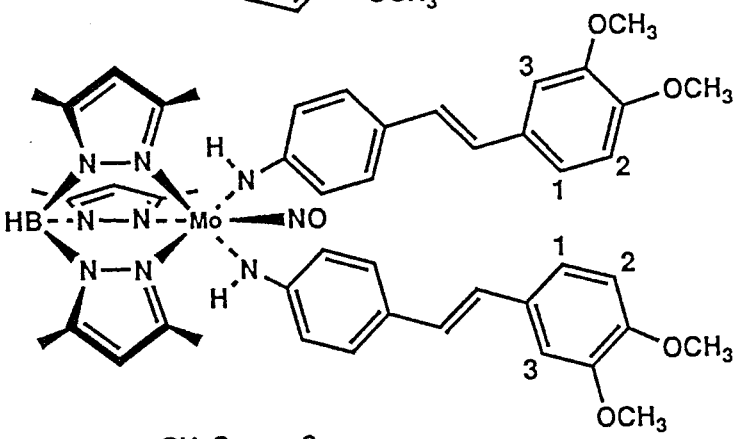


[123] E = O
[131] E = NH

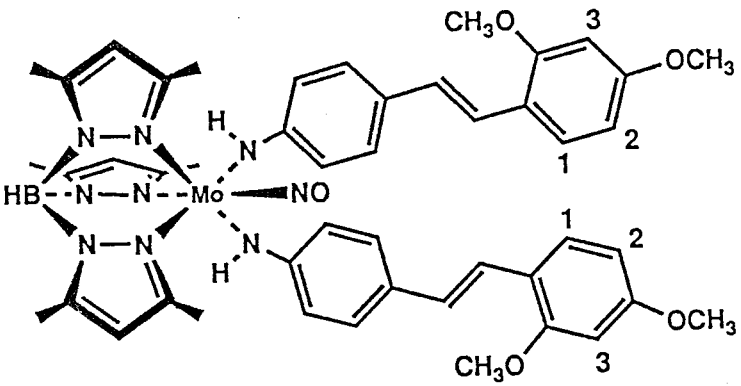
Fig. 47 (*Continued*)



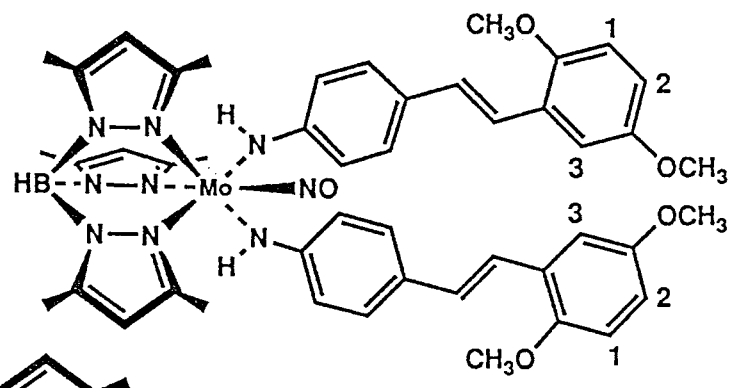
[127] E = O
[135] NH



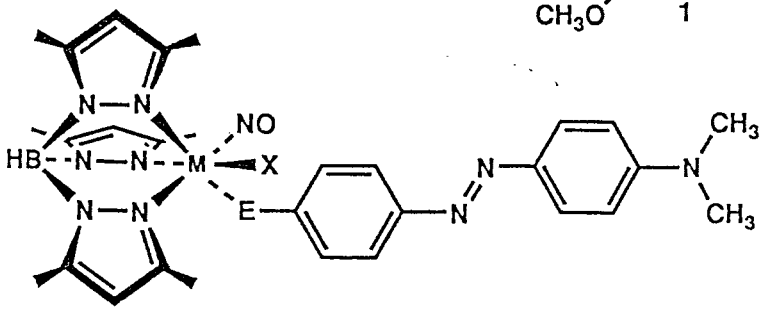
[139]



[143]



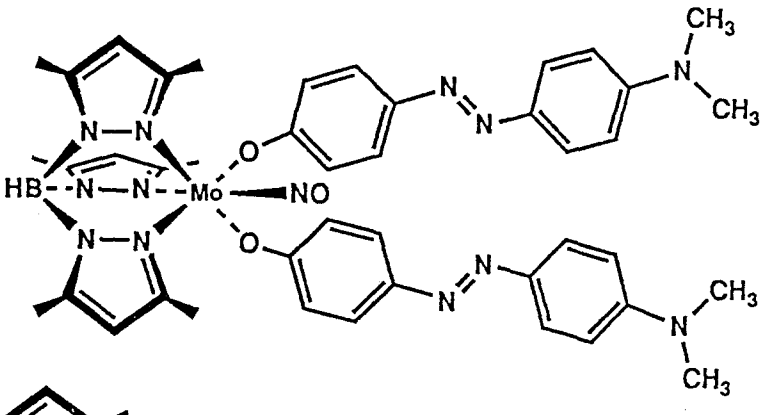
[147]



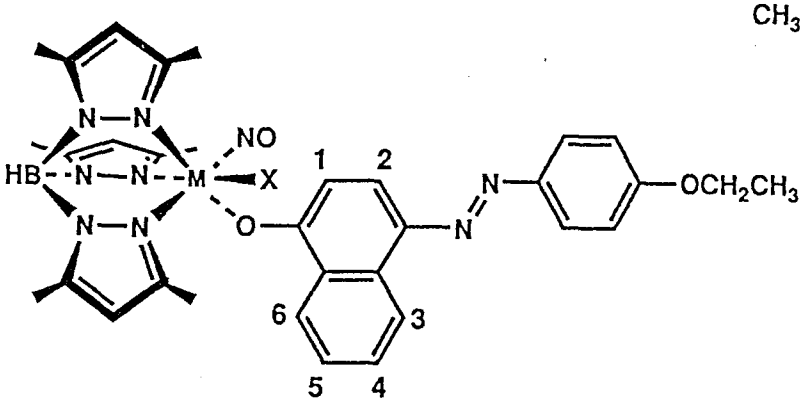
E = O { [149] M = Mo X = Cl; [150] I; [152] W Cl }

E = NH { [153] M = Mo X = Cl; [154] I; [155] W Cl }

Fig. 47 (*Continued*)



[151]



[156] M = Mo X = Cl
[157] I
[158] W Cl

CHAPTER FOUR

MOLYBDENUM MONONITROSYL COMPLEXES INCORPORATING LONG CHAIN ALKYL SUBSTITUENTS FOR POTENTIAL LIQUID CRYSTAL APPLICATIONS

V-1 DISCUSSION

As has been discussed earlier, the field of metallomesogens has attracted considerable interest in recent years, and complexes of many different metals have been found to form liquid crystal mesophases. However, there has to date been only one report of molybdenum-containing metallomesogens.[164] This very recent work concerns some dimolybdenum tetracarboxylate compounds containing Mo-Mo quadruply bonded units which possess potential for electronic tuning of redox behavour. These complexes of formulation $[Mo_2(O_2C(CH_2)_nCH_3)_4]$ form discotic mesophases for n = 3-9, with both the onset point and the mesophase temperature range found to vary significantly with hydrocarbyl chain length. No liquid crystal behaviour was found when n = 1, 2, or 16. Dimetal tetra-carboxylates are known for numerous transition metals, and discotic mesophases had previously been found in related complexes of rhodium, having M-M single bonds,[263] copper, having weaker M-M single bonds,[264] and ruthenium, having M=M double bonds.[265]

As has been described earlier, molybdenum mononitrosyl derivatives of formula [Mo(NO)L*(X)(Y)] (L* = tris(3,5-dimethyl-pyrazolyl)hydroborate; X and Y = halide, phenoxide, or arylamide) are redox-active, highly coloured species which are capable of exhibiting various interesting molecular electronic properties including NLO effects. These characteristics would make them attractive candidates for liquid crystal applications if complexes with the necessary mesogenic behaviour could be produced. The creation of liquid crystalline complexes containing bulky

trispyrazolylborate ligands would also represent a significant departure from the classes of complex currently receiving attention in the metallomesogens research field.

To this end, a number of complexes containing the {Mo(NO)L*} unit attached to long alkyl chain-bearing aromatic ligands have been prepared, characterised by the usual physical techniques, and their thermal properties investigated using polarising hot-stage microscopy and differential scanning calorimetry (DSC). The simplest complexes were made using the commercially available mono-aryl ligands 4-n-decylaniline and n-dodecyl-4-hydroxybenzoate. In order to prepare complexes containing larger more structurally anisotropic rigid aromatic sections typical of organic thermotropic species, several biphenyl and stilbenyl ligands were synthesised. Since chiral cholesteric liquid crystals are of great interest particularly for thermochromic applications,[266] several cholesterolate complexes have been prepared using commercial cholesterol.

V-1.1 LIGANDS AND LIGAND PRECURSORS

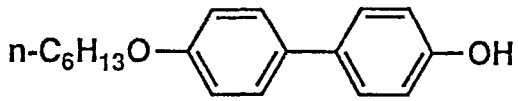
The biphenyl ligands used in this work are 4-n-alkyloxy-4'-hydroxybiphenyls in which the alkyloxy group has one of three different chain lengths, with the alkyl groups being hexyl [159], octyl [160], or dodecyl [161]. These compounds are known thermotropic liquid crystalline organics and they were prepared by straightforward monoalkylation of 4,4'-dihydroxybiphenyl using n-alkylbromides according to literature reports.[267,268]

The stilbene compounds 4-n-hexyloxy- [162] and 4-n-octyloxy-4'-nitrostilbene [163] have also previously been found to possess mesogenic behaviour, and were prepared by the condensation of 4-nitrophenylacetic acid with 4-n-alkyloxybenzaldehydes using a variation on a report by other workers.[269] The new compound 4-n-dodecyloxy-4'-nitrostilbene [164] was prepared in a similar fashion, and reduction of these three nitro derivatives using zinc and ammonium chloride gave the 4-n-alkyloxy-4'-stilbenamines

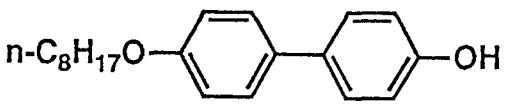
[165], [166], and [167] for use as ligands. The structures of these three classes of organic compounds are shown in Fig. 48.

Fig. 48

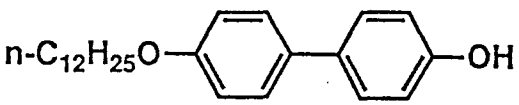
Hydroxybiphenyl Ligands, Aminostilbene Ligands, and Nitrostilbene Ligand Precursors



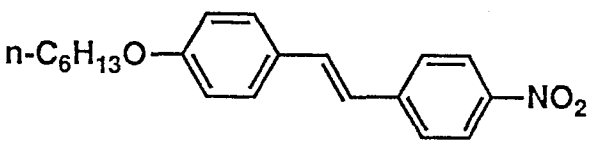
[159]



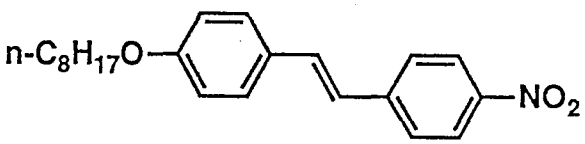
[160]



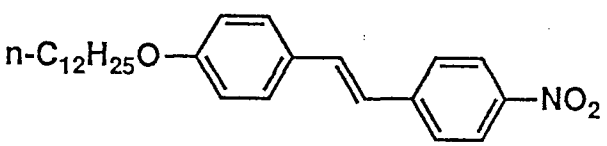
[161]



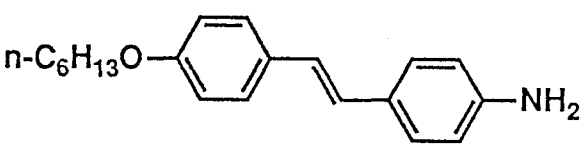
[162]



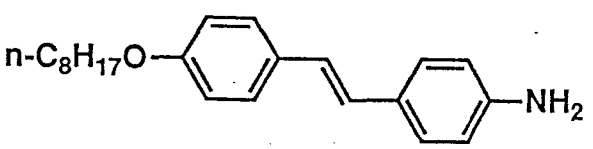
[163]



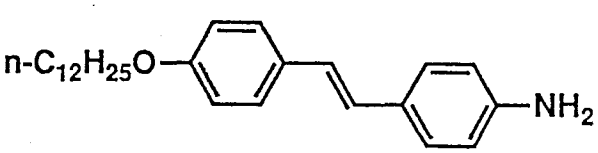
[164]



[165]



[166]



[167]

V-1.2 COMPLEXES

All complexes were prepared from [Mo(NO)L*(Cl)$_2$] or [Mo(NO)L*(I)$_2$] using the usual methods described earlier in Chapters Two and Three. The bis-stilbenamide complexes have been found to show some decomposition when subjected to column chromatography on silica

gel, and yields have been improved greatly by using alumina 90 as the stationary phase.

The unusual hydroxy-stilbenamide complex [Mo(NO)L*(OH)($HNC_6H_4CH{=}CHC_6H_4OC_6H_{13}$)] [186] was prepared fortuitously by the rapid hydrolysis of [Mo(NO)L*($HNC_6H_4CH{=}CHC_6H_4OC_6H_{13}$)$_2$] [185] on activated alumina in dichloromethane/n-hexane.

The mono-halo cholesterolate derivatives [193] and [194] were prepared readily under the usual conditions for production of alkoxide complexes, but an attempt to produce a bis-cholesterolate derivative by reaction of [Mo(NO)L*(I)$_2$] with excess cholesterol in the presence of triethylamine failed to give other than mono-substitution. This is likely to be due to the steric demands of the bulky cholesteryl unit which prevent more than one such molecule from entering the molybdenum coordination sphere.

The mixed alkoxide complex [Mo(NO)L*(OR)(OR')] (R = n-octyl, R' = cholesteryl) [196] was prepared in an attempt to produce a species with a lower melting point than the mono halo cholesterolate derivatives by replacing the second halide with a long chain ligand. A reaction between [L*Mo(NO)(I)(OR')] [194] and n-octanol did not produce the desired complex, but displacement of both iodide and cholesterol was found to occur giving the bis-octyloxide derivative [Mo(NO)L*(OR)$_2$] [195]. Since it had earlier been established that a bis-cholesterolate derivative could not be prepared, the reaction of the bis-octyloxide with excess cholesterol was then carried out and this proved a successful route to the mixed alkoxide complex [196].

V-1.3 PHYSICAL CHARACTERISATION OF COMPLEXES

All of the new complexes were characterised using i.r. and ^{1}H n.m.r. spectroscopy, EI mass spectrometry, elemental analyses, and cyclic voltammetry. U.v.-visible absorption spectra were recorded for the complexes of mono-aryl ligands but not for the other stilbenyl or biphenyl derivatives.

V-1.3(a) Elemental Analyses

All of the compounds show satisfactory analyses for C, H, and N, but it was found that many retain between 0.3 and 1 mole of dichloromethane of crystallisation which may also be detected by ^1H n.m.r. spectroscopy. The bis-amide complex [Mo(NO)L*($HNC_6H_4C_{10}H_{21}$)$_2$] [173] was isolated in solvated form with one mole of n-pentane present, but since n-hexane rather than n-pentane was used in all subsequent recrystallisations, this solvent is not found in any other products. Samples were dried for extended periods under vacuum at *ca* 70 °C, although in most cases this was clearly insufficient to remove solvent. Higher temperatures were not used in case of decomposition.

V-1.3(b) Infra-Red Spectroscopy

All of the complexes exhibit $\nu_{max.}$(BH) at *ca* 2550 cm^{-1} as well as $\nu_{max.}$(NO) at frequencies which are in accord with their formulations. In addition, the benzoate derivatives exhibit $\nu_{max.}$(CO) at 1715-1710 cm^{-1} attributable to the carboxylate moiety, while the arylamide derivatives exhibit $\nu_{max.}$(NH) at 3320-3260 cm^{-1} due to the amide moiety. The hydroxide complex [186] shows $\nu_{max.}$(OH) at 3480 cm^{-1} due to the coordinated hydroxyl group, and has $\nu_{max.}$(NO) at 1640 cm^{-1} which is almost as low as those for the bis-stilbenamide complexes [185], [189], and [192]. This implies that bound hydroxide acts as a considerably better donor of charge to the metal centre than does a phenoxide ligand, a conclusion entirely in keeping with expectations.

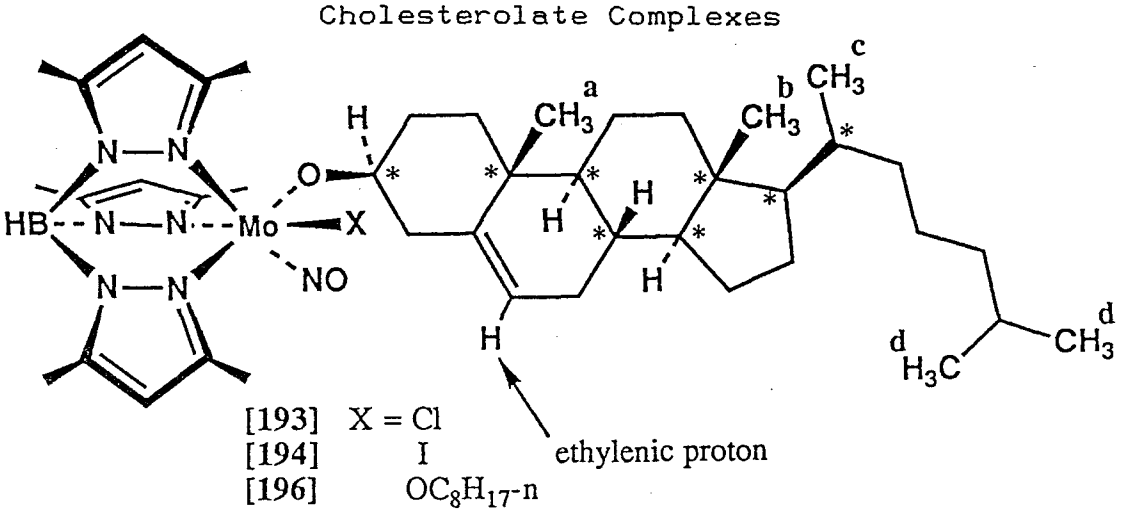
V-1.3(c) ^1H n.m.r. Spectroscopy

All of the complexes exhibit the expected signals attributable to the L* ligand as well as signals due to aryl and alkyl ligands. In all cases where a long alkyloxy chain is present the signals have been assigned as far as possible with the OCH_2-, OCH_2-CH_2-, and $OC_2H_4-CH_2-$ methylene groups and the terminal methyl giving rise to discernable triplet, quintet, quintet, and triplet signals

respectively. In most cases the mono-substituted complexes give the usual three signals due to the pyrazolyl 4-protons along with six discrete signals due to the pyrazolyl 3,5-methyl groups, and the bis-substituted give two proton and four methyl signals due to the symmetry conditions described earlier. The hydroxystilbenamide complex [186] gives a sharp signal attributable to the coordinated hydroxyl at 6.48 ppm.

Fig. 49

Cholesterolate Complexes



[193] X = Cl
[194] I
[196] OC_8H_{17}-n

The cholesterolate derivatives (Fig. 49) give rise to complex spectra owing to the nature of the steroidal fragment and the presence of optical isomerism at the molybdenum centre. The cholesteryl moiety is chiral but of only one configuration (the ligand used was commercial (-)-cholesterol) and hence the two configurations at the octahedral metal centre (*R* and *S*) give two possible diastereomeric forms which have slightly different proton resonance frequencies. The pyrazolyl signals show some splitting, but the clearest evidence for isomers is seen in the occurrence of two doublet signals attributable to the cholesteryl ethylenic proton which integrate for a single proton. These occur at roughly the same chemical shift as in free cholesterol, and their relative intensities indicate that for both chloride [193] and iodide [194] the ratio of isomers is *ca.* 1:1. The single proton adjacent to the coordinated oxygen is shifted markedly downfield by *ca.* 2 ppm due to deshielding by the molybdenum centre, but two multiplets are

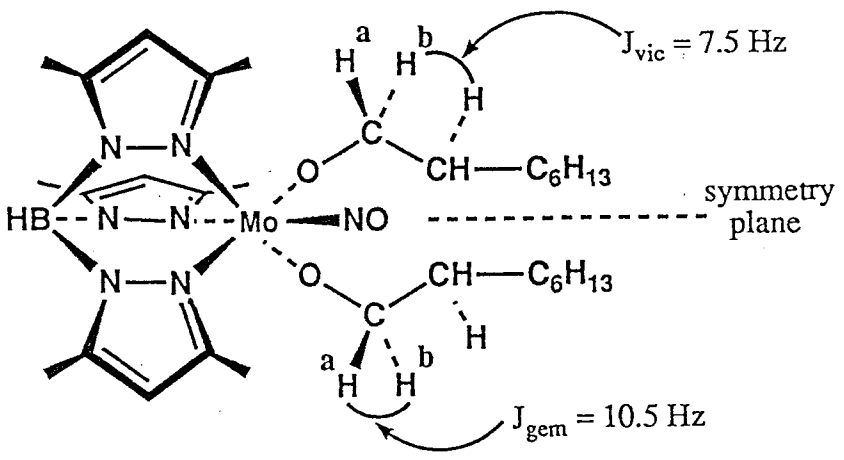
not discernable. The cholesteryl methyl and methylene signals also show signs of isomerism.

The bis-octyloxide complex [195] (Fig. 50) has a relatively simple spectrum owing to the presence of a molecular symmetry plane. However, the OCH_2 groups give rise to splitting patterns which at first sight appear rather complicated. Coordination to the metal centre renders the α-methylene protons a and b on each carbon inequivalent, and it is therefore possible to observe both geminal and vicinal coupling within separate multiplet signals attributable to the two protons, a, and two protons b. The two protons a give a signal which is in fact a triplet of doublets (not a sextet) with a vicinal coupling constant J_{vic} owing to the adjacent methylene group of *ca* 7.5 Hz, and a geminal coupling constant J_{gem} owing to the protons b of *ca* 10.5 Hz. The two protons b are split similarly, and the shift difference between the a and b multiplets is *ca* 0.3 ppm.

Fig. 50

Bis-n-octyloxide Complex

[195]



V-1.3(d) Mass Spectrometry

All of the mono- and most of the bis-substituted complexes show molecular ion envelopes of low intensity. Owing to the presence of a large number of possible isotope combinations of the elements Mo, B, Cl, and I these envelopes have complex forms with

the highest peak often not corresponding to exactly the fragmental mass calculated from relative atomic mass values. In most cases the highest peak and not the averaged fragment mass is quoted. The only complexes which show no evidence of a molecular ion are the hydroxide derivative [186] and the largest bis-stilbenamide [Mo(NO)L*(HNC$_6$H$_4$CH=CHC$_6$H$_4$OC$_{12}$H$_{25}$)$_2$] [192]. In all cases a number of significant fragments have been assigned, and these correspond to the expected fragmentation patterns for such complexes. Several unidentified ion envelopes of high intensity are also reported.

V-1,3(e) Cyclic Voltammetry

All of the phenoxide and arylamide complexes show reversible, quasi-reversible, or irreversible one-electron reduction waves at potentials which are in accord with expectations. These show the usual large cathodic shift of *ca* 400 mV in moving from phenoxide to arylamide due to the greater electron donating capability of the nitrogen donor ligands. They also demonstrate rather well how aryl substituents can influence the metal reduction potential.

Comparison of the mono-phenoxide complexes [Mo(NO)L*(Cl)(OC$_6$H$_4$CO$_2$C$_{12}$H$_{25}$)] [168] and [Mo(NO)L*(Cl)(OC$_6$H$_4$C$_6$H$_4$OC$_n$H$_{2n+1}$)] ([174], [177], and [179]) reveals a cathodic shift of 130 mV in moving from carboxylate to alkoxyphenyl substituent, and for the corresponding bis-phenoxide derivatives an even larger cathodic shift of 230 mV is observed. This large difference arises from the fact that the ester function is a relatively strong electron withdrawing group and effective communication via the phenyl ring enables it to significantly deplete the electron density at the metal. Similarly, the reduction potential of [Mo(NO)L*(Cl)(HNC$_6$H$_4$C$_{10}$H$_{21}$)] [171] is found to be 90 mV more cathodic than that for the stilbenamides [Mo(NO)L*(Cl)(HNC$_6$H$_4$CH=CHC$_6$H$_4$OC$_n$H$_{2n+1}$)] [183], [187], and [190] which is because the ethenyl moiety behaves as an electron accepting group when compared to a simple saturated alkyl chain. For the corresponding bis-amides the shift is increased to 200 mV. Not surprisingly, the length of the alkyl chain has no detectable influence on the reduction potential in either the biphenyl or stilbenyl complexes.

The hydroxide complex [186] has a reduction potential which is almost the same as those of the bis-stilbenamides. This is in accord with the i.r. data in that the $\nu_{max.}$(NO) value demonstrates that the hydroxide ligand is substantially more efficient at donating charge to the metal than is a phenoxide ligand.

The cholesterolate chloro- and iodo-complexes show a marked difference in electrochemical behaviour. The mono-chloride [193] exhibits an irreversible reduction wave at -0.71 V (ΔE_p = 210 mV) which is typical for a mono-chloro alkoxide complex, but the iodide [194] gives a wave which is both chemically and electrochemically irreversible, implying that rapid decomposition is taking place. Previous work has shown that chloride complexes tend to show more nearly reversible electrochemical behaviour than iodides due to the occurrence of iodide dissociation from reduced species,[209] but these two complexes provide an unusually stark contrast. The bis-octyloxide [195] and mixed octyloxide/ cholesterolate [196] complexes both show irreversible reduction waves at highly cathodic potentials of -1.35 and -1.37 V respectively.

V-1.4 THERMAL STUDIES

Typical melting points for complexes of the type described here, and which contain phenoxide or arylamide ligands with methyl substituents, are in excess of 200 °C; *e.g.* 210-215 °C for [Mo(NO)L*(Cl)(OC_6H_4-4-CH_3)] and 250-255 °C for [Mo(NO)L*(Cl)(HNC_6H_4-4-CH_3)]. As expected, the incorporation of the long alkyl chain substituents leads to a marked reduction in the melting points of these compounds. Many of the aryl complexes show melting points below 200 °C, and in the case of the bis-phenoxide derivative [Mo(NO)L*($OC_6H_4CO_2C_{12}H_{25}$)$_2$] [170] an unusually low melting point of 41-44 °C has been observed. In order to assess whether these materials exhibit any liquid crystalline behaviour, the complexes were examined by polarising hot-stage microscopy and DSC.

The complexes of mono-aryl ligands gave the most interesting results with all showing some sort of fairly well defined melting

event, but no evidence of mesophases was observed. The thermal behaviour of these six complexes will now be discussed in detail.

V-1.4(a) Complexes of Mono-aryl Ligands

[Mo(NO)L*(Cl)($OC_6H_4CO_2C_{12}H_{25}$)] [168]

When viewed under the polarising microscope, this compound showed a melting event at 100 °C which corresponded with an endothermic event in the DSC trace with T_{ON} = 104 °C (ΔH = 31.13 J g^{-1}). Another event was observed at 122 °C which involved a darkening of the sample. This corresponded with an exothermic event in the DSC trace with ΔH = -3.95 J g^{-1}. Although the sample appeared birefringent on melting at 100 °C, this was in fact unmelted crystallites in an isotropic environment.

[Mo(NO)L*(I)($OC_6H_4CO_2C_{12}H_{25}$)] [169]

This compound showed no changes until the material melted with some apparent decomposition at 106 °C. Cooling the freshly melted sample at 10 K min^{-1} failed to show any birefringent textures. The DSC trace revealed two fairly well-resolved endothermic events with a combined enthalpy of 47.9 J g^{-1}. The former had T_{ON} = 107 °C (ΔH = 46.6 J g^{-1}), while the latter, which peaked at about 124.5 °C, accounted for 1.3 J g^{-1}. Nothing corresponding with this second event could be observed by microscopy and its origin is thus unclear.

[Mo(NO)L*($OC_6H_4CO_2C_{12}H_{25}$)$_2$] [170]

This compound melted at 43 °C corresponding with two poorly resolved events in the DSC trace having T_{ON} = 42.5 °C (ΔH = 33.6 J g-1) and T_{peak} = 46 °C (ΔH = 20.3 J g^{-1}). Cooling the resulting fluid to -40 °C revealed nothing by either microscopy or DSC study.

[Mo(NO)L*(Cl)($HNC_6H_4C_{10}H_{21}$)] [171]

This complex melted into an isotropic fluid over a broad range at about 110 °C. The DSC study revealed a broad endothermic event with T_{ON} = 92.6 °C (ΔH = 27 J g^{-1}). No other events were observed on cooling.

[$Mo(NO)L^*(I)(HNC_6H_4C_{10}H_{21})$] [172]

Heating this complex at 10 K min^{-1} revealed the onset of melting at 186.7 °C, a possible second event at 189.7 °C, and finally clearing at 190.5 °C. Despite the birefringent appearance of the material between the highest and lowest temperatures, the melting of solid crystallites into an isotropic background showed that this is not a liquid crystalline phase. On heating the DSC showed two fairly well-resolved events with T_{ON} = 175 °C (ΔH = 19 J g^{-1}) and T_{peak} = 186 °C (ΔH = 18.5 J g^{-1}), while on cooling the trace was featureless. This suggests that the first event may be a transition between two crystalline modifications while the second is associated with melting, apparently without decomposition. Although the sample solidifies at around 136 °C on cooling under the microscope, no thermal evidence of solidificaction was observed by DSC.

[$Mo(NO)L^*(HNC_6H_4C_{10}H_{21})_2$] [173]

This material could not be freed of solvent and it became more fluid on heating to 64 °C before turning black and decomposing at 74 °C. No evidence of any liquid crystalline behaviour was observed.

V-1.4(b) Nitro- and Amino-stilbene Compounds

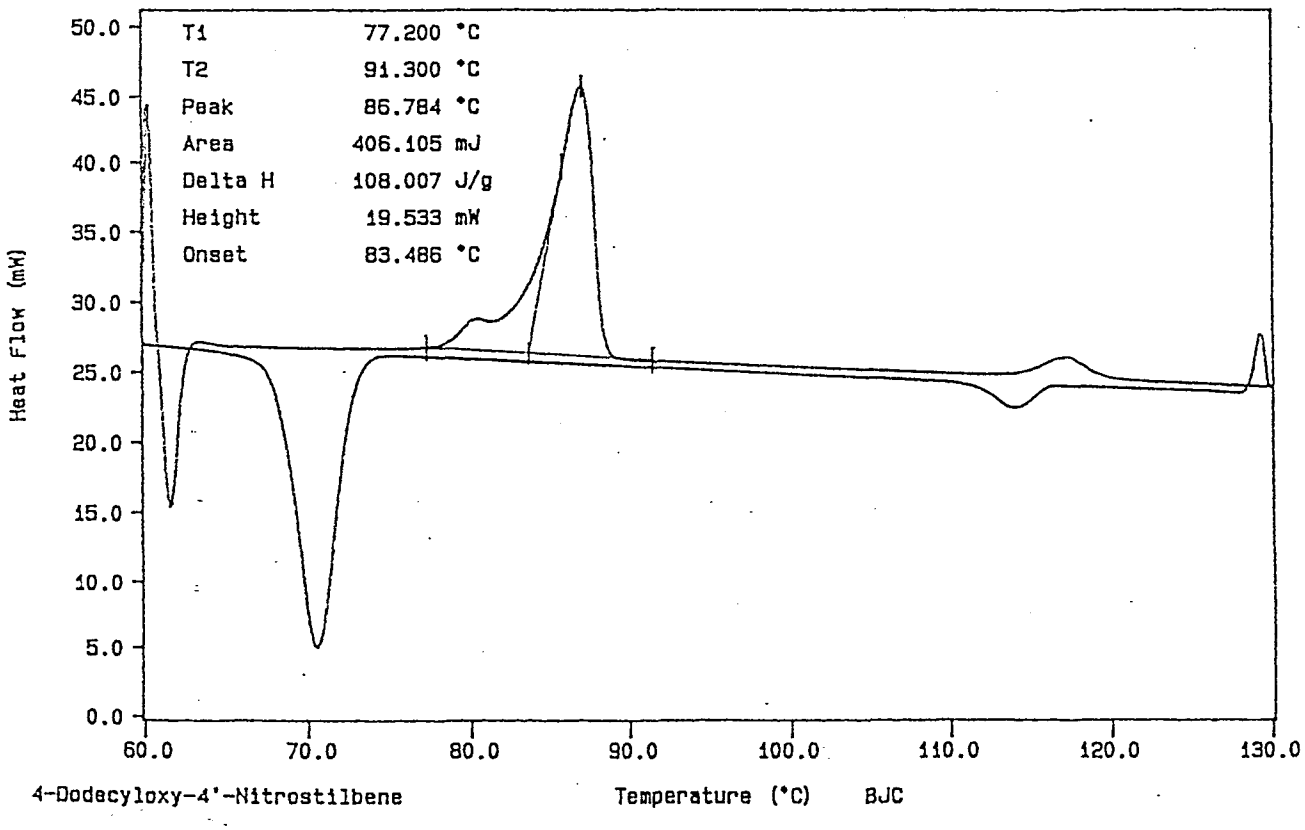
The nitrostilbene precursors to the stilbenamine ligands used were investigated under the polarising microscope and the occurrence of extensive fluid birefringence, characteristic of liquid crystalline phases, was observed in all three. Both of the previously reported hexyloxy [162] and octyloxy [163] derivatives melted at about 100 °C and the new dodecyloxy derivative [164] at about 80 °C. Since their mesogenic properties have already been reported elsewhere,[269] the hexyloxy and octyloxy compounds will not be further discussed here. The thermal behaviour of 4-dodecyloxy-4'-nitrostilbene [164] is described below, and a DSC trace for this compound is shown in Fig. 51.

Under the microscope a crystal to fluid transition was observed at about 85 °C and the birefringent texture of a smectic A

phase was seen until clearing occurred at about 115 °C. A DSC study gave more precise evidence for these transitions. On heating at 10 K min^{-1} a minor endothermic event peaking at 80.0 °C was found before a major event with T_{ON} = 83.5 °C (for both events combined ΔH = 108.0 J g^{-1}). The main peak represents the K-S_A (crystal to smectic) transition but the origin of the small pre-peak is unclear. A second endothermic event corresponding to the S_A-I (smectic to isotropic liquid) transition was detected with T_{ON} = 114.5 °C (ΔH = 7.9 J g^{-1}). Upon cooling from 130 °C at 10 K min^{-1} both of these events proved to be fully reversible with exothermic events at T_{ON} = 116.1 °C (ΔH = -8.0 J g^{-1}) and at T_{ON} = 72.7 °C (ΔH = -101.5 J g^{-1}).

Fig. 51

DSC Trace for 4-Dodecyloxy-4'-nitrostilbene



The three stilbenamine ligands [165], [166], and [167] were also investigated. These showed ill-defined behaviour, all melting at about 120 °C with no evidence for liquid crystalline phases.

This is perhaps unsurprising as terminal amino groups are not generally thought of as desirable for the stabilisation of mesophases. The vast majority of known thermotropic organic compounds possess terminal cyano, halo, nitro, alkoxy, or alkyl groups,[270] and the absence of mesogenic behaviour in these amines may well reflect the presence of opportunities for hydrogen bonding between the amino hydrogens and the oxygen of the alkoxy function.

DSC and microscopy studies on the biphenyloxy, stilbenamide, and cholesterolate complexes were carried out, but none revealed signs of any liquid crystalline behaviour. Indeed, under the microscope most of these compounds were observed to melt over very broad ranges of 10-20 °C, and many DSC traces failed to show any detectable events whatsoever. Their extremely strong visible absorptions render even very thin layers highly coloured, and the crystalline samples appeared almost black without the analyser in place. This makes the observation of optical effects difficult because so little light is able to penetrate the sample. The only series of compounds for which any meaningful data could be obtained are the bis-biphenyloxy and the cholesterolate complexes. A brief discussion of the results of these studies follows below, taking the compounds in five different groups.

V-1.4(c) Mono-substituted Biphenyloxy Complexes: $[Mo(NO)L^*(X)(OC_6H_4C_6H_4OC_nH_{2n+1})]$

These compounds proved to be extremely high melting. For both chloride and iodide complexes it was found that the hexyloxy and octyloxy derivatives melt at around the same temperature, whilst the dodecyloxy derivatives have somewhat lower melting points. All three iodide complexes were observed to melt at higher temperatures than their chloride analogues. These complexes represent materials which have higher melting points than the simple $[Mo(NO)L^*(Cl)(OC_6H_4\text{-}4\text{-}CH_3)]$ complex mentioned earlier, and since no birefringence was detected under the polarising microsope, they were not studied further using DSC. Approximate melting points for these complexes are shown in Table XIX.

TABLE XIX

Approximate Melting Points for Mono-substituted Biphenyloxy Complexes [Mo(NO)L*(X)($OC_6H_4C_6H_4OC_nH_{2n+1}$)]

X	n	m.p./°C	complex no.
Cl	6	230	[174]
	8	230	[177]
	12	195	[180]
I	6	245	[175]
	8	245	[178]
	12	225	[181]

V-1,4(d) Mono-substituted Stilbenamide Complexes: [Mo(NO)L*(X)($HNC_6H_4CH=CHC_6H_4OC_nH_{2n+1}$)]

Again, generally high melting points were observed under the microscope (Table XX) although these are significantly lower than for the biphenyl derivatives.

TABLE XX

Approximate Melting Points for Mono-substituted Stilbenamide Complexes [Mo(NO)L*(X)($HNC_6H_4CH=CHC_6H_4OC_nH_{2n+1}$)]

X	n	m.p./°C	complex no.
Cl	6	130	[183]
	8	210	[187]
	12	175	[190]
I	6	210	[184]
	8	130	[188]
	12	110	[191]
OH	6	190	[186]

For the octyloxy and dodecyloxy derivatives the iodide complexes melt at considerably lower temperatures than their chloride analogues with the longest chain species having the lowest melting points. However, the hexyloxy/chloride derivative [183] has a far lower melting point than its iodo analogue [184] and than its longer chain homologues [187] and [190], providing a curious exception to the trends found for other types of complex. The hydroxide derivative [186] is also high melting with apparent decomposition occuring at 190 °C. No evidence for liquid crystalline behaviour was observed in any of these compounds.

V-1.4(e) Bis-substituted Biphenyloxy Complexes: $[Mo(NO)L^*(OC_6H_4C_6H_4OC_nH_{2n+1})_2]$

These complexes proved to have greatly reduced melting points when compared to their mono-substituted counterparts. However, these values are still somewhat higher than those of the mono-aryl ligand complexes described earlier. When viewed under the microscope at a heating rate of 10 K min^{-1} all three showed fairly wide range melting behaviour with no birefringence at all, and a single broad endothermic melting event was observed in their DSC traces. The results of the DSC studies are summarised in Table XXI.

TABLE XXI

DSC Data for Bis-substituted Biphenyloxy Complexes $[Mo(NO)L^*(OC_6H_4C_6H_4OC_nH_{2n+1})_2]$

n	T_{ON}/°C	ΔH/J g^{-1}	T_{peak}/°C	complex no.
6	106.3	9.2	115	[176]
8	142.4	37.5	149	[179]
12	102.4	28.5	110	[182]

The hexyloxy derivative [176] showed an extremely broad second event with T_{peak} = 137 °C, the origin of which is unclear. It is

perhaps of some interest to note that the hexyloxy [176] and dodecyloxy [182] complexes have very similar melting points but that the octyloxy derivative [179] melts at about 40 °C higher than these two. None of these samples showed any thermal evidence of solidification in the cooling trace which implies that the compounds cool to form amorphous glassy solids. In keeping with this observation, repeating the heating process failed to show the endothermic events found in the initial traces.

V-1.4(f) Bis-substituted Stilbenamide Complexes:

$[Mo(NO)L^*(HNC_6H_4CH{=}CHC_6H_4OC_nH_{2n+1})_2]$

These also showed reduced melting points which were found to decrease with increasing chain length as shown in Table XXII.

TABLE XXII

Approximate Melting Points for Bis-substituted Stilbenamide Complexes $[Mo(NO)L^*(HNC_6H_4CH{=}CHC_6H_4OC_nH_{2n+1})_2]$

n	m.p./°C	complex no.
6	105	[185]
8	90	[189]
12	70	[192]

The bis(dodecyloxystilbenamide) complex [192] represents the only compound other than $[Mo(NO)L^*(OC_6H_4CO_2C_{12}H_{25})_2]$ [170] which melts significantly below 100 °C. However, these compounds did not show any birefringence under the microscope and DSC study failed to show any features in heating or cooling modes.

V-1.4(g) Cholesterolate Complexes:

$[Mo(NO)L^*(X)(OR)]$ (R = cholesteryl)

Both the chloro- [193] and iodo-cholesterolate [194] complexes were found to melt at disappointingly high temperatures of about

210 °C and 230 °C respectively, but it was found that the replacement of halide by an n-octyloxy group produces a significant drop in melting point to 180 °C for the mixed alkoxide derivative [196]. Owing to the relatively weak visible absorptions of these compounds, some birefringence was observed in the crystalline samples. Although the octyloxy complex appeared birefringent on melting at 180 °C, this was in fact simply unmelted crystallites in an isotropic environment. No liquid crystalline textures were observed, but each complex showed a broad melting event in the DSC trace and the results of these studies are shown in Table XXIII.

TABLE XXIII

DSC Data for Cholesterolate Complexes

[Mo(NO)L*(X)(OR)] (R = cholesteryl)

X	T_{ON}/°C	ΔH/J g^{-1}	T_{peak}/°C	complex no.
Cl	198.3	17.2	209 (220)	[193]
	241.0	45.5	252	
I	220.5	48.5	230	[194]
OC_8H_{17}	172.4	25.9	184	[196]

The second peak quoted for the chloro derivative [193] corresponds to a minor event of unknown origin after the initial peak, and the third event is due to sample decomposition as evidenced by a darkening when viewed under the microscope. The other two complexes were not heated to high enough temperatures to cause decomposition. For comparison the bis-octyloxide complex [195] melts at about 140 °C showing that replacement of one octyloxy ligand by cholesterol produces an increase in melting point of some 40 °C. Once again, all compounds gave featureless cooling traces showing that these materials do not recrystallise but form glassy solids.

V-1.5 SUMMARY OF RESULTS AND POSSIBLE FURTHER WORK

Although several of the complexes described were found to melt at unusually low temperatures for such molybdenum mononitrosyl derivatives, and indeed for coordination complexes in general, none show any signs of mesomorphic behaviour. The molten complexes generally appear rather viscous but show completely isotropic optical properties when viewed under the polarising microscope. The complexes with the lowest melting points are the bis-substituted derivatives [Mo(NO)L*($OC_6H_4CO_2C_{12}H_{25}$)$_2$] [170] (m.p. = 44 °C) and [Mo(NO)L*($HNC_6H_4CH{=}CHC_6H_4OC_{12}H_{25}$)$_2$] [192] (m.p. = 70 °C), and in general a considerable decrease in melting point is brought about by substitution of the second iodide to produce bis-substituted complexes.

The observation of very broad melting events in the DSC, or even no detectable enthalpy change at all, indicates that these complexes are generally isolated as poorly crystalline materials. This tendency to form partially amorphous solids has already been noted in some of the complexes of ferrocenyl and other organic ligands discussed in Chapters Two and Three, but is clearly more significant in the complexes containing long alkyl chain substituents.

Further trends in melting behaviour related to hydrocarbon chain length, halide, or other aspects of ligand structure are not evident when considering all of the complexes discussed. In some cases changing chloride for iodide seems to have little effect on melting point, whereas in others it results in large variations. Similarly, although complexes containing dodecyl chains often have the lowest melting points, this is not the case for all types of complex. Whether the presence of dichloromethane in many of the samples has significant effects upon thermal behaviour is questionable. Although it is likely that this included solvent may render melting less well defined, it does not alter the general result that these complexes show no mesomorphic properties because samples which did contain solvent showed similar behaviour to those which did not.

The reasons why none of these complexes shows any liquid

crystalline behaviour are unclear, but the most obvious factor must be the steric properties of the tris(3,5-dimethylpyrazol-1-yl)hydroborate ligand. Although its steric bulk is important in increasing the thermal stability of complexes, the overall shape of this ligand is certainly somewhat untypical of hitherto discovered mesogenic compounds because it represents a highly non-planar structure. When attached to a liquid crystalline organic fragment in a monosubstituted complex the {Mo(NO)L*} centre will act as a bulky hydrophobic moiety which does not lie neatly in the plane of the aromatic fragment but extends outwards in all directions. It will hence be likely to interfere with any fluid ordering and make the formation of stable mesophases less likely. In the case of a bis-substituted complex the geometry will be that of a V-shape possessing considerable three-dimensional character.

One possible way of reducing this three-dimensional nature of such molybdenum complexes would be to make use of the unsubstituted tris(pyrazol-1-yl)hydroborate ligand in which the absence of methyl groups reduces considerably the size of the tripodal ligand. Other interesting but synthetically more involved approaches could involve the attachment of long alkyl chains to either the pyrazolyl rings or to the tetrahedral boron atom. Both variations in pyrazole substitution and boron substitution have already been achieved by other workers. These have involved pyrazole substituents such as isopropyl,[172] and t-butyl,[271] and boron substituents such as phenyl.[272] Hence, there is no reason why ligands containing long alkyl-chain bearing pyrazoles should not be prepared, and the known substituted phenyl derivatives {4-X-C_6H_4-B(pz)$_3$} (where pz = pyrazolyl, and X = Br, CO_2H)[273] used to make {4-n-C_nH_{2n+1}-C_6H_4-B(pz)$_3$} or {4-n-$C_nH_{2n+1}O_2C$-C_6H_4-B(pz)$_3$} ligands. In fact, cobalt complexes of formulation [Co{4-X-C_6H_4-B(pz)$_3$}$_2$] (where X = n-butyl, or -CO_2CH_3) have already been reported.[273]

Moving to related complexes such as molybdenum cyclopentadienyl derivatives might prove fruitful since these would involve a rather less bulky metal centre than trispyrazolylborate systems, although reduced thermal stability might prove a problem in such compounds. Considering the nature of the aromatic co-ligand, its extension to species containing three

or even four phenyl rings is a possibility which could be readily realised by further organic synthesis. This would serve to increase the overall molecular structural anisotropy, but the steric effects of the {Mo(NO)L*} centre thought to prevent sufficient fluid ordering might still prove critical.

Although the complexes described here are themselves not mesomorphic, there are several ways in which {Mo(NO)L*} species might conceivably be incorporated into liquid crystalline materials. One possibility is that the lowest melting complexes could be used as dopant molecules in a known organic mesogen of similar structure to the aryl ligand fragment. In practice this approach would probably encounter problems of complex insolubility along with doped mesophase instability. Also the inevitable dilution of useful complex properties such as NLO activity (possible in noncentrosymmetric LC phases such as chiral tilted smectics) would be undesirable. Another possibility is that the molybdenum centres could somehow be attached to a polymeric structure which would give increased ordering of the organic ligand portions, perhaps interspersed with purely organic liquid crystalline polymer substituents. In fact neither of these strategies would be simple to carry out and the creation of simple monomeric complexes which are mesogenic remains a more realistic goal at present.

Clearly there exists much scope for further work into the creation of liquid crystalline materials containing molybdenum mononitrosyl centres, and the lack of success from this limited study should not preclude the possibility of future interesting advances. To this end, some work is currently in progress involving molybdenum complexes of 4-n-alkyloxy-stilbazole ligands which are known to form metallomesogens with other heavy transition metals.[160]

V-2 EXPERIMENTAL

[Mo(NO)L*$(I)_2$] was prepared by a previously described method.[187] [Mo(NO)L*$(Cl)_2$] was prepared by a previously described method,[186] and also using the new technique described in Chapter Two. The diiodide is considered as its mono toluene solvate [Mo(NO)L*$(I)_2$].C_7H_8 when calculating yields. Triethylamine was dried over sodium and stored over activated alumina, and hexamine was recrystallised from absolute ethanol and dried under vacuum. Other reagents were used as supplied, and all reaction solvents were redistilled from drying agents according to standard methods prior to use. All reactions were performed under an atmosphere of dry nitrogen but the reaction products were handled in air. Column chromatography was carried out using silica gel 60 (70-230 mesh) or alumina 90 (70-230 mesh), and column dimensions of 40 x 2 cm unless otherwise specified.

V-2.1 LIGANDS AND LIGAND PRECURSORS

4-n-Dodecyloxy-4'-nitrostilbene [164]

A solution of 4-n-dodecyloxybenzaldehyde (4.0 g, 13.8 mmol), 4-nitrophenylacetic acid (2.74 g, 15.1 mmol) and piperidine (10 cm^3) was stirred under reflux in pyridine (50 cm^3) for 22 h. The mixture was cooled and the solvent removed under reduced pressure. The bright yellow product was purified by two recrystallisations from ethanol to yield bright yellow crystals of 4-n-dodecyloxy-4'-nitrostilbene (0.90 g, 16%).

$C_{12}H_{25}OC_6H_4CH{=}CHC_6H_4{-}NO_2$, m.p. 95→113 °C (Found: C, 76.5; H, 8.5; N, 3.4. $C_{26}H_{35}NO_3$ requires C, 76.3; H, 8.6; N, 3.4); $\nu_{max.}(NO_2)$ 1500s and 1330s cm^{-1}; $\delta_H(CDCl_3)$ 8.19 and 7.58 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, $C_6H_4{-}NO_2$], 7.48 and 6.91 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, $C_6H_4{-}OC_{12}H_{25}$], 7.22 and 6.99 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, $CH{=}CH$], 3.98 [2 H, t, J(HH) 6.6 Hz, $OCH_2{-}C_{11}H_{23}$], 1.80 [2 H, qn, $OCH_2{-}CH_2{-}C_{10}H_{21}$], 1.46 [2 H, qn, OCH_2CH_2-

CH_2-C_9H_{19}], 1.27 [16 H, br s, OC_3H_6-C_8H_{16}-CH_3], 0.88 [3 H, t, J(HH) 7.0 Hz, CH_3].

4-n-Hexyloxy-4'-nitrostilbene [162]

This compound was prepared in an identical manner to [164] using 4-n-hexyloxybenzaldehyde (2.85 g, 13.8 mmol) in place of 4-n-dodecyloxybenzaldehyde. Recrystallisation afforded bright yellow crystals of 4-n-hexyloxy-4'-nitrostilbene (0.85 g, 19%) $C_6H_{13}OC_6H_4CH{=}CHC_6H_4{-}NO_2$, m.p. 99→106 °C (Found: C, 73.8; H, 7.0; N, 4.6. $C_{20}H_{23}NO_3$ requires C, 73.8; H, 7.1; N, 4.3); $\nu_{max.}(NO_2)$ 1500s and 1330s cm^{-1}; $\delta_H(CDCl_3)$ 8.19 and 7.58 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-NO_2], 7.48 and 6.91 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-OC_6H_{13}], 7.22 and 6.99 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, CH=CH], 3.99 [2 H, t, J(HH) 6.6 Hz, OCH_2-C_5H_{11}], 1.80 [2 H, qn, OCH_2-CH_2-C_4H_9], 1.47 [2 H, qn, OCH_2CH_2-CH_2-C_3H_7], 1.37-1.31 [4 H, c m, OC_3H_6-C_2H_4-CH_3], 0.91 [3 H, t, J(HH) 7.0 Hz, CH_3].

4-n-Octyloxy-4'-nitrostilbene [163]

This compound was prepared in an identical manner to [164] using 4-n-octyloxybenzaldehyde (3.23 g, 13.8 mmol) in place of 4-n-dodecyloxybenzaldehyde. Recrystallisation afforded bright yellow needles of 4-n-octyloxy-4'-nitrostilbene (0.98 g, 20%) $C_8H_{17}OC_6H_4CH{=}CHC_6H_4{-}NO_2$, m.p. 95→109 °C (Found: C, 75.1; H, 7.7; N, 4.0. $C_{22}H_{27}NO_3$ requires C, 74.8; H, 7.7; N, 4.0); $\nu_{max.}(NO_2)$ 1500s and 1330s cm^{-1}; $\delta_H(CDCl_3)$ 8.19 and 7.58 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-NO_2], 7.48 and 6.91 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-OC_8H_{17}], 7.22 and 6.99 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, CH=CH], 3.98 [2 H, t, J(HH) 6.6 Hz, OCH_2-C_7H_{15}], 1.80 [2 H, qn, OCH_2-CH_2-C_6H_{13}], 1.46 [2 H, qn, OCH_2CH_2-CH_2-C_5H_{11}], 1.40-1.20 [8 H, br m, OC_3H_6-C_4H_8-CH_3], 0.89 [3 H, t, J(HH) 7.0 Hz, CH_3].

4-n-Hexyloxy-4'-stilbenamine [165]

A solution of [162] (1.1 g, 3.38 mmol) and ammonium chloride (1.1 g, 20.56 mmol) in acetone (100 cm^3) and water (20 cm^3) was heated to reflux. Zinc powder (1.0 g, 15.30 mmol) was added and

the mixture stirred under reflux for 1 h. Further ammonium chloride (0.5 g) and zinc powder (0.5 g) were added and the mixture was stirred under reflux for a further 4 h. The colour of the solution changed from yellow to almost colourless during this time. The reaction mixture was cooled and the zinc powder removed by filtration. The acetone was removed *in vacuo*. and water (50 cm^3) and dichloromethane (50 cm^3) were added. The pale yellow-orange organic layer was separated and the aqueous layer extracted with further dichloromethane (3 x 20 cm^3). The combined organic extracts were evaporated to yield 4-n-hexyloxy-4'-stilbenamine as a beige powder (0.89 g, 89%).

$C_6H_{13}OC_6H_4CH=CHC_6H_4-NH_2$ (Found: C, 78.7; H, 8.2; N, 4.8 $C_{20}H_{25}NO.0.13CH_2Cl_2$ requires C, 78.9; H, 8.3; N, 4.6); $\nu_{max.}(NH_2)$ 3380s and 3315s cm^{-1}; $\delta_H(CDCl_3)$ 7.39 and 6.86 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, $C_6H_4-NH_2$], 7.30 and 6.66 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, $C_6H_4-OC_6H_{13}$], 6.87 [2 H, s, $CH=CH$], 3.96 [2 H, t, J(HH) 6.6 Hz, $OCH_2-C_5H_{11}$], 3.72 [2 H, vbr s, NH_2], 1.78 [2 H, qn, $OCH_2-CH_2-C_4H_9$], 1.45 [2 H, qn, $OCH_2CH_2-CH_2-C_3H_7$], 1.37-1.31 [4 H, c m, $OC_3H_6-C_2H_4-CH_3$], 0.91 [3 H, t, J(HH) 7.0 Hz, CH_3].

4-n-Octyloxy-4'-stilbenamine [166]

This compound was prepared in an identical manner to [165] using [163] (1.19 g, 3.38 mmol) in place of [162]. Due to lower solubility, the reaction was allowed to proceed for a total reflux time of 22 h. This afforded 4-n-octyloxy-4'-stilbenamine as a beige powder (0.69 g, 63%).

$C_8H_{17}OC_6H_4CH=CHC_6H_4-NH_2$ (Found: C, 80.5; H, 8.8; N, 4.5 $C_{22}H_{29}NO.0.06CH_2Cl_2$ requires C, 80.6; H, 8.9; N, 4.3); $\nu_{max.}(NH_2)$ 3380s and 3315s cm^{-1}; $\delta_H(CDCl_3)$ 7.39 and 6.86 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, $C_6H_4-NH_2$], 7.30 and 6.66 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, $C_6H_4-OC_8H_{17}$], 6.87 [2 H, s, $CH=CH$], 3.96 [2 H, t, J(HH) 6.6 Hz, $OCH_2-C_7H_{15}$], 3.72 [2 H, vbr s, NH_2], 1.78 [2 H, qn, $OCH_2-CH_2-C_6H_{13}$], 1.45 [2 H, qn, $OCH_2CH_2-CH_2-C_5H_{11}$], 1.40-1.25 [4 H, br m, $OC_3H_6-C_4H_8-CH_3$], 0.89 [3 H, t, J(HH) 7.0 Hz, CH_3].

4-n-Dodecyloxy-4'-stilbenamine [167]

This compound was prepared in an identical manner to [165]

using [164] (1.38 g, 3.38 mmol) in place of [162]. Due to lower solubility, the reaction was allowed to proceed for a total reflux time of 22 h. This afforded 4-n-dodecyloxy-4'-stilbenamine as a beige powder (0.62 g, 48%).

$C_{12}H_{25}OC_6H_4CH{=}CHC_6H_4{-}NH_2$ (Found: C, 80.6; H, 9.5; N, 3.0 $C_{26}H_{37}NO.0.11CH_2Cl_2$ requires C, 80.6; H, 9.6; N, 3.6); $\nu_{max.}(NH_2)$ 3380s and 3315s cm^{-1}; $\delta_H(CDCl_3)$ 7.39 and 6.86 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, $C_6H_4{-}NH_2$], 7.30 and 6.66 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, $C_6H_4{-}OC_8H_{17}$], 6.87 [2 H, s, $CH{=}CH$], 3.96 [2 H, t, J(HH) 6.6 Hz, $OCH_2{-}C_{11}H_{23}$], 3.72 [2 H, vbr s, NH_2], 1.78 [2 H, qn, $OCH_2{-}CH_2{-}C_6H_{13}$], 1.45 [2 H, qn, $OCH_2CH_2{-}CH_2{-}C_9H_{19}$], 1.26 [16 H, br s, $OC_3H_6{-}C_8H_{16}{-}CH_3$], 0.88 [3 H, t, J(HH) 7.0 Hz, CH_3].

V-2.2 COMPLEXES

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl($OC_6H_4CO_2C_{12}H_{25}$)] [168]

A solution of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] (0.30 g, 0.61 mmol), n-dodecyl-4-hydroxybenzoate (0.23 g, 0.75 mmol) and hexamine (0.05 g, 0.36 mmol) was stirred under reflux in toluene (20 cm^3) for 3 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The resulting brown solid was purified by column chromatography on silica using dichloromethane as the eluent. The major brown band was collected and crystallised from a dichloromethane/n-hexane mixture to afford the golden brown product (0.36 g, 77%). m.p. 102-107 °C (Found: C, 53.2; H, 6.7; N, 12.7%; M^+, 765. $C_{34}H_{51}BClMoN_7O_4$ requires C, 53.5; H, 6.7; N, 12.8%; M, 764); $\lambda_{max.}(CH_2Cl_2)$ 450 (ε 7,200 $dm^3mol^{-1}cm^{-1}$) and 312 nm (8,400); $\nu_{max.}(CO)$ 1710s, $\nu_{max.}(NO)$ 1690s cm^{-1}; $\delta_H(CDCl_3)$ 8.11 and 7.34 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 5.93, 5.92, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.31 [2 H, t, J(HH) 6.5 Hz, $OCH_2{-}C_{11}H_{23}$], 2.56, 2.43, 2.41, 2.39, 2.17, and 2.05 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 1.77 [2 H, qn, $OCH_2{-}CH_2{-}C_{10}H_{21}$], 1.5-1.2 [18 H, br m, $OC_2H_4{-}C_9H_{18}{-}CH_3$], 0.88 [3 H, t, J(HH) 6.8 Hz, CH_3]; *m/z* 765 (M^+), 735 (M - NO), 729 (M - Cl), 460 (M - $OC_6H_4CO_2C_{12}H_{25}$), 430 (M - $OC_6H_4CO_2C_{12}H_{25}$ - NO), 424 (M -

$OC_6H_4CO_2C_{12}H_{25}$ - Cl), 138 ($HOC_6H_4CO_2H$). E_f = -0.20 V, ΔE_p = 115 mV, ΔE_p(Fc) = 125 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I($OC_6H_4CO_2C_{12}H_{25}$)] [169]

This compound was prepared in an identical manner to [168] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and n-dodecyl-4-hydroxybenzoate (0.21 g, 0.67 mmol). A red-brown solid was obtained (0.28 g, 62%). m.p. 105-109 °C (Found: C, 47.6; H, 6.2; N, 11.4%; M^+, 857. $C_{34}H_{51}BIMoN_7O_4$ requires C, 47.7; H, 6.0; N, 11.5%; M, 855); $\lambda_{max.}$(CH_2Cl_2) 450 (ε 10,500 $dm^3mol^{-1}cm^{-1}$) and 324 nm (5,600); $\nu_{max.}$(CO) 1715s, $\nu_{max.}$(NO) 1685s cm^{-1}; δ_H($CDCl_3$) 8.07 and 7.46 [2 H, d, J(HH) 8.6 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 5.91, 5.86, and 5.85 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.30 [2 H, t, J(HH) 6.5 Hz, OCH_2-$C_{11}H_{23}$], 2.53, 2.45, 2.40, 2.37, 2.28, and 1.97 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.76 [2 H, qn, OCH_2-CH_2-$C_{10}H_{21}$], 1.5-1.2 [18 H, br m, OC_2H_4-C_9H_{18}-CH_3], 0.88 [3 H, t, J(HH) 6.8 Hz, CH_3]; *m/z* 857 (M^+), 827 (M - NO), 730 (M - I), 552 (M - $OC_6H_4CO_2C_{12}H_{25}$), 522 (M - $OC_6H_4CO_2C_{12}H_{25}$ - NO), 424 (M - $OC_6H_4CO_2C_{12}H_{25}$ - I), 138 ($HOC_6H_4CO_2H$), 128 (I). E_f = -0.18 V, ΔE_p = 125 mV, ΔE_p(Fc) = 160 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}($OC_6H_4CO_2C_{12}H_{25}$)$_2$] [170]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) and n-dodecyl-4-hydroxybenzoate (0.40 g, 1.31 mmol) using the procedure described for [168] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A dark green-brown solid was obtained (0.46 g, 85%). m.p. 41-44 °C (Found: C, 61.4; H, 8.0; N, 9.0%; M^+, 1034. $C_{53}H_{80}BMoN_7O_7$ requires C, 61.6; H, 7.8; N, 9.5%; M, 1034); $\lambda_{max.}$(CH_2Cl_2) 407 nm (ε 5,700 $dm^3mol^{-1}cm^{-1}$); $\nu_{max.}$(CO) 1710s, $\nu_{max.}$(NO) 1665s cm^{-1}; δ_H($CDCl_3$) 8.00 and 7.02 [4 H, d, J(HH) 8.8 Hz; 4 H, d, J(HH) 8.8 Hz, 2 x C_6H_4], 5.89 and 5.70 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.29 [4 H, t, J(HH) 6.6 Hz, 2 x OCH_2-$C_{11}H_{23}$], 2.43, 2.41, 2.21, and 1.95 [6 H, s; 3 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.76 [4 H, qn, 2 x OCH_2-CH_2-$C_{10}H_{21}$], 1.5-1.2 [36 H, br m, 2 x OC_2H_4-C_9H_{18}-CH_3], 0.88 [6 H, t, J(HH) 6.2 Hz, 2 x CH_3]; *m/z* 1034 (M^+),

1003 (M - NO), 848 (M - $OC_{12}H_{25}$), 728 (M - $OC_6H_4CO_2C_{12}H_{25}$), 698 (M - $OC_6H_4CO_2C_{12}H_{25}$ - NO), 427 (M - 2 x $OC_6H_4CO_2C_{12}H_{25}$), 138 ($HOC_6H_4CO_2H$). E_f = -0.44 = V, ΔE_p = 145 mV, ΔE_p(Fc) = 140 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl($HNC_6H_4C_{10}H_{21}$)] [171]

This compound was prepared in similar manner to [168] using 4-n-decylaniline (0.18 g, 0.75 mmol) in place of n-dodecyl-4-hydroxybenzoate and triethylamine (0.5 cm^3) in place of hexamine. Column chromatography using 20% n-hexane/dichloromethane yielded a red-brown solid (0.23 g, 55%). m.p. 105 °C (Found: C, 54.0; H, 7.0; N, 16.3%; M^+, 692. $C_{31}H_{48}BClMoN_8O$ requires C, 53.9; H, 7.0; N, 16.2%; M, 691); $\lambda_{max.}$(CH_2Cl_2) 446 (ε 14,800 $dm^3mol^{-1}cm^{-1}$) and 292 nm (5,100); $\nu_{max.}$(NH) 3260w, $\nu_{max.}$(NO) 1655s cm^{-1}; δ_H($CDCl_3$) 12.73 [1 H, s, N*H*], 7.39 and 7.22 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.2 Hz, C_6H_4], 5.86 and 5.78 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 2.69, 2.42, 2.38, 2.37, 2.36, and 2.01 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 2.64 [2 H, t, J(HH) 7.7 Hz, C_6H_4-CH_2-C_9H_{19}], 1.63 [2 H, qn, CH_2-CH_2-C_8H_{17}], 1.31 and 1,27 [14 H, s, s, C_2H_4-C_7H_{14}-CH_3], 0.88 [3 H, t, J(HH) 6.5 Hz, CH_3]; *m/z* 692 (M^+), 662 (M - NO), 656 (M - Cl), 623 (M - NO - Cl), 566 (M - C_9H_{19}), 460 (M - $HNC_6H_4C_{10}H_{21}$), 430 (M - $HNC_6H_4C_{10}H_{21}$ - NO), 424 (M - $HNC_6H_4C_{10}H_{21}$ - Cl), 233 ($H_2NC_6H_4C_{10}H_{21}$), 106 ($H_2NC_6H_4CH_2$). E_f = -0.87 V, ΔE_p = 115 mV, ΔE_p(Fc) = 115 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I($HNC_6H_4C_{10}H_{21}$)] [172]

This compound was prepared in identical manner to [171] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-n-decylaniline (0.16 g, 0.69 mmol). A dark brown solid was obtained (0.36 g, 85%). m.p. 110 °C (Found: C, 48.0; H, 6.3; N, 14.6%; M^+, 784. $C_{31}H_{48}BIMoN_8O$ requires C, 47.6; H, 6.2; N, 14.3%; M, 782); $\lambda_{max.}$(CH_2Cl_2) 468 (ε 13,900 $dm^3mol^{-1}cm^{-1}$) and 400 nm (7,000); $\nu_{max.}$(NH) 3280w, $\nu_{max.}$(NO) 1660s cm^{-1}; δ_H($CDCl_3$) 13.20 [1 H, s, N*H*], 7.54 and 7.18 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 5.92, 5.85, and 5.76 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 2.71, 2.47, 2.46, 2.37, and 1.98 [3 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 2.55 [2 H, t, J(HH) 7.7 Hz, C_6H_4-CH_2-C_9H_{19}], 1.63 [2 H, qn, CH_2-CH_2-C_8H_{17}], 1.31 and 1,27 [14

H, s, s, C_2H_4-C_7H_{14}-CH_3], 0.88 [3 H, t, J(HH) 6.6 Hz, CH_3]; *m/z* 784 (M^+), 657 (M - I), 566 (M - $C_6H_4C_{10}H_{21}$), 233 ($H_2NC_6H_4C_{10}H_{21}$), 106 ($H_2NC_6H_4CH_2$). E_f = -0.83 V, ΔE_p = 110 mV, ΔE_p(Fc) = 125 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}($HNC_6H_4C_{10}H_{21}$)$_2$] [173]

Sodium (0.1 g, 4.35 mmol) was heated under reflux in dry thf (35 cm^3) for 30 min. Naphthalene (0.1 g, 0.78 mmol) was then added and the mixture stirred for 1 h under reflux during which time the solution became dark green. The mixture was then filtered under nitrogen, to remove excess sodium, and 4-n-decylaniline (0.1 g, 0.43 mmol) was added to the filtrate. After stirring the resulting solution for 30 min at room temperature, [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I($HNC_6H_4C_{10}H_{21}$)] (0.1 g, 0.13 mmol) was added and the mixture stirred for a further 2.5 h. The final dark green mixture was filtered in air to give a dark purple filtrate from which the solvent was removed *in vacuo*. The product was purified by column chromatography on silica using 20% n-hexane/dichloromethane as eluent, the major purple fraction being collected. Further purification was effected by recrystallisation from n-pentane to yield a dark purple solid (0.11 g, 57%) (Found: C, 64.8; H, 8.5; N, 12.5%; M^+, 889. $C_{47}H_{74}BMoN_9O.C_5H_{12}$ requires C, 65.1; H, 9.0; N, 13.1%; M, 888); $\lambda_{max.}$(CH_2Cl_2) 549 (ε 12,600 $dm^3mol^{-1}cm^{-1}$) and 369 nm (11,400); $\nu_{max.}$(NH) 3320w, $\nu_{max.}$(NO) 1630s cm^{-1}; δ_H($CDCl_3$) 8.78 [2 H, s, 2 x N*H*], 7.19 and 7.03 [4 H, d, J(HH) 8.1 Hz; 4 H, d, J(HH) 8.4 Hz, 2 x C_6H_4], 5.94 and 5.72 [1 H, s; 2 H, s, ($Me_2C_3N_2H$)$_3$], 2.47, 2.34, and 2.24 [3 H, s; 9 H, s; 6 H, s, ($Me_2C_3N_2H$)$_3$], 2.53 [4 H, t, J(HH) 7.7 Hz, 2 x C_6H_4-CH_2-C_9H_{19}], 1.60 [4 H, qn, 2 x CH_2-CH_2-C_6H_{17}], 1.40-1.20 [28 + 12 H, br m, 2 x C_2H_4-C_7H_{14}-CH_3 + C_5H_{12}], 0.88 [6 H, t, J(HH) 6.6 Hz, 2 x CH_3]; *m/z* 889 (M^+), 656 (M - $HNC_6H_4C_{10}H_{21}$), 624 (M - $HNC_6H_4C_{10}H_{21}$ - NO), 566 (M - $HNC_6H_4C_{10}H_{21}$ - NO - C_4H_9), 425 (M - 2 x $HNC_6H_4C_{10}H_{21}$), 233 ($H_2NC_6H_4C_{10}H_{21}$). E_f = -1.40 V, ΔE_p = 200 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl($OC_6H_4C_6H_4OC_6H_{13}$)] [174]

This compound was prepared in similar manner to [168] using 4-n-hexyloxy-4'-hydroxybiphenyl (0.20 g, 0.74 mmol) in place of

n-dodecyl-4-hydroxybenzoate. The product was purified by column chromatography on silica using 50% dichloromethane/n-hexane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.33 g, 75%). (Found: C, 52.2; H, 5.9; N, 13.5; M^+, 729. $C_{33}H_{43}BClMoN_7O_3.0.4CH_2Cl_2$ requires C, 52.7; H, 5.8; N, 12.9%; M, 728); $\nu_{max.}$(NO) 1680 cm^{-1}; $\delta_H(CDCl_3)$ 7.61 and 6.97 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4-OMo], 7.56 and 7.39 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4-OC_6H_{13}], 5.93, 5.89, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.01 [2 H, t, J(HH) 6.6 Hz, C_6H_4-OCH_2-C_5H_{11}], 2.60, 2.42, 2.39, 2.21, and 2.09 [3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 1.81 [2 H, qn, $C_6H_4OCH_2$-CH_2-C_4H_9], 1.48 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_3H_7], 1.40-1.30 [4 H, c m, OC_3H_6-C_2H_4-CH_3], 0.92 [3 H, t, J(HH) 6.7 Hz, CH_3]; *m/z* 729 (M^+), 699 (M - NO), 693 (M - Cl), 460 (M - $OC_6H_4C_6H_4OC_6H_{13}$), 430 (M - $OC_6H_4C_6H_4OC_6H_{13}$ - NO), 424 (M - $OC_6H_4C_6H_4OC_6H_{13}$ - Cl), 270 ($HOC_6H_4C_6H_4OC_6H_{13}$), 186 ($HOC_6H_4C_6H_4OH$). E_f = -0.33 V, ΔE_p = 140 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I($OC_6H_4C_6H_4OC_6H_{13}$)] [175]

This compound was prepared in identical manner to [174] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-n-hexyloxy-4'-hydroxy-biphenyl (0.18 g, 0.67 mmol). A deep violet solid was obtained (0.30 g, 70%). (Found: C, 47.1; H, 5.5; N, 11.7; M^+, 821. $C_{33}H_{43}BIMoN_7O_3.0.4CH_2Cl_2$ requires C, 47.0; H, 5.2; N, 11.5%; M, 819); $\nu_{max.}$(NO) 1670 cm^{-1}; $\delta_H(CDCl_3)$ 7.58 and 7.51 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-OC_6H_{13}], 7.56 and 6.96 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-Mo], 5.91, 5.85, and 5.84 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 4.00 [2 H, t, J(HH) 6.6 Hz, C_6H_4-OCH_2-C_5H_{11}], 2.59, 2.45, 2.40, 2.38, 2.32, and 2.01 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 1.81 [2 H, qn, $C_6H_4OCH_2$-CH_2-C_4H_9], 1.48 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_3H_7], 1.40-1.30 [4 H, c m, OC_3H_6-C_2H_4-CH_3], 0.92 [3 H, t, J(HH) 7.0 Hz, CH_3]; *m/z* 821 (M^+), 791 (M - NO), 694 (M - I), 552 (M - $OC_6H_4C_6H_4OC_6H_{13}$), 522 (M - $OC_6H_4C_6H_4OC_6H_{13}$ - NO), 424 (M - $OC_6H_4C_6H_4OC_6H_{13}$ - I), 270 ($HOC_6H_4C_6H_4OC_6H_{13}$), 186 ($HOC_6H_4C_6H_4OH$), 128 (I). E_f = -0.28 V, ΔE_p = 120 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}($OC_6H_4C_6H_4OC_6H_{13}$)$_2$] [176]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) and 4-n-hexyloxy-4'-hydroxybiphenyl (0.36 g, 1.33 mmol) using the procedure described for [168] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A dark brown solid was obtained (0.45 g, 90%). (Found: C, 61.4; H, 6.4; N, 9.8%; M^+, 961. $C_{61}H_{64}BMoN_7O_5.0.5CH_2Cl_2$ requires C, 61.6; H, 6.5; N, 9.8%; M, 962); $\nu_{max.}$(NO) 1655 cm^{-1}; δ_H($CDCl_3$) 7.53 and 7.23 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.6 Hz, 2 x C_6H_4-OC_6H_{13}], 7.52 and 6.94 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.8 Hz, 2 x C_6H_4-Mo], 5.85 and 5.76 [2 H, s; 1 H, s ($Me_2C_3N_2H$)$_3$], 3.99 [4 H, t, J(HH) 6.6 Hz, C_6H_4-OCH_2-C_6H_{11}], 2.42, 2.41, 2.27, and 2.14 [3 H, s; 6 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.80 [4 H, qn, 2 x $C_6H_4OCH_2$-CH_2-C_4H_9], 1.48 [4 H, qn, 2 x $C_6H_4OC_2H_4$-CH_2-C_3H_7], 1.40-1.30 [8 H, c m, 2 x OC_3H_6-C_2H_4-CH_3], 0.91 [6 H, t, J(HH) 7.0 Hz, 2 x CH_3]; *m/z* 961 (M^+), 933 (M - NO), 694 (M - $OC_6H_4C_6H_4OC_6H_{13}$), 664 (M - $OC_6H_4C_6H_4OC_6H_{13}$ - NO), 424 (M - 2 x $OC_6H_4C_6H_4OC_6H_{13}$), 270 ($HOC_6H_4C_6H_4OC_6H_{13}$), 186 ($HOC_6H_4C_6H_4OH$). E_f = -0.67 V, ΔE_p = 135 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl($OC_6H_4C_6H_4OC_8H_{17}$)] [177]

This compound was prepared in similar manner to [168] using 4-n-octyloxy-4'-hydroxybiphenyl (0.22 g, 0.74 mmol) in place of n-dodecyl-4-hydroxybenzoate. The product was purified by column chromatography on silica using 50% dichloromethane/n-hexane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.37 g, 80%). (Found: C, 55.9; H, 6.3; N, 12.6; M^+, 757. $C_{35}H_{47}BClMoN_7O_3$ requires C, 55.6; H, 6.3; N, 13.0%; M, 756); $\nu_{max.}$(NO) 1675 cm^{-1}; δ_H($CDCl_3$) 7.61 and 6.97 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-OMo], 7.56 and 7.39 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4-OC_8H_{17}], 5.93, 5.89, and 5.77 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.00 [2 H, t, J(HH) 6.6 Hz, C_6H_4-OCH_2-C_7H_{15}], 2.60, 2.42, 2.41, 2.39, 2.21, and 2.09 [3 H, s; 3 H, s, 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.80 [2 H, qn, $C_6H_4OCH_2$-CH_2-C_6H_{13}], 1.48 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_5H_{11}], 1.40-1.30 [8 H, c m, OC_3H_6-C_4H_8-CH_3], 0.88 [3 H, t, J(HH) 6.7 Hz, CH_3]; *m/z* 757 (M^+), 727 (M - NO), 460 (M - $OC_6H_4C_6H_4OC_8H_{17}$), 430 (M -

$OC_6H_4C_6H_4OC_8H_{17}$ - NO), 298 ($HOC_6H_4C_6H_4OC_8H_{17}$), 186 ($HOC_6H_4C_6H_4OH$). E_f = -0.33 V, ΔE_p = 120 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I($OC_6H_4C_6H_4OC_8H_{17}$)] [178]

This compound was prepared in identical manner to [177] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-n-octyloxy-4'-hydroxybiphenyl (0.20 g, 0.67 mmol). A deep violet solid was obtained (0.32 g, 73%). (Found: C, 49.3; H, 5.5; N, 11.8; M^+, 849. $C_{35}H_{47}BIMoN_7O_3$ requires C, 49.6; H, 5.6; N, 11.6%; M, 847); $\nu_{max.}$(NO) 1665 cm^{-1}; δ_H($CDCl_3$) 7.58 and 7.51 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-OC_8H_{17}], 7.56 and 6.96 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-Mo], 5.91, 5.85, and 5.84 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.00 [2 H, t, J(HH) 6.6 Hz, C_6H_4-OCH_2-C_7H_{15}], 2.59, 2.45, 2.40, 2.38, 2.32, and 2.01 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.81 [2 H, qn, $C_6H_4OCH_2$-CH_2-C_6H_{13}], 1.48 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_5H_{11}], 1.40-1.30 [8 H, c m, OC_3H_6-C_4H_8-CH_3], 0.89 [3 H, t, J(HH) 7.0 Hz, CH_3]; *m/z* 849 (M^+), 819 (M - NO), 722 (M - I), 552 (M - $OC_6H_4C_6H_4OC_8H_{17}$), 522 (M - $OC_6H_4C_6H_4OC_8H_{17}$ - NO), 424 (M - $OC_6H_4C_6H_4OC_8H_{17}$ - I), 298 ($HOC_6H_4C_6H_4OC_8H_{17}$), 186 ($HOC_6H_4C_6H_4OH$), 128 (I). E_f = -0.28 V, ΔE_p = 110 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}($OC_6H_4C_6H_4OC_8H_{17}$)$_2$] [179]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) and 4-n-octyloxy-4'-hydroxybiphenyl (0.40 g, 1.34 mmol) using the procedure described for [168] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A dark brown solid was obtained (0.50 g, 95%). (Found: C, 61.7; H, 6.7; N, 9.8%; M^+, 1019. $C_{55}H_{72}BMoN_7O_5.0.75CH_2Cl_2$ requires C, 61.9; H, 6.8; N, 9.1%; M, 1018); $\nu_{max.}$(NO) 1650 cm^{-1}; δ_H($CDCl_3$) 7.53 and 7.23 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.6 Hz, 2 x C_6H_4-OC_8H_{17}], 7.52 and 6.94 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.8 Hz, 2 x C_6H_4-Mo], 5.85 and 5.76 [2 H, s; 1 H, s ($Me_2C_3N_2H$)$_3$], 3.99 [4 H, t, J(HH) 6.6 Hz, C_6H_4-OCH_2-C_7H_{15}], 2.42, 2.41, 2.27, and 2.14 [3 H, s; 6 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.80 [4 H, qn, 2 x $C_6H_4OCH_2$-CH_2-C_6H_{13}], 1.47 [4 H, qn, 2 x $C_6H_4OC_2H_4$-

CH_2-C_5H_{11}], 1.40-1.30 [16 H, c m, 2 x OC_3H_6-C_4H_8-CH_3], 0.91 [6 H, t, J(HH) 7.0 Hz, 2 x CH_3]; *m/z* 1019 (M^+), 722 (M - $OC_6H_4C_6H_4OC_8H_{17}$), 648 (M - $OC_6H_4C_6H_4OC_8H_{17}$ - C_5H_{11}), 424 (M - 2 x $OC_6H_4C_6H_4OC_8H_{17}$), 298 ($HOC_6H_4C_6H_4OC_8H_{17}$), 186 ($HOC_6H_4C_6H_4OH$). E_f = -0.67 V, ΔE_p = 150 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl($OC_6H_4C_6H_4OC_{12}H_{25}$)] [180]

This compound was prepared in similar manner to [168] using 4-n-dodecyloxy-4'-hydroxybiphenyl (0.26 g, 0.73 mmol) in place of n-dodecyl-4-hydroxybenzoate. The product was purified by column chromatography on silica using 50% dichloromethane/n-hexane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.45 g, 91%). (Found: C, 56.2; H, 7.1; N, 12.0; M^+, 813. $C_{39}H_{55}BClMoN_7O_3.0.33CH_2Cl_2$ requires C, 56.2; H, 6.7; N, 11.7%; M, 812); $\nu_{max.}$(NO) 1680 cm^{-1}; δ_H($CDCl_3$) 7.61 and 6.97 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-OMo], 7.56 and 7.39 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4-$C_{12}H_{25}$], 5.93, 5.89, and 5.77 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.00 [2 H, t, J(HH) 6.6 Hz, C_6H_4-OCH_2-C_7H_{15}], 2.60, 2.42, 2.39, 2.21, and 2.09 [3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.81 [2 H, qn, $C_6H_4OCH_2$-CH_2-$C_{10}H_{21}$], 1.48 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_9H_{19}], 1.27 [16 H, br s, OC_3H_6-C_8H_{16}-CH_3], 0.88 [3 H, t, J(HH) 6.7 Hz, CH_3]; *m/z* 813 (M^+), 783 (M - NO), 777 (M - Cl), 460 (M - $OC_6H_4C_6H_4OC_{12}H_{25}$), 430 (M - $OC_6H_4C_6H_4OC_{12}H_{25}$ - NO), 354 ($HOC_6H_4C_6H_4OC_{12}H_{25}$), 186 ($HOC_6H_4C_6H_4OH$). E_f = -0.33 V, ΔE_p = 110 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I($OC_6H_4C_6H_4OC_{12}H_{25}$)] [181]

This compound was prepared in identical manner to [180] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(I)_2$].C_7H_8 (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] and 4-n-dodecyloxy-4'-hydroxy-biphenyl (0.24 g, 0.68 mmol). A deep violet solid was obtained (0.36 g, 77%). (Found: C, 49.9; H, 6.0; N, 10.9; M^+, 905. $C_{39}H_{55}BIMoN_7O_3.0.5CH_2Cl_2$ requires C, 50.2; H, 6.0; N, 10.4%; M, 904); $\nu_{max.}$(NO) 1665 cm^{-1}; δ_H($CDCl_3$) 7.58 and 7.51 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4-$OC_{12}H_{25}$], 7.56 and 6.96 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4-Mo], 5.91, 5.85, and 5.84 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 4.00 [2 H, t, J(HH) 6.6 Hz,

C_6H_4-OCH_2-$C_{11}H_{23}$], 2.59, 2.45, 2.40, 2.38, 2.32, and 2.01 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.81 [2 H, qn, $C_6H_4OCH_2$-CH_2-$C_{10}H_{21}$], 1.48 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_9H_{19}], 1.27 [16 H, br s, OC_3H_6-C_8H_{16}-CH_3], 0.88 [3 H, t, J(HH) 6.6 Hz, CH_3]; *m/z* 905 (M^+), 875 (M - NO), 778 (M - I), 552 (M - $OC_6H_4C_6H_4OC_{12}H_{25}$), 522 (M - $OC_6H_4C_6H_4OC_{12}H_{25}$ - NO), 424 (M - $OC_6H_4C_6H_4OC_{12}H_{25}$ - I), 354 ($HOC_6H_4C_6H_4OC_{12}H_{25}$), 186 ($HOC_6H_4C_6H_4OH$), 128 (I). E_f = -0.28 V, ΔE_p = 105 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}($OC_6H_4C_6H_4OC_{12}H_{25}$)$_2$] [182]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) and 4-n-dodecyloxy-4'-hydroxybiphenyl (0.48 g, 1.35 mmol) using the procedure described for [168] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A dark brown solid was obtained (0.55 g, 94%). (Found: C, 63.4; H, 7.4; N, 8.6%; M^+, 1129. $C_{63}H_{88}BMoN_7O_5.CH_2Cl_2$ requires C, 63.3; H, 7.5; N, 8.1%; M, 1130); $\nu_{max.}$(NO) 1650 cm^{-1}; δ_H($CDCl_3$) 7.53 and 7.23 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.6 Hz, 2 x C_6H_4-$OC_{12}H_{25}$], 7.52 and 6.94 [4 H, d, J(HH) 8.6 Hz; 4 H, d, J(HH) 8.8 Hz, 2 x C_6H_4-Mo], 5.85 and 5.76 [2 H, s; 1 H, s ($Me_2C_3N_2H$)$_3$], 3.99 [4 H, t, J(HH) 6.6 Hz, C_6H_4-OCH_2-$C_{11}H_{23}$], 2.42, 2.41, 2.27, and 2.14 [3 H, s; 6 H, s; 6 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.80 [4 H, qn, 2 x $C_6H_4OCH_2$-CH_2-$C_{10}H_{21}$], 1.47 [4 H, qn, 2 x $C_6H_4OC_2H_4$-CH_2-C_9H_{19}], 1.27 [32 H, br s, 2 x OC_3H_6-C_8H_{16}-CH_3], 0.88 [6 H, t, J(HH) 6.6 Hz, 2 x CH_3]; *m/z* 1129 (M^+), 776 (M - $OC_6H_4C_6H_4OC_{12}H_{25}$), 648 (M - $OC_6H_4C_6H_4OC_{12}H_{25}$ - C_5H_{11}), 424 (M - 2 x $OC_6H_4C_6H_4OC_{12}H_{25}$), 354 ($HOC_6H_4C_6H_4OC_{12}H_{25}$), 186 ($HOC_6H_4C_6H_4OH$). E_f = -0.67 V, ΔE_p = 180 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl(HNC_6H_4CH=$CHC_6H_4OC_6H_{13}$)] [183]

This compound was prepared in similar manner to [168] using 4-n-hexyloxy-4'-stilbenamine (0.22 g, 0.74 mmol) in place of n-dodecyl-4-hydroxybenzoate and triethylamine (0.5 cm^3) in place of hexamine, with a reaction time of 2 h. The product was purified by column chromatography on silica using 60% dichloromethane/n-hexane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.32 g, 70%). (Found: C, 53.6; H, 6.0; N, 14.5; M^+, 754. $C_{35}H_{46}BClMoN_8O_2.0.5CH_2Cl_2$ requires C, 53.6; H, 6.0; N,

14.1%; M, 753); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1655 cm^{-1}; $\delta_H(CDCl_3)$ 12.60 [1 H, s, N*H*], 7.54 and 7.45 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-OC_6H_{13}], 7.45 and 6.90 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-NHMo], 7.09 and 6.98 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 5.87 and 5.79 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.98 [2 H, t, J(HH) 6.4 Hz, C_6H_4-OCH_2-C_5H_{11}], 2.69, 2.42, 2.39, 2.38, 2,37, and 2.03 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$], 1.79 [2 H, qn, $C_6H_4OCH_2$-CH_2-C_4H_9], 1.47 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_3H_7], 1.40-1.30 [4 H, c m, OC_3H_6-C_2H_4-CH_3], 0.91 [3 H, t, J(HH) 6.7 Hz, CH_3]; *m/z* 754 (M^+), 724 (M - NO), 718 (M - Cl), 682 (M - C_5H_{11}), 652 (M - OC_6H_{13}), 628 (M - 125), 295 ($H_2NC_6H_4CH$=$CHC_6H_4OC_6H_{13}$), 252 ($H_2NC_6H_4CH$=$CHC_6H_4OC_3H_6$), 211 ($H_2NC_6H_4CH$=CHC_6H_4OH), 107 ($H_2CC_6H_4OH$). E_f = -0.78 V, ΔE_p = 140 mV, ΔE_p(Fc) = 105 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I(HNC_6H_4CH=$CHC_6H_4OC_6H_{13}$)] [184]

This compound was prepared in identical manner to [183] using [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(I)_2$].C_7H_8 (0.40 g, 0.52 mmol) in place of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] and 4-n-hexyloxy-4'-stilbenamine (0.20 g, 0.68 mmol). A deep violet solid was obtained (0.33 g, 75%). (Found: C, 47.8; H, 5.5; N, 13.5; M^+, 846. $C_{35}H_{46}BIMoN_6O_2$.0.5CH_2Cl_2 requires C, 48.1; H, 5.3; N, 12.6%; M, 844); $\nu_{max.}$(NH) 3275w, $\nu_{max.}$(NO) 1655 cm^{-1}; $\delta_H(CDCl_3)$ 13.06 [1 H, s, N*H*], 7.61 and 7.46 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-OC_6H_{13}], 7.49 and 6.89 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-NHMo], 7.18 and 6.94 [1 H, d, $J(HH)_{trans}$ 16.1 Hz; 1 H, d, $J(HH)_{trans}$ 16.1 Hz, C*H*=C*H*], 5.93, 5.86, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.98 [2 H, t, J(HH) 6.7 Hz, C_6H_4-OCH_2-C_5H_{11}], 2.72, 2.48, 2.46, 2.38, 2,37, and 2.00 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$], 1.80 [2 H, qn, $C_6H_4OCH_2$-CH_2-C_4H_9], 1.47 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_3H_7], 1.40-1.30 [4 H, c m, OC_3H_6-C_2H_4-CH_3], 0.91 [3 H, t, J(HH) 6.9 Hz, CH_3]; *m/z* 846 (M^+), 719 (M - 125), 295 ($H_2NC_6H_4CH$=$CHC_6H_4OC_6H_{13}$), 211 ($H_2NC_6H_4CH$=CHC_6H_4OH), 128 (I). E_f = -0.74 V, ΔE_p = 125 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}(HNC_6H_4CH=$CHC_6H_4OC_6H_{13})_2$] [185]

This compound was prepared in similar manner to [173] using

[184] (0.11 g, 0.13 mmol) in place of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I($HNC_6H_4C_{10}H_{21}$)] and 4-n-hexyloxy-4'-stilbenamine (0.06 g, 0.20 mmol) in place of 4-decylaniline. Upon addition of [184] the solution was stirred under reflux for 2 h, and cooled before filtration. The product was purified by column chromatography on alumina 90 using 40% n-hexane/dichloromethane. This afforded a deep emerald green solid (0.11 g, 84%) (Found: C, 63.4; H, 6.9; N, 11.4; M^+, 1013. $C_{55}H_{70}BMoN_9O_3.0.5CH_2Cl_2$ requires C, 63.2; H, 6.8; N, 12.0%; M, 1012); $\nu_{max.}$(NH) 3300m, $\nu_{max.}$(NO) 1635 cm^{-1}; δ_H($CDCl_3$) 8.90 [2 H, s, 2 x NH], 7.40 and 7.27 [4 H, d, J(HH) 8.7 Hz; 4 H, d, J(HH) 8.7 Hz, 2 x C_6H_4-OC_6H_{13}], 7.40 and 6.87 [4 H, d, J(HH) 8.7 Hz; 4 H, d, J(HH) 8.7 Hz, 2 x C_6H_4-NHMo], 6.93 [4 H, s, 2 x CH=CH], 5.96 and 5.75 [1 H, s; 2 H, s, ($Me_2C_3N_2H$)$_3$], 3.97 [4 H, t, J(HH) 6.6 Hz, 2 x C_6H_4-OCH_2-C_5H_{11}], 2.47, 2.35, and 2.27 [3 H, s; 9 H, s; 6 H, s, ($Me_2C_3N_2H$)$_3$], 1.78 [4 H, qn, 2 x $C_6H_4OCH_2$-CH_2-C_4H_9], 1.46 [4 H, qn, 2 x $C_6H_4OC_2H_4$-CH_2-C_3H_7], 1.40-1.30 [8 H, c m, 2 x OC_3H_6-C_2H_4-CH_3], 0.91 [6 H, t, J(HH) 6.9 Hz, 2 x CH_3]; *m/z* 1013 (M^+), 989 (M - 23), 982 (M - NO), 927 (M - C_6H_{13}), 911 (M - OC_6H_{13}), 295 ($H_2NC_6H_4CH$=$CHC_6H_4OC_6H_{13}$), 211 ($H_2NC_6H_4CH$=CHC_6H_4OH). E_f = -1.20 V, ΔE_p = 230 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}OH(HNC_6H_4CH=$CHC_6H_4OC_6H_{13}$)] [186]

This compound was prepared by the rapid hydrolysis of [185] (0.10 g, 0.10 mmol) on an activated alumina column in dichloromethane. A dark brown solid was produced (0.046 g, 64%) (Found: C, 55.6; H, 6.2; N, 14.3; $C_{36}H_{47}BMoN_6H_3.0.33CH_2Cl_2$ requires C, 55.6; H, 6.3; N, 14.7%; M, 735); $\nu_{max.}$(OH) 3480w br, $\nu_{max.}$(NH) 3300w, $\nu_{max.}$(NO) 1640 cm^{-1}; δ_H($CDCl_3$) 10.46 [1 H, s, NH], 7.46 and 7.26 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-OC_6H_{13}], 7.43 and 6.88 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-NHMo], 7.01 and 6.94 [1 H, d, $J(HH)_{trans}$ 16 Hz; 1 H, d, $J(HH)_{trans}$ 16 Hz, CH=CH], 6.48 [1 H, s, OH], 5.84, 5.81, and 5.76 [1 H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 3.97 [2 H, t, J(HH) 6.7 Hz, C_6H_4-OCH_2-C_5H_{11}], 2.61, 2.40, 2.37, 2.36, 2.33, and 2.10 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.79 [2 H, qn, $C_6H_4OCH_2$-CH_2-C_4H_9], 1.46 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_3H_7], 1.40-1.30 [4 H, c m, OC_3H_6-C_2H_4-CH_3], 0.91 [3 H, t, J(HH) 6.9 Hz, CH_3]; *m/z* 706 (M - NO), 691 (M -

NO - OH), 650 (M - C_6H_{13}), 295 ($H_2NC_6H_4CH{=}CHC_6H_4OC_6H_{13}$), 211 ($H_2NC_6H_4CH{=}CHC_6H_4OH$). E_f = -1.19 V, ΔE_p = 250 mV, ΔE_p(Fc) = 105 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl(HNC_6H_4CH=CH$C_6H_4OC_8H_{17}$)] [187]

This compound was prepared in similar manner to [168] using 4-n-octyloxy-4'-stilbenamine (0.24 g, 0.74 mmol) in place of n-dodecyl-4-hydroxybenzoate and triethylamine (0.5 cm^3) in place of hexamine, with a reaction time of 2 h. The product was purified by column chromatography on silica using 20% n-hexane/dichloromethane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.31 g, 65%). (Found: C, 54.2; H, 6.3; N, 14.0; M^+, 782. $C_{37}H_{50}BClMoN_8O_2.0.6CH_2Cl_2$ requires C, 54.3; H, 6.2; N, 13.5%; M, 781); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1655 cm^{-1}; δ_H($CDCl_3$) 12.60 [1 H, s, N*H*], 7.54 and 7.45 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-OC_8H_{17}], 7.45 and 6.90 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-NHMo], 7.09 and 6.98 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 5.87 and 5.79 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 3.98 [2 H, t, J(HH) 6.4 Hz, C_6H_4-OCH_2-C_7H_{15}], 2.69, 2.42, 2.39, 2.38, 2,37, and 2.03 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, ($Me_2C_3N_2H$)$_3$], 1.79 [2 H, qn, $C_6H_4OCH_2$-CH_2-C_6H_{13}], 1.46 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_5H_{11}], 1.40-1.30 [8 H, c m, OC_3H_6-C_4H_8-CH_3], 0.89 [3 H, t, J(HH) 6.7 Hz, CH_3]; *m/z* 782 (M^+), 752 (M - NO), 746 (M - Cl), 656 (M - 125), 323 ($H_2NC_6H_4CH{=}CHC_6H_4OC_8H_{17}$), 252 ($H_2NC_6H_4CH{=}CHC_6H_4OC_3H_6$), 211 ($H_2NC_6H_4CH{=}CHC_6H_4OH$), 107 ($H_2CC_6H_4OH$). E_f = -0.78 V, ΔE_p = 160 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I(HNC_6H_4CH=CH$C_6H_4OC_8H_{17}$)] [188]

This compound was prepared in identical manner to [187] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) in place of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-n-octyloxy-4'-stilbenamine (0.22 g, 0.68 mmol). A deep violet solid was obtained (0.38 g, 84%). (Found: C, 49.3; H, 5.6; N, 12.2; M^+, 874. $C_{37}H_{50}BIMoN_8O_2.0.5CH_2Cl_2$ requires C, 49.2; H, 5.6; N, 12.2%; M, 873); $\nu_{max.}$(NH) 3275w, $\nu_{max.}$(NO) 1655 cm^{-1}; δ_H($CDCl_3$) 13.06 [1 H, s, N*H*], 7.61 and 7.46 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-OC_6H_{13}], 7.49 and 6.89 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-NHMo], 7.18 and 6.94 [1 H, d, $J(HH)_{trans}$ 16.1 Hz; 1 H, d,

$J(HH)_{trans}$ 16.1 Hz, C*H*=C*H*], 5.93, 5.86, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.98 [2 H, t, J(HH) 6.7 Hz, C_6H_4-OCH_2-C_7H_{15}], 2.72, 2.48, 2.46, 2.38, 2,37, and 2.00 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(MeC_3N_2H)_3$], 1.80 [2 H, qn, $C_6H_4OCH_2$-CH_2-C_6H_{13}], 1.47 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_5H_{11}], 1.40-1.30 [8 H, c m, OC_3H_6-C_4H_8-CH_3], 0.89 [3 H, t, J(HH) 6.9 Hz, CH_3]; *m/z* 874 (M^+), 747 (M - 125), 323 ($H_2NC_6H_4CH$=$CHC_6H_4OC_8H_{17}$), 211 ($H_2NC_6H_4CH$=CHC_6H_4OH), 128 (I). E_f = -0.74 V, ΔE_p = 120 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(HNC_6H_4CH=$CHC_6H_4OC_8H_{17}$)$_2$] [189]

This compound was prepared in similar manner to [173] using [188] (0.11 g, 0.13 mmol) in place of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I(HN$C_6H_4C_{10}H_{21}$)] and 4-n-octyloxy-4'-stilbenamine (0.065 g, 0.20 mmol) in place of 4-decylaniline. Upon addition of [188] the solution was stirred under reflux for 2 h, and cooled before filtration. The product was purified by column chromatography on alumina 90 using 40% n-hexane in dichloromethane. This afforded a deep emerald green solid (0.11 g, 82%) (Found: C, 65.3; H, 7.4; N, 10.3; M^+, 1069. $C_{59}H_{78}BMoN_9O_3.0.25CH_2Cl_2$ requires C, 65.3; H, 7.3; N, 11.6%; M, 1068); $\nu_{max.}$(NH) 3300m, $\nu_{max.}$(NO) 1635 cm^{-1}; $\delta_H(CDCl_3)$ 8.90 [2 H, s, 2 x N*H*], 7.40 and 7.27 [4 H, d, J(HH) 8.7 Hz; 4 H, d, J(HH) 8.7 Hz, 2 x C_6H_4-OC_8H_{17}], 7.40 and 6.87 [4 H, d, J(HH) 8.7 Hz; 4 H, d, J(HH) 8.7 Hz, 2 x C_6H_4-NHMo], 6.93 [4 H, s, 2 x C*H*=C*H*], 5.96 and 5.75 [1 H, s; 2 H, s, $(Me_2C_3N_2H)_3$], 3.97 [4 H, t, J(HH) 6.6 Hz, 2 x C_6H_4-OCH_2-C_7H_{15}], 2.47, 2.35, and 2.27 [3 H, s; 9 H, s; 6 H, s, $(MeC_3N_2H)_3$], 1.78 [4 H, qn, 2 x $C_6H_4OCH_2$-CH_2-C_6H_{13}], 1.46 [4 H, qn, 2 x $C_6H_4OC_2H_4$-CH_2-C_5H_{11}], 1.40-1.30 [16 H, c m, 2 x OC_3H_6-C_4H_8-CH_3], 0.89 [6 H, t, J(HH) 6.9 Hz, 2 x CH_3]; *m/z* 1069 (M^+), 1037 (M - NO), 990 (M - 78), 926 (M - C_6H_{13}), 323 ($H_2NC_6H_4CH$=$CHC_6H_4OC_8H_{17}$), 211 ($H_2NC_6H_4CH$=CHC_6H_4OH). E_f = -1.20 V, ΔE_p = 290 mV, ΔE_p(Fc) = 105 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl(HNC_6H_4CH=$CHC_6H_4OC_{12}H_{25}$)] [190]

This compound was prepared in similar manner to [168] using 4-n-dodecyloxy-4'-stilbenamine (0.28 g, 0.74 mmol) in place of n-dodecyl-4-hydroxybenzoate and triethylamine (0.5 cm^3) in place of hexamine, with a reaction time of 2 h. The product was purified by

column chromatography on silica using 20% n-hexane/dichloromethane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.37 g, 73%). (Found: C, 57.6; H, 6.8; N, 12.7; M^+, 838. $C_{41}H_{58}BClMoN_8O_2.0.3CH_2Cl_2$ requires C, 57.5; H, 6.8; N, 13.0%; M, 837); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1655 cm^{-1}; $\delta_H(CDCl_3)$ 12.60 [1 H, s, NH], 7.54 and 7.45 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-$OC_{12}H_{25}$], 7.45 and 6.90 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-NHMo], 7.09 and 6.98 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, CH=CH], 5.87 and 5.79 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.98 [2 H, t, J(HH) 6.4 Hz, C_6H_4-OCH_2-$C_{11}H_{23}$], 2.69, 2.42, 2.39, 2.38, 2,37, and 2.03 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 1.79 [2 H, qn, $C_6H_4OCH_2$-CH_2-$C_{10}H_{21}$], 1.46 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_9H_{19}], 1.40-1.30 [16 H, c m, OC_3H_6-C_8H_{16}-CH_3], 0.88 [3 H, t, J(HH) 6.7 Hz, CH_3]; *m/z* 838 (M^+), 807 (M - NO), 802 (M - Cl), 712 (M - 125), 379 ($H_2NC_6H_4CH$=$CHC_6H_4OC_{12}H_{25}$), 252 ($H_2NC_6H_4CH$=$CHC_6H_4OC_3H_6$), 211 ($H_2NC_6H_4CH$=CHC_6H_4OH), 107 ($H_2CC_6H_4OH$). E_f = -0.78 V, ΔE_p = 200 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I(HNC_6H_4CH=CH$C_6H_4OC_{12}H_{25}$)] [191]

This compound was prepared in identical manner to [190] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) in place of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$] and 4-n-dodecyloxy-4'-stilbenamine (0.26 g, 0.68 mmol). A deep violet solid was obtained (0.36 g, 75%). (Found: C, 50.2; H, 6.0; N, 11.8; M^+, 930. $C_{41}H_{58}BIMoN_8O_2$.$0.8CH_2Cl_2$ requires C, 50.4; H, 6.0; N, 11.2%; M, 929); $\nu_{max.}$(NH) 3275w, $\nu_{max.}$(NO) 1655 cm^{-1}; $\delta_H(CDCl_3)$ 13.06 [1 H, s, NH], 7.61 and 7.46 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-$OC_{12}H_{25}$], 7.49 and 6.89 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4-NHMo], 7.18 and 6.94 [1 H, d, $J(HH)_{trans}$ 16.1 Hz; 1 H, d, $J(HH)_{trans}$ 16.1 Hz, CH=CH], 5.93, 5.86, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.98 [2 H, t, J(HH) 6.7 Hz, C_6H_4-OCH_2-$C_{11}H_{23}$], 2.72, 2.48, 2.46, 2.38, 2,37, and 2.00 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 1.80 [2 H, qn, $C_6H_4OCH_2$-CH_2-$C_{10}H_{21}$], 1.47 [2 H, qn, $C_6H_4OC_2H_4$-CH_2-C_9H_{19}], 1.40-1.30 [16 H, c m, OC_3H_6-C_8H_{16}-CH_3], 0.88 [3 H, t, J(HH) 6.9 Hz, CH_3]; *m/z* 930 (M^+), 803 (M - 125), 379 ($H_2NC_6H_4CH$=$CHC_6H_4OC_{12}H_{25}$), 211 ($H_2NC_6H_4CH$=CHC_6H_4OH), 128 (I). E_f = -0.74 V, ΔE_p = 110 mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(HNC_6H_4CH=$CHC_6H_4OC_{12}H_{25}$)$_2$] [192]

This compound was prepared in identical manner to [173] using [191] (0.12 g, 0.13 mmol) in place of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I($HNC_6H_4C_{10}H_{21}$)] and 4-n-dodecyloxy-4'-stilbenamine (0.075 g, 0.20 mmol) in place of 4-decylaniline. Upon addition of [191] the solution was stirred at reflux for 2 h, and cooled before filtration. The product was purified by column chromatography on alumina 90 using 40% n-hexane in dichloromethane. This afforded a deep emerald green solid (0.070 g, 46%) (Found: C, 68.1; H, 8.4; N, 9.4. $C_{67}H_{94}BMoN_9O_3$ requires C, 68.2; H, 8.0; N, 10.7%; M, 1180); $\nu_{max.}$(NH) 3300m, $\nu_{max.}$(NO) 1635 cm^{-1}; δ_H($CDCl_3$) 8.90 [2 H, s, 2 x N*H*], 7.40 and 7.27 [4 H, d, J(HH) 8.7 Hz; 4 H, d, J(HH) 8.7 Hz, 2 x C_6H_4-$OC_{12}H_{25}$], 7.40 and 6.87 [4 H, d, J(HH) 8.7 Hz; 4 H, d, J(HH) 8.7 Hz, 2 x C_6H_4-NHMo], 6.93 [4 H, s, 2 x C*H*=C*H*], 5.96 and 5.75 [1 H, s; 2 H, s, ($Me_2C_3N_2H$)$_3$], 3.97 [4 H, t, J(HH) 6.6 Hz, 2 x C_6H_4-OCH_2-$C_{11}H_{23}$], 2.47, 2.35, and 2.27 [3 H, s; 9 H, s; 6 H, s, ($Me_2C_3N_2H$)$_3$], 1.78 [4 H, qn, 2 x $C_6H_4OCH_2$-CH_2-$C_{10}H_{21}$], 1.46 [4 H, qn, 2 x $C_6H_4OC_2H_4$-CH_2-C_9H_{19}], 1.40-1.30 [32 H, c m, 2 x OC_3H_6-C_8H_{16}-CH_3], 0.88 [6 H, t, J(HH) 6.9 Hz, 2 x CH_3]; *m/z* 1037 (M - NO - C_8H_{17}), 990, 925 (M - $OC_{12}H_{25}$ - C_5H_{11}), 895 (M - $OC_{12}H_{25}$ - C_5H_{11} - NO), 379 ($H_2NC_6H_4CH$=$CHC_6H_4OC_{12}H_{25}$), 211 ($H_2NC_6H_4CH$=CHC_6H_4OH). E_f = -1.20 V, ΔE_p = 230 mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl($OC_{27}H_{45}$)] [193]

This compound was prepared in similar manner to [168] using (-)-cholesterol (0.26 g, 0.67 mmol) in place of n-dodecyl-4-hydroxybenzoate and triethylamine (0.5 cm^3) in place of hexamine, with a reaction time of 1 h. The product was purified by column chromatography on silica using dichloromethane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a pale blue-purple solid (0.36 g, 71%). m.p. 230 °C (dec.) (Found: C, 59.5; H, 7.8; N, 11.7; M^+, 843. $C_{42}H_{67}BClMoN_7O_2$ requires C, 59.8; H, 8.0; N, 11.6%; M, 844); $\nu_{max.}$(NO) 1665 cm^{-1}; δ_H($CDCl_3$) 6.06 [1 H, o, Mo-OC*H*], 5.90, 5.89, 5.84, and 5.76 [½ H, s; ½ H, s; 1 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 5.63 and 5.38 [1 H, d, d, =C*H*], 3.15 and 2.73 [1 H, dd, dd, OCH-C*H*], 2.53, 2.52, 2.42, 2.39, 2.38, and 2.36 [18 H, s, s, s, s, s, s, ($Me_2C_3N_2H$)$_3$], 2.20-0.80 [39 H, c m, $C_{27}H_{39}$, inc. CH_3

at 1.04(a), 0.88(c), 0.88(c), 0.86(d), and 0.86(d)], 0.69 [3 H, s, CH_3(b)], ; *m/z* 843 (M^+), 809 (M - Cl), 460 (M - $OC_{27}H_{45}$), 424 (M - $OC_{27}H_{45}$ - Cl), 386 ($OC_{27}H_{45}$), 369 ($OC_{27}H_{45}$ - O - H). E_f = -0.71 V, ΔE_p = 210 mV, ΔE_p(Fc) = 120 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}I($OC_{27}H_{45}$)] [194]

This compound was prepared in identical manner to [193] using [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(I)_2$].C_7H_8 (0.40 g, 0.52 mmol) in place of [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] and (-)-cholesterol (0.25 g, 0.65 mmol). A pale lime green solid was obtained (0.43 g, 88%). m.p. 230 °C (dec.) (Found: C, 53.7; H, 7.2; N, 10.7; M^+, 934. $C_{42}H_{67}BIMoN_7O_2$ requires C, 53.9; H, 7.2; N, 10.5%; M, 936); $\nu_{max.}$(NO) 1670 cm^{-1}; $\delta_H(CDCl_3)$ 5.95-5.75 [4 H, inc. br m, Mo-OC*H*; 5.86, 5.85, and 5.82 ($Me_2C_3N_2H)_3$], 5.62 and 5.37 [1 H, d, d, =C*H*], 3.23 and 2.83 [1 H, dd, dd, OCH-C*H*], 2.54, 2.53, 2.49, 2.40, 2.39, 2.36, and 2.35 [18 H, s, s, s, s, s, s, s, ($Me_2C_3N_2H)_3$], 2.20-0.80 [39 H, c m, $C_{27}H_{39}$, inc. CH_3 at 1.04(a), 0.88(c), 0.88(c), 0.86(d), and 0.86(d)], 0.69 [3 H, s, CH_3(b)], ; *m/z* 934 (M^+), 808 (M - I), 551 (M - $OC_{27}H_{45}$), 424 (M - $OC_{27}H_{45}$ - I), 386 ($OC_{27}H_{45}$), 369 ($OC_{27}H_{45}$ - O - H). Irreversible wave at E_p^c = -0.67 V.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(OC_8H_{17})_2$] [195]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(I)_2$].C_7H_8 (0.40 g, 0.52 mmol) and n-octanol (0.5 g, 3.84 mmol) using the procedure described for [168] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine, with a reaction time of 30 min. Purification was carried out using column chromatography on silica with dichloromethane as eluent, the major pink band being collected. Recrystallisation from diethyl ether produced a pale pink solid (0.29 g, 82%). (Found: C, 54.0; H, 8.5; N, 14.6%; M^+, 682. $C_{31}H_{55}BMoN_7O_3$ requires C, 54.6; H, 8.3; N, 14.4%; M, 682); $\nu_{max.}$(NO) 1640 cm^{-1}; $\delta_H(CDCl_3)$ 5.79 and 5.72 [2 H, s; 1 H, s ($Me_2C_3N_2H)_3$], 5.52 and 5.29 [2 H, td, $J(HH)_{gem}$ 10.4 Hz, $J(HH)_{vic}$ 7.5 Hz; 2 H, td, $J(HH)_{gem}$ 10.5 Hz, $J(HH)_{vic}$ 7.4 Hz, 2 x OCH_2-C_7H_{15}], 2.55 and 2.31 [6 H, s; 12 H, s, ($Me_2C_3N_2H)_3$], 1.78 [4 H, qn, 2 x OCH_2-CH_2-C_6H_{13}], 1.50-1.20 [20 H, c m, 2 x OC_2H_4-C_5H_{10}-CH_3], 0.89 [6 H, t, J(HH) 7.0 Hz, 2 x CH_3]; *m/z* 682 (M^+), 652 (M - NO), 553 (M -

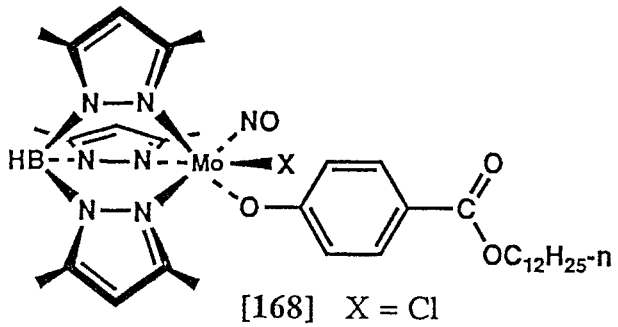
OC_8H_{17}), 538 (M - OC_8H_{17} - CH_3), 523 (M - OC_8H_{17} - NO), 424 (M - 2 x OC_8H_{17}), 410 (M - OC_8H_{17} - NO - C_8H_{17}), 394 (M - 2 x OC_8H_{17} - NO). E_f = -1.35 V, ΔE_p = 500 mV, ΔE_p(Fc) = 85 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(OC_8H_{17})($OC_{27}H_{45}$)] [196]

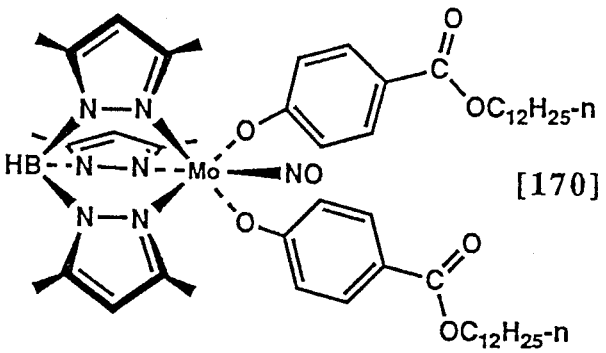
This compound was prepared from [195] (0.15 g, 0.22 mmol) and (-)-cholesterol (1.0 g, 2.59 mmol) using the procedure described for [168] except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine, with a reaction time of 17 h. Purification was carried out using column chromatography on silica with 40% n-hexane/dichloromethane as eluent, the major pink band being collected. This was repeated to ensure purity. Recrystallisation from diethyl ether produced a pale pink solid (0.14 g, 68%). (Found: C, 63.5; H, 9.4; N, 10.7; M^+, 938. $C_{60}H_{84}BMoN_7O_3$ requires C, 64.0; H, 9.0; N, 10.5%; M, 938); $\nu_{max.}$(NO) 1640 cm^{-1}; $\delta_H(CDCl_3)$ 5.78 and 5.72 [2 H, s; 1 H, s, ($Me_2C_3N_2H$)$_3$], 5.55-5.25 [4 H, c m, OCH_2, OCH, =CH], 2.80 [1 H, dd, OCH-CH], 2.57, 2.55, 2.50, 2.48, and 2.31 [18 H, s, s, s, s, s, ($Me_2C_3N_2H$)$_3$], 2.10-0.60 [54 H, c m, C_7H_{15} + $C_{27}H_{39}$, inc. CH_3 at 1.03(a), 0.94, 0.91, 0.88(c), 0.88(c), 0.86(d), 0.86(d)], 0.69 [3 H, s, CH_3(b)], ; *m/z* 937 (M^+), 907 (M - NO), 809 (M - OC_8H_{17}), 552 (M - $OC_{27}H_{45}$), 424 (M - OC_8H_{17} - $OC_{27}H_{45}$). E_f = -1.37 V, ΔE_p = 490 mV, ΔE_p(Fc) = 85 mV.

Fig. 52

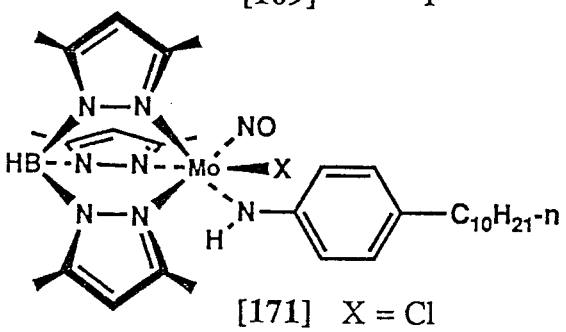
Complexes Prepared in Chapter Four



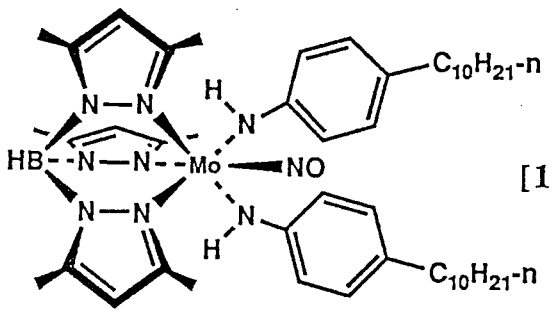
[168] X = Cl
[169] I



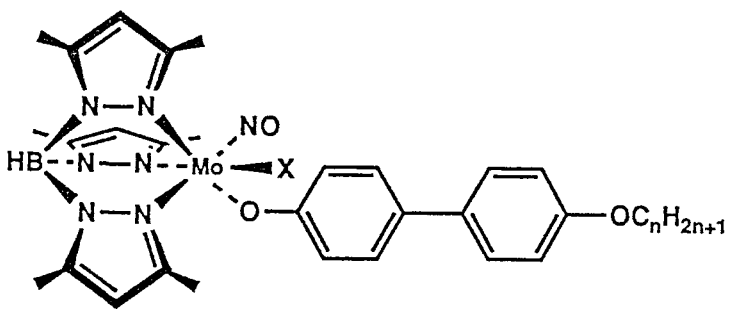
[170]



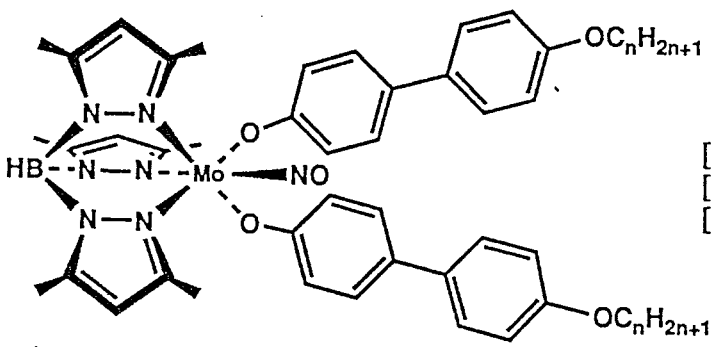
[171] X = Cl
[172] I



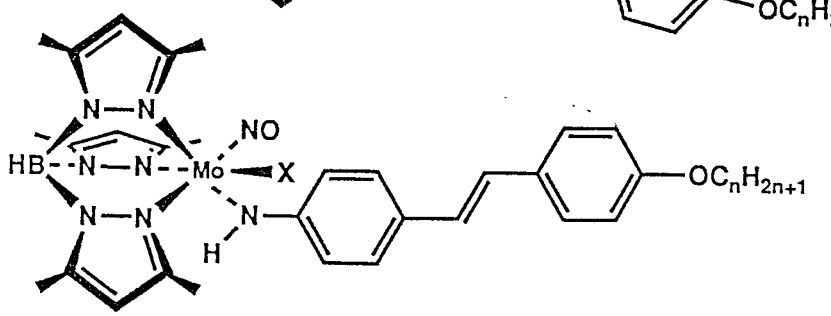
[173]



[174]	n = 6	X = Cl
[175]		I
[177]	8	Cl
[178]		I
[180]	12	Cl
[181]		I

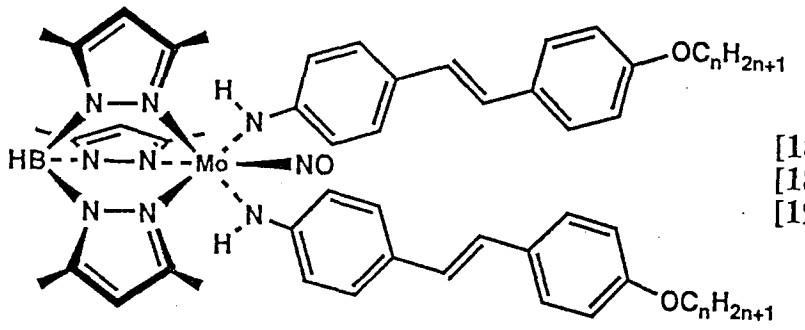


[176]	n = 6
[179]	8
[182]	12

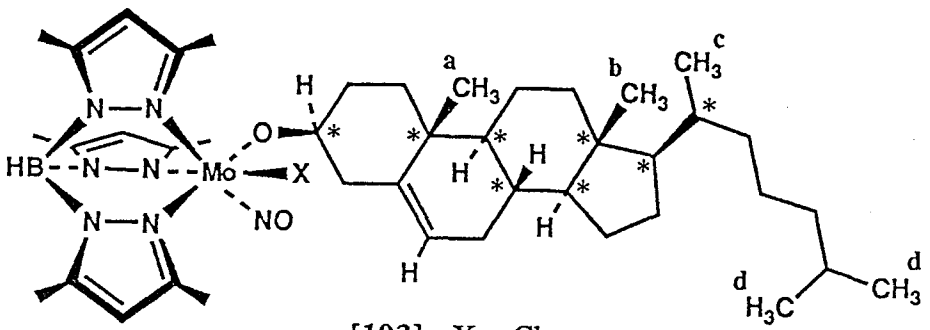


[183]	n = 6	X = Cl
[184]		I
[186]		OH
[187]	8	Cl
[188]		I
[190]	12	Cl
[191]		I

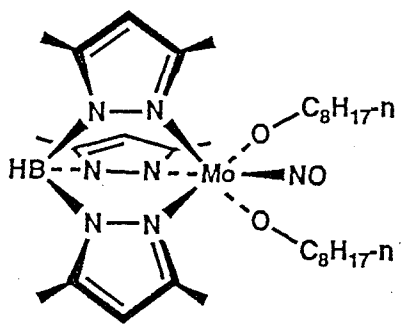
Fig. 52 (*Continued*)



[185] n = 6
[189] 8
[192] 12



[193] X = Cl
[194] I
[196] OC_8H_{17}-n



[195]

CHAPTER FIVE

MISCELLANEOUS MOLYBDENUM MONONITROSYL COMPLEXES: CHIRAL, BIMETALLIC, POLYENE, AND CHARGED SPECIES

VI-1 DISCUSSION

In the preceding Chapters Two and Three only relatively simple complexes were examined in which achiral donor-substituted ligands are attached to molybdenum or tungsten mononitrosyl centres. All of the compounds prepared are neutral and contain a single, 16-electron $\{M(NO)L^*\}^{2+}$ (M = Mo or W) metal centre which is thought to act as an electron acceptor function. However, the chemistry of molybdenum mononitrosyl complexes of trispyrazolylborate and other ligands is extremely diverse, and many aspects remain to be explored with the aim of preparing compounds for NLO. In this Chapter, the objective is to utilise some of these aspects to prepare complexes which might be of interest for second or third order NLO effects.

VI-1.1 CHIRAL SYSTEMS

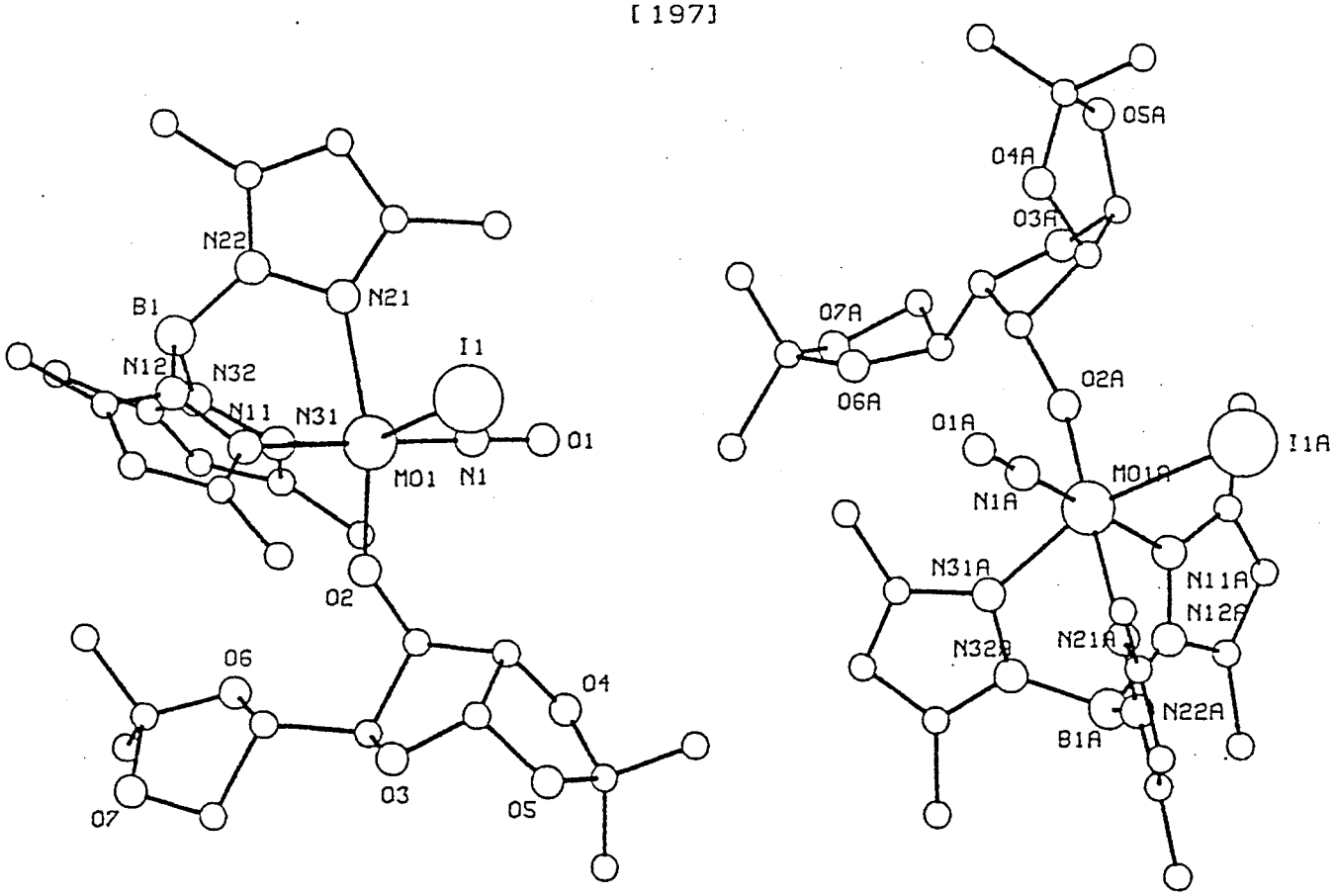
Although the octahedral metal centre in complexes of formula [M(NO)L*(X)(Y)] (where M = Mo or W, X ≠ Y) is chiral, attempts at resolution of the two enantiomeric forms have only proven possible in rare cases where a chiral co-ligand is present. Hence the three complexes [Mo(NO)L*(I){3-*O*-1,2:5,6-di-isopropylidene-α-D-gluco-furanoate}] [197], [Mo(NO)L*(Cl){(1*S*,2*R*,5*S*)-(+)-mentholate}] [198], and [Mo(NO)L*(Cl){(*R*)-(+)-methylbenzamide}] [199], the structures of which are shown in Figs. 53 and 54, have recently been isolated in the form of single pure diastereomers and characterised by single crystal X-ray structural determinations.[274,275]

Fig. 53

X-ray Crystal Structure of

[Mo(NO)L*(I){3-*O*-1,2:5,6-di-isopropylidene-α-D-glucofuranoate}][274]

[197]



Two of these resolved complexes and the resolved tungsten analogue of [199] have been tested for SHG using the Kurtz powder test at 1,907 nm, but only exhibit weak if any SHG. Harmonic intensities with respect to urea powder are 0.245 for [197], 0.074 for [198], and zero for [W(NO)L*(Cl){(*R*)-(+)-methylbenzamide}].[145] The saturated nature of the parts of these ligands bound to the metal centre may account for these disappointing results in that the molecules are not highly polarisable in the region of the acceptor substituent. However, there may also be structural reasons for the low SHG intensities observed. The single crystal X-ray structure of the sugar complex [197] shows that this molecule crystallises in the monoclinic space group *P*2$_1$ with two independent molecules in the asymmetric unit (Fig. 53). It has previously been demonstrated that, under these circumstances, it

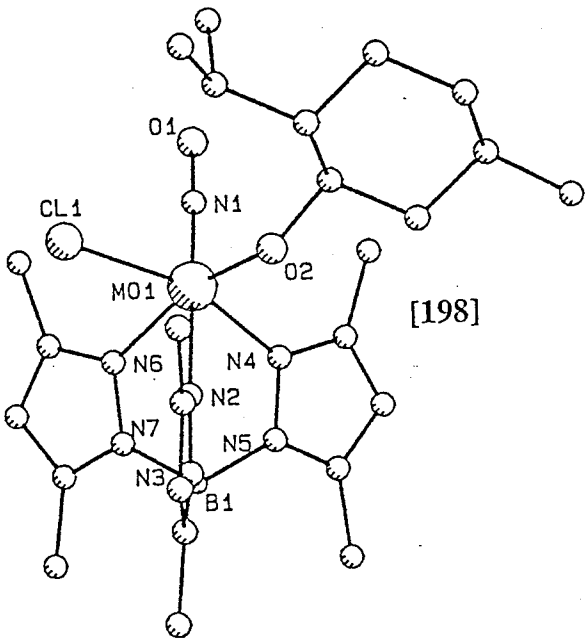
is possible for the molecular hyperpolarisability, β, of one molecule in the unit cell to be orientated so as to oppose that of the other molecule.[58] This produces a pseudo-centrosymmetric situation with respect to the hyperpolarisability, resulting in low SHG intensities despite the presence of a chiral molecule.

Fig. 54

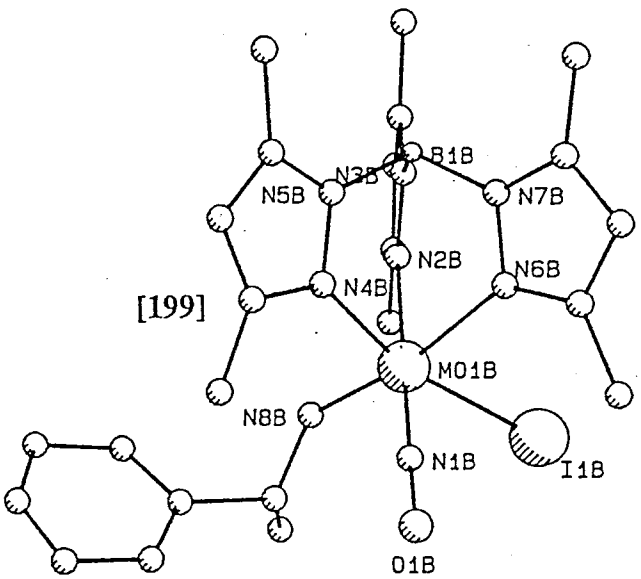
X-ray Crystal Structures of

[Mo(NO)L*(Cl){(1*S*,2*R*,5*S*)-(+)-mentholate}][275] [198]

and [Mo(NO)L*(Cl){(*R*)-(+)-methylbenzamide}][275] [199]



[198]



[199]

It is apparent from these results that merely isolating resolved {M(NO)L*} complexes with chiral co-ligands is insufficient to produce materials exhibiting strong SHG. The single crystal X-ray diffraction studies reported in Chapter Two show that the complexes [M(NO)L*(Cl)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] (M = Mo or W) undergo spontaneous resolution through each enantiomer forming discrete crystals which exclude the other. However, this represents a fortuitous result which is not general for {M(NO)L*} complexes of achiral co-ligands. If the controlled resolution of [M(NO)L*(X)(Y)] complexes containing highly polarisable achiral co-ligands could be achieved, then this would facilitate the preparation of materials likely to exhibit bulk NLO properties.

VI-1.1(a) Resolution of Metal Complexes

The resolution of metal complexes containing a chiral metal centre, but no chiral ligands, is of interest for a number of reasons other than their use in NLO. Particularly attractive to chemists is the potential held by such compounds for asymmetric organic synthesis by stereocontrolled reactions of metal-bound species.[276] However, apart from the use of chromatographic techniques in the resolution of various charged complexes,[277] success in resolving chiral complexes has to date been achieved with only a small number of species.

In this context the findings of greatest significance have come from work carried out over the last 20 years involving neutral cyclopentadienyl complexes of manganese and iron,[278] which has recently attracted industrial interest. The approach used in these studies has been one of asymmetric induction, whereby diastereomeric complexes are resolved and the chiral ligand then replaced by an achiral one with retention of stereochemistry at the metal centre. The chiral ligand chosen is usually a menthyl derivative, and resolution is achieved using solubility differences. Very recently, some chiral cationic cyclopentadienyl molybdenum complexes of 2H-pyran have been resolved and used to effect the enantiospecific synthesis of various pyran derivatives.[279] Other workers have reported the successful liquid chromatographic resolution of chiral metallocene derivatives using β-cyclodextrin as a chiral stationary phase.[280]

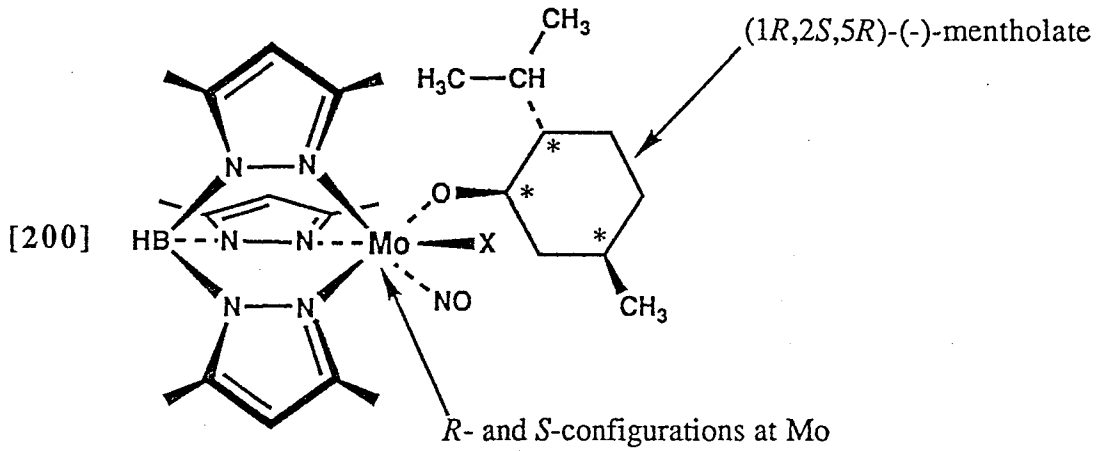
VI-1.1(b) Asymmetric Induction Experiments

An asymmetric induction approach has been attempted with molybdenum mononitrosyl derivatives along the following lines. The known mentholate chloride complex [Mo(NO)L*(Cl){OC_6H_{11}}] [200] (Fig. 55) was prepared in straightforward fashion by reaction of [Mo(NO)L*$(Cl)_2$] with commercial (−)-menthol, and resolved into two diastereomers by column chromatography. Resolution of the iodo analogue was not successful. One chloride diastereomer was then reacted with various aromatic ligands and the products analysed by

polarimetry. Aniline and thiophenol were found to give only low degrees of menthol displacement even in the presence of triethylamine under reflux. However, reaction with 4-nitrophenol did give significant replacement, and the phenolate product was separated by column chromatography. Polarimetric study revealed that this product had zero optical rotation and was therefore racemic.

Fig. 55

[Mo(NO)L*(Cl){(1*R*,2*S*,5*R*)-(-)-mentholate}]



A timed reaction between resolved [200] and 4-nitrophenol was also carried out, but samples removed at a number of intervals showed only a smooth gradual decline in rotation which is likely to be a result of loss of mentholate complex and shows no evidence for the formation of a resolved chiral product.

Hence this approach was not pursued further, the conclusion being that, although significant replacement of menthol can occur, no resolved products were isolated. This may either be because the mechanism of substitution is such that no retention of stereochemistry occurs, or because a chiral product is formed but racemises rapidly under the conditions of the experiment.

VI-1.1(c) Chiral Chromatography Experiments

Several experiments using β-cyclodextrin as a chiral column chromatographic support were also carried out. These involved the

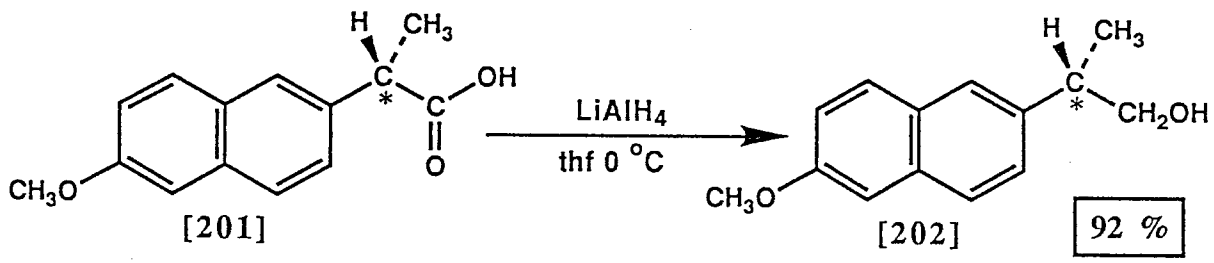
racemic molybdenum complexes [Mo(NO)L*(Cl)(HNC$_6$H$_4$-4-Fc)], [Mo(NO)L*(Cl){OC$_6$H$_4$CO$_2$C$_{12}$H$_{25}$}], [Mo(NO)L*(Cl)(OC$_6$H$_4$N=NC$_6$H$_4$-4-Fc)], and [Mo(NO)L*(Cl){HNC$_6$H$_4$-4-NH$_2$}], but polarimetic measurements on various fractions revealed no separation of enantiomers. The lack of ready availability of other possible chiral stationary phases precluded any further work in this area.

VI-1.1(d) Complexes of a Chiral Naphthalene Derivative

The chiral naphthalene derivative (-)-2-(6-methoxy-2-naphthyl)-1-propanol [202], which has found use as an analgesic,[281] was prepared readily via a lithium aluminium hydride reduction of commercial (+)-2-(6-methoxy-2-naphthyl)-1-propanoic acid [201] as shown in Fig. 56. Other workers have employed diborane in thf to carry out this reduction,[281] but a slightly improved yield is achieved by use of LiAlH$_4$.

Fig. 56

Synthesis of (-)-2-(6-Methoxy-2-naphthyl)-1-propanol [202]

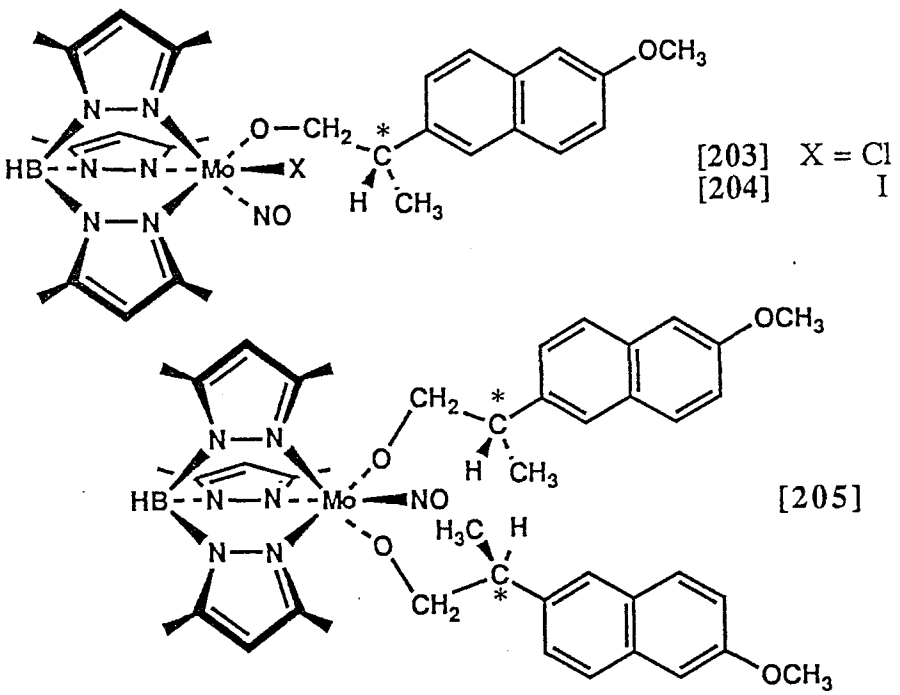


This alcohol was chosen because it possesses a donor-substituted aromatic portion as well as being a resolved chiral molecule. It was used to prepare three {Mo(NO)L*} complexes, the mono-chloride [203], mono-iodide [204], and bis-substituted [205] derivatives (Fig. 57) using the usual synthetic techniques. These were all fully characterised using the standard physical techniques, but were not separated into discrete diastereomers. All gave good elemental analyses for C, H, and N, exhibited $\nu_{max.}$(NO) at the expected frequencies, showed molecular ion envelopes along with the predictable fragmentation patterns, and gave reduction waves at potentials in accord with their

formulations. ^1H n.m.r. spectroscopy confirmed that all three compounds were isolated as mixtures of diastereomers, as evidenced by the occurrence of up to nine signals for the pyrazolyl methyl groups. Also, the chiral ligand OCH_2 protons give two or more multiplets, and the CH_3 groups give a pair of doublets in each case. For the bis-substituted complex the α-proton also shows as two discrete multiplets, the ratio of which is roughly 1:1. Both of the monosubstituted derivatives, [203] and [204] were tested for powder SHG at 1,907 nm but gave only very weak signals of 0.004 and 0.007 times urea respectively.

Fig. 57

Complexes of the (-)-2-(6-Methoxy-2-naphthyl)-1-propoxide Ligand

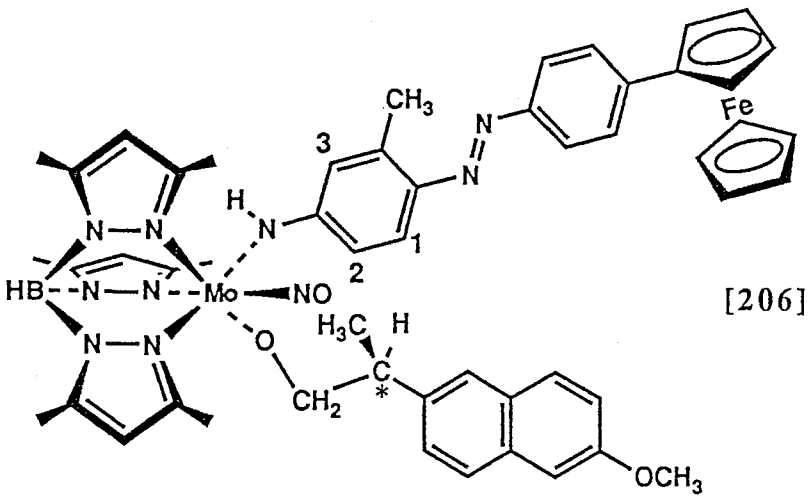


Also prepared using this chiral ligand was a mixed-ligand complex [206] (Fig. 58) containing the ferrocenyl amine ligand 4-amino-2-methyl-4'-ferrocenylazobenzene. This was synthesised by reaction of $[Mo(NO)L^*(I)(HNC_6H_3\text{-}3\text{-}CH_3\text{-}4\text{-}N{=}NC_6H_4\text{-}4\text{-}Fc)]$ with [202] in the presence of triethylamine. Initial purification was effected by column chromatography which yielded a mixture of at least three diastereomers. This mixture was characterised by i.r., elemental analyses, mass spectrometry, and cyclic voltammetry. The mass spectrum did not show a molecular ion, but a number of envelopes

have been assigned to fragments which are in keeping with the proposed formulation. The elemental analyses were carried out on a sample which was dried at 50 °C for 24 h, and this shows the presence of large amounts of both dichloromethane and n-hexane. These solvents were also detected by ^{1}H n.m.r. spectroscopy.

Fig. 58

Mixed Complex Containing (-)-2-(6-Methoxy-2-naphthyl)-1-propoxide and 4-Amido-2-methyl-4'-ferrocenylazobenzene Ligands



[206]

VI-1.1(d)(i) Separation of Diastereomers of [206]

Separation of the isomers present in complex [206] was carried out using a large (65 x 2½ cm) silica column with a 35% n-hexane/dichloromethane solution as eluent. Three fractions were collected and these were studied by ^{1}H n.m.r. spectroscopy.

Fraction 1 (206-F1): accounted for 56% of the whole, and appears to contain two diastereomers as evidenced by the presence of a single signal for the amide proton at 9.66 ppm, but multiple signals for most other protons. The pyrazolyl 4-protons show six singlets and the pyrazolyl methyls twelve. Also, the naphthyl ligand OCH_2 and α-protons show two or more multiplets, and the ferrocenyl C_5H_4 signals show evidence of two triplets for each pair. The complete spectrum for 206-F1 is shown in Fig. 59, and an expansion of the region 5.9-4.9 ppm, showing the pyrazolyl 4-proton and naphthyl ligand OCH_2 signals, is shown in Fig. 60.

Fig. 59

^{1}H n.m.r. spectrum of 206-F1

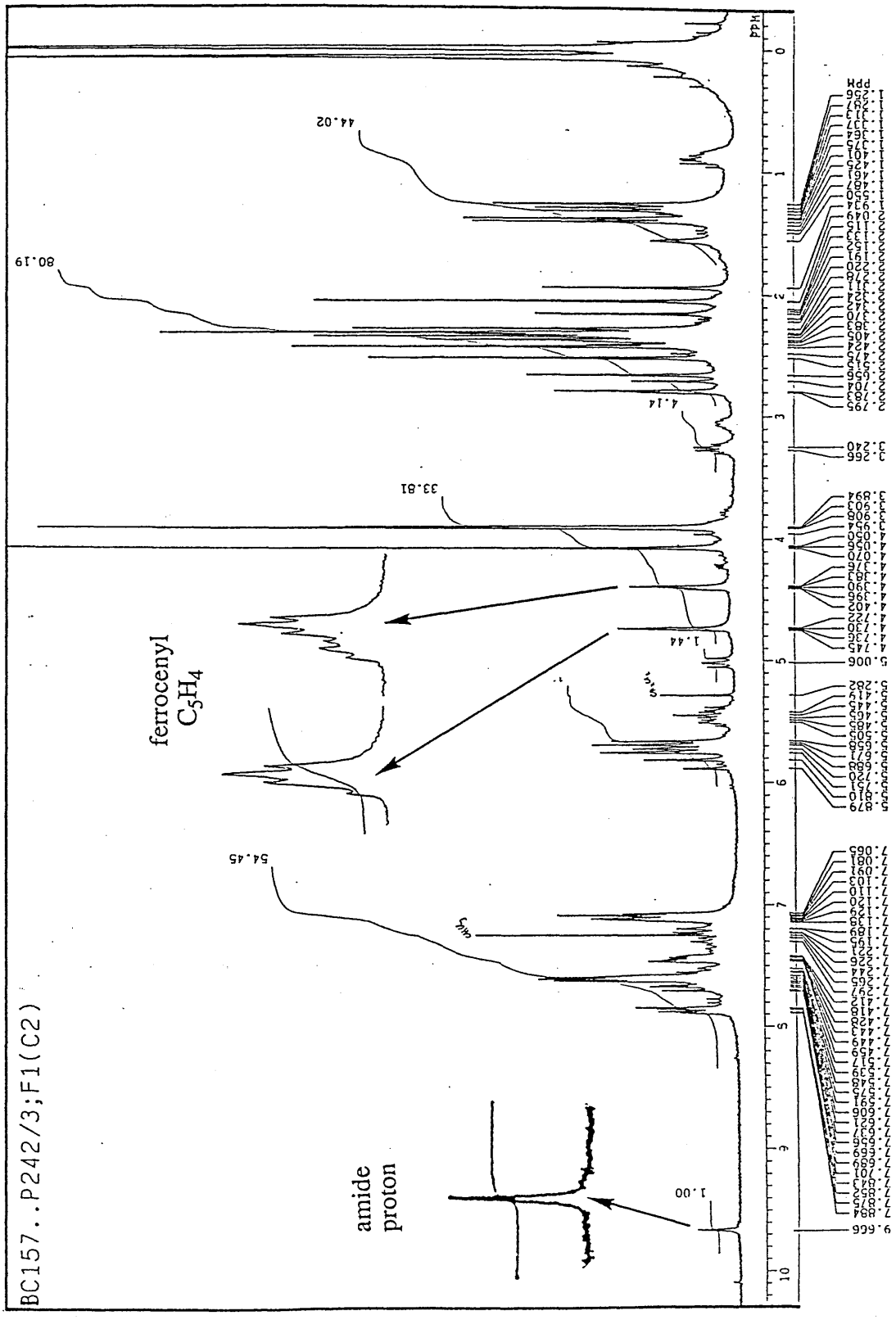
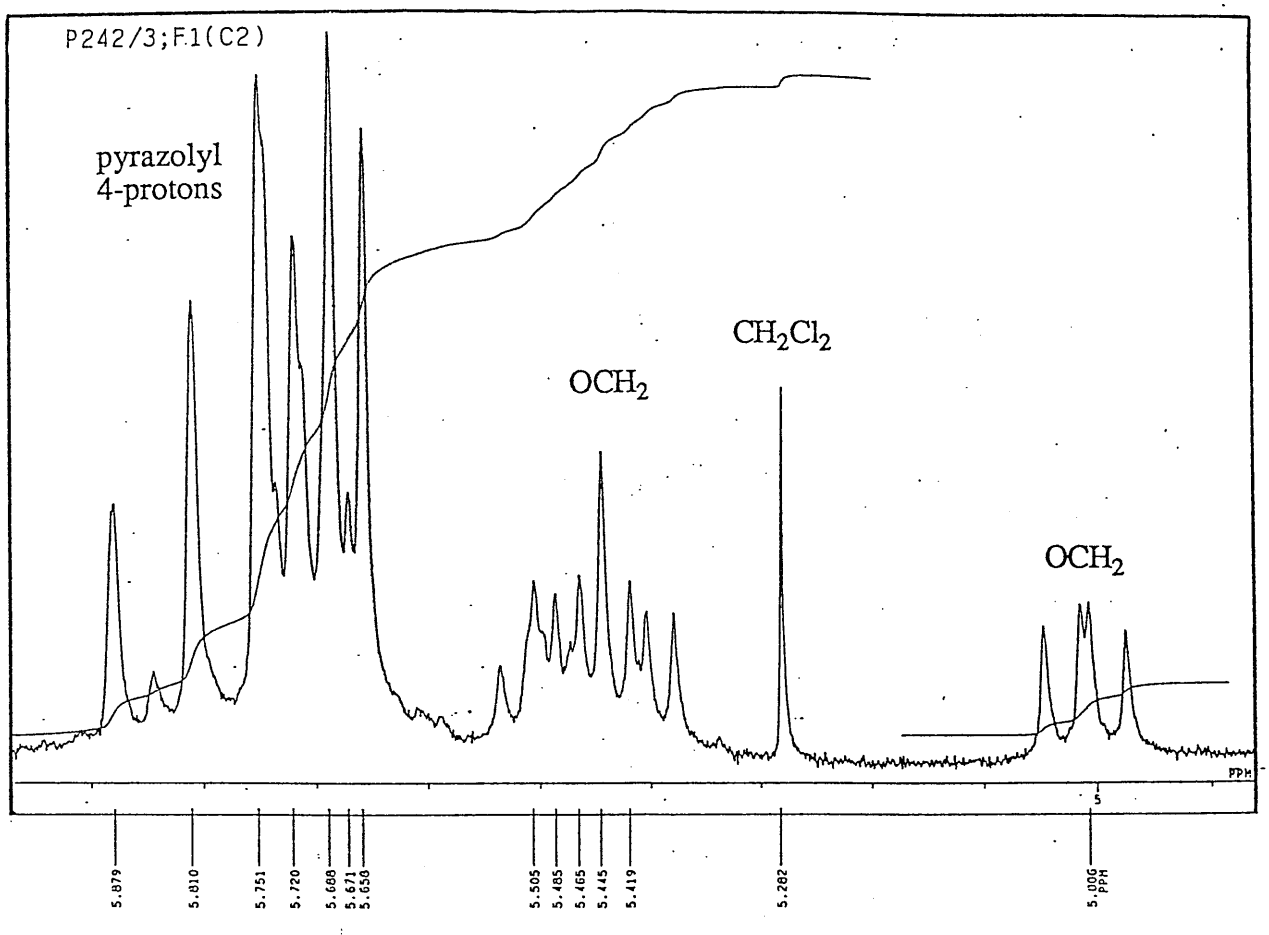


Fig. 60

Expansion of the region 5.9-4.9 ppm for 206-F1



Fraction 2 (206-F2): represented 21% of the whole, and also contains a mixture of diastereomers. Two amide signals at 9.66 and 9.62 ppm in a ratio of roughly 2:1 along with very complex patterns for other regions are observed. The complete spectrum for 206-F2 is shown in Fig. 61.

Fraction 3 (206-F3): accounted for 23% of the whole, and seems to consist of only one single diastereomer. The ^1H n.m.r. spectrum shows a single amide signal at 9.62 ppm, only three pyrazolyl 4-proton signals, two OCH_2 multiplets, one α-proton multiplet, and six pyrazolyl methyl singlets. Although traces of impurity can be seen in the spectrum, this fraction indicates a successful resolution of a diastereomer, and gave $[\alpha]_{546} = -2315°(CH_2Cl_2)$.

The complete spectrum for 206-F3 is shown in Fig. 62, and an expansion of the region 6.0-5.2 ppm, showing the pyrazolyl 4-proton and naphthyl ligand OCH_2 signals, is shown in Fig. 63.

Fig. 61

^{1}H n.m.r. spectrum of 206-F2

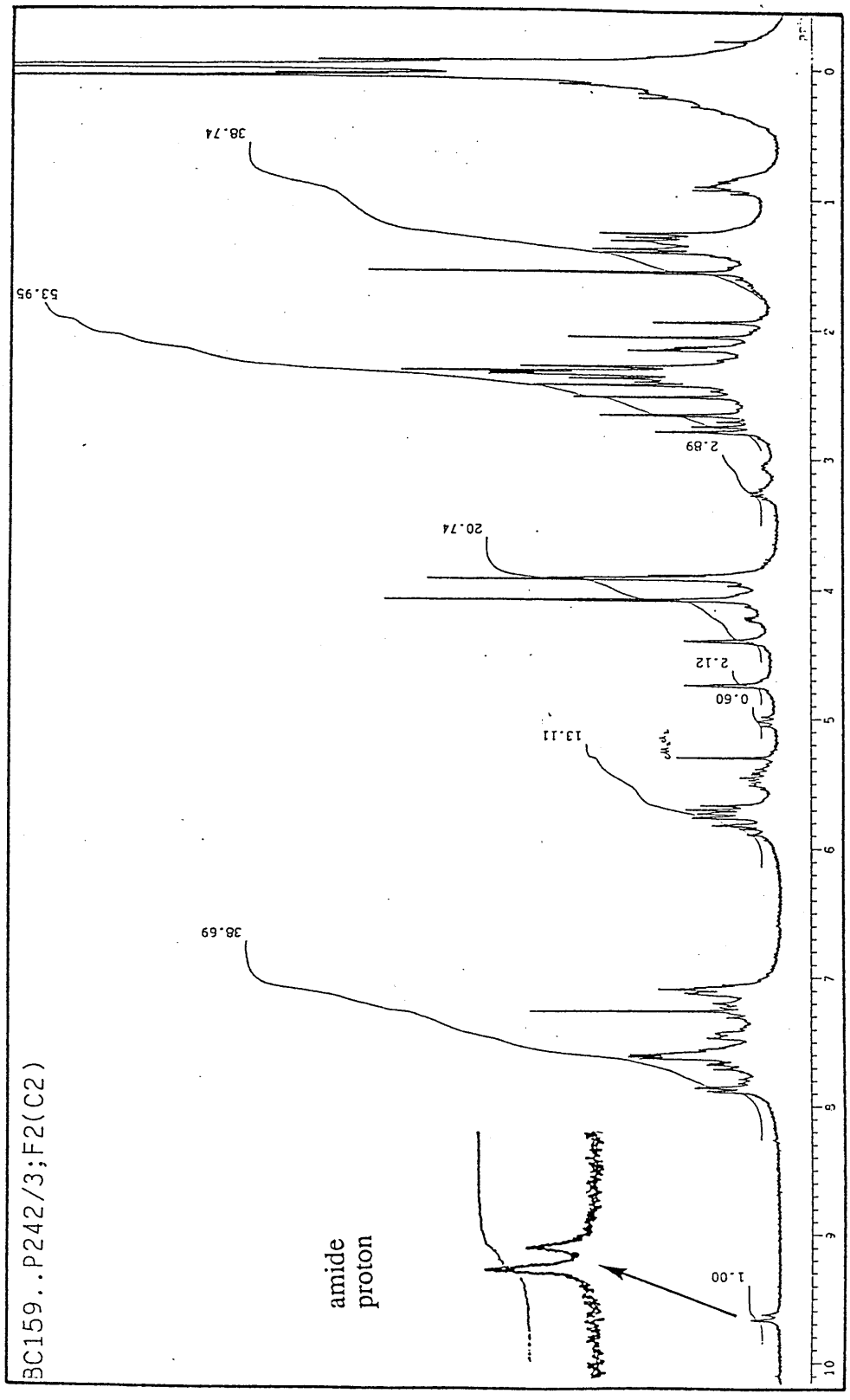


Fig. 62

^{1}H n.m.r. spectrum of 206-F3

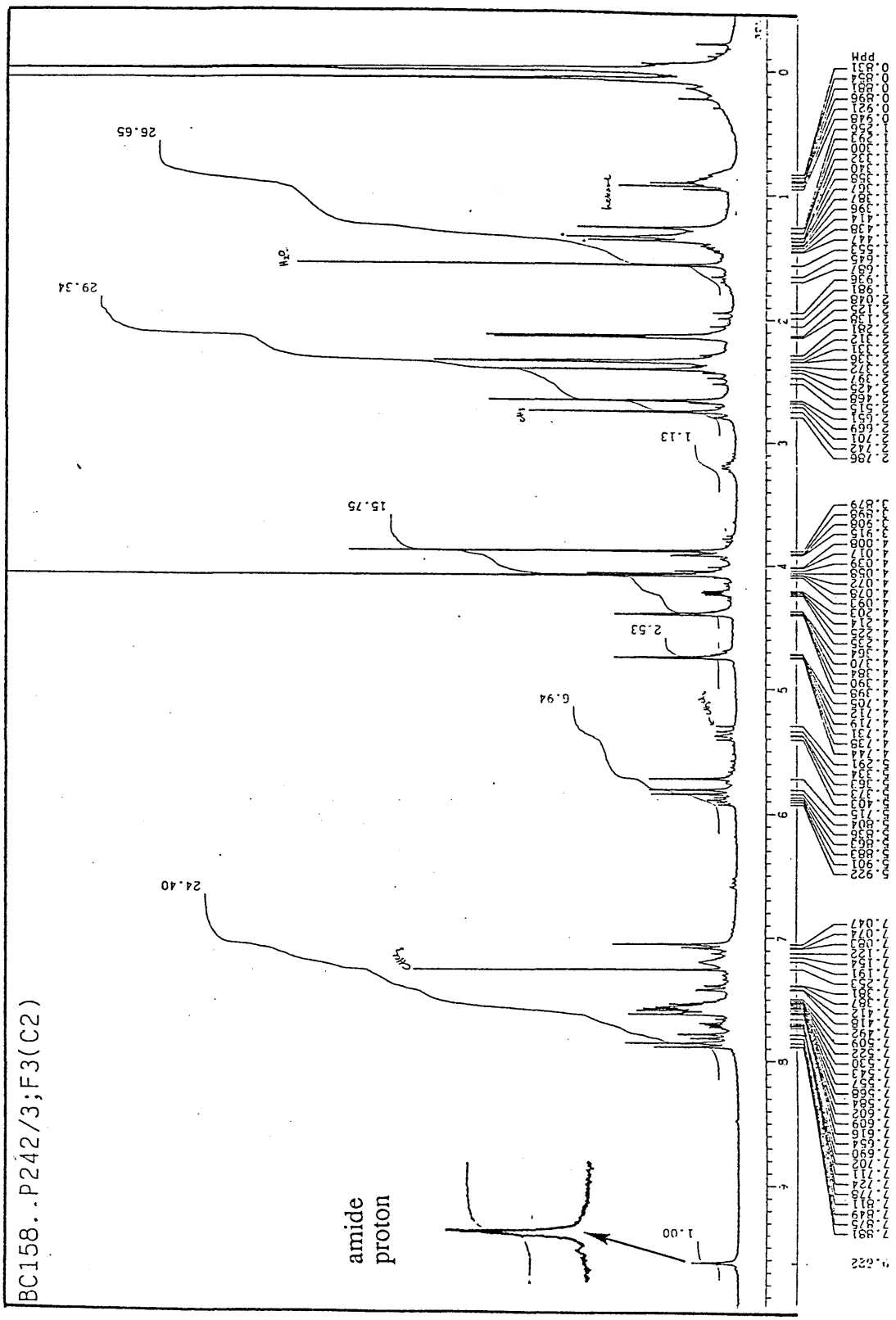
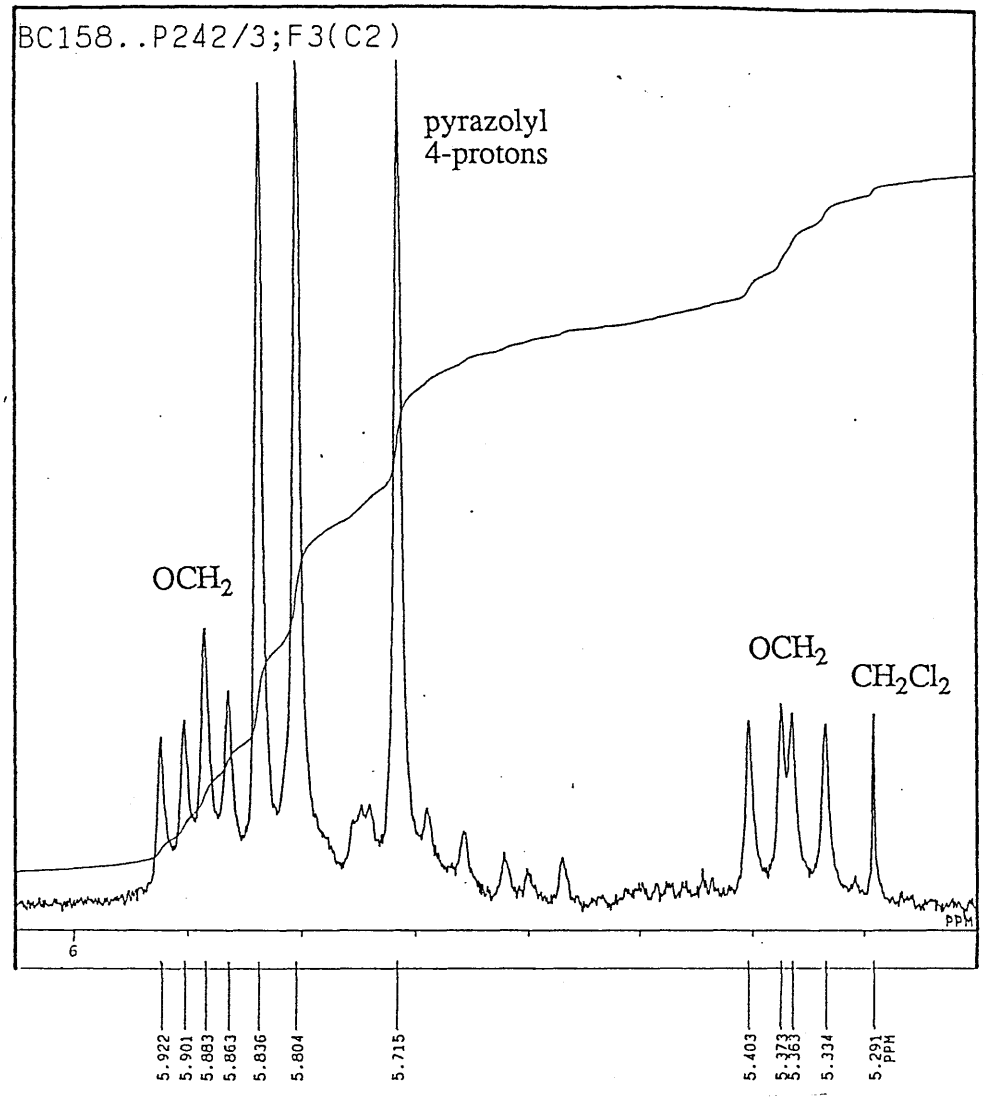


Fig. 63

Expansion of the region 6.0-5.2 ppm for 206-F3



It seems that 206-F1 contains the (-) hand of the naphthyl ligand, along with both *R* and *S* hands at molybdenum. 206-F3 must then contain the other hand of the ligand (*i.e.* (+)) but only *R* or *S* configuration at the metal centre. Quite why a fourth diastereomer is not observed is unclear. 206-F2 is clearly a mixture of fractions 1 and 3 (roughly 66% of 1 and 33% of 3 according to the ratio of amide proton signals). The shifting of the amide signal by about 12 Hz owing to the change in ligand chirality is small but noteworthy.

Unfortunately, complex [206] was not isolated in sufficient quantity to allow NLO evaluation by the Kurtz powder test.

VI-1.1(d)(ii) Ligand Racemisation

The assumption that fraction 206-F1 contains the chiral ligand in its original (-) form, whilst 206-F3 contains the (+) hand, is made on the grounds that dissociation of the chiral α-proton has led to some racemisation of the ligand. It seems logical that the (-) hand should still be present in excess over the (+) form, and working from yields of the three fractions shows that about 30% of the product contains (+) rather than the originally used (-) ligand. This indicates significant acidity of the α-proton, presumably enhanced by initial coordination to molybdenum.

To test the validity of this assertion, an experiment was carried out to investigate whether racemisation of the pure ligand precursor (+)-2-(6-methoxy-2-naphthyl)-1-propanoic acid [201] could be detected in the absence of any molybdenum complex. The carboxylate group is electron-withdrawing and could be expected to exert a similar labilising effect on the α-proton as might be caused by a coordinated {Mo(NO)L*} centre. The results of this study are presented in Table XXIV.

TABLE XXIV

Optical Rotations* for (+)-2-(6-Methoxy-2-naphthyl)-1-Propanoic Acid

		no base	with added base	
λ/nm	pure ligand	Δ 8 h	Δ 5.5 h	Δ 24.5 h
589	65	62	57.5	34.5
578	68.5	65	60	36
546	79.5	75	69	42
436	148.5	141	129	79
365	274	262	238	145

* All rotations measured to the nearest 0.5° in toluene at ambient temperature. Values represent positive degrees with respect to pure toluene rotation = 0.000°. Concentrations *ca* 2 x 10^{-3} g cm^{-1}.

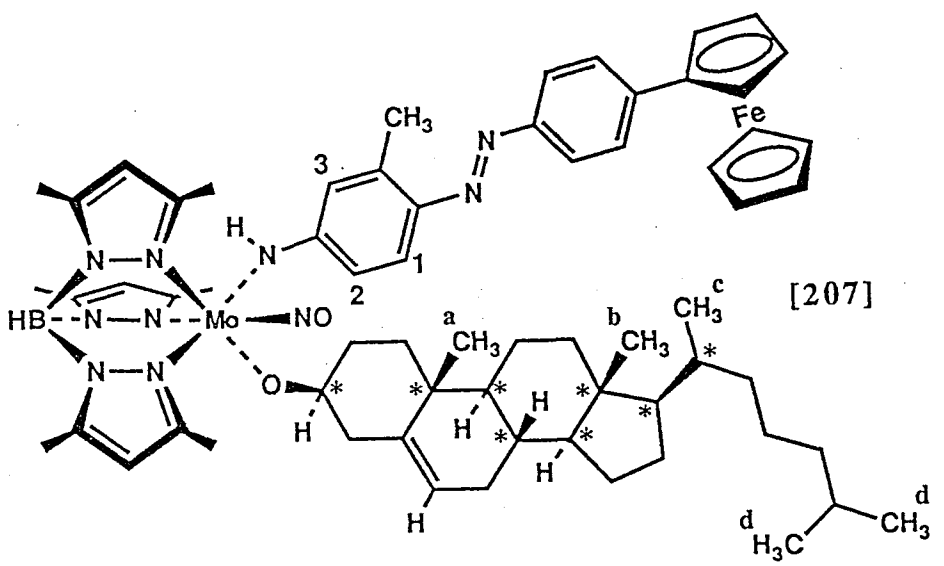
The data in Table XXIV clearly shows that, although heating under reflux in toluene for 8 h produces only a very small degree of racemisation, heating in the presence of excess triethylamine base gives considerable conversion as evidenced by a marked decrease in optical rotation. After just over 24 hours the rotation values indicate about 25% racemisation of the original acid. This is perhaps a little less than that produced on coordination after a reaction time of only 4 hours. The results of this study make the observation of some ligand racemisation unsurprising.

VI-1.1(e) Cholesterolate Complex

Another mixed-ligand complex of a chiral ligand was prepared by reaction of [Mo(NO)L*(I)(HNC$_6$H$_3$-3-CH$_3$-4-N=NC$_6$H$_4$-4-Fc)] with commercial (-)-cholesterol. The product [207] (Fig. 64) was fully characterised by the usual physical techniques, but was not resolved into discrete diastereomers.

Fig. 64

Mixed Complex Containing (-)-Cholesterolate
and 4-Amido-2-methyl-4'-ferrocenylazobenzene Ligands



[207]

The ^{1}H n.m.r. spectrum of [207] reveals the presence of two isomers in roughly equal proportion as evidenced by amide proton

signals at 9.54 and 9.49 ppm (a difference of 14 Hz). EI mass spectrometry failed to show any peaks above *m/z* 760 which suggests that the compound is involatile. One point worth noting is that this reaction also produced 13% of the mono-iodo cholesterolate complex [194], presumably resulting from direct replacement of the azo-anilide ligand by cholesterol. A similar result was not observed with the chiral naphthol ligand. Complex [207], apart from being chemically interesting, contains a ferrocenyl fragment found in complexes possessing NLO activity as well as the cholesteryl group which can form chiral liquid crystalline phases. Unfortunately, the small quantities of product isolated were insufficient for powder test study of SHG.

VI-1,2 BIMETALLIC MOLYBDENUM COMPLEXES

By reaction of $[Mo(NO)L^*(Cl)_2]$, $[Mo(NO)L^*(I)_2]$ or $[W(NO)L^*(Cl)_2]$ with difunctional organic ligands, both hetero- and homo-bimetallic complexes containing the {M(NO)L*} moiety may be readily prepared.[103,104,209] Electrochemical and e.p.r. studies have been used to investigate metal-metal interactions through saturated and unsaturated organic bridges in reduced mixed-valence products, and a considerable body of knowledge has been accumulated over the last decade. In particular, complexes of 1,4-diaminobenzene and 1,4-dihydroxybenzene ligands show strong inter-metallic communication,[103] and some very recent studies have revealed extremely large electronic coupling between {Mo(NO)L*(Cl)} centres across bipyridyl bridges.[106] The coupling in these bipyridyl complexes, as evidenced by electrochemical studies, is an order of magnitude larger than that found in their penta-ammine Ru(II) counterparts.

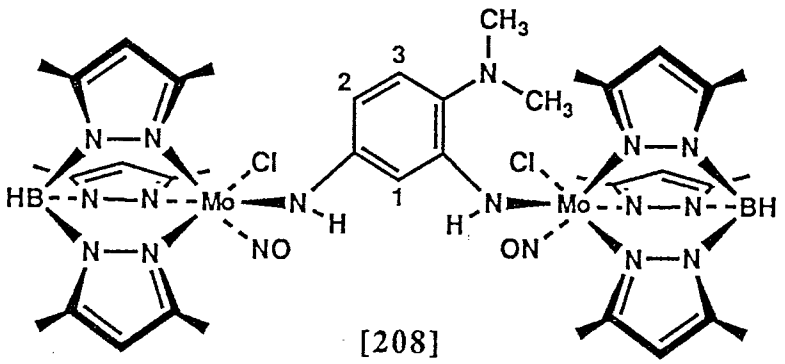
In view of their relatively facile synthesis, and more importantly, the evidence for efficient intermetallic communication, several bimetallic molybdenum complexes were prepared with the aim of producing NLO-active molecules in which two chiral {Mo(NO)L*(Cl)} centres are present.

VI-1,2(a) Synthesis and Isomer Characterisation of Di-anilido Complexes

The difunctional ligand 2,4-diamino-N,N-dimethylaniline was prepared as a precursor to 2,4-bisferrocenyl-N,N-dimethylaniline (see Chapter One). Its homobimetallic derivative [208] (Fig. 65), prepared along the usual lines, contains a powerful dimethylamino electron donor group along with *para* and *ortho* molybdenum-amido electron acceptor centres. The occurrence of *R* and *S* configurations at the two metal centres coupled with the asymmetry introduced by the dimethylamino group would be expected to give rise to a total of four distinct diastereomers with configurations *RR*, *RS*, *SS*, and *SR*.

Fig. 65

[Mo(NO)L*(Cl){HNC_6H_3-2-$N(CH_3)_2$-5-NH}Mo(NO)L*(Cl)]



[208]

Column chromatography on silica gel was successful in separating the product into two fractions (denoted 208-F1 and 208-F2) which have identical i.r. and mass spectra, and elemental analyses, which are all in accord with their proposed formulation. ^1H n.m.r. spectroscopy shows both to have two amide proton signals which are separated by some 0.47 ppm for 208-F1 and 0.58 ppm for 208-F2. These result from the steric and electronic inequivalence of the two metal centres. Some very small shifts between the two fractions are seen for the three aryl protons, and 208-F1 shows eight pyrazolyl-methyl signals whilst 208-F2 shows nine. The latter observation proves that both fractions contain more than one diastereomer, which is in keeping with the expectation that a

total of four isomers should be produced. It seems likely that one fraction contains the complexes with *RS* and *SR* metal centres, and the other the *RR* and *SS* products, but this remains a speculative suggestion in the absence of further data.

Both diastereomeric mixtures were also studied by cyclic voltammetry. This revealed for both two reversible one-electron reduction waves separated by some 430 mV, indicating that the two mutually *meta* molybdenum centres are coupled fairly strongly.[103] As expected, the difference in stereochemistry between the two fractions did not produce any significant change in electrochemical behaviour. Each also showed a strong irreversible wave at +0.97 V, perhaps attributable to oxidation of the dimethylamino function.

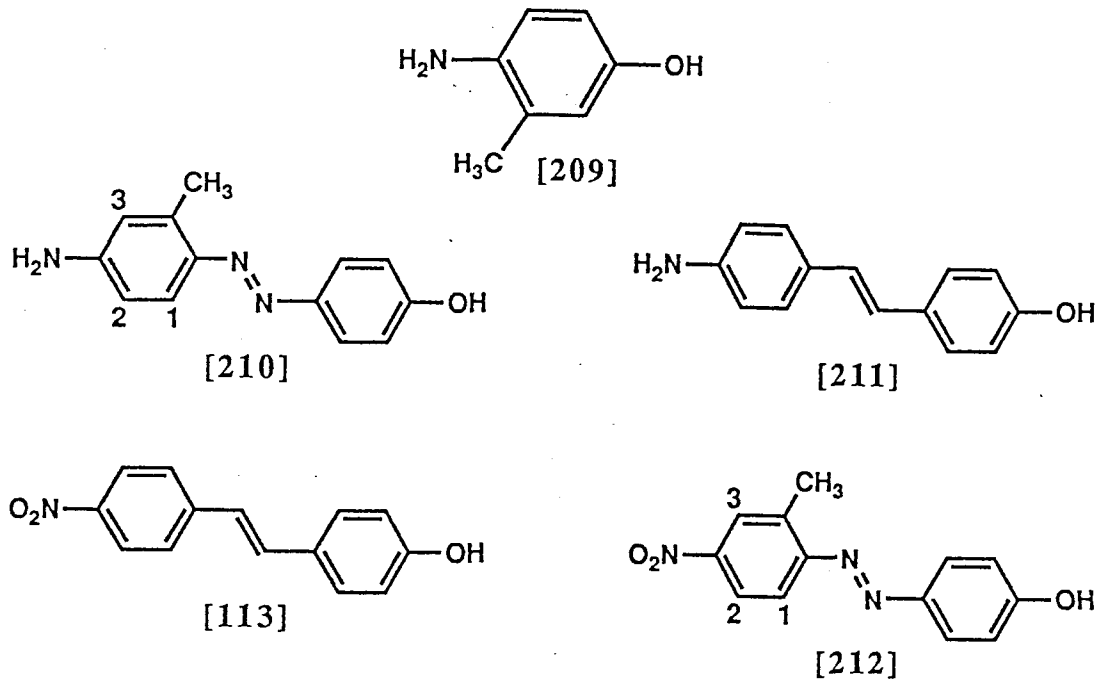
VI-1.2(b) Synthesis of Phenoxy-anilido Complexes

Also prepared were three homobimetallic complexes of amino-phenolic ligands. The ligands used were commercial 4-amino-3-methylphenol [209], and 4-amino-2-methyl-4'-hydroxyazobenzene [210] and 4-amino-4'-hydroxystilbene [211] which were prepared using simple organic reactions. 4-Hydroxy-4'-nitrostilbene [113] was synthesised by the condensation of 4-hydroxybenzaldehyde and 4-nitrophenylacetic acid.[282] This compound was then reduced to its amino derivative [211] using tin chloride and hydrochloric acid.[283] 4-Nitro-2-methyl-4'-hydroxyazobenzene [212] was prepared from a diazonium coupling reaction between the diazonium salt of 2-methyl-4-nitroaniline and phenol.[284] Reduction to [210] was carried out using aqueous sodium sulphide.[284] The structures of these ligands and precursors are shown in Fig. 66.

The primary objective of making bimetallic complexes from these ligands is to utilise molybdenum centres as both the electron acceptor and donor in dipolar polarisable molecules. It was envisaged, that if the oxygen bound metal centre could be selectively reduced, then the reduced 17-electron metal should act as the donor group whilst the unreduced nitrogen-bound metal behaves as an acceptor. This approach will be discussed in more detail later in section VI-1.3.

Fig. 66

Amino-phenolic Ligands and Nitro-phenolic Ligand Precursors



Di(molybdenum mononitrosyl) derivatives of all three ligands were prepared without difficulty, and also isolated were monometallic derivatives of [209] and [211]. All of these new complexes are shown in Fig. 67.

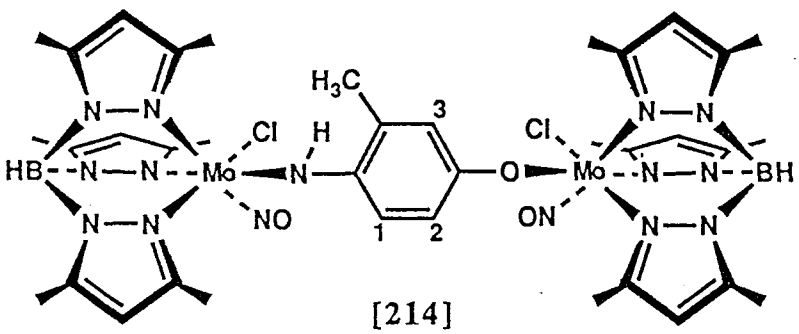
These reactions demonstrate an interesting fact about the reactivity of {Mo(NO)L*} with amino-phenolic ligands. In both cases, the monometallic complexes isolated were found to be phenoxy derivatives with free amino groups, and no traces of any anilido complexes with free hydroxy groups were detected. This proves that, given a choice between the two groups in the same aryl molecule, the molybdenum shows a strong preference for hydroxy rather than amino, and no amino binding occurs until the free hydroxy has reacted. This may be a result of zwitterion formation by the difunctional ligand to give a phenoxide-ammonium derivative of form $^{-}O-Ar-NH_3^{+}$ owing to the differing pK_a values of the amino and hydroxy functions. Hence the amino group will be blocked from reacting whilst the phenoxy group becomes strongly activated as a nucleophilic function. The presence of triethylamine may also influence the course of the reaction.

These results do not necessarily contradict earlier observations concerning the {Mo(NO)L*} system that reaction appears to proceed faster with amino than with alcohol ligands,[209] but merely describe the situation for a particular class of difunctional ligands under certain reaction conditions. More detailed studies involving kinetic measurements are required in order to obtain a fuller understanding of the reactivity of {Mo(NO)L*} towards different donor functions.

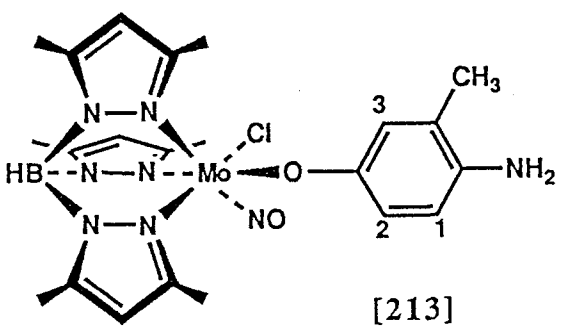
As a side point to this result, the complexes with free amino groups could also be interesting from the point of view of NLO because they represent donor-substituted monometallics. Furthermore, structural effects due to possible hydrogen-bonding involving free $-NH_2$ groups might be expected in compounds of this type.

Fig. 67

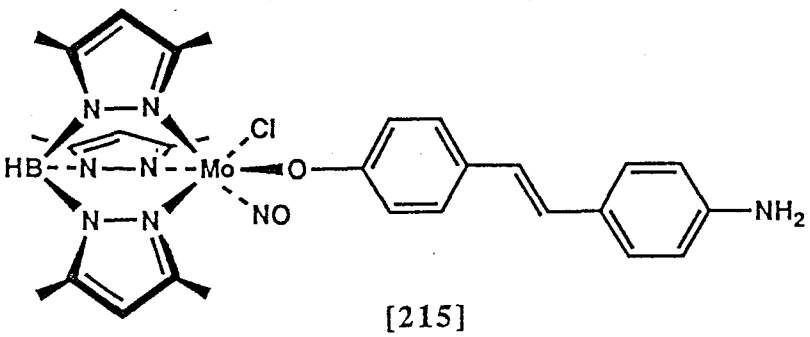
Monometallic and Bimetallic Complexes of Amino-phenolic Ligands



[214]

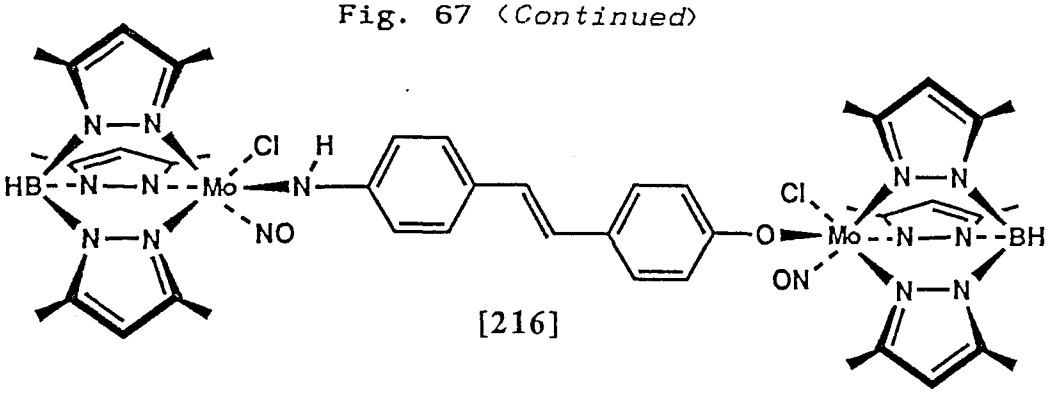


[213]

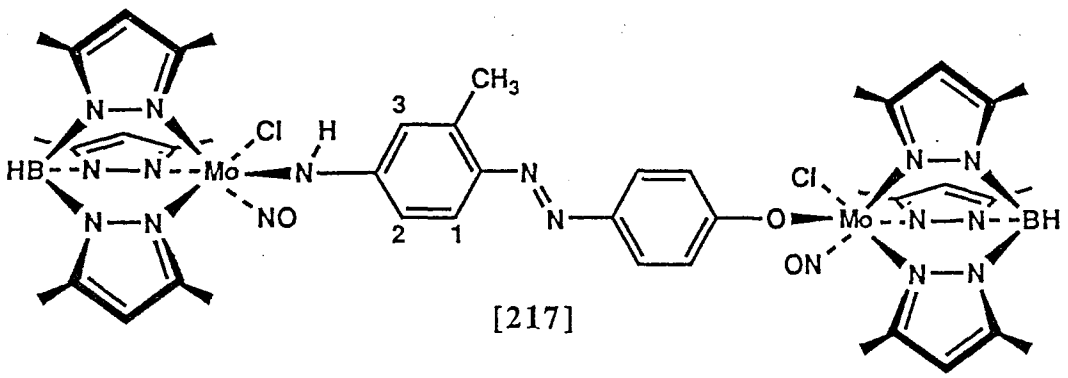


[215]

Fig. 67 (*Continued*)



[216]



[217]

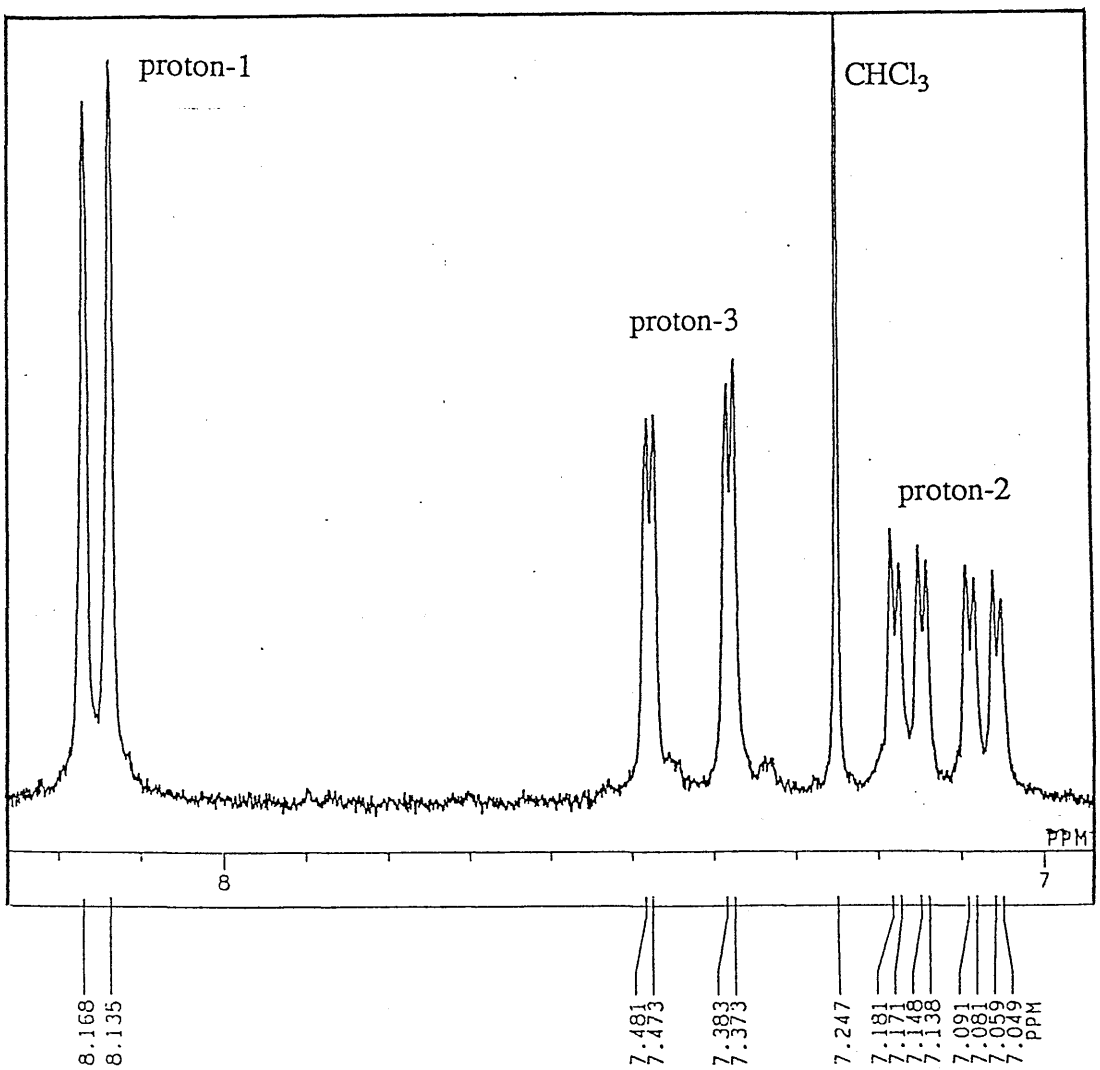
VI-1.2(c) Physical Characterisation of Phenoxy-anilido Complexes

All of the new complexes, both bimetallic and monometallic, were fully characterised by the usual physical techniques. All gave elemental analyses in accord with their formulations, except for the bimetallic stilbene complex [216] which gave a good C analysis but an N value which remains some 2% low for several different samples. The reason for this discrepancy is unclear, but the identity of this complex is not in doubt. The monometallic stilbene complex [215] contains a small amount of dichloromethane shown by elemental analyses as well as ^{1}H n.m.r. spectroscopy. All three bimetallic phenoxy-amido complexes gave broad $\nu_{max.}$(NO) at about 1660 cm^{-1}, showing that resolution of the two nitrosyl stretches, which should be separated by about 20 cm^{-1}, is not possible in such species. The bimetallic species all have molecular masses in excess of 1,000, and proved to be insufficiently volatile to show molecular ions or even any peaks above *m/z* = 600.

The ^1H n.m.r. spectrum for the mono-aryl bimetallic [214] is interesting in that some splitting of the signals, which may be attributed to diastereomers, is observed which is not found in the stilbenyl or azobenzene species. Two signals for the amide proton are detected very close together, and some splitting is also seen for two of the aryl protons (Fig. 68). Proton 3 gives two doublets (split by proton 2 with J(23) = 2.5 Hz), and proton 2 gives a pair of doubly split doublets (split by proton 1 with J(12) = 8.9 Hz and split by proton 3 with J(23) = 2.7 Hz). Proton 1 gives only one doublet (split by proton 2 with J(12) = 8.9 Hz), suggesting that perhaps the sample contains only one metal configuration at the NH-linked Mo centre, but both *R* and *S* at the O-linked Mo.

Fig. 68

Aromatic Region of the ^1H n.m.r. spectrum for [214]



Cyclic Voltammetric studies reveal several noteworthy results. The monometallic complexes containing free amino functions show irreversible oxidation waves at +0.89 V for [213] and +0.83 V for [215] which are not present in the bimetallic derivatives, and can therefore be assigned to oxidation of the amino group. The three bimetallic complexes each show two quasi-reversible or irreversible molybdenum reduction waves and the mono-aryl derivative [214] shows a very large $\Delta E_{\frac{1}{2}}$ value of 1070 mV. This is similar to the previously reported values of 1010 mV for [Mo(NO)L*(Cl)(OC_6H_4NH)Mo(NO)L*(Cl)] and 1040 mV for [Mo(NO)L*(Cl)(HNC_6H_4NH)Mo(NO)L*(Cl)].[209] However, the stilbenyl and azobenzene bridged bimetallic derivatives show rather smaller wave separations of 530 mV and 520 mV respectively.

These results show how the inter-metallic communication is substantially reduced by increasing the size of the aromatic linkage, and also imply that the ethenyl and azo functions allow roughly similar degrees of interaction. Furthermore, comparison of the reduction potentials for the monometallic and bimetallic complexes shows that complexation of the free amino group produces a 200 mV anodic shift with the mono-aryl linkage, but only a modest 40 mV anodic shift with the stilbenyl linkage. This shows that the electron-withdrawing effect of the amide-linked metal centre is much larger in the former species, again due to the greater degree of inter-metallic electronic-coupling.

VI-1.3 CHARGED COMPLEXES

Although most of the organic materials studied earlier for their NLO properties are neutral molecules, more recently a considerable number of organic salt compounds have been investigated and found to possess marked NLO behaviour. Zwitterionic merocyanine dyes have been known for some time to possess extremely large molecular hyperpolarisability values, β,[285] and of particular interest are reports of very high powder SHG from the stilbazolinium salts of a range of anions including halides, tosylate and mesylate.[28] In such materials coulombic interactions can override the deleterious

dipolar interactions that encourage an unfavourable centrosymmetric crystal packing. Various zwitterionic phenoxide-pyridinium compounds have also been the subject of recent attention in the search for second-order NLO effects.[286]

Combining organic and inorganic species, a novel class of salt has recently been reported in which a polarisable organic quaternary ammonium cation is crystallised with an inorganic dihydrogenphosphate anion.[287] Such materials are transparent in the visible region, making them amenable to frequency doubling of a 1,064 nm laser fundamental, unlike the highly coloured dye-related compounds mentioned above. Also, several of the reports of NLO-active organometallic and coordination compounds have concerned salt compounds.[28,144,130,135]

VI-1.3(a) Trispyrazolylborate Complexes

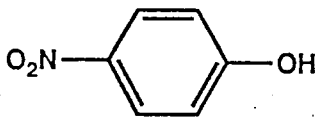
Electrochemical studies indicate that in reduced anionic 17-electron $[Mo(NO)L^*(X)(Y)]^-$ complexes the $\{Mo(NO)\}^{2+}$ centre acts as an efficient donor of electrons,[103] rather than displaying the acceptor behaviour ascribed to the $\{Mo(NO)\}^{3+}$ moiety in neutral 16-electron complexes. In order to incorporate the reduced centre into dipolar polarisable complexes for NLO, the attachment of acceptor-substituted aromatic ligands is necessary prior to reduction of the 16-electron complexes.

The acceptor function chosen was the nitro group, and phenolic ligands were chosen because their complexes are reduced rather more readily than anilido derivatives. The ligands used were 4-nitrophenol (commercial) [218], 4-hydroxy-4'-nitrostilbene [113],[282] 4-hydroxy-4'-nitroazobenzene [219],[288] 4-hydroxy-2'-methyl-4'-nitroazobenzene [212],[284] 4-hydroxy-2-methyl-2'-methyl-4'-nitroazobenzene [220],[284] and 4-nitrophenylazo-1-naphthol (commercial) [221]. The non-commercial ligands were synthesised using established chemistry as described earlier. The four phenolic ligands not previously illustrated are shown in Fig. 69.

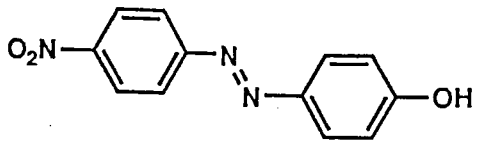
Using established methods, mono-chloro complexes containing each of these ligands were synthesised, along with the bis(4-nitrophenoxide) derivative. These are shown in Fig. 70.

Fig. 69

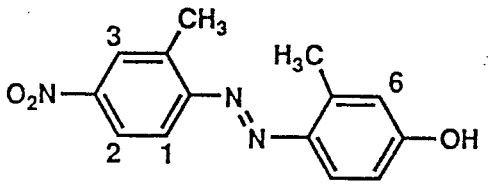
Nitro-phenolic Ligands



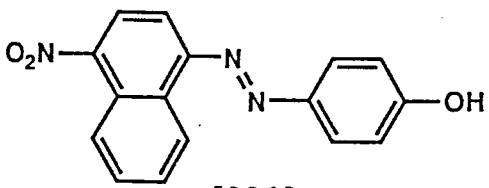
[218]



[219]



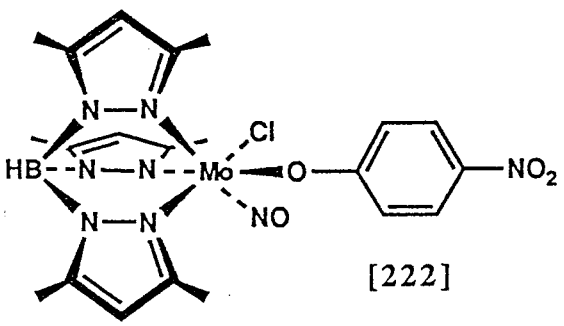
[220]



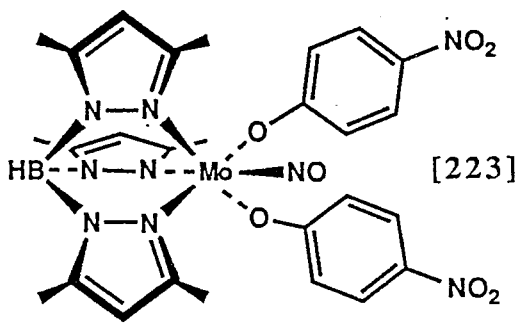
[221]

Fig. 70

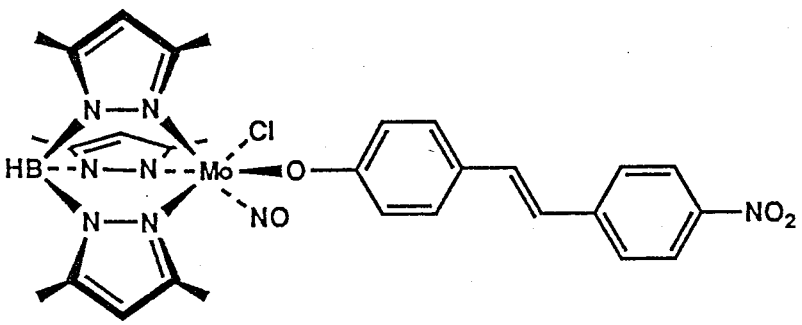
Complexes of Nitro-phenoxide Ligands



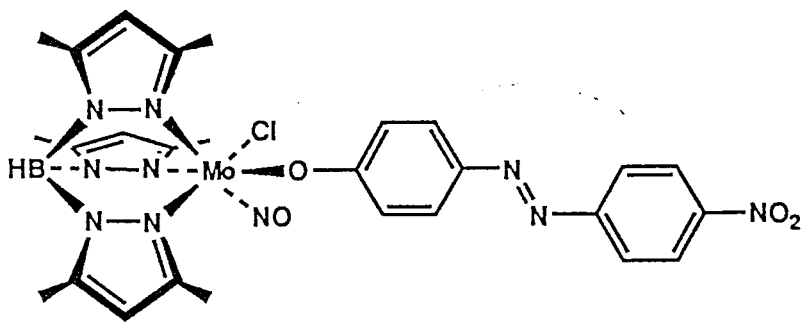
[222]



[223]

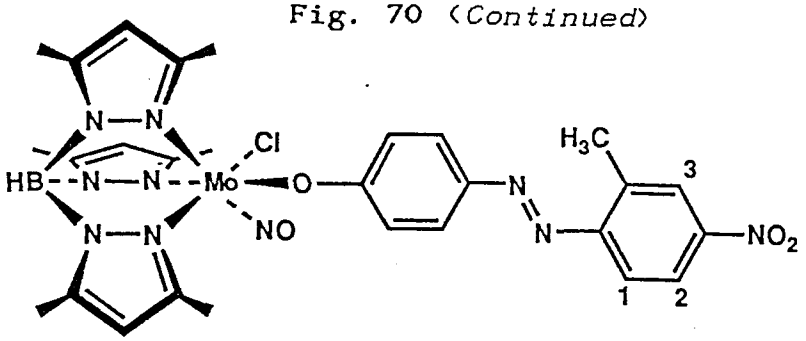


[224]

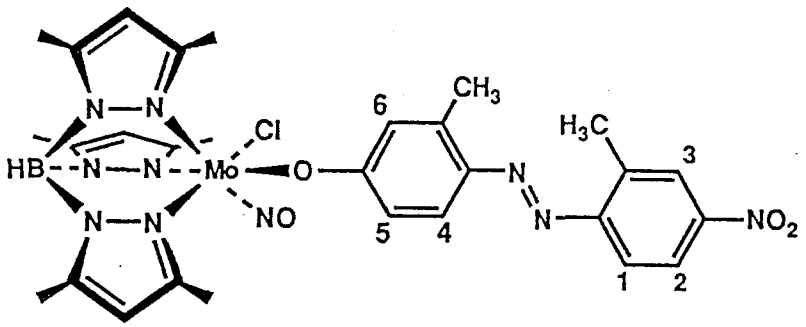


[225]

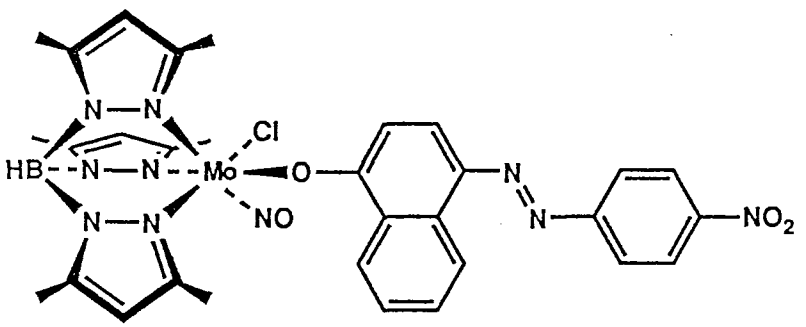
Fig. 70 (*Continued*)



[226]



[227]



[228]

All of the new complexes were fully characterised using the usual physical techniques, and all of the physical data was found to be in accord with proposed formulations. Cyclic voltammetry revealed an extra irreversible reduction wave between -1.0 and -1.5 V for all of the mono-substituted complexes. This is likely to be due to the nitro group. The four azo complexes showed a third irreversible reduction process in the region -0.84-0.90 V, which is likely to be associated with reduction of the azo moiety.

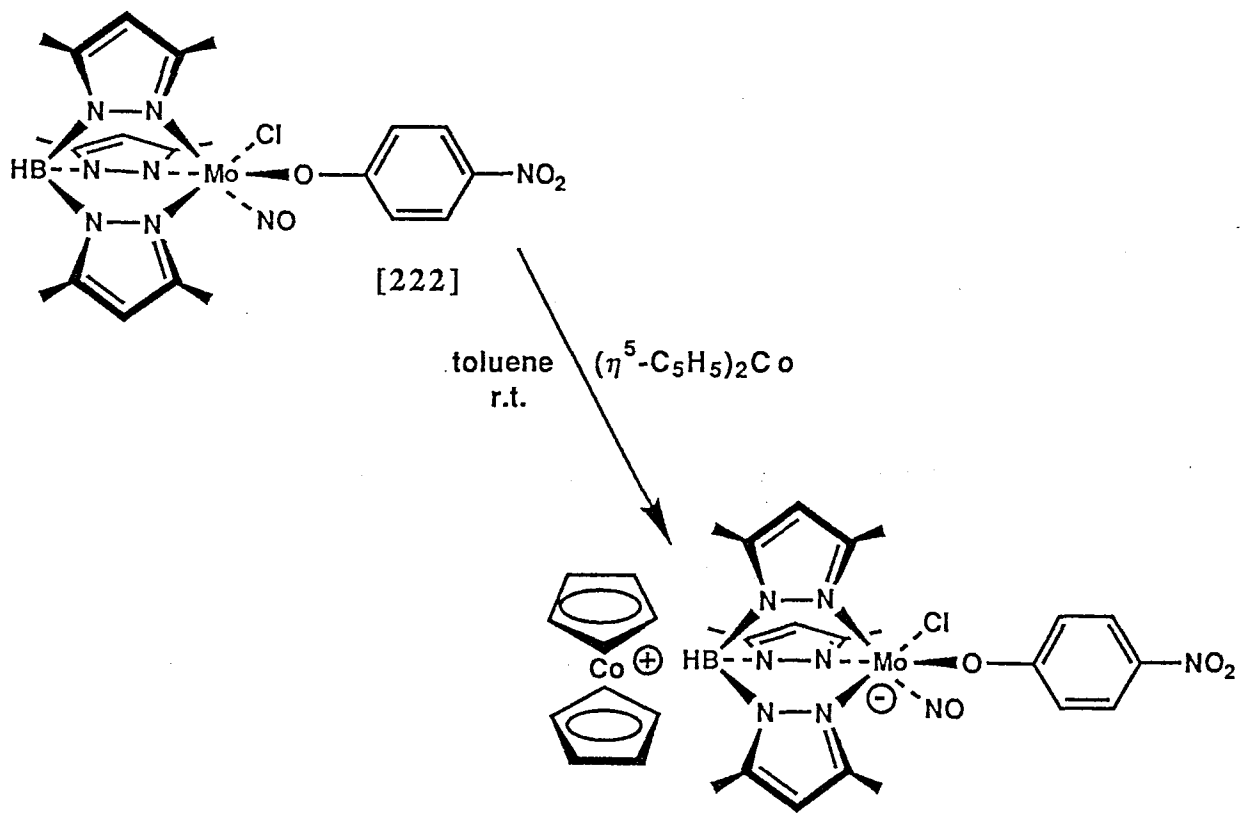
VI-1,3(a)(i) Reduction of Neutral Complexes

Cobaltocene has been used previously in the chemical reduction of {Mo(NO)L*} complexes prior to e.p.r. study,[106,208] and this

compound was considered a suitable choice to carry out the reduction of the nitro-substituted phenoxide complexes. All six of the mono-substituted complexes, along with the three bimetallic phenoxy-anilide derivatives described earlier, were reduced and the products characterised by i.r. spectroscopy, elemental analyses, and cyclic voltammetry. In each case, the appropriate complex was dissolved in dry toluene with 1.5 eq. of cobaltocene and the mixture stirred at ambient temperature under a dry nitrogen atmosphere for one hour. A precipitate was formed which was collected by filtration and washed in air with further dry toluene. The darkly coloured powders thus obtained were dried under vacuum at 100 °C for 48 hours prior to submission for elemental analysis. A proposed reduction for complex [222] is shown in Fig. 71.

Fig. 71

Proposed Reduction by Cobaltocene of Complex [222]



VI-1.3(a)(ii) Characterisation of Reduced Products

For each product, i.r. spectroscopy revealed a strong sharp $\nu_{max.}$(NO) at 1590-1580 cm^{-1} which is as expected for a reduced 17-electron complex. However, the products from the two complexes which have the most cathodic reduction potentials, [224] (E_f = -0.25 V) and [227] (E_f = -0.17 V) also have smaller peaks at 1685 cm^{-1}, indicating incomplete reduction of the 16-electron complex. Redissolution and stirring with further cobaltocene failed to eliminate these peaks. The other complexes all have E_f equal to -0.15 V or less (even as low as -0.08 V for [222]), and are hence more readily reduced by cobaltocene. For the bimetallic complexes, the extent of reduction cannot be established solely from i.r. because a peak due to the amide-linked metal centre will always be present. Also found in all spectra are weak $\nu_{max.}$(BH) at about 2540 cm^{-1} and a medium peak at 3090 cm^{-1} attributable to cyclopentadienyl.

Elemental analyses were recorded only for those products which did not contain unreduced complex, and results are shown in Table XXV.

Considering the values that would be expected for the desired 1:1 salt products, C and H percentages show fairly good agreement, but the N percentages are up to 5% too low. Drying under vacuum for extended periods did not significantly alter these results which indicates that if solvent is present then it must be included in the crystal lattices. Despite many attempts to explain these anomalous results, the only sensible conclusion appears to be that somehow loss of nitrogen takes place upon reduction, *i.e.* an irreversible chemical decomposition, perhaps involving loss of nitro groups, is occurring. In order to test this idea, the product from the reduction of [225] was treated with silver(I) acetate to see if the reduced species could be re-oxidised to the original complex. This reaction involved an excess of silver(I) in dry dichloromethane under a dry nitrogen atmosphere. After 2 hours reaction under reflux, a considerable quantity of [225] was recovered by column chromatography on silica.

TABLE XXV

Physical Data for Cobaltocene Reduction Products

products from [Mo(NO)L*(Cl)(Y)]:

Y[a]	colour	$\nu_{max.}$(NO)[b]	Elemental Analyses: %found(calc.)[c] C	H	N
OΦNO_2	khaki	1590	45.0(47.4)	4.3(4.6)	9.6(14.3)
OΦN=NΦNO_2	brown	1585	49.3(49.9)	4.3(4.5)	9.9(15.7)
OΦN=NØNO_2	brown	1590	49.8(50.5)	4.4(4.7)	10.1(15.5)
OΘN=NΦNO_2	indigo	1580	50.8(52.4)	4.2(4.5)	9.4(14.9)

product from [Mo(NO)L*(Cl){Z}Mo(NO)L*(Cl)]:

Z[a]	colour	$\nu_{max.}$(NO)[b]		Elemental Analyses: %found(calc.)[c] C	H	N
HNØO	blue	1650	1585	45.0(46.0)	4.9(5.0)	15.6(17.1)

[a] Φ = $-C_6H_4-$, Ø = $-C_6H_3-2-CH_3-$, Θ = $-C_{10}H_6-$. [b] in cm^{-1}, recorded as KBr disc. [c] Calculated analyses for desired 1:1 salt product;
[$(\eta^5-C_5H_5)_2Co$]$^+$[Mo(NO)L*(Cl)(Y)]$^-$ or
[$(\eta^5-C_5H_5)_2Co$]$^+$[Mo(NO)L*(Cl){Z}Mo(NO)L*(Cl)]$^-$.

Cyclic voltammetry in dichloromethane solution was carried out on all of the reduced products (solubility is low but sufficient for the quantities involved). In each case, this revealed the molybdenum and other waves found for the original unreduced complex along with a large irreversible wave at about -0.80 V which must be due to the cobaltocene. This is further evidence that no irreversible chemical decomposition takes place upon reduction, but the precise nature of the products isolated is still unclear.

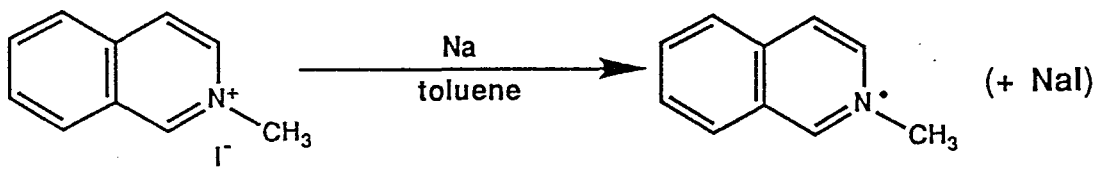
Several of the reduced products were tested for magnetic

susceptibility to establish whether paramagnetic salts had formed. These studies revealed moments of μ_{eff} = 3.34 B.M. for the reduced product from [222], 2.15 B.M. for that from [225], and 2.31 for the product from [226]. However, these values are based upon the assumption that the products are the desired 1:1 cobaltocenium salts. Since this has not been proven, the μ_{eff} values quoted are not of great significance beyond proving the paramagnetic nature of the products.

Finally, an attempt to reduce [225] using the organic radical [230] generated by sodium reduction of N-methyl isoquinolinium [229] in toluene (Fig. 72), gave some reduction, but less than that caused by cobaltocene. Further experiments with other reducing agents might lead to a better understanding of the products formed in these reduction reactions.

Fig. 72

Preparation of an N-Methyl Isoquinoline Radical



[229] [230]

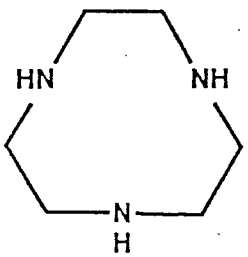
VI-1.3(b) Triazacyclononane Complexes

Over the past decade or so, work has been carried out on complexes of the small macrocycle 1,4,7-triazacyclononane with chromium, molybdenum, and tungsten in low oxidation states. This has involved the preparation of air- and moisture-stable neutral carbonyl and cationic mononitrosyl complexes, *e.g.* $[M(NO)(9\text{-ane-}N_3)(CO)_2]^+$ (M = Cr, Mo, or W), via nitrosylation of $[M(9\text{-ane-}N_3)(CO)_3]$ with nitric acid,[289] as well as analogous species involving the more sterically demanding trimethylated ligand N,N',N"-trimethyl-1,4,7-triazacyclononane (Fig. 73).[290] In general, the presence of the three methyl groups prevents the formation of dimeric species with two edge-sharing octahedra,[291] and study of such complexes has

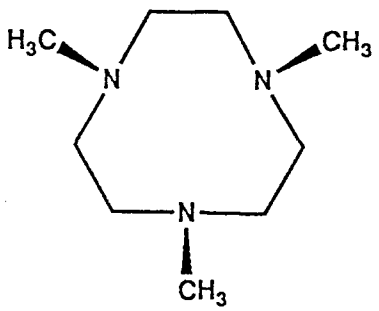
led to halide derivatives of formula $[M(NO)L^N(X)_2]^+$ (L^N = N,N',N''-trimethyl-1,4,7-triazacyclononane; M = Mo, X = Br, Cl; M = W, X = Br).[292] The metal in these complexes is formally in a +2 oxidation state, and is coordinatively unsaturated, having a formal valence electron count of 16. Reduction by chemical or electrochemical means affords paramagnetic neutral 17-electron species $[M(NO)L^N(X)_2]$. Furthermore, alkoxide derivatives such as $[Mo(NO)L^NCl(OEt)]^+.PF_6^-$ have been prepared by halide displacement.[292] The synthesis of these complexes for M = Mo is shown in Fig. 74.

Fig. 73

1,4,7-Triazacyclononane Ligands



(i) 1,4,7-triazacyclononane



(ii) N,N',N''-trimethyl-1,4,7-triazacyclononane = L^N

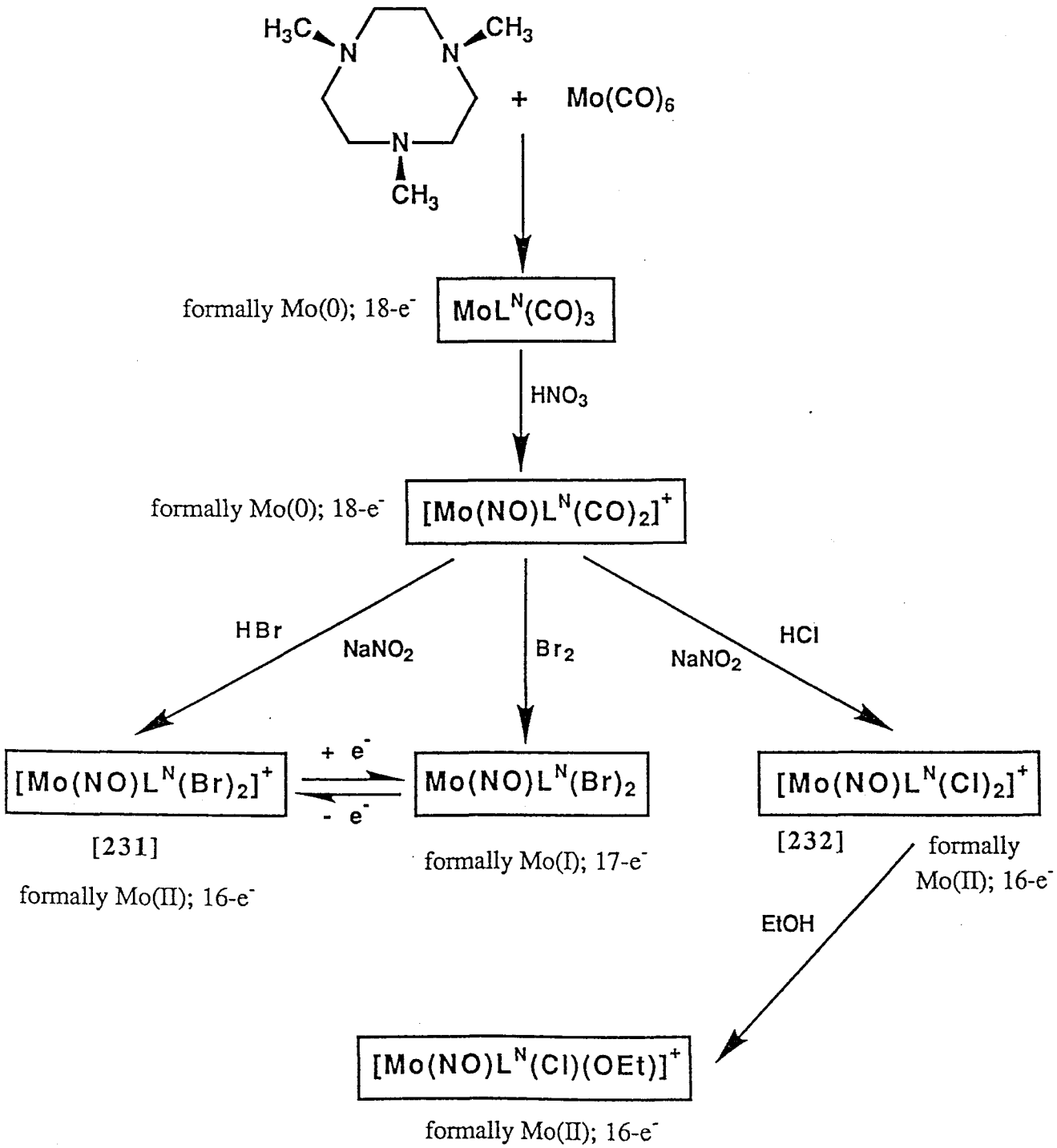
During these recent studies, similarities between complexes of the cyclic triamine and trispyrazolylborate ligands have become apparent. The obvious structural and electronic differences between the two types of ligand do not prevent close parallels in the simple derivative chemistry described above, but a more extensive study of reactions of $\{M(NO)L^N\}$ halides with organic ligands has yet to be attempted. Hence it is not known whether these macrocyclic complexes will display such a widespread derivative chemistry as their versatile heterocyclic counterparts.

In the context of preparing complexes which might show NLO effects, it was decided to carry out some reactions of the complexes $[Mo(NO)L^N(X)_2]^+.PF_6^-$ (X = Br [231], Cl [232]) with aromatic ligands, with the aim of preparing cationic analogues of the neutral tris(3,5-dimethylpyrazol-1-yl)hydroborate, L*, complexes described earlier. The presence of the positive charge

might be expected to render the molybdenum centre a more powerful electron-acceptor, and structural effects in such salt systems could be of interest.

Fig. 74

Synthetic Scheme for Molybdenum Mononitrosyl Complexes of the N,N',N"-Trimethyl-1,4,7-triazacyclononane Ligand



VI-1.3(b)(i) Reactions with $[Mo(NO)L^{N}(Cl)_2]^+.PF_6^-$

Reactions of the pale brown dichloride complex [232] with several ligands were carried out under conditions similar to those used for the preparation of derivatives of $[Mo(NO)L^{*}(Cl)_2]$. It was found that the use of triethylamine as base resulted in the production of reduced species with $\nu_{max.}(NO)$ at about 1590 cm^{-1} and no $\nu_{max.}(PF_6)$ in the i.r. Further characterisation of these products was not attempted, and subsequent reactions were carried out without added base.

Heating of [232] with excess phenol for several hours in dry dichloromethane or acetonitrile gave rise to a deep purple coloration. Evaporation of the solvent followed by i.r. study of the solid revealed a strong $\nu_{max.}(NO)$ at 1665 cm^{-1} as well as a small peak due to unreacted dichloride at 1710 cm^{-1} and a strong $\nu_{max.}(PF_6)$. Recrystallisation from acetonitrile/toluene yielded a purple powder with only $\nu_{max.}(NO)$ at 1665 cm^{-1} and strong $\nu_{max.}(PF_6)$. However, hopes that this compound was the mono-phenoxide derivative $[Mo(NO)L^{N}(Cl)(OPh)]^+.PF_6^-$ were proven incorrect by an absence of any aromatic proton signals in the ^1H n.m.r. spectrum. Elemental analyses also revealed considerably lower C and N percentages than would be required for such a formulation.

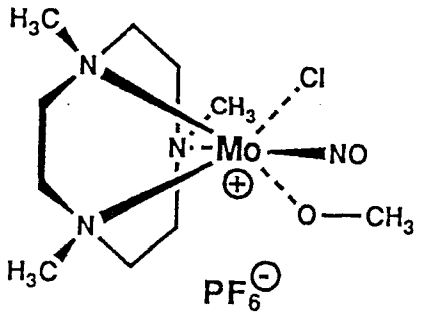
Since the supply of [232] was limited, further study of this reaction was abandoned, and a reaction with 4-ferrocenylphenol was undertaken instead. This afforded a brown product with $\nu_{max.}(NO)$ at 1660 cm^{-1} and strong $\nu_{max.}(PF_6)$, but again an absence of any aromatic signals in the ^1H n.m.r. spectrum. A control experiment, involving the heating of [232] in dry acetonitrile also yielded a khaki product with strong $\nu_{max.}(PF_6)$ and $\nu_{max.}(NO)$ at 1660 cm^{-1}. Addition of phenol to this in solution failed to produce any purple coloration.

Heating of [232] with 4-amino-2-methyl-4'-ferrocenylazobenzene [47] in dichloromethane, followed by filtration, afforded a brown-green powder with $\nu_{max.}(NO)$ at 1655 cm^{-1}, and strong $\nu(PF_6)$. However, an extremely low C analysis showed that this material did not contain the ferrocenyl amine ligand which was recovered unchanged in the filtrate solution.

The methoxide derivative $[Mo(NO)L^N(Cl)(OMe)]^+.PF_6^-$ [233] (Fig. 75) was prepared by the same method used to make the ethoxide derivatives,[292] and characterised by elemental analyses, i.r. and ^1H n.m.r. spectroscopy. A number of attempts were undertaken to displace the methoxide ligand using [47] in refluxing dichloromethane or toluene, but the i.r. spectra of the products failed to show any signs of a reaction having occurred.

Fig. 75

$[Mo(NO)L^N(Cl)(OMe)]^+.PF_6^-$



[233]

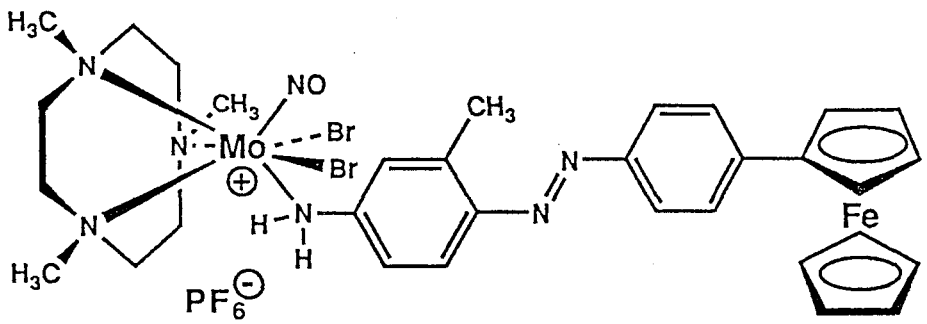
VI-1,3(b)(ii) Reactions with $[Mo(NO)L^N(Br)_2]^+.PF_6^-$

Reaction of orange [231] with 4-amino-2-methyl-4'-ferrocenyl-azobenzene [47] under reflux in dichloromethane followed by filtration in air afforded a dark red-purple powder. This displayed $\nu_{max.}(NO)$ at 1585 cm^{-1}, strong $\nu_{max.}(PF_6)$ at 830 cm^{-1}, and also sharp absorptions for $\nu_{max.}(NH_2)$ at 3470 and 3380 cm^{-1}, suggesting a coordinated amino group. Elemental analyses confirmed that this was a pure sample of the complex $[Mo(NO)L^N(Br)_2(H_2NC_6H_3\text{-}3\text{-}CH_3\text{-}4\text{-}N{=}NC_6H_4\text{-}4\text{-}Fc)]^+.PF_6^-$ [234] resulting from addition of the neutral ferrocenyl-amine ligand without any loss of bromide ion. Repeated experiments produced the same product. [234] was also characterised by FAB-m.s. and cyclic voltammetry, but its paramagnetic nature precludes study by ^1H n.m.r. spectroscopy. A magnetic moment of μ_{eff} = 3.13 B.M. was recorded which indicates a triplet state (2 unpaired electrons), and a sample was sent for study by e.p.r. spectroscopy. Unfortunately, the result of this experiment was too complicated to analyse, owing to the complex nature of triplet state behaviour.

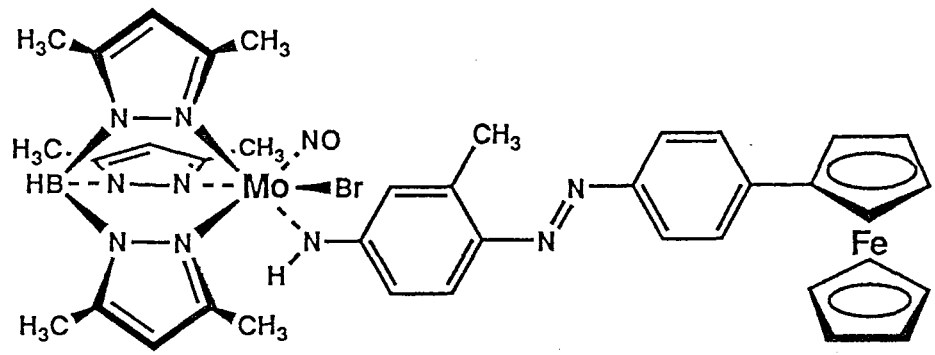
Although chromium(II) and tungsten(II) complexes are often paramagnetic, paramagnetism in molybdenum(II) coordination complexes is very rare.[293] Monomeric Mo(I) and Mo(III) complexes are always paramagnetic, but the four d-electrons of the Mo(II) ion tend to pair up to give diamagnetic species. However, a suitable crystal field splitting should be capable of giving rise to a triplet state for Mo(II), and all of the physical evidence confirms that this is indeed the case in complex [234].

Fig. 76

Products from Reaction of $[Mo(NO)L^*(Br)_2]$ or $[Mo(NO)L^N(Br)_2]^+.PF_6^-$ with 4-Amino-2-methyl-4'-ferrocenylazobenzene



[234]



[90]

The unexpected production of [234] provides a clear and useful comparison between the reactions of $[Mo(NO)L^*(Br)_2]$ and [231] with the ligand [47]. In the case of $[Mo(NO)L^*(Br)_2]$, described earlier, a simple bromide displacement occurs to give the six-coordinate 16-electron, neutral product $[Mo(NO)L^*(Br)(HNC_6H_3\text{-}3\text{-}CH_3\text{-}4\text{-}N{=}NC_6H_4\text{-}4\text{-}Fc)]$ [90]. However, with [231], the product is the seven-coordinate, 18-electron, cationic [234] (Fig. 76). Clearly, the steric bulk of the L^N ligand is insufficient to prevent expansion

of the molybdenum coordination sphere which is prevented in [Mo(NO)L*(Br)$_2$] by the shape of the bulky L* ligand. Furthermore, the ability of [231] to accept an electron pair and become reduced by the aniline ligand is a reflection of the poorer electron donating properties of the neutral macrocycle as compared to the uninegative L* ligand. This is confirmed by comparison of the electrochemical properties of these complexes (see section VI-1.3(b)(iii)).

A coordination number of seven is not at all unusual for Mo(II) complexes.[293] For example, the neutral bimetallic amine complex [(Mo(S_2CNEt_2)$_2$(CO)$_2$)$_2$(μ-$H_2NC_2H_4NH_2$)][294] has two 7-coordinate metals, and the complex [Mo(NO)(9-ane-N_3)(CN)$_3$][289] is an example with a formulation somewhat similar to [234] In such complexes, the metal is often found in a mono-capped octahedral geometry.

Reaction of [231] with several other potential amine ligands, followed by i.r. spectroscopic studies, failed to reveal any identifiable products. With 4-amino-4'-nitroazobenzene or 2-methyl-4-nitroaniline no reaction was detected even after extended periods under reflux in dichloromethane. Aniline, 4-ferrocenyl-2-methylaniline, and triethylamine all gave reduced products with $\nu_{max.}$(NO) at 1585 cm^{-1} but which contained no $\nu_{max.}$(PF_6) or new ligand absorptions. From these limited experiments, it appears that amines which are sufficiently basic simply reduce the dibromide without forming an adduct, whereas amines rendered less basic by strongly electron-withdrawing groups do not react at all. In the case of [47] it would seem that, rather fortuitously, a situation somewhere in between these two extremes occurs. Whether factors other than simple basicity are in operation is unclear.

Finally, an attempt to eliminate HBr from [234] and form the amide using sodium hydride in dry acetonitrile gave a reduced product with $\nu_{max.}$(NO) at 1590 cm^{-1}, but no $\nu_{max.}$(NH_2) or $\nu_{max.}$(PF_6). This clearly was not the desired [Mo(NO)L^N(Br)(HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-Fc)]$^+$.PF_6^-, and no further work on this reaction was undertaken.

Complex [234] was tested for powder SHG at 1,907 nm using the apparatus at Durham, but gave no detectable signal, suggesting that it crystallises in a centrosymmetric space group. In view of

the considerable differences between the molecular structure of [234] and of its neutral SHG-active L* analogue [90], this is not a surprising result.

VI-1.3(b)(iii) Cyclic Voltammetry

The electrochemical properties of the cationic dihalide complexes [231] and [232] have previously been investigated in DMF or acetonitrile solution using cyclic voltammetry.[292] The objectives of the investigations carried out in this study are to provide direct comparisons between the redox behaviour of these complexes and their neutral counterparts containing L*, as well as to study the properties of the unusual 7-coordinate amine complex [234]. Results are shown in Table XXVI.

TABLE XXVI

Cyclic Voltammetry Data for Dihalide Complexes

Complex	E_f[Mo]/V[a] (ΔE_p/mV)	
	DCM	MeCN
$[Mo(NO)L^*(Cl)_2]$	-	+0.09 (70)
$[Mo(NO)L^N(Cl)_2]^+.PF_6^-$	+0.53 (175)[b]	+0.41 (195)[b]
$[Mo(NO)L^*(Br)_2]$	+0.21 (95)	-
$[Mo(NO)L^N(Br)_2]^+.PF_6^-$	+0.67 (80)	+0.56 (80)

[a] All potentials measured relative to SCE using a platinum-bead working electrode with 0.2 M $[NBu_4][BF_4]$ as supporting electrolyte; scan rate 200 mV s^{-1}. [b] Some splitting of reduction wave detected.

Inspection of the data in Table XXVI shows that, in dichloromethane, the dibromide complex [231] has a reduction potential which is some 460 mV more anodic than that of its counterpart containing L*. Also, the dichloride [232] has a reduction potential which is about 320 mV more anodic than that of its non-macrocyclic analogue in acetonitrile solution. Hence it

can be concluded that the molybdenum mononitrosyl dihalide complexes of the L^N ligand are reduced much more readily than L* derivatives. This explains the empirical observation that reduction rather than coordination is likely with donor ligands and the {Mo(NO)L^N} dihalides.

In acetonitrile solution the complex [234] shows an irreversible molybdenum reduction wave at E_f = -1.53 V (ΔE_p = 120 mV) and an irreversible ferrocenyl oxidation wave at +0.51 V (ΔE_p = 110 mV). The highly cathodic molybdenum potential is in keeping with the reduced nature of the complex, representing a shift of 970 mV from the 16-electron dibromide precursor [231]. The free ligand 4-amino-2-methyl-4'-ferrocenylazobenzene [47] has an oxidation at +0.46 V (ΔE_p = 80 mV) in acetonitrile, so a 50 mV anodic shift is produced upon coordination to the cationic metal centre. This compares with an anodic shift of 30 mV (in dichloromethane) when the anilide ligand forms the neutral complex [Mo(NO)L*(Br)(HNC_6H_3-3-CH_3-4-N=NC_6H_4-4-Fc)] [90].

VI-1.4 POLYENE SPECIES

Conjugated polyene molecules have been the focus of much research in the field of molecular electronics for a number of reasons. Polyacetylene and polydiacetylene compounds are semiconductors which can be doped to produce materials exhibiting metallic electrical conductivity comparable to that of copper.[295] In photochemically active molecules, carotenoid groups act as molecular antennae for photon trapping, and these have been used in the construction of artificial molecules designed to mimic natural photosynthetic systems.[296] Various carotenoid derivatives, such as zwitterionic carioviologens, are also being investigated as "molecular wires" for use in future molecular electronic systems.[297] Furthermore, polyene molecules have been found to possess marked nonlinear optical responses,[18,298] both second and third order, because they contain extensive delocalisation of π-electrons. This has recently led to the fabrication of prototype waveguiding devices using polydiacetylene thin films,[299] but

considerable developments are necessary before these materials could become commercially viable.

Small donor-acceptor substituted polyene molecules ("push-pull" polyenes) containing between four and eight conjugated double bonds have been found, from solution EFISH measurements, to possess exceptionally high β values.[26,300] They can also show marked SHG in powder form,[301] and high $\chi^{(2)}$ values when cast as L-B films.[26] There have recently been reports of SHG from L-B films of the natural molecule retinal and retinal schiff-base derivatives.[302] Hence, polyene ligand complexes containing the $\{Mo(NO)L^*(Cl)\}^+$ electron acceptor centre could be of interest for both second and third-order NLO effects.

VI-1.4(a) Reactions with Retinol

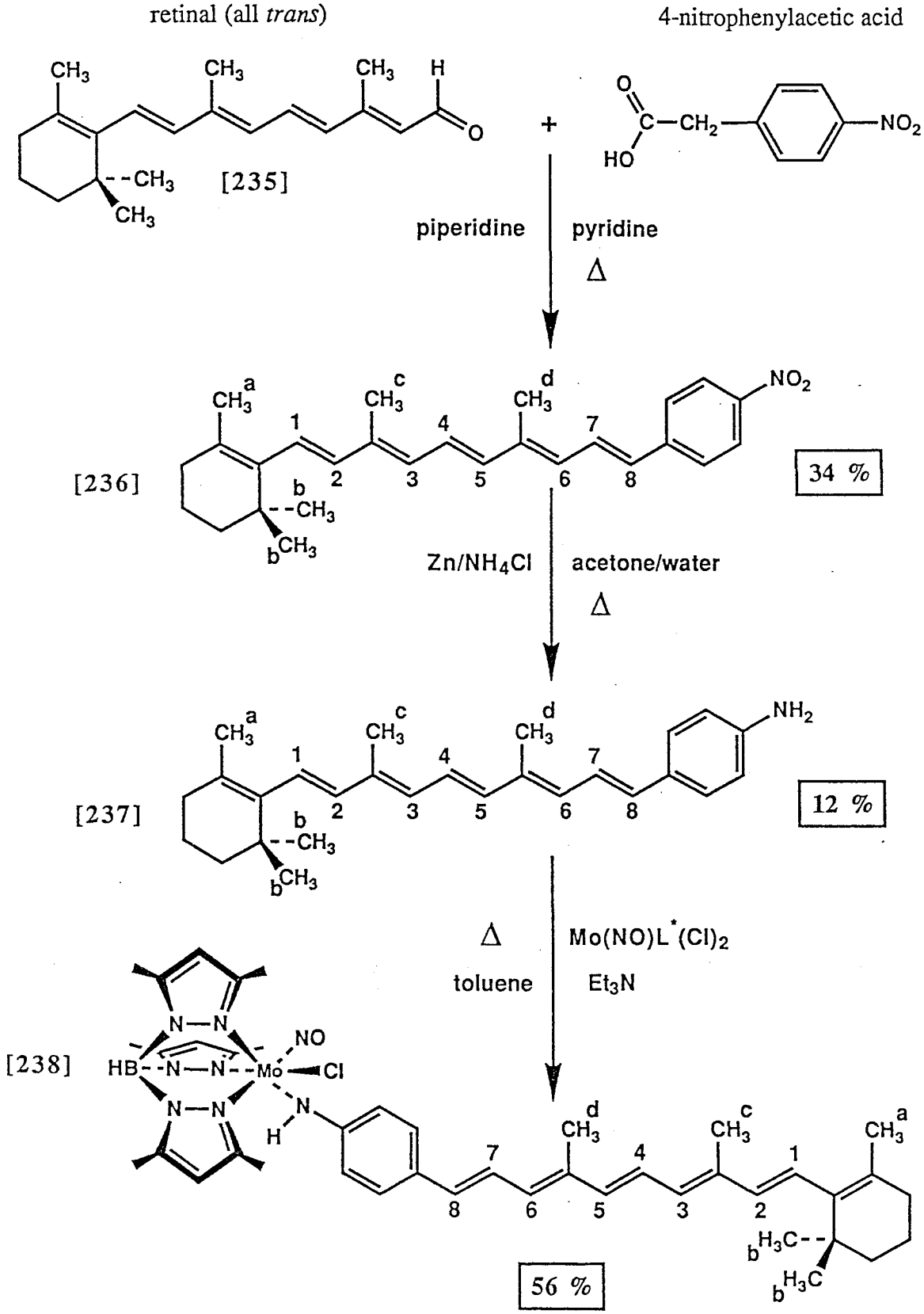
Some reactions between commercial retinol (vitamin A_1) and $[Mo(NO)L^*(Cl)_2]$ were carried out, but no complexes containing the polyene ligand were isolated. Several fractions were collected from column chromatography and studied by i.r. and ^1H n.m.r. spectroscopy, but none contained the retinyl group. This could be largely due to the presence of significant quantities of water in the retinol sample, but also the particularly sensitive nature of the retinol molecule to photochemical degradation may be important.

VI-1.4(b) Synthesis and Complexation of a Retinyl Aniline Ligand

An alternative approach to the preparation of the first $\{Mo(NO)L^*\}$-polyene complex involved taking commercial retinal as a starting material. A Perkin-type reaction of the sort employed in the synthesis of stilbene ligands was used to prepare a novel aryl polyene ligand for complexation to a molybdenum mononitrosyl electron-acceptor centre. The synthetic scheme for the preparation of the retinyl ligand and its complexation to molybdenum is shown in Fig. 77.

Fig. 77

Synthesis of a Retinylanilide Complex



Retinal (95% *trans*) [235] was condensed with 4-nitrophenyl-acetic acid in pyridine and piperidine to yield the orange crystalline product 4-[4,8-dimethyl-10-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,3,5,7,9-decapentaenyl]-nitrobenzene (95% all *trans*) [236] in reasonable yield. A zinc-ammonium chloride reduction of [236] produced the amine 4-[4,8-dimethyl-10-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,3,5,7,9-decapentaenyl]-aniline (95% all *trans*) [237] in low yield. [237] appeared to be somewhat air-sensitive, and was stored under a nitrogen atmosphere prior to physical characterisation and complexation studies.

Reaction of [237] with $[Mo(NO)L^*(Cl)_2]$ under the usual conditions afforded a good yield of the mono-chloro anilide complex [238] which was purified by column chromatography and isolated as a black powder. Further column chromatography was used to separate this into major (93%) and minor (7%) black fractions. The minor fraction, believed to be the complex of the 5-*cis* ligand, was characterised only by i.r. spectroscopy owing to there being insufficient quantity for further study. The major fraction was found to be the all *trans* complex and was fully characterised by the usual physical techniques which gave results in accord with the proposed formulation.

Complex [238] was tested for powder SHG at 1,907 nm using the apparatus at Durham, but no detectable signal was observed. Further NLO testing, particularly for third-order $\chi^{(3)}$ effects which can occur even in centrosymmetric media, would perhaps be of interest, but is unfortunately beyond the scope of this study.

VI-2 EXPERIMENTAL

$[Mo(NO)L^*(I)_2]$, $[Mo(NO)L^N(Cl)_2]^+.PF_6^-$, and $[Mo(NO)L^N(Br)_2]^+.PF_6^-$ were prepared by previously described methods.[187,292] $[Mo(NO)L^*(Cl)_2]$ was prepared by a previously described method,[186] and also using the new technique described in Chapter Two. The diiodide is considered as its mono toluene solvate $[Mo(NO)L^*(I)_2].C_7H_8$ when calculating yields. Triethylamine was dried over sodium and stored over

activated alumina, and hexamine was recrystallised from absolute ethanol and dried under vacuum. Other organic reagents were prepared by literature methods referenced in section VI-1, or obtained commercially and used as supplied. All reaction solvents were redistilled from drying agents according to standard methods prior to use, and all reactions were performed under an atmosphere of dry nitrogen but the reaction products handled in air. Column chromatography was carried out using silica gel 60 (70-230 mesh) and column dimensions of 40 x 2 cm unless otherwise specified.

VI-2.1 LIGANDS AND LIGAND PRECURSORS

(-)-2-(6-Methoxy-2-naphthyl)-1-propanol [202]

(+)-2-(6-methoxy-2-naphthyl)-1-propanoic acid (0.75 g, 3.26 mmol) was added to a stirred solution of $LiAlH_4$ (0.30 g, 7.8 mmol) in dry thf (30 cm^3) kept at 0 °C in an ice-water bath. After initial effervescence, the mixture was stirred at 0 °C for 5 h and then allowed to warm to r.t. and stirred for 15 h. Methanol (10 cm^3) was added followed by water (10 cm^3) to destroy any residual $LiAlH_4$. Dichloromethane (30 cm^3) was added and the mixture filtered using a no. 2 sinter to remove inorganic hydroxides. The dichloromethane layer was separated and the aqueous layer extracted with further dichloromethane (2 x 20 cm^3). The combined organic extracts were evaporated *in vacuo* to yield the crude white product which was purified by recrystallisation from ethanol/water to afford a white powder (0.65 g, 92%) m.p. 87-89 °C (lit.,[201] 88-89 °C); $[\alpha]_D$ = -15°(CH_2Cl_2) (lit.,[201] -18°($CHCl_3$) (Found: C, 77.9; H, 7.8%; M^+, 216. $C_{14}H_{16}O_2$ requires C, 77.8; H, 7.5%; M, 216); $\nu_{max.}$(OH) 3350s cm^{-1}; $\delta_H(CDCl_3)$ 7.73-7.12 [6 H, c m, $C_{10}H_6$], 3.91 [3 H, s, OCH_3], 3.77 [2 H, t, Mo-OCH_2], 3.08 [1 H, sx, -$CH(CH_3)$], 1.35 [3 H, d, J(HH) 7.0 Hz, -$CH(CH_3)$]; *m/z* 216 (M^+), 198 (M - H_2O), 185 (M - $HOCH_2$ or OCH_3), 170 (M - $HOCH_2$ - CH_3), 157 (M - $CH(CH_3)CH_2OH$), 154 (M - $HOCH_2$ - OCH_3), 141 (M - $HOCH_2$ - CH - OCH_3), 128 ($C_{10}H_8$),

4-[4,8-Dimethyl-10-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,3,5,7,9-decapentaenyl]-nitrobenzene (*E,E,?,E,E,E*) [236]

A solution of retinal (95% *trans*, 0.5 g, 1.76 mmol), 4-nitrophenylacetic acid (0.4 g, 2.21 mmol), and piperidine (5 cm^3) was stirred under reflux in pyridine (20 cm^3) for 4 h. The mixture was cooled and the solvent removed under reduced pressure. The product was purified by column chromatography on silica using 35% dichloromethane/n-hexane as eluent. The major orange band was collected and evaporated to yield the orange product (0.24 g, 34%). This was further purified by recrystallisation from methanol to afford orange needles. T.l.c. investigation revealed major and minor yellow-orange fractions likely to be due to two isomeric forms resulting from the presence of 5% *cis* in the original retinal.

$C_9H_{15}CH{=}CH{-}C(CH_3){=}CH{-}CH{=}CH{-}C(CH_3){=}CH{-}CH{=}CH{-}C_6H_4{-}4{-}NO_2$ m.p. 110–125 °C (Found: C, 75.2; H, 7.6; N, 2.7; M^+, 403. $C_{27}H_{33}NO_2.0.5CH_2Cl_2$ requires C, 75.2; H, 7.8; N, 3.2%; M, 403); $\nu_{max.}(NO_2)$ 1510s and 1345s cm^{-1}; $\delta_H(CDCl_3)$ 8.17 and 7.52 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4], 7.36 and 7.30 [½ H, d, J(67) 11.7 Hz; ½ H, d, J(67) 11.4 Hz, J(78) 15.4 Hz, =C*H*(7)], 6.81 and 6.75 [½ H, d, J(34) 11.9 Hz; ½ H, d, J(34) 11.4 Hz, J(45) 14.9 Hz, =C*H*(4)], 6.60 [1 H, d, J(78) 15.7 Hz, =C*H*(8)], 6.39 [1 H, d, J(45) 15.0 Hz, =C*H*(5)], 6.31 [1 H, d, J(67) 11.5 Hz, =C*H*(6)], 6.21–6.11 [3 H, c m, =C*H*(1,2,3)], 2.09 [3 H, s, CH_3(d)], 2.00 [3 H, s, CH_3(c)], 1.73 [3 H, s, CH_3(a)], 1.67–1.45 [6 H, c m, 3 x CH_2], 1.04 [6 H, s, CH_3(b)]; *m/z* 403 (M^+), 388 (M – O), 373 (M – NO), 372 (M – O_2).

4-[4,8-Dimethyl-10-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,3,5,7,9-decapentaenyl]-aniline (*E,E,?,E,E,E*) [237]

A solution of [236] (0.2 g, 0.50 mmol) and ammonium chloride (0.16 g, 3.0 mmol) in acetone (25 cm^3) and water (5 cm^3) was heated to reflux. Zinc powder (0.2 g) was added and the mixture stirred under reflux for 1 h. Further ammonium chloride (0.2 g) and zinc powder (0.2 g) were added and the mixture was stirred under reflux for a further 4 h. The colour of the solution changed from orange to yellow during this time. The reaction mixture was cooled and the zinc powder removed by filtration. The acetone was removed *in vacuo*, and water (10 cm^3) and dichloromethane (10 cm^3) were added. The yellow organic layer was separated and the aqueous layer

extracted with further dichloromethane (3 x 10 cm^3). The combined organic extracts were evaporated to yield the crude product as a yellow oil. This was purified by column chromatography on silica using dichloromethane as eluent, collecting the major yellow band. This yielded the product as a golden solid (0.022 g, 12%) which was further purified by recrystallisation from dichloromethane/ n-hexane. This product was found to turn brown upon prolonged exposure to air, and was stored under a nitrogen atmosphere prior to physical characterisation and complexation studies.

$C_9H_{15}CH{=}CH{-}C(CH_3){=}CH{-}CH{=}CH{-}C(CH_3){=}CH{-}CH{=}CH{-}C_6H_4{-}4{-}NH_2$

(Found: C, 86.5; H, 9.4; N, 3.8; M^+, 373. $C_{27}H_{35}N$ requires C, 86.8; H, 9.4; N, 3.8%; M, 373); $\nu_{max.}(NH_2)$ 3450w and 3360m cm^{-1}; $\delta_H(CDCl_3)$ 7.24 and 6.61 [2 H, d, J(HH) 8.2 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 7.00 and 6.94 [½ H, d, J(67) 11.4 Hz; ½ H, d, J(67) 11.4 Hz, J(78) 15.4 Hz, =C*H*(7)], 6.65 and 6.59 [½ H, d, J(34) 11.4 Hz; ½ H, d, J(34) 11.4 Hz, J(45) 15.4 Hz, =C*H*(4)], 6.49 [1 H, d, J(78) 15.4 Hz, =C*H*(8)], 6.37 [1 H, d, J(45) 15.0 Hz, =C*H*(5)], 6.25 [1 H, d, J(67) 11.5 Hz, =C*H*(6)], 6.17-6.11 [3 H, c m, =C*H*(1,2,3)], 3.70 [2 H, br s, NH_2], 2.00 [3 H, s, CH_3(d)], 1.97 [3 H, s, CH_3(c)], 1.72 [3 H, s, CH_3(a)], 1.67-1.45 [6 H, c m, 3 x CH_2], 1.03 [6 H, s, CH_3(b)]; *m/z* 373 (M^+), 358 (M - NH_2).

VI-2.2 COMPLEXES

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{(-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3}] [203]

A solution of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.30 g, 0.61 mmol), (-)-2-(6-methoxy-2-naphthyl)-1-propanol (0.16 g, 0.73 mmol) and triethylamine (0.5 cm^3) was stirred under reflux in toluene (20 cm^3) for 45 min. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The resulting blue solid was purified by column chromatography on silica using dichloromethane as eluent. The major turquoise band was collected and crystallised from a dichloromethane/n-hexane mixture to afford the turquoise product (0.28 g, 68%). m.p. *ca* 230 °C (Found: C, 51.8; H, 5.8; N, 14.4%; M^+, 674. $C_{29}H_{37}BClMoN_7O_3$ requires C, 51.7; H, 5.5; N, 14.6%; M, 674); $\nu_{max.}$(NO) 1670s cm^{-1}; $\delta_H(CDCl_3)$ 7.70-7.09 [6 H, c m, $C_{10}H_6$],

6.12-5.90 [2 H, c m, Mo-OCH_2], 5.85, 5.80, 5.72, and 5.69 [3 H, all s, ($Me_2C_3N_2H$)$_3$], 3.92 and 3.91 [3 H, s, s, OCH_3], 3.53 [1 H, c m, -CH(CH_3)], 2.52, 2.51, 2.38, 2.35, 2.35, 2.32, 2.30, 2.19, and 2.12 [18 H, all s, ($Me_2C_3N_2H$)$_3$], 1,55, and 1.48 [3 H, d, d, J(HH) 7.0 Hz, -CH(CH_3)]; *m/z* 674 (M^+), 644 (M - NO), 638 (M - Cl), 608 (M - Cl - NO), 460 (M - (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3), 430 (M - (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3 - NO), 216 ((-)-2-$HOCH_2CH(CH_3)C_{10}H_6$-6-OCH_3). E_f = -0.62 V, ΔE_p = 150 mV; ΔE_p(Fc) = 75 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{(-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3}] [204]

This compound was prepared in similar manner to [203] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.40 g, 0.52 mmol) in place of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)$_2$], (-)-2-(6-methoxy-2-naphthyl)-1-propanol (0.13 g, 0.60 mmol) and hexamine (0.05 g, 0.36 mmol) in place of triethylamine, with a reaction time of 1 h. A lime green solid was obtained (0.34 g, 86%). m.p. *ca* 230 °C (Found: C, 45.3; H, 4.8; N, 12.9%; M^+, 765. $C_{29}H_{37}BIMoN_7O_3$ requires C, 45.5; H, 4.9; N, 12.8%; M, 765); $\nu_{max.}$(NO) 1670s cm^{-1}; δ_H($CDCl_3$) 7.68-7.08 [6 H, c m, $C_{10}H_6$], 5.86-5.58 [5 H, c m, ($Me_2C_3N_2H$)$_3$ and Mo-OCH_2], 3.91 and 3.91 [3 H, s, s, OCH_3], 3.50 [1 H, c m, -CH(CH_3)], 2.49, 2.40, 2.37, 2.34, 2.33, 2.31, 2.25, 2.14, and 2.11 [18 H, all s, ($Me_2C_3N_2H$)$_3$], 1.48 and 1.44 [3 H, d, d, J(HH) 7.0 Hz, -CH(CH_3)]; *m/z* 765 (M^+), 735 (M - NO), 640 (M - I), 610 (M - I - NO), 552 (M - (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3), 522 (M - (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3 - NO), 424 (M - (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3 - I), 216 ((-)-2-$HOCH_2CH(CH_3)C_{10}H_6$-6-OCH_3). E_f = -0.55 V, ΔE_p = 110 mV; ΔE_p(Fc) = 75 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{(-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3}$_2$] [205]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(I)$_2$].C_7H_8 (0.25 g, 0.33 mmol) and (-)-2-(6-methoxy-2-naphthyl)-1-propanol (0.16 g, 0.74 mmol) using the procedure described for [203]. A red-brown solid was obtained (0.15 g, 55%). m.p. *ca* 195 °C (Found: C, 60.2; H, 5.9; N, 11.5%; M^+, 854. $C_{43}H_{45}BMoN_7O_5$ requires C, 60.5; H, 6.1; N, 11.5%; M, 854); $\nu_{max.}$(NO) 1640s cm^{-1}; δ_H($CDCl_3$) 7.70-7.08 [12 H, c m, 2 x $C_{10}H_6$], 5.75-4.98 [7 H, c m, ($Me_2C_3N_2H$)$_3$ and 2 x Mo-OCH_2], 3.90 [6 H, s, 2 x OCH_3], 3.26 and 3.06 [1 H, c m;

1 H, c m, 2 x -C*H*(CH_3)], 2.51, 2.47, 2.34, 2.31, 2.28, and 2.05 [18 H, all s, ($Me_2C_3N_2H$)$_3$], 1.39 and 1.30 [6 H, d, d, J(HH) 6.7 Hz, 2 x -CH(C*H*$_3$)]; *m/z* 854 (M^+), 824 (M - NO), 640 (M - (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3), 610 (M - (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3 - NO), 423 (M - 2 x (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3), 216 ((-)-2-$HOCH_2CH(CH_3)C_{10}H_6$-6-OCH_3). E_f = -1.24 V, ΔE_p = 240 mV; ΔE_p(Fc) = 75 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{(-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3}{HNC_6H_3-3-CH_3-4-$N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [206]

A solution of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I{HNC_6H_3-3-CH_3-4-$N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [88] (0.10 g, 0.11 mmol), (-)-2-(6-methoxy-2-naphthyl)-1-propanol (0.065 g, 0.30 mmol) and triethylamine (0.5 cm^3) was stirred under reflux in toluene (10 cm^3) for 4 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The resulting deep crimson solid was purified by column chromatography on alumina using 30% n-hexane/dichloromethane as the eluent. Unreacted [88] was removed as a second purple band, and the first major crimson band was collected and evaporated to afford the deep crimson product (0.049 g, 45%). Further details of isomer separation by column chromatography and ^{1}H n.m.r. spectroscopic data can be found in section VI-1.1(d)(i). (Found: C, 55.0; H, 6.4; N, 10.5%; M^+, 918. $C_{62}H_{57}BFeMoN_{10}O_3.2.4CH_2Cl_2.1.1C_6H_{14}$ requires C, 55.0; H, 5.8; N, 10.5%; M, 1033); $\nu_{max.}$(NH) 3300w, $\nu_{max.}$(NO) 1635s cm^{-1}; *m/z* 912 (M - Fe(η^5-C_5H_5)), 848 (M - $CH(CH_3)C_{10}H_6$-6-OCH_3), 818 (M - (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3), 640 (M - HNC_6H_3-3-CH_3-4-$N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 610 (M - HNC_6H_3-3-CH_3-4-$N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - NO), 424 (M - HNC_6H_3-3-CH_3-4-$N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5) - (-)-2-$OCH_2CH(CH_3)C_{10}H_6$-6-OCH_3), 395 ($H_2NC_6H_3$-3-CH_3-4-$N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)), 216 ((-)-2-$HOCH_2CH(CH_3)C_{10}H_6$-6-OCH_3). E_f[Mo] = -1.05 V, ΔE_p = 185 mV; E_f[Fe] = +0.60 V, ΔE_p = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}{$OC_{27}H_{45}$}{HNC_6H_3-3-CH_3-4-$N{=}NC_6H_4$-4-(η^5-C_5H_4)Fe(η^5-C_5H_5)}] [207]

This compound was prepared in identical manner to [206] using cholesterol (0.19 g, 0.49 mmol) in place of (-)-2-(6-methoxy-2-

naphthyl)-1-propanol, and a reaction time of 3 h. Column chromatography on silica using 40% n-hexane/dichloromethane as eluent yielded three major fractions. The first was lime green [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}I($OC_{27}H_{45}$)] [194] (0.011 g, 13%). Unreacted [88] was recovered as a purple third band (0.031 g, 31%), and the second deep crimson band was collected and evaporated to afford the deep crimson product (0.049 g, 37%). (Found: C, 64.5; H, 7.4; N, 11.3%; $C_{65}H_{87}BFeMoN_{10}O_2$ requires C, 64.9; H, 7.3; N, 11.6%; M, 1203); $\nu_{max.}$(NH) 3300w, $\nu_{max.}$(NO) 1640s cm^{-1}; δ_H($CDCl_3$) 9.54 and 9.49 [1 H, s, s, N*H*], 7.83 and 7.57 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.2 Hz, C_6H_4], 7.82 [1 H, d, J(12) 8.6 Hz, C_6H_3(1)], 7.77 and 7.74 [1 H, d, d, J(23) 2.5 Hz, J(12) 8.6 Hz, C_6H_3(2)], 7.09 [1 H, br s, C_6H_3(3)], 5.85, 5.84, and 5.71 [3 H, s, s, s, ($Me_2C_3N_2H$)$_3$], 5.55 [1 H, c m, Mo-OC*H*], 5.36 [1 H, br s, =C*H*], 4.72 and 4.38 [2 H, d, J(HH) 1.2 Hz; 2 H, t, J(HH) 2.0, 1.7 Hz, C_5H_4], 4.06 [5 H, s, C_5H_5], 2.75, 2.71, 2.63, 2.60, 2.40, 2.35, 2.34, 2.13, and 2.12 [21 H, all s, C_6H_3-CH_3 and ($Me_2C_3N_2H$)$_3$], 2.10-0.80 [43 H, c m, $C_{27}H_{43}$, inc. CH_3 at 0.94, 0.93, 0.90, 0.88, 0.88, 0.86, and 0.85], 0.66 [3 H, s, CH_3(b)]; E_f[Mo] = -1.09 V, ΔE_p = 180 mV; E_f[Fe] = +0.60 V, ΔE_p = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{HNC_6H_3-2-N(CH_3)$_2$-5-NH}Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl] [208]

This compound was prepared in similar manner to [203] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}($Cl)_2$] (0.34 g, 0.69 mmol) and 2,4-diamino-N,N-dimethylaniline (0.050 g, 0.33 mmol) in place of (-)-2-(6-methoxy-2-naphthyl)-1-propanol, with a reaction time of 3 h. Column chromatography yielded two deep purple-brown fractions which were evaporated to afford deep purple solids (total yield 0.088 g, 25%).

Fraction 1 (208-F1) (0.049 g, 14%). (Found: C, 42.3; H, 5.2; N, 22.0%; M^+, 1065. $C_{38}H_{56}B_2Cl_2Mo_2N_{17}O_2$ requires C, 42.8; H, 5.2; N, 22.3%; M, 1066); $\nu_{max.}$(NH) 3275w, $\nu_{max.}$(NO) 1650s cm^{-1}; δ_H($CDCl_3$) 13.38 and 12.90 [1 H, s; 1 H, s, 2 x N*H*], 8.21 and 8.18 [½ H, d, J(12) 2.2 Hz; ½ H, d, J(12) 2.2 Hz, J(23) 8.7 Hz, C_6H_3(2)], 7.63 [1 H, d, J(12) 2.0 Hz, C_6H_3(1)], 7.30 [1 H, d, J(23) 8.7 Hz, C_6H_3(3)], 5.86, 5.83, and 5.76 [6 H, all s, 2 x ($Me_2C_3N_2H$)$_3$], 2.70, 2.60,

2.44, 2.43, 2.41, 2.38, 2.37, 2.35, 2.16, and 2.05 [42 H, all s, $-N(CH_3)_2$ and 2 x $(Me_2C_3N_2H)_3$]; *m/z* 1065 (M^+), 1035 (M - NO), 941 (M - 124), 936 (M - 129), 608 (M - Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl), 578 (M - Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl - NO), 458 (M - {HNC_6H_3-2-$N(CH_3)_2$-5-NH}Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl), 424 (M - {HNC_6H_3-2-$N(CH_3)_2$-5-NH}Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl - Cl). E_f = -0.81 V, ΔE_p = 65 mV; E_f = -1.24 V, ΔE_p = 70 mV, ΔE_f = 430 mV; ΔE_p(Fc) = 65 mV.

Fraction 2 (208-F2) (0.039 g, 11%). (Found: C, 42.6; H, 5.4; N, 21.8%; M^+, 1066. $C_{38}H_{56}B_2Cl_2Mo_2N_{17}O_2$ requires C, 42.8; H, 5.2; N, 22.3%; M, 1066); $\nu_{max.}$(NH) 3275w, $\nu_{max.}$(NO) 1650s cm^{-1}; $\delta_H(CDCl_3)$ 13.39 and 12.81 [1 H, s; 1 H, s, 2 x N*H*], 8.00 and 7.97 [½ H, d, J(12) 2.5 Hz; ½ H, d, J(12) 2.5 Hz, J(23) 8.7 Hz, C_6H_3(2)], 7.62 [1 H, d, J(12) 2.5 Hz, C_6H_3(1)], 7.31 [1 H, d, J(23) 8.7 Hz, C_6H_3(3)], 5.90, 5.86, 5.83, 5.77, and 5.72 [6 H, all s, 2 x $(Me_2C_3N_2H)_3$], 2.71, 2.61, 2.44, 2.44, 2.43, 2.39, 2.38, 2.36, 2.11, and 2.08 [42 H, all s, $-N(CH_3)_2$ and 2 x $(Me_2C_3N_2H)_3$]; *m/z* 1066 (M^+), 1036 (M - NO), 941 (M - 124), 936 (M - 129), 608 (M - Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl), 578 (M - Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl - NO), 458 (M - {HNC_6H_3-2-$N(CH_3)_2$-5-NH}Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl), 424 (M - {HNC_6H_3-2-$N(CH_3)_2$-5-NH}Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl - Cl). E_f = -0.81 V, ΔE_p = 75 mV; E_f = -1.25 V, ΔE_p = 75 mV, ΔE_f = 440 mV; ΔE_p(Fc) = 65 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}Cl(OC_6H_3-3-CH_3-4-NH_2)] [213]

This compound was prepared in similar manner to [203] using [Mo(NO){HB(3,5-$Me_2C_3N_2H)_3$}$(Cl)_2$] (0.30 g, 0.61 mmol) and 4-amino-3-methylphenol (0.086 g, 0.70 mmol) in place of (-)-2-(6-methoxy-2-naphthyl)-1-propanol, with a reaction time of 2 h. Column chromatography gave a major deep blue band which was evaporated to yield a deep indigo solid. (0.21 g, 59%). (Found: C, 45.3; H, 5.0; N, 19.1%; M^+, 582. $C_{22}H_{30}BClMoN_8O_2$ requires C, 45.5; H, 5.2; N, 19.3%; M, 581); $\nu_{max.}$(NH_2) 3460w, 3360m; $\nu_{max.}$(NO) 1660s cm^{-1}; $\delta_H(CDCl_3)$ 7.13 and 7.10 [2 H, s, d, J(23) 2.6 Hz, C_6H_3(2 and 3)], 6.67 [1 H, d, J(12) 8.2 Hz, C_6H_3(1)], 5.91, 5.84, and 5.75 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.70 [2 H, vbr s, NH_2], 2.61, 2.40, 2.39, 2.38, 2.20, and 2.05 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s, $-CH_3$ and $(Me_2C_3N_2H)_3$]; *m/z* 582 (M^+), 552 (M - NO), 460 (M

- OC_6H_3-3-CH_3-4-NH_2), 430 (M - OC_6H_3-3-CH_3-4-NH_2 - NO). E_f = -0.46 V, ΔE_p = 260 mV; ΔE_p(Fc) = 65 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{OC_6H_3-3-CH_3-4-NH}Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)] [214]

This compound was prepared in similar manner to [203] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.81 mmol) and 4-amino-3-methylphenol (0.048 g, 0.39 mmol) in place of (-)-2-(6-methoxy-2-naphthyl)-1-propanol, with a reaction time of 1.5 h. Column chromatography gave a major deep blue band which was evaporated to yield a deep purple solid. (0.20 g, 50%). (Found: C, 42.5; H, 5.2; N, 19.9%; $C_{37}H_{51}B_2Cl_2Mo_2N_{15}O_3$ requires C, 42.8; H, 5.0; N, 20.2%; M, 1038); $\nu_{max.}$(NH) 3290w, $\nu_{max.}$(NO) 1660br s cm^{-1}; δ_H($CDCl_3$) 12.81 and 12.80 [1 H, s, s, N*H*], 8.15 [1 H, d, J(12) 8.9 Hz, C_6H_3(1)], 7.48 and 7.38 [½ H, d, J(23) 2.2 Hz; ½ H, d, J(23) 2.5 Hz, C_6H_3(3)], 7.16 and 7.07 [½ H, dd, J(23) 2.7 Hz, J(12) 8.9 Hz; ½ H, dd, J(23) 2.7 Hz, J(12) 8.8 Hz, C_6H_3(2)], 5.93, 5.88, 5.87, 5.81, and 5.78 [6 H, all s, 2 x ($Me_2C_3N_2H$)$_3$], 2.70, 2.59, 2.58, 2.43, 2.41, 2.39, 2.38, 2.37, 2.23, 2.22, 2.18, 2.09, 2.05, 2.03, and 1.98 [39 H, all s, -CH_3 and 2 x ($Me_2C_3N_2H$)$_3$]; Mass spec. nothing > *m/z* = 600. E_f = -0.26 V, ΔE_p = 150 mV; E_f = -1.33 V, ΔE_p = 290 mV, ΔE_f = 1070 mV; ΔE_p(Fc) = 65 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl(OC_6H_4CH=CHC_6H_4-4-NH_2)] [215]

This compound was prepared in similar manner to [203] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.30 g, 0.61 mmol) and 4-amino-4'-hydroxystilbene (0.14 g, 0.66 mmol) in place of (-)-2-(6-methoxy-2-naphthyl)-1-propanol, with a reaction time of only 5 min. Column chromatography gave two major bands; the first blue band yielded the purple bimetallic product (0.024 g, 7%), and the second major deep purple band was evaporated to yield a deep blue solid. (0.073 g, 18%). (Found: C, 51.3; H, 5.2; N, 16.9%; $C_{29}H_{34}BClMoN_8O_2$ .0.1CH_2Cl_2 requires C, 51.6; H, 5.1; N, 16.5%; M, 669); $\nu_{max.}$(NH_2) 3460w, 3360m; $\nu_{max.}$(NO) 1670s cm^{-1}; δ_H($CDCl_3$) 7.53 and 7.32 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.34 and 6.67 [2 H, d, J(HH) 8.4 Hz; 2 H, d, J(HH) 8.4 Hz, C_6H_4], 7.02 and 6.95 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 5.93, 5.88,

and 5.76 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 3.75 [2 H, br s, NH_2], 2.59, 2.41, 2.39, 2.20, and 2.06 [3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 639 (M - NO), 578 (M - $C_6H_4NH_2$), 564 (M - $CHC_6H_4NH_2$), 551 (M - $CH{=}CHC_6H_4NH_2$), 460 (M - $OC_6H_4CH{=}CHC_6H_4NH_2$), 424 (M - $OC_6H_4CH{=}CHC_6H_4NH_2$ - Cl), 211 ($HOC_6H_4CH{=}CHC_6H_4NH_2$). E_f = -0.33 V, ΔE_p = 65 mV; ΔE_p(Fc) = 65 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$OC_6H_4CH{=}CHC_6H_4$-4-NH}Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)] [216]

This compound was prepared in similar manner to [203] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.81 mmol) and 4-amino-4'-hydroxystilbene (0.082 g, 0.39 mmol) in place of (-)-2-(6-methoxy-2-naphthyl)-1-propanol. Column chromatography was carried out using 20% n-hexane/dichloromethane as eluent, collecting the major deep blue band which was evaporated to yield a deep purple solid. (0.19 g, 44%). (Found: C, 46.9; H, 5.1; N, 16.9%; $C_{44}H_{55}B_2Cl_2Mo_2N_{15}O_3$ requires C, 46.9; H, 4.9; N, 18.7%; M, 1126); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1660br s cm^{-1}; $\delta_H(CDCl_3)$ 12.60 [1 H, s, N*H*], 7.59 and 7.48 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.58 and 7.35 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.19 and 7.10 [1 H, d, $J(HH)_{trans}$ 16.1 Hz; 1 H, d, $J(HH)_{trans}$ 16.3 Hz, C*H*=C*H*], 5.93, 5.90, 5.88, 5.87, 5.80, and 5.77 [6 H, all s, 2 x $(Me_2C_3N_2H)_3$], 2.70, 2.59, 2.42, 2.42, 2.39, 2.38, 2.37, 2.21, 2.07, and 2.05 [3 H, s; 3 H, s; 6 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 2 x $(Me_2C_3N_2H)_3$]; *m/z* 578 (M - (Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl) - $C_6H_4NH_2$), 564 (M - (Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl) - $CHC_6H_4NH_2$), 551 (M - (Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl) - $CH{=}CHC_6H_4NH_2$), 460 (M - (Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl) - $OC_6H_4CH{=}CHC_6H_4NH_2$), 424 (M - (Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl) - $OC_6H_4CH{=}CHC_6H_4NH_2$ - Cl), 211 ($HOC_6H_4CH{=}CHC_6H_4NH_2$). E_f = -0.29 V, ΔE_p = 100 mV; E_f = -0.82 V, ΔE_p = 120 mV, ΔE_f = 530 mV; ΔE_p(Fc) = 65 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl{$OC_6H_4N{=}NC_6H_3$-2-CH_3-4-NH}Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(Cl)] [217]

This compound was prepared in similar manner to [203] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.40 g, 0.81 mmol) and 4-amino-2-methyl-4'-hydroxyazobenzene (0.089 g, 0.39 mmol) in place of (-)-

2-(6-methoxy-2-naphthyl)-1-propanol, with a reaction time of 4.5 h. Column chromatography was carried out using 20% n-hexane/dichloromethane as eluent, collecting the major deep pink-purple band which was evaporated to yield a deep purple solid. (0.29 g, 62%). (Found: C, 45.2; H, 4.9; N, 21.0%; $C_{43}H_{55}B_2Cl_2Mo_2N_{17}O_3$ requires C, 45.2; H, 4.9; N, 20.8%; M, 1142); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1660br s cm^{-1}; $\delta_H(CDCl_3)$ 12.52 [1 H, s, N*H*], 8.03 and 7.45 [2 H, d, J(HH) 8.9 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4], 7.78 [1 H, d, J(12) 8.7 Hz, $C_6H_3(1)$], 7.52 [1 H, br s, $C_6H_3(3)$], 7.30 [1 H, d, J(12) 8.9 Hz, $C_6H_3(2)$], 5.94, 5.93, 5.89, 5.88, 5.82, and 5.78 [6 H, all s, 2 x $(Me_2C_3N_2H)_3$], 2.79, 2.70, 2.58, 2.43, 2.43, 2.42, 2.40, 2.39, 2.37, 2.21, 2.10, and 2.05 [21 H, all s, $-CH_3$ and 2 x $(Me_2C_3N_2H)_3$]; Mass spec. nothing > *m/z* = 600. E_f = -0.20 V, ΔE_p = 90 mV; E_f = -0.72 V, ΔE_p = 110 mV, ΔE_f = 520 mV; ΔE_p(Fc) = 65 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl(OC_6H_4-4-NO_2)] [222]

A solution of [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.30 g, 0.61 mmol), 4-nitrophenol (0.085 g, 0.61 mmol) and triethylamine (0.5 cm^3) was stirred under reflux in toluene (20 cm^3) for 9 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The resulting brown solid was purified by column chromatography on silica using 20% n-hexane/dichloromethane as eluent. The major yellow-brown band was collected and crystallised from a dichloromethane/n-hexane mixture to afford the brown product (0.25 g, 68%). (Found: C, 42.2; H, 4.6; N, 18.7%; M^+, 598. $C_{21}H_{26}BClMoN_8O_4$ requires C, 42.3; H, 4.4; N, 18.8%; M, 597); $\nu_{max.}$(NO) 1680s cm^{-1}; $\delta_H(CDCl_3)$ 8.31 and 7.38 [2 H, d, J(HH) 9.3 Hz; 2 H, d, J(HH) 9.2 Hz, C_6H_4], 5.97, 5.96, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.53, 2.45, 2.42, 2.40, 2.15, and 2.07 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 598 (M^+), 582 (M - O), 568 (M - NO), 562 (M - Cl), 460 (M - $OC_6H_4NO_2$), 430 (M - $OC_6H_4NO_2$ - NO). E_f[Mo] = -0.08 V, ΔE_p = 95 mV; E_f[NO_2] = -1.43 V, ΔE_p = 350 mV; ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}(OC_6H_4-4-NO_2)$_2$] [223]

This compound was prepared from [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(I)_2$] .C_7H_8 (0.40 g, 0.52 mmol) and 4-nitrophenol (0.20 g, 1.44 mmol)

using the procedure described for [222], with a reaction time of 6 h. Column chromatography followed by recrystallisation yielded the product as a yellow-green solid (0.31 g, 84%) (Found: C, 45.4; H, 3.8; N, 17.4%; M^+, 699. $C_{27}H_{30}BMoN_9O_7.0.25CH_2Cl_2$ requires C, 45.4; H, 4.3; N, 17.5%; M, 699); $\nu_{max.}$(NO) 1675s cm^{-1}; $\delta_H(CDCl_3)$ 8.18 and 6.84 [4 H, d, J(HH) 9.2 Hz; 4 H, d, J(HH) 9.2 Hz, 2 x C_6H_4], 5.96, and 5.65 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.47, 2.41, 2.24, and 1.77 [6 H, s; 3 H, s; 6 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 699 (M^+), 683 (M - O), 669 (M - NO), 563 (M - $OC_6H_4NO_2$), 533 (M - $OC_6H_4NO_2$ - NO), 424 (M - 2 x $OC_6H_4NO_2$). E_f[Mo] = -0.21 V, ΔE_p = 185 mV; ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl(OC_6H_4CH=CHC_6H_4-4-NO_2)] [224]

This compound was prepared in identical manner to [222] using 4-hydroxy-4'-nitrostilbene (0.15 g, 0.62 mmol) in place of 4-nitrophenol, and with a reaction time of 3 h. Column chromatography followed by recrystallisation yielded the product as a deep pink-purple solid (0.35 g, 83%) (Found: C, 50.0; H, 4.9; N, 16.3%; M^+, 700. $C_{29}H_{32}BClMoN_8O_4$ requires C, 49.8; H, 4.6; N, 16.0%; M, 699); $\nu_{max.}$(NO) 1675s cm^{-1}; $\delta_H(CDCl_3)$ 8.20 and 7.62 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4], 7.62 and 7.38 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.6 Hz, C_6H_4], 7.31 and 7.11 [1 H, d, $J(HH)_{trans}$ 16.3 Hz; 1 H, d, $J(HH)_{trans}$ 16.1 Hz, C*H*=C*H*], 5.94, 5.91, and 5.77 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.58, 2.43, 2.42, 2.40, 2.20, and 2.07 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 700 (M^+), 684 (M - O), 670 (M - NO), 664 (M - Cl), 564 (M - CHC_6H_4-4-NO_2), 460 (M - OC_6H_4CH=CHC_6H_4-4-NO_2), 430 (M - OC_6H_4CH=CHC_6H_4-4-NO_2 - NO), 241 (HOC_6H_4CH=CHC_6H_4-4-NO_2). E_f[Mo] = -0.25 V, ΔE_p = 105 mV; $E_f[NO_2]$ = -1.02 V, ΔE_p = 205 mV; ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl(OC_6H_4N=NC_6H_4-4-NO_2)] [225]

This compound was prepared in identical manner to [222] using 4-hydroxy-4'-nitroazobenzene (0.15 g, 0.62 mmol) in place of 4-nitrophenol, and with a reaction time of 3 h. Column chromatography followed by recrystallisation yielded the product as a deep crimson solid (0.33 g, 79%) (Found: C, 44.8; H, 4.1; N, 19.6%; M^+, 702. $C_{27}H_{30}BClMoN_{10}O_4.0.3CH_2Cl_2$ requires C, 45.1; H, 4.2;

N, 19.3%; M, 701); $\nu_{max.}$(NO) 1685s cm^{-1}; $\delta_H(CDCl_3)$ 8.38 and 8.02 [2 H, d, J(HH) 9.0 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4], 8.09 and 7.48 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 9.0 Hz, C_6H_4], 5.95, 5.94, and 5.78 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.57, 2.44, 2.43, 2.41, 2.21, and 2.09 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 702 (M^+), 686 (M - O), 672 (M - NO), 666 (M - Cl), 552 (M - $N{=}NC_6H_4$-4-NO_2), 460 (M - $OC_6H_4N{=}NC_6H_4$-4-NO_2), 430 (M - $OC_6H_4N{=}NC_6H_4$-4-NO_2 - NO). E_f[Mo] = -0.15 V, ΔE_p = 120 mV; E_f = -0.88 V, ΔE_p = 145 mV; E_f = -1.44 V, ΔE_p = 310 mV; ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl($OC_6H_4N{=}NC_6H_3$-2-CH_3-4-NO_2)] [226]

This compound was prepared in identical manner to [222] using 4-hydroxy-2'-methyl-4'-nitroazobenzene (0.16 g, 0.62 mmol) in place of 4-nitrophenol, and with a reaction time of 3 h. Column chromatography followed by recrystallisation yielded the product as a deep crimson solid (0.29 g, 66%) (Found: C, 47.4; H, 4.6; N, 19.9%; M^+, 716. $C_{28}H_{32}BClMoN_{10}O_4$ requires C, 47.1; H, 4.5; N, 19.6%; M, 715); $\nu_{max.}$(NO) 1685s cm^{-1}; $\delta_H(CDCl_3)$ 8.23 [1 H, d, J(23) 2.2 Hz, C_6H_3(3)], 8.15 and 8.12 [½ H, d, J(23) 2.4 Hz; ½ H, d, J(23) 2.7 Hz, J(12) 9.0 Hz, C_6H_3(2)], 7.71 [1 H, d, J(12) 8.8 Hz, C_6H_3(1)], 8.08 and 7.48 [2 H, d, J(HH) 8.8 Hz; 2 H, d, J(HH) 8.8 Hz, C_6H_4], 5.95, 5.94, and 5.79 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.79, 2.57, 2.44, 2.43, 2.41, 2.20, and 2.11 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $-CH_3$ and $(Me_2C_3N_2H)_3$]; *m/z* 716 (M^+), 700 (M - O), 686 (M - NO), 680 (M - Cl), 460 (M - $OC_6H_4N{=}NC_6H_3$-2-CH_3-4-NO_2), 430 (M - $OC_6H_4N{=}NC_6H_3$-2-CH_3-4-NO_2 - NO), 257 ($HOC_6H_4N{=}NC_6H_3$-2-CH_3-4-NO_2). E_f[Mo] = -0.15 V, ΔE_p = 100 mV; E_f = -0.88 V, ΔE_p = 110 mV; E_f = -1.39 V, ΔE_p = 225 mV; ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl(OC_6H_3-3-CH_3-4-$N{=}NC_6H_3$-2-CH_3-4-NO_2)] [227]

This compound was prepared in identical manner to [222] using 4-hydroxy-2-methyl-2'-methyl-4'-nitroazobenzene (0.17 g, 0.62 mmol) in place of 4-nitrophenol, and with a reaction time of 3 h. Column chromatography followed by recrystallisation yielded the product as a deep crimson solid (0.27 g, 60%) (Found: C, 46.6; H, 5.0; N, 18.9%; M^+, 730. $C_{29}H_{34}BClMoN_{10}O_4.0.25CH_2Cl_2$ requires C, 46.8; H, 4.6; N, 18.7%; M, 729); $\nu_{max.}$(NO) 1685s cm^{-1}; $\delta_H(CDCl_3)$ 8.22 [1 H,

d, J(23) 2.2 Hz, C_6H_3(3)], 8.14 and 8.10 [½ H, d, J(23) 2.2 Hz; ½ H, d, J(23) 2.2 Hz, J(12) 8.9 Hz, C_6H_3(2)], 7.69 [1 H, d, J(12) 8.7 Hz, C_6H_3(1)], 7.86 [1 H, d, J(45) 8.9 Hz, C_6H_3(4)], 7.35 [1 H, d, J(56) 2.0 Hz, C_6H_3(6)], 7.25 and 7.21 [½ H, d, J(56) 2.5 Hz; ½ H, d, J(56) 2.7 Hz, J(45) 9.0 Hz, C_6H_3(5)], 5.95, 5.94, and 5.78 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.83, 2.80, 2.58, 2.44, 2.43, 2.40, 2.20, and 2.12 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 2 x $-CH_3$ and $(Me_2C_3N_2H)_3$]; *m/z* 730 (M^+), 714 (M - O), 700 (M - NO), 694 (M - Cl), 565 (M - $N{=}NC_6H_3$-2-CH_3-4-NO_2), 535 (M - $N{=}NC_6H_3$-2-CH_3-4-NO_2 - NO), 460 (M - OC_6H_3-3-CH_3-4-$N{=}NC_6H_3$-2-CH_3-4-NO_2), 430 (M - OC_6H_3-3-CH_3-4-$N{=}NC_6H_3$-2-CH_3-4-NO_2 - NO). E_f[Mo] = -0.17 V, ΔE_p = 105 mV; E_f = -0.90 V, ΔE_p = 130 mV; E_f = -1.45 V, ΔE_p = 270 mV; ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl($OC_{10}H_6$-4-$N{=}NC_6H_4$-4-NO_2)] [228]

This compound was prepared in identical manner to [222] using 4-nitrophenylazo-1-naphthol (0.18 g, 0.62 mmol) in place of 4-nitrophenol, and with a reaction time of 3 h. Column chromatography followed by recrystallisation yielded the product as a black solid (0.091 g, 20%) (Found: C, 49.3; H, 4.4; N, 18.4%; M^+, 752. $C_{31}H_{32}BClMoN_{10}O_4$ requires C, 49.6; H, 4.3; N, 18.7%; M, 751); $\nu_{max.}$(NO) 1685s cm^{-1}; $\delta_H(CDCl_3)$ 8.98, 8.23, 7.89, 7.71-7.63, and 7.44 [1 H, d, J(HH) 8.4 Hz; 1 H, d, J(HH) 8.4 Hz; 1 H, d, J(HH) 8.7 Hz; 2 H, c m; 1 H, t, $C_{10}H_6$], 8.42 and 8.14 [2 H, d, J(HH) 9.1 Hz; 2 H, d, J(HH) 8.9 Hz, C_6H_4], 5.98, 5.87, and 5.79 [1 H, s; 1 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.60, 2.48, 2.45, 2.16, and 1.78 [3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s, $(Me_2C_3N_2H)_3$]; *m/z* 752 (M^+), 642 (M - 110), 612 (M - 110 - NO), 552 (M - 200), 516 (M - 236), 460 (M - $OC_{10}H_6$-4-$N{=}NC_6H_4$-4-NO_2), 430 (M - $OC_{10}H_6$-4-$N{=}NC_6H_4$-4-NO_2 - NO), 293 ($HOC_{10}H_6$-4-$N{=}NC_6H_4$-4-NO_2). E_f[Mo] = -0.11 V, ΔE_p = 90 mV; E_f = -0.84 V, ΔE_p = 100 mV; E_f = -1.38 V, ΔE_p = 235 mV; ΔE_p(Fc) = 70 mV.

[Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}Cl
{HNC_6H_4-4-CH=CH-CH=C(CH_3)-CH=CH-CH=C(CH_3)-CH=CH-C_9H_{15}}] [238]

This compound was prepared in similar manner to [222] using [Mo(NO){HB(3,5-$Me_2C_3N_2H$)$_3$}$(Cl)_2$] (0.10 g, 0.20 mmol) and 4-[4,8-

dimethyl-10-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,3,5,7,9-decapentaenyl]-aniline (*E,E,?,E,E,E*) [237] (0.091 g, 0.24 mmol) in place of 4-nitrophenol, with a reaction time of 4 h. The product was purified by column chromatography on silica using 40% n-hexane/dichloromethane as eluent. The major black band was collected and evaporated to afford the black product (0.10 g, 60%). Further careful column chromatography was used to separate this into major (93%) and minor (7%) black fractions. The minor fraction, believed to be the complex of the 5-*cis* ligand, was characterised only by i.r. spectroscopy owing to there being insufficient quantity for further study. The two fractions were indistinguishable by i.r. spectra. The major fraction was found to be the all *trans* complex. (Found: C, 60.7; H, 6.9; N, 13.1%; M^+, 832. $C_{42}H_{56}BClMoN_8O$ requires C, 60.7; H, 6.9; N, 13.5%; M, 831); $\nu_{max.}$(NH) 3270w, $\nu_{max.}$(NO) 1655s cm^{-1}; $\delta_H(CDCl_3)$ 12.54 [1 H, s, N*H*], 7.48 and 7.43 [2 H, d, J(HH) 8.7 Hz; 2 H, d, J(HH) 8.7 Hz, C_6H_4], 7.22 and 7.16 [½ H, d, J(67) 11.6 Hz; ½ H, d, J(67) 11.4 Hz, J(78) 15.5 Hz, =C*H*(7)], 6.73 and 6.67 [½ H, d, J(34) 11.4 Hz; ½ H, d, J(34) 11.4 Hz, J(45) 15.5 Hz, =C*H*(4)], 6.60 [1 H, d, J(78) 15.1 Hz, =C*H*(8)], 6.40 [1 H, d, J(45) 14.6 Hz, =C*H*(5)], 6.32 [1 H, d, J(67) 11.4 Hz, =C*H*(6)], 6.19-6.16 [3 H, c m, =C*H*(1,2,3)], 5.87, and 5.79 [2 H, s; 1 H, s, $(Me_2C_3N_2H)_3$], 2.69, 2.42, 2.38, and 2.07 [3 H, s; 3 H, s; 9 H, s; 3 H, s, $(Me_2C_3N_2H)_3$], 2.02 [3 H, s, CH_3(d)], 1.99 [3 H, s, CH_3(c)], 1.73 [3 H, s, CH_3(a)], 1.70-1.45 [6 H, c m, 3 x CH_2], 1.04 [6 H, s, CH_3(b)]; *m/z* 832 (M^+), 802 (M - NO), 796 (M - Cl), 766 (M - Cl - NO), 709 (M - C_9H_{15}), 706 (M - 126), 460 (M - $HNC_6H_4C_9H_{15}$), 430 (M - $HNC_6H_4C_9H_{15}$ - NO), 373 ($H_2NC_6H_4C_{21}H_{29}$). E_f = -0.75 V, ΔE_p = 165 mV; ΔE_p(Fc) = 75 mV.

Elemental Analyses for N,N',N"-trimethyl-1,4,7-triazacyclononane dihalides (obtained from Prof. K. Wieghardt, Bochum, Germany):

[Mo(NO){N,N',N"-$Me_3C_6N_3H_{12}$}$(Cl)_2$].PF_6 [232]: Found: C, 22.2; H, 4.5; N, 10.7. $C_9H_{21}Cl_2F_6MoN_4OP$ requires C, 21.1; H, 4.1; N, 10.9.

[Mo(NO){N,N',N"-$Me_3C_6N_3H_{12}$}$(Br)_2$].PF_6 [231]: Found: C, 18.6; H, 3.7; N, 9.2. $C_9H_{21}Br_2F_6MoN_4OP$ requires C, 18.0; H, 3.5; N, 9.3.

[Mo(NO){N,N',N"-$Me_3C_6N_3H_{12}$}Cl(OCH_3)].PF_6 [233]

A suspension of [Mo(NO){N,N',N"-$Me_3C_6N_3H_{12}$}$(Cl)_2$].PF_6 (0.21 g, 0.41 mmol) in methanol (20 cm^3) was stirred under reflux for 4 h. The reaction mixture was allowed to cool to room temperature, and then filtered to remove a small amount of a pale green solid material, which was discarded. A saturated aqueous solution of $NaPF_6$ (5 cm^3) was added to the filtrate. The solution was cooled to 0 °C and, upon evaporation of some of the methanol *in vacuo*, a dark green solid precipitated. This was collected by filtration, washed with cold water, and dried under vacuum at 100 °C for 24 h to yield the product as a dark olive-green powder (0.14 g, 66%). (Found: C, 22.9; H, 4.4; N, 11.8%. $C_{10}H_{24}ClF_6MoN_4O_2P$ requires C, 23.6; H, 4.8; N, 11.0%); $\nu_{max.}$(NO) 1670s, $\nu_{max.}$(PF_6) 830s cm^{-1}; δ_H(CD_3COCD_3) 5.50 [3 H, s, OCH_3], 4.0–3.0 [12 H, c m, 6 x CH_2], 3.23, 2.90, and 2.80 [3 H, s; 3 H, s; 3 H, s, 3 x N–CH_3].

[Mo(NO){N,N',N"-$Me_3C_6N_3H_{12}$}$(Br)_2${$H_2NC_6H_3$-3-CH_3-4-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η_5-C_5H_5)}].PF_6 [234]

A solution of [Mo(NO){N,N',N"-$Me_3C_6N_3H_{12}$}$(Br)_2$].PF_6 (0.15 g, 0.25 mmol) and 4-amino-2-methyl-4'-ferrocenylazobenzene (0.11 g, 0.28 mmol) was stirred under reflux in dry dichloromethane (20 cm^3) for 3.5 h. The reaction mixture was cooled and filtered in air. The dark red-purple solid was washed with further dry dichloromethane (*ca* 50 cm^3) until the orange filtrate became colourless. The product was dried under vacuum at 100 °C for 24 h to yield a dark red-purple powder (0.17 g, 69%). (Found: C, 38.6; H, 4.2; N, 9.6%; M^+, 853. $C_{32}H_{42}Br_2F_6FeMoN_7OP$ requires C, 38.5; H, 4.2; N, 9.8%; M, 852); $\nu_{max.}$(NH_2) 3470w, 3380m, $\nu_{max.}$(NO) 1585s, $\nu_{max.}$(PF_6) 830s cm^{-1}; *m/z* 853 (M^+), 823 (M – NO), 772 (M – Br), 707 (M – N,N',N"-$Me_3C_6N_3H_{12}$), 692 (M – Br_2), 670 (M – (η^5-C_5H_4)Fe(η_5-C_5H_5)), 580 (M – NC_6H_4-4-(η^5-C_5H_4)Fe(η_5-C_5H_5)), 459 (M – $H_2NC_6H_3(CH_3)$-N=NC_6H_4-4-(η^5-C_5H_4)Fe(η_5-C_5H_5)), 428 (M – $H_2NC_6H_3(CH_3)$N=NC_6H_4-4-(η^5-C_5H_4)Fe(η_5-C_5H_5) – NO), 396 ($H_2NC_6H_3(CH_3)$N=NC_6H_4-4-(η^5-C_5H_4)Fe(η_5-C_5H_5)); E_f[Mo] = –1.53 V, ΔE_p = 120 mV; E_f[Fe] = +0.51 V, ΔE_p = 110 mV; μ_{eff} = 3.13 BM.

SUMMARY OF CONCLUSIONS AND PROSPECTS FOR FUTURE WORK

The results which have emerged from this study make it clear that the {M(NO)L*} system is extremely well suited for use in the creation of NLO-active transition metal complexes. Both favourable electronic and structural factors result in the observation of high SHG efficiencies from complexes of the type [M(NO)L*(X)(HN-Z-4-Fc)] (where M = Mo, X = Cl, Br, or I; M = W, X = Cl; Fc = ferrocenyl, and Z = a stilbenyl or diphenylazo moiety). The significant electronic effect of changing Mo for W demonstrates that the chiral metal centre is not merely playing a passive structural role, but is behaving as a powerful electron acceptor as was envisaged at the outset.

The absence of any SHG from polarisable dipolar {M(NO)L*} complexes lacking the ferrocenyl donor substituent demonstrates how the bulky organometallic group also plays a crucial structural as well as electronic role. Furthermore, it has been shown that nitro-arylferrocenyl compounds such as 4-Fc-C_6H_4N=NC_6H_3-2-CH_3-4-NO_2 have a tendency to crystallise centrosymmetrically and hence exhibit no bulk NLO properties. Therefore, a general conclusion is that the presence of both ferrocenyl and {M(NO)L*} moieties are necessary for the formation of NLO-active materials. In addition, these groups need to be linked via an amido-azobenzene or -stilbenyl function.

Unfortunately, the semi-quantitative nature of the powder SHG measurements serves to limit greatly the establishment of structure-activity relationships, and in cases where no SHG is detected very little can be concluded in the absence of crystallographic data. Further structural studies involving some of the complexes found to be SHG-inactive are necessary to provide a fuller understanding of the solid state structures adopted by dipolar {M(NO)L*} complexes. Also, the ferrocenylstilbene compound 4-Fc-C_6H_4CH=CHC_6H_4-4-NO_2 shows significant SHG, and a single crystal study of this compound would be of interest. In the absence of such information, the structural differences found in the nitro-

arylferrocenyl compounds remain surprising and largely unexplained.

The fact that several of the complexes described in Chapter Five could not be tested for SHG, and that those which were did not show any detectable signals is disappointing. However, scope remains for further investigations, particularly into the nature and physical properties of the reduced anionic 17-electron complexes. The creation of materials which exhibit NLO effects and are also paramagnetic is of considerable interest; all of the NLO-active metal-organic species reported to date are diamagnetic and the author is only aware of one stable organic radical possessing simultaneously bulk NLO and magnetic properties.[303]

The further study of {M(NO)L*} complexes containing polyene ligands could also yield interesting results. Indeed, some work is at present underway involving complexes of pyridyl polyenes with a view to creating materials for third-order NLO effects.

The extremely limited aryl ligand derivative chemistry of the cationic {Mo(NO)L^{N}} system effectively precludes the need for further work in this area, but a structural study of the one amino complex isolated could be of some value.

Much current attention is paid to the measurement of molecular hyperpolarisability β values using EFISH in solution, as this gives quantitative results and is hence often regarded as more informative than simply recording powder SHG signals. However, very few studies of this kind involving metal-organic compounds have so far been reported.[137] Therefore the subjection of some {M(NO)L*} complexes, both SHG-active and inactive, to EFISH study would be of considerable interest. This could facilitate precise comparison of electronic effects such as changing Mo for W, amido NH for phenoxide O, or halide ligand variations in the absence of complications introduced by working with solid materials.

Overall, the prospects for future work and the resultant gaining of further insights into the NLO properties of {M(NO)L*} complexes appear very good. In reality it is likely that such work will be limited only by the resources made available for its pursuance coupled with the ingenuity and practical skills of those who might be involved.

APPENDIX: EXPERIMENTAL TECHNIQUES

All physical measurements described in this thesis were carried out at the University of Birmingham unless otherwise stated. Ambient conditions were used in all cases except for the thermal studies.

Spectroscopic Measurements

I.r. spectra were recorded as KBr discs unless otherwise stated using a Perkin-Elmer 297 spectrophotometer. ^1H n.m.r. spectra were obtained as solutions in $CDCl_3$ unless otherwise stated using a JEOL GX-270 (270 MHz) instrument with trimethylsilane (TMS) as an internal reference. U.v.-visible spectra were recorded as solutions in CH_2Cl_2 unless otherwise stated using a Perkin-Elmer M330 spectrophotometer. Mass spectra were recorded by electron impact using a Kratos MS80RF instrument, except for that of complex [243] which was recorded by FAB at Swansea University.

Electrochemical Measurements

Cyclic voltammetric measurements were made using an EG&G model 174A polarographic analyzer, with approximately 10^{-3} M solutions under a nitrogen atmosphere in dry CH_2Cl_2 unless otherwise stated. A platinum-bead working electrode was used with 0.2 M $[Bu_4N][BF_4]$ as supporting electrolyte and a scan rate of 200 mV s^{-1}. Potentials were measured versus a standard saturated calomel reference electrode, and in most cases ferrocene was added as an internal standard.

Thermal Measurements

DSC measurements were carried out at Sheffield University using a Perkin-Elmer DSC7 instrument with samples (typically 1.4-3 mg) being hermetically sealed in 10 μl aluminium pans. In all cases heating and cooling rates of 10 K min^{-1} were used. Polarising

microscopy studies were carried out using a CZ Scientific Labpol system equipped with a Link-Am PR600 controller and TH600 hot-stage. Heating rates were 10 K min^{-1} unless otherwise stated. Melting points were obtained using a Gallenkamp melting point apparatus.

NLO Measurements

SHG measurements carried out at Durham University were made using a Spectra-Physics Quanta-Ray DCR-11 Nd^{3+}:YAG laser operating in Q-switch mode at 1,064 nm, a modified Quanta-Ray RS-1 Raman shifter, and a Hughes Aircraft Co. Series 5000 helium-neon visible laser for system alignment. Signals were detected using a Thorn-EMI B2F/RFI photomultiplier tube, averaged by a Stanford Research Systems Inc. Gated Integrator and Boxcar Averager, and displayed on a Tektronix 2467B 400 MHz cathode ray oscilloscope.

Other Techniques

All weights were recorded using a Mettler AE100 six-figure balance. Elemental analyses for C, H, and N were carried out by the Micro-analytical Laboratory, School of Chemistry, University of Birmingham. T.l.c. was carried out on Merck aluminium sheets coated with silica gel 60 F_{254} or alumina 60 F_{254} to a thickness of 0.2 mm. Magnetic moments were recorded using a Johnson Matthey magnetic susceptibility balance. Optical rotations were recorded using a Perkin-Elmer 241 polarimeter.

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