THE CHEMICAL CHARACTERISTICS OF TRANSITION-METAL ORGANOMETALLIC NITROSYL COMPLEXES

by

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We accept this thesis as conforming to the required standard

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MAY 1983

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ABSTRACT

The reactions of \((\eta^5-C_5H_5)Cr(NO)2\) with halogens result in either \((\eta^5-C_5H_5)Cr(NO)_2X\) (X=Cl or Br) or \([((\eta^5-C_5H_5)Cr(NO)I)_2\). Further treatment of the iodo-complex with excess \(I_2\) or NO leads to the formation of \((\eta^5-C_5H_5)Cr(NO)_2I\). This complex also results from thermal decomposition of the dimeric iodo-complex. Reaction of \((\eta^5-C_5H_5)Cr(NO)(PPh_3)\) with halogens, or cleavage of the iodide bridges in \([((\eta^5-C_5H_5)Cr(NO)I)_2\) with Lewis bases, results in a series of stable paramagnetic complexes, \((\eta^5-C_5H_5)Cr(NO)LX\) (L=Lewis base, X=halide). In addition, the reactions of halogens with \((\eta^5-C_5Me_5)M(CO)_2(NO)\) (M=Cr, Mo and W) are described.

Reaction of \([((\eta^5-C_5H_5)W(NO)I)_2\) with thallium or sodium cyclopentadienide results in the electron-rich complexes \((C_5H_5)_2W(NO)X\) (X=I or \(\eta^1-C_5H_5\)). The fluxional behaviour and instantaneous molecular structures of these complexes are discussed. Reduction of \([((\eta^5-C_5H_5)Mo(NO)I)_2\) with Na/Hg in the presence of non-cyclic conjugated dienes produces \((\eta^5-C_5H_5)Mo(NO)(\eta^4-diene)\); the diene is coordinated in the rare \(s_{trans}\) conformation.
An unusual solvent control is observed in the reaction of \((\text{C}_5\text{H}_5)\text{}_2\text{Mo(NO)}\text{I}\) with the silver (I) salts, \(\text{AgBF}_4\) or \(\text{AgSbF}_6\). In \(\text{CH}_3\text{CN}\), salts of the \([(\text{C}_5\text{H}_5)\text{}_2\text{Mo(NO)}(\text{CH}_3\text{CN})]\) cation are formed in high yield, while in aqueous acetone the trimetallic species, \([(\eta^5-\text{C}_5\text{H}_5)\text{Mo(NO)}(\text{OH})]_3\text{O}]Y \ (Y=\text{BF}_4 \text{ of } \text{SbF}_6)\), result. In \(\text{CH}_2\text{Cl}_2\), a non-coordinating solvent, the insoluble adducts, \((\text{C}_5\text{H}_5)\text{}_2\text{Mo(NO)}\text{I}.\text{AgY} \ (Y=\text{BF}_4 \text{ or } \text{SbF}_6)\), precipitate in high yield, the organometallic reactant presumably functioning as a "soft" Lewis base. Reaction of \((\text{C}_5\text{H}_5)\text{}_2\text{Mo(NO)}\text{I}\) with \(\text{AlCl}_3\), effects halide abstraction to give the unsolvated cation, \([(\eta^5-\text{C}_5\text{H}_5)\text{}_2\text{Mo(NO)}]\) *.

Addition of the strong acids \(\text{HBF}_4.\text{OMe}_2\) or \(\text{HPF}_6(\text{aq})\) to a \(\text{CH}_2\text{Cl}_2\) solution of \((\eta^5-\text{C}_5\text{H}_4\text{Me})\text{Mn}_3(\text{NO})_3\) (1) results in the reversible formation of the novel hydroxyimido complexes, \([(\eta^5-\text{C}_5\text{H}_4\text{Me})\text{Mn}_3(\text{NO})_3(\text{NOH})]Y \ (2a, \ Y=\text{BF}_4; \ 2b, \ Y=\text{PF}_6)\). Further treatment with acid induces reduction of the \(\text{N-O}\) bond to give \([(\eta^5-\text{C}_5\text{H}_4\text{Me})\text{Mn}_3(\text{NO})_3(\text{NH})]Y \ (3a, \ Y=\text{BF}_4; \ 3b, \ Y=\text{PF}_6)\). X-ray crystallographic analyses of \(2a\) and \(3b\) have been performed in order to characterise the novel \((\mu_3-\text{NOH})\) and \((\mu_3-\text{NH})\) groups. The trimetallic imido complex is also one of the products of the reaction of \([(\eta^5-\text{C}_5\text{H}_4\text{Me})\text{Mn(CO)}(\text{NO})]_2\) with \(\text{HBF}_4.\text{OMe}_2\). In addition, the new amido complex, \([(\eta^5-\text{C}_5\text{H}_4\text{Me})\text{Mn}_2(\text{NO})_2(\text{CO})(\text{NH}_2)]\text{BPh}_4\), can be isolated from the reaction mixture after treatment with aqueous \(\text{NaBPh}_4\).
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### Abbreviations And Stylistic Notes

In general, the abbreviations used in this thesis are those recommended in "Handbook for Authors of Papers in American Chemical Society Publications", published by the American Chemical Society. Figures, Tables, Schemes and Equations are numbered (x,y), where x represents the Chapter and y resets to 1 at the beginning of each Chapter. Bibliographic references are indicated by [xx] in the running text; footnotes are represented by superscripts. In addition, the following abbreviations are also used:—

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>Å</td>
<td>Angstrom ($10^{-10}$ m)</td>
</tr>
<tr>
<td>a&lt;N&gt;</td>
<td>electron/nucleus hyperfine coupling constant (N=coupled nucleus)</td>
</tr>
<tr>
<td>B</td>
<td>Base</td>
</tr>
<tr>
<td>BM</td>
<td>Bohr Magnetons</td>
</tr>
<tr>
<td>bpy</td>
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<tr>
<td>Cp</td>
<td>($\eta^5$-C$_5$H$_5$)</td>
</tr>
<tr>
<td>Cp''</td>
<td>($\eta^5$-C$_5$Me$_5$)</td>
</tr>
<tr>
<td>dec</td>
<td>decomposed</td>
</tr>
<tr>
<td>dmpe</td>
<td>1,2-bis(dimethylphosphino)ethane</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>E</td>
<td>Main Group element</td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>Half-wave potential</td>
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E_p\alpha \quad \text{Anodic peak potential}

g \quad \text{g-value of the unpaired electron}

G \quad \text{gauss}

J(\text{X-Y}) \quad \text{Inter-nuclear coupling constant between nuclei X and Y}

L \quad \text{2-electron donor ligand}

\text{NO}_x \quad \text{a mixture of nitrogen oxides}

R \quad \text{organic alkyl group}

\text{SCE} \quad \text{saturated calomel electrode}

\text{trpy} \quad \text{2,6-bis(2'-pyridyl)pyridine}

\text{THF} \quad \text{Tetrahydrofuran}

X \quad \text{halide}

\eta^* \quad \text{The eta-nomenclature indicates the number of atoms (x) in the ligand which are within bonding distance of the metal atom}

\mu_x \quad \text{The mu-nomenclature indicates the number of metal atoms (x) within bonding distance of the ligand}

\delta \quad \text{chemical shift downfield from teramethylsilane}

\nu \quad \text{infrared stretching absorption}

\chi_m \quad \text{molar magnetic susceptibility}

\mu(\text{eff}) \quad \text{effective magnetic moment}

\lambda \quad \text{wavelength}

\Lambda m \quad \text{molar conductivity}

\Omega \quad \text{ohms}.
Acknowledgements

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"Experiments are the only means of knowledge at our disposal. The rest is poetry, imagination."

MAX PLANCK
CHAPTER ONE

INTRODUCTION

The principal impetus for the current interest in the characteristic chemistry of coordinated nitrogen monoxide, NO, derives from the widespread occurrence of oxides of nitrogen (NOx) as an environmental hazard produced in many combustion processes [1]. Previous studies had been stimulated by the fact that NO is only a proton and an electron removed from CO [2]. However, recently there has been a shift in emphasis away from these comparative studies of nitrosyl and carbonyl complexes, towards the possible use of transition-metal complexes in the effective removal of NO from exhaust gases, and conversion into less harmful and potentially more useful products.

(i) NO As An Environmental Hazard

In 1975, 24.4 million tons of nitrogen oxides (NOx) were produced in the U.S. from fossil fuel combustion processes. In addition, a further 2.1 million tons originated from Canadian sources [3]. The major sources of
these emissions are vehicle exhausts, electric power plants and industrial boilers. At the elevated temperatures required for these processes, nitrogen and oxygen react to produce NO which is then converted into NO$_2$ by aerial oxidation in the atmosphere.

\[
N_2 + O_2 \rightarrow 2NO \quad (1.1)
\]

\[
2NO + O_2 \rightarrow 2NO_2 \quad (1.2)
\]

The released nitrogen oxides (NO + NO$_2$), commonly referred to as NOx, are involved in the formation of two environmental problems:

a) photochemical smog, and

b) acid rain.

(a) **Photochemical Smog**

One of the most discomforting features of life in urban areas of industrialised nations is the frequent presence of smog, the prime example being the South Coast Air Basin in California [4]. Smog is characterised by a relatively high level of oxidants in the atmosphere, which irritate the eyes and throat and aggravate respiratory problems. These oxidants include ozone (O$_3$), nitrogen dioxide (NO$_2$), hydrogen peroxide (H$_2$O$_2$) and peroxyacynitrates (RCO$_3$NO$_2$).
While the exact nature of the photochemical reactions involved in smog formation has not yet been completely determined, it has been demonstrated that the most important reaction sequence is the so-called nitrogen dioxide photolytic cycle [5].

\[ \text{NO}_2 + h\nu(<0.38\mu m) \rightarrow \text{NO} + \text{O} \quad \ldots \quad (1.3) \]

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad \ldots \quad (1.4) \]

\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad \ldots \quad (1.5) \]

However, this simple model does not account for the high concentrations of \( \text{O}_3 \) observed (Figure 1.1). Analysis of the steady-state kinetics requires that \([\text{NO}_2]/[\text{NO}]\) must be 10 or greater, but the observed ratio emitted is typically about 0.05 [5]. Hence, the large quantities of ozone and nitrogen dioxide observed can be explained only if additional mechanisms for the oxidation of NO to \( \text{NO}_2 \) can be established.

Two such mechanisms have been cited which lead to increased \( \text{NO}_2 \) and \( \text{O}_3 \) concentrations [6,7]. Both involve atomic oxygen as an initiator, the substrate being either unsaturated organic compounds or water. The important steps in the mechanisms are given below:
Figure 1.1 Daily Variation Of NO, NO₂ And O₃ Concentrations
In Los Angeles, July 19, 1965.

(a)

\[
\begin{align*}
O + \text{olefin} & \rightarrow R^\cdot + \text{RCO}^\cdot \ldots (1.6) \\
O_3 + \text{olefin} & \rightarrow \text{RCHO} + \text{RO}^\cdot + \text{RCO}^\cdot \ldots (1.7) \\
R^\cdot + O_2 & \rightarrow \text{ROO}^\cdot \ldots (1.8) \\
\text{RCO}^\cdot + O_2 & \rightarrow \text{RCO}_3^\cdot \ldots (1.9) \\
\text{ROO}^\cdot + \text{NO} & \rightarrow \text{RO}^\cdot + \text{NO}_2 \ldots (1.10)
\end{align*}
\]
RCO$_3$· + NO$_2$ → RCO$_3$NO$_2$ ...(1.11)

(b)

O + H$_2$O → 2OH· ...(1.12)

OH· + O$_3$ → HO$_2$· + O$_2$ ...(1.13)

OH· + CO → CO$_2$ + H· ...(1.14)

HO$_2$· + NO → NO$_2$ + OH· ...(1.15)

Even with inclusion of these two mechanisms, the situation is still oversimplified. However, a comparison of average concentrations of pollutants in a typical Los Angeles smog, with a simulated smog which initially contained propylene and NO (Figure 1.2) indicates that inclusion of processes which involve hydrocarbons gives a good qualitative match to the observed situation [5].

In summary, photochemical smog involves the initial photodissociation of NO$_2$ to produce atomic oxygen. Chain reactions, involving molecular oxygen, water vapour and unsaturated organic substrates lead to a rapid buildup in atmospheric oxidants. As a result, the reduction of smog effects will require a substantial reduction in the amount of NOx emitted.
Figure 1.2 A Comparison Of (a) A Typical Los Angeles Smog And (b) A Simulated Smog Initially Containing Propylene And NO.

(a)

(b)
(b) Acid Rain

Acid rain will probably be the most politically emotive environmental issue to face the industrialised nations during the next 2–3 decades. Unlike photochemical smog which is local in nature, the problem is international in scope. For instance, it has been claimed that only 17% of the acid rain which falls on the lakes and mountains of Scandinavia actually originates from Scandinavian sources, the majority of it being carried by the prevailing winds from the industrial heartland of Europe [8] (Table 1.1). A similar situation exists in N. America where it has been estimated that 50% of the acid rain falling on Northern Ontario originates from the U.S. [8]. Of course, the polluting countries tend to dispute these results, and it is evident that much work still needs to be done to determine the exact causes and nature of acid rain.

It is presently thought that acid rain is formed in the rain clouds, by a combination of oxidation and hydrolysis of SO$_2$ and NOx [5,7]. These gases are produced from industrial processes, as well as from natural sources, such as volcanoes and electrical storms.

\[ 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{HNO}_3 \ldots (1.16) \]

\[ 3\text{NO}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_3 + \text{NO} \ldots (1.17) \]
Table 1.1 Sources Of Scandinavian Acid Rain

<table>
<thead>
<tr>
<th>Country</th>
<th>%Contribution</th>
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<tr>
<td>Sweden/Norway</td>
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<td>E. Germany</td>
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<td>W. Germany</td>
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<tr>
<td>Poland</td>
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<tr>
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\[
\text{NO}_2 + \cdot \text{OH} \rightarrow \text{HNO}_3 \quad (1.18)
\]

\[
\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \quad (1.19)
\]

\[
\text{H}_2\text{SO}_3 + [\text{O}] \rightarrow \text{H}_2\text{SO}_4 \quad (1.20)
\]

where \([\text{O}] = \text{OH}, \text{O}_3, \text{OH}_2, \text{or H}_2\text{O}_2\).

It has been estimated that in the eastern states and provinces ≈70% of the acid rain results from sulphur dioxide emissions produced by non-ferrous smelters and coal-burning power stations [9]. In the west, however, the acidity of the
Rain is almost entirely due to nitric acid. Since the nitrogen oxides are part of the natural nitrogen cycle it has also been claimed that a distinction can be made between harmful SO$_2$ emissions and beneficial NO$_x$. However, it is the increased acidity of the rain and not the nature of the anions which seems to have the most profound effect on the environment.

"Pure" rain has a pH of 5.6 due to dissolution of carbon dioxide. Over the last 10–15 years an increasing area of N. America and Northern Europe has experienced acidic rainfall with pH's in the range 4.0–4.5. The most acidic rainfall ever recorded had a pH of 1.5 (i.e., $\approx 10,000$ times more acidic than "pure" rain [3]). The effect of this acidic rainfall on the environment depends on a number of factors, which include the buffering capacity and mineral content of the soil. Neutralisation of the rain leaches out the metal ions from the soils. This has two important consequences:—first, elements which are nutrients (e.g. Ca, Mg) are removed from the soil [10] and second, toxic elements such as aluminum, manganese and mercury which are normally fixed as harmless insoluble compounds are mobilised and dissolved as lethal sulphates and nitrates [11]. Many lakes and rivers in affected areas no longer support aquatic life due to the high concentrations of toxic metals and the general high acidity.
Acid rain is also very corrosive. For instance, the increased acidity of the rain is causing an escalation of corrosion of car bodies as well as erosion of stone structures; those constructed of limestone being particularly susceptible [12]. Furthermore, the higher acidity of domestic tap water is causing concern, as this produces an increase in toxic copper levels [10].

To summarise, the increasing acidity of global precipitation is having grave environmental consequences, which can only be alleviated by a reduction in the $SO_2$ and NOx emissions.

(ii) Abatement And Control Of NOx Emissions

Present methods for the reduction of NOx emissions can be categorised according to two classifications:—
a) abatement, i.e. reduction of the amount of NOx produced by modifying the combustion process, and
b) control — removal of the NOx produced by various catalytic and non-catalytic processes.

While improvements in the design of the burner and furnace have been made they have, in general, resulted in a reduction in the efficiency of combustion. On the other hand, the methods presently employed to remove the NOx are either somewhat inefficient or very expensive. For instance, the most common process — Exxon's Thermal "Denox" — involves
the gas phase reaction

$$4\text{NH}_3 + 4\text{NO} + \text{O}_2 \longrightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \ ...(1.21)$$

in the combustion zone. The drawbacks of this process are the low NOx removal (<70%) and the large amount of expensive NH$_3$ required [13]. Recently, some success in effecting the removal of NOx using homogeneous catalysts has been reported, [14-16]. The overall process involves the reaction between carbon monoxide and nitrogen monoxide to give the much less toxic gases, carbon dioxide and dinitrogen monoxide.

$$\text{CO} + 2\text{NO} \longrightarrow \text{CO}_2 + \text{N}_2\text{O} \ ...(1.22)$$

The catalyst systems studied were acidic aqueous or ethanolic solutions of PdCl$_2$ [14], CuCl$_2$ [14], RhCl$_3$ [15] and [Rh(CO)$_2$Cl$_2$]$^-$ [15,16].

While these processes have been successful in removing nitrogen monoxide from exhaust gases to varying degrees, the emphasis of most of the work has been to accomplish the conversion of NO into less noxious products, principally N$_2$ and to a lesser extent N$_2$O. However, both of these products are quite non-reactive, and further expensive transformations must be effected in order to convert the nitrogen into important chemicals such as fertilizers. An
alternative approach, which merits investigation, is to convert the NO directly into more useful species. This approach, if successful, would not only lead to a reduction of NOx emissions but may also pay for itself from the sales of the products thus obtained. The first step in the strategy involves trapping of the nitrogen monoxide on an electron–rich transition–metal centre to form a nitrosyl complex. Once obtained, the reactivity of the coordinated nitrosyl ligand may be exploited to obtain the desired objective. At present, ample precedent exists in the literature [17] for the first step, while the reactivity of coordinated NO in coordination complexes has been studied [18,19]. However, in most of these complexes, the NO ligands are attached to transition metals in high, rather than low, formal oxidation states.

(iii) The Reaction Of NO With Transition Metal Complexes

It has been established that NO reacts with appropriate transition metal complexes to effect 3 principal types of transformations [17]:–

a) simple adduct formation

b) substitution, and

c) reductive nitrosylation.
(a) Simple Adduct Formation

This type of reaction occurs when the transition-metal complex is either a 15- or 17-electron species, lacking one or three electrons from the inert gas configuration [20-22] e.g.

\[ \text{Cr(NR}_2\text{)}_3 + \text{NO} \rightarrow \text{Cr(NO)(NR}_2\text{)}_3 \quad (1.23) \]

\[ \text{CoCl}_2\text{L}_2 + \text{NO} \rightarrow \text{Co(NO)Cl}_2\text{L}_2 \quad (1.24) \]

\[ \text{Cr(OPPh}_3\text{)}_2\text{X}_2 + \text{NO} \rightarrow \text{Cr(NO)}_2\text{(OPPh}_3\text{)}_2\text{X}_2 \quad (1.25) \]

(b) Substitution

Reaction of nitrogen monoxide with many coordinatively saturated transition metal complexes results in the substitution of ligand(s) capable of donating 3n electrons to the metal centre [23-26] e.g.

\[ \text{Cr(CO)}_6 + 4\text{NO} + h\nu \rightarrow \text{Cr(NO)}_4 + 6\text{CO} \quad (1.26) \]

\[ [(\eta^5-C_5\text{H}_5)\text{V(CO)}_3\text{CN}]^- + \text{NO} \rightarrow (\eta^5-C_5\text{H}_5)\text{V(NO)}_2(\text{CO}) + 2\text{CO} + \text{CN}^- \quad (1.27) \]
\[
\left[ (\eta^5-C_5H_5)Cr(CO)_3 \right]_2 + 2\text{NO} \rightarrow 2(\eta^5-C_5H_5)Cr(CO)_2(\text{NO}) + 2\text{CO} \\
\ldots(1.28)
\]

\[
2(\eta^5-C_5H_5)\text{Co(CO)}_2 + 2\text{NO} \rightarrow [(\eta^5-C_5H_5)\text{Co(NO)}]_2 + 4\text{CO} \\
\ldots(1.29)
\]

(c) **Reducive Nitrosylation**

Many transition metal halides are reduced by NO gas, the oxidised product in these reactions usually being NOCl [27-29]. e.g.

\[
\text{MoCl}_5 + 5\text{NO} \rightarrow [\text{Mo(NO)}_2\text{Cl}_2] + 3\text{NOCl} \ldots(1.30)
\]

\[
(\eta^3-C_3H_5)\text{Fe(CO)}_2\text{CL} + 2\text{NO} \rightarrow (\eta^3-C_3H_5)\text{Fe(CO)(NO)L} + \text{NOCl} \\
\ldots(1.31)
\]

\[
2\text{CoCl}_2 + 6\text{NO} + 2\text{B} + 2\text{ROH} \rightarrow [\text{Co(NO)}_2\text{Cl}]_2 + 2\text{BH}^+ + 2\text{Cl}^- + 2\text{RONO} \ldots(1.32)
\]

(iv) **The Bonding And Reactivity Of Transition Metal Nitrosyl Complexes**

Once incorporated into the transition metal's coordination sphere, the nitrosyl ligand can engage in one
of three principal bonding modes, all of which involve metal-to-nitrogen rather than M—ON interactions [19]:—

a) terminal, linear M—NO groups,

b) terminal, bent M—NO groups

c) bridging NO groups.

It is here that one notices the first difference between NO and CO as a ligand, since carbon monoxide does not function in the bent mode.

(a) **Terminal, Linear M—NO Bonds**

This is the most common type of M—NO bonding, particularly in organometallic complexes. In this type of bonding the NO group functions as a 3—electron donor (i.e. formally NO⁺). The linear mode, as shown in resonance structures (a) and (b),

![Resonance structures](image)

parallels directly CO coordination involving a synergic coupling of σ and π components [30]. As with carbonyl coordination, the degree of metal-to-ligand π-backbonding is influenced by the complex charge, metal oxidation state or the nature of ancillary ligands.
Resonance structures (a) and (b) above represent two extremes of the continuum and this formalism illustrates how the degree of backbonding influences the nitrosyl stretching frequency, $\nu$(NO), of the complex. When relatively little electron density is transferred to the nitrosyl by this interaction, as evidenced by a $\nu$(NO) > 1880 cm$^{-1}$, the nitrosyl exhibits NO$^+$ character and is activated towards nucleophilic attack at nitrogen [31] e.g.

$$[\text{IrCl}_3(\text{NO})(\text{PPh}_3)_2]^+ + \text{OEt}^- \rightarrow \text{IrCl}_3(\text{N(O)OEt})(\text{PPh}_3)_2$$

...(1.33)

On the other hand, species having particularly low values of $\nu$(NO) may be expected to be liable to attack by electrophiles, particularly at the O atom. For instance, it has been shown that Lewis Acids such as AlCl$_3$, SnCl$_4$, TiCl$_4$, and $(\eta^5-\text{C}_5\text{H}_5)_3\text{Ln}$ form isonitrosyl linkages with $(\eta^5-\text{C}_5\text{H}_5)_2\text{M(CO)}_2(\text{NO})_2$ (M=Cr,Mo,W). [32,33].

$$\text{M-NO} + \text{EX}_n \rightarrow \text{M-NO-EX}_n$$

...(1.34)
(b) **Terminal, Bent M—NO Bonds**

This type of bonding is relatively common for late transition-metal nitrosyl coordination complexes, but is rare in organometallic nitrosyls. In this type of bonding the NO group functions as a 1-electron donor (formally NO⁻). i.e.

\[
\text{M} - \text{N} = \text{O}^* \quad \theta
\]

The bond angle is typically 120° (i.e. the nitrogen is essentially sp² hybridised), but there are many complexes which have M—N—O bond angles intermediate between 120° (bent) and 180° (linear). Structural studies of nitrosyls of this type have also shown that the bent NO ligand invariably occurs at the apical position of a square based pyramid or a distorted octahedron [34].

Since the nitrogen atom possesses a nonbonding pair of electrons, the charge affinity of the nitrogen atom has been inverted from that found in linear nitrosyls. Whereas, the linear nitrosyl undergoes nucleophilic attack at N (providing ν(NO) is high enough), the bent nitrosyl reacts with electrophiles [35] e.g.
OsCl(CO)(NO)(PPh₃)₂ + HCl → OsCl₂(CO)(HNO)(PPh₃)₂
...(1.35)

(c) Bridging NO Linkages

The bridging mode of NO coordination is relatively rare. It occurs in a few bi- and tri-metallic cyclopentadienyl derivatives and in a few mixed carbonylnitrosyl clusters, e.g. [((η⁵-C₅H₅)Cr(NO)₂]₂ [36], (η⁵-C₅H₅)₃Mn₃(NO)₄ [37], [((η⁵-C₅H₅)Fe(NO)]₂ [38] and H₃Os₄(CO)₁₂(NO) [39]. Bridging NO linkages can be classified in 3 categories:

(a) doubly-bridging (μ₂-NO) supported by a M-M bond e.g.

(b) doubly-bridging (μ₂-NO) unsupported by a M-M bond e.g.
The oxygen atom in all types of bridging NO groups is basic, the order of increasing basicity being \((\mu_3\text{-NO}) \approx (\mu_2\text{-NO}) < \text{terminal NO}\) [40]. Surprisingly, this order is the reverse of that found for carbonyl complexes [41]. The nitrogen atom in bridging systems should be activated towards nucleophilic

\[^1\text{The three hydrogen atoms were not located in the structure determination.}\]
attack, and in fact this has been demonstrated in the reaction of t-BuLi with \([\eta^5\text{C}_5\text{H}_5]\text{Cr(NO)}_2\), which gives the complex

\[
\begin{align*}
\text{Bu}^t \quad &\text{OH} \\
\text{Cr} &\quad \text{N} \\
\text{ON} &\quad \text{N} \\
\text{NO} &\quad \text{NO}
\end{align*}
\]

after hydrolysis [42]. Similarly, the reaction of the chromium complex with \(\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)]_2\) results in the formation of \((\eta^5\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_3(\text{NH}_2)\) and \((\eta^5\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_2(\text{NH}_2)_2\) in low to moderate yields [43].

(v) A Comparison Of Nitrosyl And Carbonyl Chemistry

Unfortunately, due to the relative underdevelopment of nitrosyl chemistry compared to carbonyl chemistry, a complete comparison of the two is not possible. However, in recent years, a few significant differences in their chemistry have been discovered.
(a) **Hydride Complexes**

A characteristic property of carbonyl hydrides is their Lowry–Bronsted acidity. Most of these hydrides react with bases to produce carbonyl anions \([44]\) e.g.

\[
H_3\text{Re}_3(\text{CO})_{12} + \text{KOH} \rightarrow \text{K}[H_2\text{Re}_3(\text{CO})_{12}] + \text{H}_2\text{O} \quad (1.36)
\]

The only nitrosyl hydride to be studied in any detail; \((\eta^5-\text{C}_5\text{H}_5)\text{W(NO)}_2\text{H}\), is, however, not acidic but hydridic in behaviour \([45]\). This is surprising in view of the fact that NO is considered to be a better \(\pi\)-acid than CO. In addition, while most carbonyl hydrides have very high field chemical shifts in their \(^1\text{H}-\text{NMR}\) spectra, \((\eta^5-\text{C}_5\text{H}_5)\text{W(NO)}_2\text{H}\) resonates downfield from TMS (62–3 depending on solvent). Without further examples, however, no definitive conclusion on the generality of this behaviour can be made.

(b) **Alkyl Complexes**

A common feature of alkylcarbonyl complexes is alkyl migration (or carbonyl insertion) resulting in the formation of an acyl complex \([46]\). For example, alkylpentacarbonylmanganese complexes rearrange in the presence of ligands such as CO, PR\(_3\), NR\(_3\) or X\(^-\) as shown in equation \((1.37)\).
\[(\text{OC})_5\text{MnR} + L \rightarrow (\text{OC})_5(\text{L})\text{Mn(COR)} \,...(1.37)\]

Detailed studies on this system suggest that the reaction occurs via initial alkyl migration. In a subsequent step, the coordinatively unsaturated acyl takes up an external ligand in the site left vacant by the migrating alkyl group.

An analogous reaction for alkynitrosyl complexes would lead to an alkynitroso species. To date, however, only one example of such a reaction has been completely characterised, although there are several reactions, which probably include such a step [47].

\[(\eta^5-\text{C}_5\text{H}_5)\text{Co}^\text{NO}_R + \text{PPh}_3 \rightarrow (\eta^5-\text{C}_5\text{H}_5)\text{Co}^\text{PPh}_3_N=O_R \,...(1.39)\]

Again, the proposed mechanism is initial alkyl migration to give the coordinatively unsaturated alkynitroso complex
which is then trapped by the phosphine ligand.

A direct comparison of the propensity of carbonyl and nitrosyl alkyls to undergo alkyl migration can be obtained from the reactions of the isoelectronic complexes \((\eta^5-C_5H_5)Cr(NO)_2Me\) and \((\eta^5-C_5H_5)Fe(CO)_2Me\) with PPh₃ (equations 1.40 and 1.41) [48,49].

\[
(\eta^5-C_5H_5)Fe(CO)_2Me + PPh₃ \rightarrow (\eta^5-C_5H_5)Fe(CO)(PPh₃)(COMe)
\]...

\[
(\eta^5-C_5H_5)Cr(NO)_2Me + PPh₃ \rightarrow N/R
\]...

On the other hand both of the alkyl complexes insert SO₂ affording the S-sulphinate M-SO₂R (equation 1.42) [50].

\[
(\eta^5-C_5H_5)M(LO)_2Me + SO₂ \rightarrow (\eta^5-C_5H_5)M(LO)_2SO₂Me
\]

\((M=Fe, \ L=C; \ M=Cr, \ L=N)\)

However, in this case, the mechanism is thought to be electrophilic cleavage of the M–C bond by attack of the electrophilic SO₂ molecule at the alkyl carbon. The fact that \((\eta^5-C_5H_5)Cr(NO)_2Me\) is amongst the most reactive alkyls to SO₂ insertion suggests that the alkyl carbon is fairly nucleophilic. Thus the reason for its inertness to alkyl migration probably is that the NO ligand is not electrophilic enough rather than a lack of nucleophilicity.
at the carbon atom.

This conclusion is not surprising in view of the charge separation in the free ligands (CO and NO), which may be determined by considering the electronegativities of C, N and O [51] or more rigourously by ab initio molecular orbital calculations [2,52]. Further chemical evidence, which confirms this conclusion can be found in the reaction of \([(\eta^5-C_5H_5)Re(CO)(NO)L]BF_4\) with hydride reagents. Depending on the conditions and reagents employed, the following products may be isolated:

\((\eta^5-C_5H_5)Re(CH_2OH)(NO)L\) or \((\eta^5-C_5H_5)Re(CH_3)(NO)L\) (L=CO,PPh_3) [53] e.g.

\[
(\eta^5-C_5H_5)Re(CO)_2(NO) + NaBH_4/H_2O \rightarrow (\eta^5-C_5H_5)Re(CO)(NO)(CHO) \ldots (1.43)
\]

\[
+ 2NaBH_4/H_2O \rightarrow (\eta^5-C_5H_5)Re(CO)(NO)(CH_2OH) \ldots (1.44)
\]

\[
+ NaBH_4/THF \rightarrow (\eta^5-C_5H_5)Re(CO)(NO)(CH_3) \ldots (1.45)
\]

All of the products result from initial reaction at the carbonyl rather than the nitrosyl ligand.

The general conclusion to be drawn from these observations is that a coordinated nitrosyl is less reactive
towards nucleophiles than a coordinated carbon monoxide ligand. In addition, it may also uniquely influence the characteristic chemistry of other ligands present in the coordination sphere.

(vi) **Objectives Of This Study**

The objectives of this study are two-fold, in line with the two main directions of study in transition-metal nitrosyl chemistry outlined above. (i.e. to investigate the effect of the NO ligand on the chemistry of other ligands in the coordination sphere and to investigate reactions which might lead to attack at the coordinated NO ligand).

In particular, Chapter 2 and Chapter 3 deal with the preparation and derivative chemistry of some cyclopentadienylhalonitrosyl derivatives of the Group VIA metals prepared by the reaction of \( (\eta^5-C_5R_5)M(CO)(NO)L \) (M=Cr, Mo, W; R=H, Me; L=CO, PPh₃) with halogens. Chapter 4 presents a detailed study of one particular reaction, that of \((C_5H_5)M(NO)I\) with silver salts, in which the solvent has a pronounced influence on the outcome of the transformations.

Chapters 5 and 6 describe the results of the reactions of \((\eta^5-C_5H_4Me)_3Mn_3(NO)\)₄ and \([((\eta^5-C_5H_4R)Mn(CO)(NO)]_2 \) (R=H or CH₃) with the strong protonic acids HBF₄-OMe₂ and HPF₆(aq). The major organometallic products of these reactions are
imido (NH) or amido (NH$_2$) complexes and result from electrophile-induced reduction of coordinated nitrogen monoxide.
CHAPTER TWO

THE REACTIONS OF HALOGENS WITH \((\eta^5-C_5R_5)M(CO)(NO)L\) \(M=Cr, R=H\) OR \(Me\), \(L=CO\) OR \(PPh_3\); \(M=Mo\) OR \(W\), \(R=Me\), \(L=CO\)

(i) Introduction

Transition-metal organometallic halides are very convenient starting materials for the synthesis of a wide variety of cationic, neutral, and anionic complexes [44]. For instance, during previous work from this laboratory, the characteristic chemistry of the chloronitrosyl compounds \((\eta^5-C_5H_5)M(NO)Cl\) \((M=Cr, Mo, W)\) was exploited to prepare some novel organometallic nitrosyl complexes, [45,54,55] i.e.

\[
(\eta^5-C_5H_5)Cr(NO)_2Cl + Zn/Hg \longrightarrow [(\eta^5-C_5H_5)Cr(NO)_2]_2 \quad \ldots(2.1)
\]

\[
(\eta^5-C_5H_5)Cr(NO)_2Cl + H^- \longrightarrow [(\eta^5-C_5H_5)Cr(NO)_2]_2 \quad \ldots(2.2)
\]

\[
(\eta^5-C_5H_5)M(NO)_2Cl + H^- \longrightarrow (\eta^5-C_5H_5)M(NO)_2H \quad \ldots(2.3)
\]

\(M=Mo, W\)
(η⁵-C₅H₅)M(NO)₂Cl + R₃Al → (η⁵-C₅H₅)M(NO)₂R ...(2.4)
R=alkyl or aryl

(η⁵-C₅H₅)W(NO)₂Cl + AgBF₄ → [(η⁵-C₅H₅)W(NO)₂]BF₄ ...(2.5)

[(η⁵-C₅H₅)W(NO)₂]BF₄ + L → [(η⁵-C₅H₅)W(NO)₂L]BF₄ ...(2.6)
L=PPh₃, C₈H₁₄, (η⁵-C₅H₅)W(NO)₂H

The products isolated from the reactions (2.1)–(2.6) are particularly interesting since their chemical properties differ markedly from those displayed by their carbonyl analogues (see Chapter 1, (iv)) [45,54–56].

In a similar vein, the synthesis of [(η⁵-C₅H₅)W(NO)I₂]₂ by the treatment of (η⁵-C₅H₅)W(CO)₂(NO) with iodine was described [57]. This iodonitrosyl complex like its molybdenum congener, also proved to be a useful precursor to a variety of new organometallic species [43,57–61] e.g.

[(η⁵-C₅H₅)W(NO)I₂]₂ + 2L → 2(η⁵-C₅H₅)W(NO)(L)I₂ ...(2.7)
L=PPh₃, P(OPh)₃, SbPh₃
\[
[(\eta^5-C_5H_5)W(NO)I_2]_2 + Sn(C_3H_5)_4 \rightarrow 2(\eta^5-C_5H_5)W(NO)(\eta^5-C_3H_5)I \quad ...(2.8)
\]

\[
[(\eta^5-C_5H_5)W(NO)I_2]_2 + H^- \rightarrow [(\eta^5-C_5H_5)W(NO)(H)I]_2 \quad ...(2.9)
\]

\[
[(\eta^5-C_5H_5)W(NO)(H)I]_2 + 2P(OPh)_3 \rightarrow 2(\eta^5-C_5H_5)W(NO)\{P(OPh)_3\}(H)I \quad ...(2.10)
\]

With a view towards extending this latter chemistry to encompass the chromium-containing analogues, it was decided to investigate the feasibility of preparing the requisite precursors by the reactions of halogens with \((\eta^5-C_5R_5)Cr(CO)(NO)L\) (R=H or Me, L=CO or PPh\(_3\)). This chapter presents the complete results of these studies. In addition, the reactions of the recently synthesised \((\eta^5-C_5Me_5)M(CO)_2(NO)\) (M=Mo, W) [62] with iodine are described.

(ii) Results And Discussion

(a) Reactions Of \((\eta^5-C_5H_5)Cr(CO)_2(NO)\) With Halogens

The products resulting from the treatment of \((\eta^5-C_5H_5)Cr(CO)_2(NO)\) with halogens do not resemble those produced by the congeneric molybdenum and tungsten compounds.
The addition of halogens to the latter compounds in 1:1 stoichiometry results in the production of the halogen-bridged dimers, \([(\eta^5-C_5H_5)M(NO)X_2]_2 \quad (M=Mo, \ X=Cl [63], \ Br [63], \ I [58,63] ; M=W, \ X=I [57] )\), which can be isolated in good yields, i.e.

\[
2(\eta^5-C_5H_5)M(CO)_2(NO) + 2X_2 \rightarrow [(\eta^5-C_5H_5)M(NO)X_2]_2 + 4CO 
\]

\[\text{...(2.11)}\]

\[M=\text{Mo or W; } X=\text{Cl, Br, I.}\]

In contrast, previous work in these laboratories has established that the reaction of \((\eta^5-C_5H_5)Cr(CO)_2(NO)\) with \(Cl_2\) affords \((\eta^5-C_5H_5)Cr(NO)_2Cl\) as the only nitrosyl-containing product [64]. The similar reaction with bromine has been performed and found to result in the rapid formation of the analogous \((\eta^5-C_5H_5)Cr(NO)_2Br\). In neither case has spectroscopic evidence been obtained for the formation of any intermediate carbonyl-nitrosyl or nitrosyl complex.

Interestingly, however, treatment of \((\eta^5-C_5H_5)Cr(CO)_2(NO)\) with iodine in a 2:1 molar ratio gives rise to the new dimeric complex, \([(\eta^5-C_5H_5)Cr(NO)I]_2\), in excellent yields, i.e.
This stoichiometry of reactants is essential for the formation of the dimeric product in optimum yields since the dimer reacts further with excess I$_2$ to yield (η$^5$-C$_5$H$_5$)Cr(NO)$_2$I as the ultimate nitrosyl-containing species. A more detailed analysis of these transformations can be effected by careful monitoring of their progress by IR spectroscopy. Thus, upon the addition of 0.5 equivalents of solid iodine to a CH$_2$Cl$_2$ solution containing 1 equivalent of (η$^5$-C$_5$H$_5$)Cr(CO)$_2$(NO), the characteristic absorptions of the organometallic reactant (i.e. ν(CO)=2020, 1945 cm$^{-1}$; ν(NO)=1680cm$^{-1}$) disappear rapidly, and three new absorbances appear in the carbonyl–nitrosyl region of the spectrum (i.e. ν(CO)=2096cm$^{-1}$; ν(NO)=1706, 1673 cm$^{-1}$). The carbonyl and higher energy nitrosyl absorptions then gradually diminish in intensity, until after 10 mins only the 1673 cm$^{-1}$ band due to [(η$^5$-C$_5$H$_5$)Cr(NO)I]$_2$ remains.

Alternatively, if an excess of I$_2$ is added to the original dicarbonylnitrosyl reactant, the initial IR spectral changes are as described in the preceding paragraph for the stoichiometric reaction. However, a new nitrosyl absorption at 1745 cm$^{-1}$ appears before the bands at 2096 and 1706 cm$^{-1}$ have completely vanished, and it attains maximum intensity after \(\approx\)2hrs. Concomitantly absorptions at 1817 and
1713 cm\(^{-1}\) (diagnostic of \((\eta^5-C_5H_5)Cr(NO)_2I\)) appear and slowly increase in intensity at the expense of the bands at 1745 and 1673 cm\(^{-1}\). After 18hrs, this iododinitrosyl complex is the only nitrosyl-containing species detectable in solution. To account for these observed spectral changes the reaction sequence presented in Scheme 2.1 is proposed.

**Scheme 2.1**

\[
\begin{align*}
2(\eta^5-C_5H_5)Cr(CO)_2(NO) &\xrightarrow{+I_2, -2CO} 2(\eta^5-C_5H_5)Cr(CO)(NO)I \\
\nu(CO) &= 2020, 1945 \text{ cm}^{-1} \\
\nu(NO) &= 1680 \text{ cm}^{-1} \\
\left[(\eta^5-C_5H_5)Cr(NO)I_2\right]_2 &\xleftarrow{+I_2} \left[(\eta^5-C_5H_5)Cr(NO)I\right]_2 \\
\nu(NO) &= 1745 \text{ cm}^{-1} \\

&\xrightarrow{-2CO} \\
\left[(\eta^5-C_5H_5)Cr(NO)I\right]_2 &\xrightarrow{+2CO} 2(\eta^5-C_5H_5)Cr(CO)(NO)I \\
\nu(NO) &= 1706 \text{ cm}^{-1} \\
\nu(NO) &= 1817, 1713 \text{ cm}^{-1}
\end{align*}
\]
It seems likely that Cl₂ and Br₂ react with \((\eta^5-C_5H_5)Cr(CO)_2(NO)\) in an analogous manner to produce \((\eta^5-C_5H_5)Cr(NO)_2X\) (X=Cl or Br) ultimately, but spectroscopic evidence to support this hypothesis is presently lacking. Nevertheless, it may be noted that \([((\eta^5-C_5H_5)Cr(NO)Cl)_2\), one of the intermediate complexes in the sequence of reactions involving Cl₂, has been previously prepared by a different synthetic route [64]. In solution, even in the absence of excess Cl₂, this complex decomposes over a period of \(\approx48\)hrs to \((\eta^5-C_5H_5)Cr(NO)_2Cl\) [65]. A similar decomposition mode is also displayed by the isolable iodo–intermediate, \([((\eta^5-C_5H_5)Cr(NO)I)_2\). In CH₂Cl₂ or THF, it eventually converts to \((\eta^5-C_5H_5)Cr(NO)_2I\) but at a rate substantially slower than in the presence of excess I₂. Again, the \(\nu(NO)\) band at 1745 cm⁻¹ which is attributed to the \([((\eta^5-C_5H_5)Cr(NO)I)_2\) species can be detected, albeit at much reduced intensity, during the course of the decomposition.

The lability of the carbonyl ligand in the proposed intermediate formed in reaction (A) of Scheme 2.1 is not without precedent, having been reported for many carbonylnitrosyl derivatives [57,64,66,67]. Also, the chloro analogue of this intermediate has been previously invoked (although not spectroscopically detected) to account for the formation in low yield of \([((\eta^5-C_5H_5)Cr(NO)Cl)_2\) as one of the products obtainable by the treatment of \([((\eta^5-C_5H_5)Cr(CO)_3)_2\)
with nitrosyl chloride [64] i.e.

\[
[(\eta^5-C_5H_5)Cr(CO)_3]_2 + 2NOCl \longrightarrow [(\eta^5-C_5H_5)Cr(CO)(NO)Cl]_2 + 4CO \quad (2.13)
\]

\[
[(\eta^5-C_5H_5)Cr(CO)(NO)Cl]_2 \longrightarrow [(\eta^5-C_5H_5)Cr(NO)Cl]_2 + 2CO 
\quad (2.14)
\]

In a separate experiment, it has been verified independently that reaction (B) of Scheme 2.1 is reversible, the iodonitrosyl dimer being cleaved by carbon monoxide. As expected, the product of this conversion exhibits the same spectral properties as the organometallic product of reaction (A). However, IR spectroscopy indicates that \((\eta^5-C_5H_5)Cr(CO)(NO)I\) is only generated in 10–20% yield and that it rapidly decarbonylates in the absence of the CO atmosphere.

The novel bis\([\eta^5\text{-cyclopentadienyl}]\text{iodonitrosyl—chromium}\) complex is a dark green solid (mp 119°C dec) which is freely soluble in benzene, CH\(_2\)Cl\(_2\), and all organic donor solvents, less soluble in CHCl\(_3\), and only very sparingly

\(1\)In the absence of definitive evidence, it is a matter of preference whether the carbonylhalonitrosyl intermediates are formulated as the 17-electron monomers, \((\eta^5-C_5H_5)Cr(CO)(NO)X\), or the 18-electron dimers, \([(\eta^5-C_5H_5)Cr(CO)(NO)X]_2\)
soluble in paraffin hydrocarbons. Although its solutions are air-sensitive and (as discussed above) thermally unstable, the solid itself is stable in air at ambient temperatures for short periods of time and can be stored unchanged indefinitely in an inert atmosphere. An IR spectrum of a fresh CH₂Cl₂ solution of the complex exhibits a single strong absorption at 1673 cm⁻¹ attributable to a terminal, linear nitrosyl ligand [68]. The compound is best formulated as the iodo-bridged dimer (either cis or trans), e.g.

![Diagram of complex structure]

since a monomeric formulation would leave the chromium atom with three electrons less than the favoured 18-electron configuration. The dimeric nature of the complex is also suggested by its mass spectrum (Table 2.1) which displays peaks due to the parent ion (m/z=548) and other Cr₂-containing ions which together contribute a significant percentage of the total ion current. However, the greater relative abundance of monometallic ions such as (C₅H₅)Cr(NO)I⁻, (C₅H₅)CrI⁻ and (C₅H₅)₂Cr⁺ indicate that the dimer is readily cleaved on vapourisation or electron
Table 2.1 Low-Resolution Mass Spectral Data For

\[(\eta^5-C_5H_5)Cr(NO)I]_2\]

<table>
<thead>
<tr>
<th>M/z</th>
<th>Rel. Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>548</td>
<td>7</td>
<td>((C_5H_5)_2Cr_2(NO)_2I_2^+)</td>
</tr>
<tr>
<td>518</td>
<td>42</td>
<td>((C_5H_5)_2Cr_2(NO)I_2^+)</td>
</tr>
<tr>
<td>488</td>
<td>21</td>
<td>((C_5H_5)_2CrI_2^+)</td>
</tr>
<tr>
<td>371</td>
<td>13</td>
<td>((C_5H_5)CrI_2^+)</td>
</tr>
<tr>
<td>304</td>
<td>9</td>
<td>((C_5H_5)Cr(NO)_2I^+)</td>
</tr>
<tr>
<td>274</td>
<td>12</td>
<td>((C_5H_5)Cr(NO)I^+)</td>
</tr>
<tr>
<td>244</td>
<td>67</td>
<td>((C_5H_5)CrI^+)</td>
</tr>
<tr>
<td>182</td>
<td>100</td>
<td>((C_5H_5)_2Cr^+)</td>
</tr>
<tr>
<td>117</td>
<td>96</td>
<td>((C_5H_5)Cr^+)</td>
</tr>
<tr>
<td>52</td>
<td>73</td>
<td>(Cr^+)</td>
</tr>
</tbody>
</table>

Probe Temp \(\approx 150^\circ C\)

impact. Interestingly, however, the complex displays significant paramagnetism, both in the solid state and in solution (Table 2.2), a feature which precludes the routine measurement of its \(^1H\)- and \(^13C\)-NMR spectra. This paramagnetism indicates that the complex may not possess a conventional 2-centre, 2-electron Cr-Cr linkage.
Table 2.2 Magnetic Susceptibility Data

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\chi_m(\text{corr}) \times 10^3$, cm$^3$ mol$^{-1}$</th>
<th>$\mu(\text{eff}),$ BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{CpCr(NO)}\text{Cl}]_2$</td>
<td>0.349±0.014 a</td>
<td>0.91±0.02 (292K)</td>
</tr>
<tr>
<td>$[\text{CpCr(NO)}\text{I}]_2$</td>
<td>0.329±0.006 b</td>
<td>0.90±0.02 (305K)</td>
</tr>
<tr>
<td>$\text{CpCr(NO)}(\text{PPh}_3)\text{Cl}$</td>
<td>1.38 c,d</td>
<td>1.86</td>
</tr>
<tr>
<td>$\text{CpCr(NO)}(\text{PPh}_3)\text{Br}$</td>
<td>1.31±0.19 c</td>
<td>1.80±0.13 (305K)</td>
</tr>
<tr>
<td>$\text{CpCr(NO)}(\text{PPh}_3)\text{I}$</td>
<td>1.44±0.10 c</td>
<td>1.89±0.07 (305K)</td>
</tr>
<tr>
<td>$\text{CpCr(NO)}{\text{P(OPh)}_3}\text{I}$</td>
<td>1.36±0.09 c</td>
<td>1.84±0.06 (305K)</td>
</tr>
<tr>
<td>$\text{CpCr(NO)}{\text{P(OEt)}_3}\text{I}$</td>
<td>1.23±0.08 c</td>
<td>1.74±0.06 (305K)</td>
</tr>
</tbody>
</table>

a Measured by the Faraday Method; taken from Ref 69.
b Measured on a Gouy Balance in the solid state.
c Measured by Evans Method (see Ref. 70).
d Taken from Ref. 71.

Alternatively, the complex may dissociate into monomeric fragments, i.e.

$$[(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}\text{I}]_2 \rightarrow 2(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}\text{I} \ldots (2.15)$$

a process which should be more facile in solution. The former explanation seems more likely, since the monomeric fragments would be 15-electron species and thus very
electron deficient (vide supra). Also, it has been proposed, on the basis of bond angles in the Cr₂Y₂ unit,¹ that the isoelectronic complex \([(η⁵-C₅H₅)Cr(NO)(OMe)]₂\) does not contain a metal–metal bond [72]. Since in the absence of a Cr–Cr linkage, a value of \(µ(\text{eff})=2.83\) BM would be expected, it is evident that some spin pairing must be occurring, possibly through the halide bridges.

In addition to the above-mentioned methoxide and chloro analogues, there exists a fairly large series of \([(η⁵-C₅H₅)Cr(NO)Y]₂\) complexes (Y=NH₂ [43], OEt [64], NMe₂ [73], NO [36,74], SR [75,76], SeR [76] or TeR [76]) in which the Y groups bridge two \((η⁵-C₅H₅)Cr(NO)\) moieties. Not surprisingly, the iodonitrosyl dimer is a synthetic precursor to the other \([(η⁵-C₅H₅)Cr(NO)Y]₂\) species, e.g.

\[
[(η⁵-C₅H₅)Cr(NO)I]₂ + NaOR \longrightarrow [(η⁵-C₅H₅)Cr(NO)(OR)]₂ + 2NaI \ldots(2.16)
\]

where R=Me, Et.

While both complexes have been previously synthesised from \((η⁵-C₅H₅)Cr(NO)₂Cl\) [64,71], the methoxide has not been fully characterised. Its mass spectrum (Table 2.3) and its IR

¹The bond angle argument is that if the Y–Cr–Y angle is greater than the Cr–Y–Cr angle, then the complex contains a Cr–Cr bond. If the reverse relationship between the angles pertains, then there is no formal Cr–Cr linkage [72].
spectrum \( \nu(\text{NO}) (\text{CH}_2\text{Cl}_2) = 1661 \text{ cm}^{-1} \) have been obtained and

Table 2.3 Low-Resolution Mass Spectral Data For

\[ [(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)(OMe)}]_2 \]

<table>
<thead>
<tr>
<th>m/z</th>
<th>Rel Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>356</td>
<td>5</td>
<td>((\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_2(\text{OMe})_2^+)</td>
</tr>
<tr>
<td>326</td>
<td>36</td>
<td>((\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})(\text{OMe})_2^+)</td>
</tr>
<tr>
<td>296</td>
<td>52</td>
<td>((\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{OMe})_2^+)</td>
</tr>
<tr>
<td>281</td>
<td>20</td>
<td>((\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{OMe})_0^+)</td>
</tr>
<tr>
<td>266</td>
<td>10</td>
<td>((\text{C}_5\text{H}_5)_2\text{Cr}_2\text{O}_2^+)</td>
</tr>
<tr>
<td>251</td>
<td>10</td>
<td>((\text{C}_5\text{H}_5)_2\text{Cr}_2\text{OH}^+)</td>
</tr>
<tr>
<td>182</td>
<td>100</td>
<td>((\text{C}_5\text{H}_5)_2\text{Cr}^+)</td>
</tr>
<tr>
<td>148</td>
<td>20</td>
<td>((\text{C}_5\text{H}_5)\text{Cr}(\text{OMe})^+)</td>
</tr>
<tr>
<td>117</td>
<td>20</td>
<td>((\text{C}_5\text{H}_5)\text{Cr}^+)</td>
</tr>
<tr>
<td>52</td>
<td>49</td>
<td>\text{Cr}^+</td>
</tr>
</tbody>
</table>

Probe Temp \( \approx 160 \text{°C} \)

are as expected.

Reaction (D) of Scheme 2.1 also has precedence in the
literature, the congeneric molybdenum complex, 

\[ [(\eta^5-C_5H_5)Mo(NO)I]_2 \]

having been reported to react readily with iodine to afford 

\[ [(\eta^5-C_5H_5)Mo(NO)I_2]_2 \].

The shift in the nitrosyl-stretching frequency accompanying reaction (D) (i.e. +72 cm\(^{-1}\)) is comparable to that observed for the molybdenum system, namely +87 cm\(^{-1}\) (1573 \(\rightarrow\) 1660 cm\(^{-1}\)) [60].

The decomposition of the iodo-dimer either in the presence or absence of excess iodine involves the transfer of nitrosyl groups between the two Cr atoms. Intermolecular transfer of a metal-bound nitrosyl ligand has been proposed to occur via formation of an intermediate \(M(\mu-NO)M'\) linkage [77,78], although recent kinetic evidence suggests that nitrogen monoxide dissociation followed by association is the preferred mechanism [79]. Although the presence of free NO has not been detected, it is proposed that the first step in reaction (E) is the slow dissociation of NO i.e.

\[ [(\eta^5-C_5H_5)Cr(NO)I_2]_2 \rightarrow [(\eta^5-C_5H_5)CrI_2]_2 + 2NO \ldots(2.17) \]

followed by rapid reaction of the liberated nitrogen monoxide with any of the three dimeric species 

\[ [(\eta^5-C_5H_5)Cr(NO)I_2]_2, \quad [(\eta^5-C_5H_5)Cr(NO)I]_2 \quad \text{or} \quad [(\eta^5-C_5H_5)CrI_2]_2 \].

It has been independently demonstrated that 

\[ [(\eta^5-C_5H_5)Cr(NO)I]_2 \]

is smoothly converted to 

\[ (\eta^5-C_5H_5)Cr(NO)_2I \], in virtually quantitative yields, by the action of NO gas. Similar reactions have been reported for
the analogous \((\eta^5-C_5H_5)CrCl_2\)_2 [64], \((\eta^5-C_5H_5)Cr(NO)Cl\)_2 [64] and \((\eta^5-C_5H_5)W(NO)I_2\)_2 [57] complexes.

(b) **Reactions Of \((\eta^5-C_5H_5)Cr(CO)(NO)(PPh_3)\) With Halogens**

The reactions of \((\eta^5-C_5H_5)Cr(CO)(NO)(PPh_3)\) with halogens are simpler than those of \((\eta^5-C_5H_5)Cr(CO)_2(NO)\) (Scheme 2.1). Indeed, only the transformations analogous to reaction (A) of the scheme occur in good yields when the phosphine-containing reactant is treated with chlorine, bromine or iodine, i.e.

\[
2(\eta^5-C_5H_5)Cr(CO)(NO)(PPh_3) + X_2 \rightarrow 2(\eta^5-C_5H_5)Cr(NO)(PPh_3)X + 2CO \quad \text{(2.18)}
\]

where \(X=\text{Cl, Br or I},\)

a feature which reflects the inertness of the triphenylphosphine ligand in the product complexes. For the case when \(X=I,\) such complexes may also be obtained by cleavage of the iodine bridges in \([(\eta^5-C_5H_5)Cr(NO)I]\)_2 with a Lewis base, \(L,\) i.e.

\[
[(\eta^5-C_5H_5)Cr(NO)I]\)_2 + 2L \rightarrow 2(\eta^5-C_5H_5)Cr(NO)(L)I \quad \text{(2.19)}
\]

where \(L=PPh_3, P(OPh)_3, \) or \(P(OEt)_3,\)
conversions which are analogous to the reverse of reaction (B) in Scheme 2.1. Of the monomeric complexes produced in reactions (2.18) and (2.19), only the chloro derivative, \((\eta^5-C_5H_5)Cr(NO)(PPh_3)Cl\), has been reported previously, having been isolated in low yield from the reaction of \((\eta^5-C_5H_5)Cr(NO)\_2Cl\) with PPh\(_3\) [71].

\[
(\eta^5-C_5H_5)Cr(NO)\_2Cl + PPh_3 \rightarrow (\eta^5-C_5H_5)Cr(NO)(PPh_3)Cl + NO 
\]

Reactions (2.18) and (2.19), as appropriate, are thus the preparative methods of choice for these organometallic compounds.

The \((\eta^5-C_5H_5)Cr(NO)(L)X\) species are green, fairly air-stable microcrystalline solids. Their solubilities depend on the nature of \(L\) and \(X\). Thus, when \(L=PPh_3\), the solubilities vary in the order \(X=Cl>Br>I\), \((\eta^5-C_5H_5)Cr(NO)(PPh_3)I\) being only moderately soluble in \(CH_2Cl_2\), less so in \(CHCl_3\), and organic donor solvents, and virtually insoluble in paraffin hydrocarbons. For \(X=I\), the solubilities in the above solvents diminish as \(L=P(OEt)_3>P(OPh)_3>PPh_3\), the triethylphosphite complex being very soluble in all organic solvents including hexanes.

All these complexes are paramagnetic, having molar magnetic susceptibilities and permanent moments \((\mu_{eff})\) indicative of one unpaired electron (Table 2.2). Toluene
solutions of the complexes at ambient temperature exhibit EPR spectra which consist of a simple two-line pattern except for \((\eta^5-C_5H_5)Cr(NO)(PPh_3)Cl\) which shows a six-line pattern with approximately equal intensities (Table 2.4 and Figure 2.1). The two-line patterns arise from the hyperfine splitting of the signal due to interaction of the odd electron with the \(^{31}P(I=0.5)\) nucleus in each molecule, whereas the six-line pattern (a doublet of triplets) results from coupling to both the \(^{31}P\) and \(^{14}N(I=1)\) nuclei. Coupling constants to \(^{31}P\) are in the range 20–33 G while the observed coupling constant to \(^{14}N\) is 4.6 G.

The \((\eta^5-C_5H_5)Cr(NO)(L)X\) complexes are relatively involatile, but their mass spectra can be obtained at elevated temperatures. These spectra (Tables 2.5 and 2.6) display peaks due to the parent ions and ions resulting from the successive loss of ligands or ion–molecule reactions.

The IR spectra of these compounds (see Table 2.7) display single, sharp nitrosyl-stretching absorptions in the range 1660–1690 \(\text{cm}^{-1}\) which are 20–40 \(\text{cm}^{-1}\) lower than that exhibited by \((\eta^5-C_5H_5)Cr(CO)(NO)I\). The decrease in \(\nu(\text{NO})\) as \(L\) varies in the order \(\text{CO} > P(\text{OPh})_3 > P(\text{OEt})_3 > PPh_3\) is consistent with the documented electron-donating and –accepting

---

1 Due to excessive fragmentation of the triethyl phosphite ligand, the low-resolution mass spectrum of \((\eta^5-C_5H_5)Cr(NO)\{P(\text{OEt})_3\}I\) cannot be assigned with certainty.
Table 2.4 Electron Paramagnetic Resonance Data

<table>
<thead>
<tr>
<th>Complex</th>
<th>g(iso)</th>
<th>$a^{14N}$,G</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpCr(NO)(PPh$_3$)Cl</td>
<td>1.994</td>
<td>20.4</td>
</tr>
<tr>
<td>CpCr(NO)(PPh$_3$)Br</td>
<td>2.014</td>
<td>24</td>
</tr>
<tr>
<td>CpCr(NO)(PPh$_3$I)</td>
<td>2.046</td>
<td>24.5</td>
</tr>
<tr>
<td>CpCr(NO)(P(OPh)$_3$I</td>
<td>2.006</td>
<td>29</td>
</tr>
<tr>
<td>CpCr(NO)(P(OEt)$_3$I</td>
<td>2.052</td>
<td>32.5</td>
</tr>
</tbody>
</table>

$a^{14N}=4.6G$

properties of these ligands [80]. Interestingly, the $\nu$(NO) values of the 17-electron chromium species occur at considerably lower frequencies than those of the analogous 18-electron manganese compounds (see Table 2.7) [67]. A similar phenomenon has recently been reported for the related $[(\eta^5-C_5H_5)M(NO)(L-L)]^+$ (M=Cr or Mn) cations [81].

The physical properties of the $(\eta^5-C_5H_5)Cr(NO)LX$ compounds described above are consistent with the complexes possessing the familiar "three-legged piano stool" molecular structure, i.e.
Figure 2.1 Electron Paramagnetic Resonance Spectra (X-Band) of Dilute Toluene Solutions Of (a) \((\eta^5-C_5H_5)Cr(NO)(PPh_3)Cl\) And (b) \((\eta^5-C_5H_5)Cr(NO)(PPh_3)I\).
Table 2.5 Low-Resolution Mass Spectral Data For
$(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)(PPh}_3)X$ (X=Cl,Br,I)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>m/z (Rel. Intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X=Cl</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)\text{Cr(NO)LX}^+$</td>
<td>444 (&lt;1)</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)\text{CrLX}^+$</td>
<td>414 (3)</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)\text{Cr(NO)L}^+$</td>
<td>409 (2)</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)\text{CrL}^+$</td>
<td>379 (2)</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})_2X_2^+$</td>
<td>364 (&lt;1)</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{NO})X_2^+$</td>
<td>334 (5)</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)_2\text{Cr}_2X_2^+$</td>
<td>304 (6)</td>
</tr>
<tr>
<td>PPh$_3^+$</td>
<td>262(100)</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)_2\text{Cr}^+$</td>
<td>182</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)\text{Cr(NO)X}^+$</td>
<td>182</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)\text{CrX}^+$</td>
<td>152 (16)</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5)\text{Cr}^+$</td>
<td>117 (10)</td>
</tr>
<tr>
<td>Cr$^+$</td>
<td>52 (16)</td>
</tr>
</tbody>
</table>

a) Probe Temp =170°C  
b) Probe Temp =180°C  
c) Probe Temp =250°C  
d) Assignment Indistinguishable at Low-Resolution
Table 2.6 Low-Resolution Mass Spectral Data For
$(\eta^5-C_5H_5)Cr(NO)\{P(OPh)_3\}I$.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Rel Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>584</td>
<td>&lt;1</td>
<td>$(C_5H_5)Cr(NO){P(OPh)_3}I^+$</td>
</tr>
<tr>
<td>554</td>
<td>1</td>
<td>$(C_5H_5)Cr{P(OPh)_3}I^+$</td>
</tr>
<tr>
<td>548</td>
<td>1</td>
<td>$(C_5H_5)_2Cr_2(NO)_2I_2^+$</td>
</tr>
<tr>
<td>518</td>
<td>10</td>
<td>$(C_5H_5)_2Cr_2(NO)I_2^+$</td>
</tr>
<tr>
<td>488</td>
<td>6</td>
<td>$(C_5H_5)_2Cr_2I_2^+$</td>
</tr>
<tr>
<td>427</td>
<td>&lt;1</td>
<td>$(C_5H_5)Cr{P(OPh)_3}^+$</td>
</tr>
<tr>
<td>310</td>
<td>100</td>
<td>$P(OPh)_3^+$</td>
</tr>
<tr>
<td>274</td>
<td>4</td>
<td>$(C_5H_5)Cr(NO)I^+$</td>
</tr>
<tr>
<td>244</td>
<td>23</td>
<td>$(C_5H_5)CrI^+$</td>
</tr>
<tr>
<td>182</td>
<td>31</td>
<td>$(C_5H_5)_2Cr^+$</td>
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<td>117</td>
<td>35</td>
<td>$(C_5H_5)Cr^+$</td>
</tr>
<tr>
<td>52</td>
<td>23</td>
<td>$Cr^+$</td>
</tr>
</tbody>
</table>

Probe Temp ≈200°C
Table 2.7 A Comparison Of The Nitrosyl-Stretching Frequencies Of The New \((\eta^5-C_5H_5)Cr(NO)LX\) With The Analogous 18-electron Manganese Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu(\text{NO}) (\text{CH}_2\text{Cl}_2), \text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M=Cr</td>
</tr>
<tr>
<td>CpM(CO)(NO)I</td>
<td>1706</td>
</tr>
<tr>
<td>CpM(NO)(PPh(_3))Cl</td>
<td>1664</td>
</tr>
<tr>
<td>CpM(NO)(PPh(_3))Br</td>
<td>1664</td>
</tr>
<tr>
<td>CpM(NO)(PPh(_3))I</td>
<td>1666</td>
</tr>
<tr>
<td>CpM(NO){P(OPh)(_3)}I</td>
<td>1686</td>
</tr>
<tr>
<td>CpM(NO){P(OEt)(_3)}I</td>
<td>1670</td>
</tr>
</tbody>
</table>

a Taken from Ref. 67.
even though they are formally isoelectronic with the carbonyl complexes \([(\eta^5-C_5H_5)Cr(CO)_2L])_2\) (L=CO [82], PPh₃ [83] or P(OMe)₃ [84]) which are diamagnetic. It must be noted, however, that the Cr–Cr linkages in the carbonyl dimers are not particularly strong [82,84]. Thus, the solid state molecular structure of \([(\eta^5-C_5H_5)Cr(CO)_3])_2\) contains a very long Cr–Cr bond (3.281Å) despite the presence of the less sterically demanding CO ligands [82]. Moreover, upon vapourisation or dissolution the dimer undergoes some dissociation into paramagnetic monomers, [82,85] i.e.

\[
[(\eta^5-C_5H_5)Cr(CO)_3]]_2 \rightarrow 2(\eta^5-C_5H_5)Cr(CO)_3 \ldots (2.21)
\]

(c) Reactions Of \((\eta^5-C_5Me_5)M(CO)_2(NO)\) (M=Cr,Mo Or W) With Halogens

Due to its increased basicity and steric requirements, the pentamethylcyclopentadienyl ligand has been employed successfully in recent years to prepare stable analogues of
unstable or transient cyclopentadienyl-transition-metal complexes [86]. The reactivity of the \((\eta^5-C_5Me_5)M(\text{CO})_2(\text{NO})\) (M=Cr, Mo or W) compounds towards halogens was therefore investigated with a view to isolating \(C_5Me_5\) analogues of various intermediate species formed during the analogous reactions of the cyclopentadienyl reactants. Specifically, it was hoped to obtain \((\eta^5-C_5Me_5)\text{Cr}(\text{CO})(\text{NO})\text{I}\) (cf Scheme 2.1) and \((\eta^5-C_5Me_5)M(\text{CO})(\text{NO})\text{I}_2\) (M=Mo, W), \(C_5H_5\) analogues of the latter complexes having been proposed for both M=Mo [58] and W [57]. Unfortunately, while all three complexes were detected as intermediates, they could not be isolated from the reaction mixture.

The only nitrosyl-containing compound isolable after treatment of \((\eta^5-C_5Me_5)\text{Cr}(\text{CO})_2(\text{NO})\) with \(\text{I}_2\) in \(\text{CH}_2\text{Cl}_2\) is \((\eta^5-C_5Me_5)\text{Cr}(\text{NO})_2\text{I}\) even if the stoichiometry of the reactants is carefully controlled at 2:1 (cf. eq. 2.12) i.e.

\[
2(\eta^5-C_5Me_5)\text{Cr}(\text{CO})_2(\text{NO}) + \text{I}_2 \rightarrow (\eta^5-C_5Me_5)\text{Cr}(\text{NO})_2\text{I}
\]

\[(2.22)\]

During the course of the transformation, however, \(C_5Me_5\) analogues of all the intermediates proposed for the \(C_5H_5\) reactant (Scheme 2.1) are detectable in solution by IR spectroscopy (Figure 2.2), but they could not be isolated by conventional techniques. In this system, at least, the
Figure 2.2 Infra-red Spectral Changes Accompanying The Reaction Of \((\eta^5-C_5Me_5)Cr(CO)_2(NO)\) With 0.5 Equivalents Of I\(_2\). Assignments Of Absorptions: A, \((\eta^5-C_5Me_5)Cr(CO)_2(NO)\); B, \((\eta^5-C_5Me_5)Cr(CO)(NO)\); C, \([(\eta^5-C_5Me_5)Cr(NO)I]\); D, \([(\eta^5-C_5Me_5)Cr(NO)I_2]\); E, \((\eta^5-C_5Me_5)Cr(NO)I_2\).
presence of the pentamethylcyclopentadienyl ligand does not seem to impart any enhanced stability to the intermediate complexes. Upon closer inspection of Figure 2.2 it is noticeable that the first step of the reaction sequence, consumption of the dicarbonylnitrosyl reactant, is significantly slower for the \( \text{C}_5\text{Me}_5 \) derivative. The consequence of this feature is that any \( [(\eta^5-\text{C}_5\text{Me}_5)\text{Cr(NO)}\text{I}]_2 \) present during the first half-hour of the reaction will react with the iodine to produce \( [(\eta^5-\text{C}_5\text{Me}_5)\text{Cr(NO)}\text{I}_2]_2 \). Thus the concentration of \( [(\eta^5-\text{C}_5\text{Me}_5)\text{Cr(NO)}\text{I}]_2 \) only builds up to a maximum after 30 mins when all the iodine has been consumed. In an attempt to trap the monoiodide dimer, \( \text{P(OPh)}_3 \) was added to the reaction mixture. Unfortunately, the \( (\eta^5-\text{C}_5\text{Me}_5)\text{Cr(NO)}\{\text{P(OPh)}_3\} \text{I} \) complex produced could not be separated from the \( (\eta^5-\text{C}_5\text{Me}_5)\text{Cr(NO)}_2 \text{I} \) present in the reaction mixture. Finally, the reaction of \( (\eta^5-\text{C}_5\text{Me}_5)\text{Cr(CO)}_2(\text{NO}) \) with \( \text{Br}_2 \) was carried out. In this case, addition of just enough \( \text{Br}_2 \) to consume the original organometallic reactant results in a mixture of \( [(\eta^5-\text{C}_5\text{Me}_5)\text{Cr(NO)}\text{Br}_2]_2 \) and \( (\eta^5-\text{C}_5\text{Me}_5)\text{Cr(NO)}_2 \text{Br} \). An unusual feature of this conversion is that the dihalodimer does not convert to the dinitrosyl species upon prolonged stirring. It is however, smoothly, transformed into \( (\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}_2 \text{Br} \) by the action of NO gas.

The new halodinitrosyl\( (\eta^5-\text{pentamethylcyclo-pentadienyl}) \) chromium complexes, are golden-brown, air-stable
solids which are soluble in all organic solvents. Their spectroscopic properties (Tables 2.8 and 2.9) are similar to those displayed by their cyclopentadienyl analogues [49,87].

The reactivity of both \((\eta^5-C_5Me_5)M(CO)_2(NO)\) (M=Mo or W) complexes is identical to that reported previously for their cyclopentadienyl analogues [57,58], namely

\[
(\eta^5-C_5R_5)M(CO)_2(NO) + I_2 \rightarrow (\eta^5-C_5R_5)M(CO)(NO)I_2 + CO
\]

...(2.23)

followed by

\[
2 (\eta^5-C_5R_5)M(CO)(NO)I_2 \rightarrow [(\eta^5-C_5R_5)M(NO)I_2]_2 + 2CO
\]

...(2.24)

M=Mo or W; R=H or Me.

The only difference is that during these sequential conversions the C_5Me_5 ligand does have a slight stabilising effect on the carbonyldiiodonitrosyl intermediates. Thus, for M=Mo, complete decarbonylation of the intermediate \((\nu(CO)=2080 \text{ cm}^{-1}, \nu(NO)=1694 \text{ cm}^{-1} \text{ in CH}_2\text{Cl}_2)\) requires 1 hr at ambient temperature when R=CH_3, whereas when R=H no such intermediate can be detected spectroscopically [58]. The most thermally stable of all the intermediate complexes, \((\eta^5-C_5Me_5)W(CO)(NO)I_2\) \([IR(CH_2Cl_2): \nu(CO) 2072 \text{ cm}^{-1}, \nu(NO) 1676 \text{ cm}^{-1}]\), requires 2–3 hrs under moderate
Table 2.8 IR And $^1$H—NMR Spectral Data For The New Pentamethylcyclopentadienyl Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>IR $\nu$(NO), cm$^{-1}$ (in CH$_2$Cl$_2$)</th>
<th>$^1$H—NMR $\delta$ (in CDCl$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp&quot;Cr(NO)$_2$Br</td>
<td>1784, 1685</td>
<td>1.82(s)</td>
</tr>
<tr>
<td>Cp&quot;Cr(NO)$_2$I</td>
<td>1784, 1687</td>
<td>1.91(s)</td>
</tr>
<tr>
<td>Cp&quot;Cr(NO){P(OPh)$_3$}I</td>
<td>1658</td>
<td></td>
</tr>
<tr>
<td>[Cp&quot;Mo(NO)I$_2$]$_2$</td>
<td>1660</td>
<td>2.05(s)</td>
</tr>
<tr>
<td>Cp&quot;Mo(NO)(PPh$_3$I$_2$</td>
<td>1658</td>
<td>1.99(s, 15H, CH$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.36(m, 15H, C$_6$H$_5$)</td>
</tr>
<tr>
<td>Cp&quot;Mo(NO){P(OPh)$_3$}I$_2$</td>
<td>1662</td>
<td>2.05(s, 15H, CH$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.07(m, 15H, C$_6$H$_5$)</td>
</tr>
<tr>
<td>[Cp&quot;W(NO)I$_2$]$_2$</td>
<td>1629</td>
<td>2.18(s)</td>
</tr>
<tr>
<td>Cp&quot;W(NO)(PPh$_3$I$_2$</td>
<td>1628</td>
<td>2.17(s, 15H, CH$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.38(m, 15H, C$_6$H$_5$)</td>
</tr>
<tr>
<td>Cp&quot;W(NO){P(OPh)$_3$}I$_2$</td>
<td>1640</td>
<td>2.18(s, 3H, CH$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.34(s, 12H, CH$_3$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.21(m, 15H, C$_6$H$_5$)</td>
</tr>
</tbody>
</table>
Table 2.9 $^{13}$C-NMR Spectral Data For The New Pentamethylcyclopentadienyl Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta$ in CDCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp&quot;Cr(NO)$_2$Br</td>
<td>112.2(C-CH$_3$) 9.7(CH$_3$)</td>
</tr>
<tr>
<td>[Cp&quot;Mo(NO)I$_2$]$_2$</td>
<td>118.6(C-CH$_3$) 13.2(CH$_3$)</td>
</tr>
<tr>
<td>Cp&quot;Mo(NO){P(OPh)$_3$}I$_2$</td>
<td>151.5(d, $J(^{31}$P-$_{13}$C)=15.3Hz;C$_1$) 129.5(C$_3$) 125.5(C$_4$(maj isomer))</td>
</tr>
<tr>
<td></td>
<td>124.2(C$<em>4$(min isomer)) 121.4(d, $J(^{31}$P-$</em>{13}$C)=6.6Hz;C$_3$(maj isomer))</td>
</tr>
<tr>
<td></td>
<td>120.6(d, $J(^{31}$P-$_{13}$C)=6.7Hz;C$_2$(min isomer)) 115.8(C-CH$_3$) 13.1(CH$_3$(min isomer))</td>
</tr>
<tr>
<td></td>
<td>12.2(CH$_3$(maj isomer))</td>
</tr>
<tr>
<td>[Cp&quot;W(NO)I$_2$]$_2$</td>
<td>117.5(C-CH$_3$) 12.8(CH$_3$)</td>
</tr>
<tr>
<td>Cp&quot;W(NO){P(OPh)$_3$}I$_2$</td>
<td>151.5(d, $J(^{31}$P-$_{13}$C)=15.2Hz;C$_1$) 129.5(C$_3$) 125.5(C$_4$(maj isomer))</td>
</tr>
<tr>
<td></td>
<td>124.2(C$<em>4$(min isomer)) 121.4(d, $J(^{31}$P-$</em>{13}$C)=3.6Hz;C$_3$(maj isomer))</td>
</tr>
<tr>
<td></td>
<td>120.6(d, $J(^{31}$P-$_{13}$C)=7.2Hz;C$_2$(min isomer)) 112.4(C-CH$_3$) 12.8(CH$_3$(min isomer))</td>
</tr>
<tr>
<td></td>
<td>12.1(CH$_3$(maj isomer))</td>
</tr>
</tbody>
</table>
vacuum at 25°C to remove completely the CO group, but it again cannot be isolated in a pure state, even when handled in an atmosphere of carbon monoxide.

The products of reaction (2.24), i.e. 
$\left[ (\eta^5-C_5Me_5)M(NO)I_2 \right]_2$ (M=Mo or W), are purple (M=Mo) or green–brown (M=W) diamagnetic solids which dissolve readily in all organic solvents except aliphatic hydrocarbons. They are best formulated as having iodo–bridged, dimeric molecular structures

![Diagram of molecular structure](image)

in order to provide each metal centre with the favoured 18–electron configuration. Their physical properties (see Tables 2.8 and 2.9) are quite similar to those displayed by their C₅H₅ analogues [57,58], although (as expected) their characteristic nitrosyl–stretching frequencies are 20–30 cm⁻¹ lower in energy. Just as for the cyclopentadienyl species, the iodine bridges in the dimers may be cleaved by Lewis bases such as triphenylphosphine or triphenylphosphite, i.e.
\[(\eta^5-C_5Me_5)M(NO)I_2\]_2 + 2L \rightarrow 2(\eta^5-C_5Me_5)M(NO)(L)I_2

...(2.25)

M=Mo or W; L=PPh\(_3\) or P(OPh)\(_3\)

to obtain in good yields the monomeric complexes (\(\eta^5-C_5Me_5\)M(NO)(L)I\(_2\) (M=Mo or W; L=PPh\(_3\) or P(OPh)\(_3\)). The physical properties of these new complexes are given in Tables 2.8 and 2.9. The only significant feature is that for the triphenylphosphite complexes both isomers (\textit{cis} and \textit{trans}) are detectable by \(^1H-\) and \(^{13}C-\)NMR.

This attribute has also been detected for the complex (\(\eta^5-C_5H_5\)Mo(NO){P(OPh)\(_3\})I_2 [58] but was not found for the analogous tungsten derivative (\(\eta^5-C_5H_5\)W(NO){P(OPh)\(_3\})I_2 [57].
(iii) **Experimental Section**

**General Procedures**

All manipulations were performed so as to maintain all chemicals under an atmosphere of prepurified nitrogen either on the bench using conventional techniques for the manipulation of air-sensitive compounds [88] or in a Vacuum Atmospheres Corp. Dri-Lab Model HE-43-2 drybox. All chemicals used were of reagent grade or comparable purity. Reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Melting points were taken in capillaries by using a Gallenkamp Melting Point apparatus and are uncorrected. All solvents were dried by standard procedures [89], distilled just prior to use and purged for 15–20 mins with nitrogen. Unless specified otherwise, the chemical reactions described were effected at ambient temperatures.

**Infrared Spectra.** Infrared spectra were recorded on Perkin–Elmer 457 or 598 spectrophotometers and were calibrated with the 1601 cm⁻¹ band of polystyrene film.

**Nuclear Magnetic Resonance Spectra.** Proton magnetic resonance spectra were obtained on Varian Associates T-60 or
EM-360 spectrometers with tetramethylsilane (Me₄Si) employed as an internal standard or on Bruker WP-80 or WH-400 spectrometers, with reference to the solvent used. Proton decoupled Carbon-13 NMR spectra were recorded on a Varian Associates CFT-20 or on the Bruker WP-80 spectrometer with reference to the solvent used. All ¹H and ¹³C chemical shifts are reported in ppm downfield from Me₄Si. For low temperature measurements the Bruker WP-80 was equipped with a Bruker B-VT-1000 variable temperature probe. Dr. S. O. Chan and Mrs. M. M. Tracey assisted in obtaining these data.

Mass Spectra. Low-resolution mass spectra were recorded at 70eV on an Atlas CH4B spectrometer using the direct insertion method with the assistance of Dr. G. K. Eigendorf and Mr. J. W. Nip.

Conductivities. Conductivities of 10⁻³ M solutions were measured with a YSI Model 31 conductivity bridge at ambient temperatures, with the help of Dr. Y. Koga.

Magnetic Susceptibility Measurements. Solution magnetic susceptibility measurements were effected by Evan's method using an 8% solution of (CH₃)₂COH in CHCl₃ as the solvent [70]. Pascal's constants were used to correct the measured molar susceptibilities for the diamagnetic contributions of the ligands [90]. Solid state measurements were recorded by
the Gouy method [91] with the assistance of Ms. K. Oliver.

**Electron Paramagnetic Resonance Spectra.** EPR spectra of $10^{-3}$M toluene solutions were recorded on a Varian E-3 spectrometer at ambient temperatures.

**Elemental Analyses.** Elemental analyses were performed by Mr. P. Borda.

**Reaction of ($\eta^5$-C$_5$H$_5$)Cr(CO)$_2$(NO) with I$_2$.** To a stirred orange solution of ($\eta^5$-C$_5$H$_5$)Cr(CO)$_2$(NO) [92] (2.03g, 10.0mmol) in CH$_2$Cl$_2$ (80mL) was added solid I$_2$ (1.24g, 4.90mmol). Reaction occurred after 5 min as evidenced by gas evolution and a colour change of the reaction mixture to green-brown. After being stirred for 1 hr to ensure completion of the reaction, the mixture was taken to dryness under reduced pressure. Crystallization of the residue from CH$_2$Cl$_2$-hexanes afforded 2.35g (88% yield) of dark green [(($\eta^5$-C$_5$H$_5$)Cr(NO)I)$_2$].

Anal. Calcd for C$_{10}$H$_{10}$N$_2$I$_2$Cr$_2$O$_2$: C, 21.92; H, 1.84; N, 5.11; I, 46.33. Found: C, 22.00; H, 1.77; N, 5.00; I, 46.08. IR (CH$_2$Cl$_2$): $\nu$(NO) 1673 cm$^{-1}$. Mp (in air) 119°C dec.

**Reaction of ($\eta^5$-C$_5$H$_5$)Cr(CO)$_2$(NO) with Br$_2$.** A bright red solution of Br$_2$ in CH$_2$Cl$_2$ was added dropwise to a rapidly stirred orange solution of ($\eta^5$-C$_5$H$_5$)Cr(CO)$_2$(NO) (0.50g,
2.5mmol) in \( \text{CH}_2\text{Cl}_2 \) (30mL). Immediately, the latter solution became blue–green in colour, and gas was evolved. The addition of bromine was continued until IR monitoring of the reaction mixture indicated that the organometallic reactant had been completely consumed. The final mixture was then concentrated in vacuo to 5mL and was transferred to the top of a Florisil column (2x6cm). Elution of the column with \( \text{CH}_2\text{Cl}_2 \) developed a golden–yellow band which was collected and taken to dryness in vacuo to obtain 0.13g (42% yield based on NO) of \( (\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}_2\text{Br} \). The product was readily identifiable by its characteristic spectroscopic properties [87] [ IR (\( \text{CH}_2\text{Cl}_2 \)) : \( \nu(\text{NO}) \) 1819, 1711 cm\(^{-1}\). \( ^1\text{H–NMR (CDCl}_3 \)) : \( \delta \) 5.74. ].

The reaction was also performed in an identical manner in THF. Solvent was removed from the final reaction mixture under reduced pressure, the residue was extracted with \( \text{CH}_2\text{Cl}_2 \) (5mL), and the extracts were filtered through a Florisil column (2x4cm) supported on a medium porosity frit. Removal of all volatiles from the filtrate in vacuo afforded microcrystalline \( (\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}_2\text{Br} \) (0.27g, 86% yield based on NO).

**Thermal decomposition of \( [(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}_2]_2 \) in \( \text{CH}_2\text{Cl}_2 \) and THF.** The two experiments were performed similarly. A sample (0.27g, 0.50mmol) of \( [(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}_2]_2 \) was dissolved in 25mL of the solvent, and the resulting solution was stirred
at room temperature. The decomposition of the organometallic complex was monitored by the disappearance of its characteristic $\nu$(NO) absorption in the IR spectrum of the solution. After decomposition was judged to be complete (45 hr in CH$_2$Cl$_2$, 200 hr in THF), the solution was taken to dryness in vacuo. The residue was extracted with CH$_2$Cl$_2$ (20mL), and the extracts were filtered through a Florisil column (2x4cm). Addition of hexanes to the filtrate and slow concentration of the resulting solution under reduced pressure induced the crystallization of golden—brown needles of (η$^5$—C$_5$H$_5$)Cr(NO)$_2$I. Both conversions produced 0.06g (40% yield based on NO) of this complex which was identified by its characteristic IR spectrum [49] ($\nu$(NO) (CH$_2$Cl$_2$): 1817,1713cm$^{-1}$).

Reaction of [(η$^5$—C$_5$H$_5$)Cr(NO)I]$_2$ with excess I$_2$. Solid I$_2$ (0.25g, 1.0mmol) was added to a rapidly stirred solution of [(η$^5$—C$_5$H$_5$)Cr(NO)I]$_2$ (0.27g, 0.50mmol) in CH$_2$Cl$_2$ (25mL). The progress of the reaction was monitored by IR spectroscopy which revealed that the transformation was complete after 18hr and that the only nitrosyl—containing product formed was (η$^5$—C$_5$H$_5$)Cr(NO)$_2$I [49].

Reaction of [(η$^5$—C$_5$H$_5$)Cr(NO)I]$_2$ with NO. A dark green solution of [(η$^5$—C$_5$H$_5$)Cr(NO)I]$_2$ (0.25g, 0.46mmol) in CH$_2$Cl$_2$ (15mL) was treated with a stream of NO gas for 10 min. The
solution rapidly turned golden-brown in colour. The reaction mixture was filtered through a Florisil column (3x3cm) supported on a medium porosity frit, and the filtrate was concentrated in vacuo to give 0.25g (89% yield) of golden ($\eta^5$-C$_5$H$_5$)Cr(NO)$_2$I [49].

Reactions of [(($\eta^5$-C$_5$H$_5$)Cr(NO)I)$_2$ with NaOR (R=Et or Me). An excess (0.22g, 3.2mmol) of solid NaOEt was added to a rapidly stirred THF solution (50mL) of [(($\eta^5$-C$_5$H$_5$)Cr(NO)I)$_2$ (0.82g, 1.5mmol). After 3 hr, removal of volatiles from the reaction mixture in vacuo afforded a green-brown oil. This oil was extracted with CH$_2$Cl$_2$ (3x15mL), and the combined extracts were filtered through a Florisil column (2x4cm) supported on a medium porosity frit. The column was washed with CH$_2$Cl$_2$ until the washings were colourless, and the volume of the filtrate was reduced to 25mL under reduced pressure. The addition of hexanes (40mL) and the slow concentration of the resulting solution in vacuo resulted in the crystallization of dark green [(($\eta^5$-C$_5$H$_5$)Cr(NO)(OEt))$_2$ (0.10g, 18% yield). The isolated product was identified by its characteristic physical properties [64], e.g. Mp (under N$_2$) 230°C dec; IR(CH$_2$Cl$_2$): $\nu$(NO) 1660 cm$^{-1}$.

Bright green microcrystals of [(($\eta^5$-C$_5$H$_5$)Cr(NO)(OMe))$_2$ were obtained in a similar manner in 15% yield from the reaction of NaOMe with the iodonitrosyl dimer.

Anal. Calcd for C$_{12}$H$_{18}$N$_2$Cr$_2$O$_4$: C, 40.45; H, 4.53; N,
7.86. Found: C, 40.30; H, 4.48; N, 7.73. IR (CH₂Cl₂): \( \nu(\text{NO}) = 1661 \text{ cm}^{-1} \). Mp (in air) 172°C dec.

**Reaction of \([(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)I}]_2\) with CO.** Carbon monoxide was bubbled through a solution of \([(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)I}]_2\) (0.27g, 0.50mmol) in CH₂Cl₂ (25mL) for a period of 1 hr. At the end of this time, an IR spectrum of the dark green solution revealed 10–20% conversion of the organometallic reactant to a new carbonylnitrosyl species (\( \nu(\text{CO})=2096\text{cm}^{-1} \), \( \nu(\text{NO})=1706\text{cm}^{-1} \)). Further exposure of the solution to CO did not, however, increase the amount of this complex produced.

**Reactions of \([(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)I}]_2\) with Lewis Bases, L (L=PPh₃, P(OPh)₃, P(OEt)₃).** The experimental procedure, using the reaction with L=P(OPh)₃ as a representative example, was as follows.

Neat triphenylphosphite (0.13mL, 0.16g, 0.50mmol) was added to a stirred CH₂Cl₂ (25mL) solution of \([(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)I}]_2\) (0.14g, 0.25mmol) and the mixture was stirred for 1 hr to ensure complete reaction. The final blue-green solution was filtered through a Florisil column (2x4cm) supported on a medium porosity frit. Hexanes (30mL) were added to the filtrate, and the resulting solution was concentrated under reduced pressure to obtain green crystals of \((\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}\{\text{P(OPh)}_3\}\text{I}\) (0.20g, 68% yield). Green microcrystals of \((\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)(PPh)}_3\)I were isolated
similarly in 64% yield.

The reaction of \([(\eta^5-C_5H_5)Cr(NO)I]\) \(_2\) and P(OME)\(_3\) was effected identically. However, the \((\eta^5-C_5H_5)Cr(NO)\{P(OEt)\}_3\)I product was obtained analytically pure (32% yield) by chromatography of the final reaction mixture on a Florisil column (2x6cm) with CH\(_2\)Cl\(_2\) as eluant and subsequent recrystallization of the material thus isolated from hexanes.

For L=PPh\(_3\): Anal. Calcd for C\(_{23}\)H\(_{20}\)NCrIOP: C, 51.51; H, 3.76; N, 2.61. Found: C, 51.21; H, 3.77; N, 2.59. IR (CH\(_2\)Cl\(_2\)): \(\nu\)(NO) 1666 cm\(^{-1}\). Mp (in air) 158°C dec.

For L=P(OPh)\(_3\): Anal. Calcd for C\(_{23}\)H\(_{20}\)NCrIO\(_4\)P: C, 47.26; H, 3.42; N, 2.40. Found: C, 47.15; H, 3.39; N, 2.40. IR (CH\(_2\)Cl\(_2\)): \(\nu\)(NO) 1686 cm\(^{-1}\). Mp (in air) 132°C.

For L=P(OEt)\(_3\): Anal. Calcd for C\(_{11}\)H\(_{20}\)NCrIO\(_4\)P: C, 30.00; H, 4.55; N, 3.18. Found: C, 29.87; H, 4.57; N, 3.30. IR (CH\(_2\)Cl\(_2\)): \(\nu\)(NO) 1670 cm\(^{-1}\). Mp (in air) 49–50°C.

Reactions of \((\eta^5-C_5H_5)Cr(CO)(NO)(PPh_3)\) with the halogens Cl\(_2\), Br\(_2\), I\(_2\). These reactions were all performed similarly, and the reaction with Cl\(_2\) is described in detail as a representative example.

A saturated solution of chlorine in CH\(_2\)Cl\(_2\) was prepared by purging 20mL of CH\(_2\)Cl\(_2\) with a stream of chlorine gas for 10 mins. An aliquot (1mL) of this solution was transferred by syringe into a dropping funnel containing CH\(_2\)Cl\(_2\) (10mL).
This diluted solution of Cl$_2$ was then added dropwise to a rapidly stirred, yellow-brown solution of ($\eta^5$-C$_5$H$_5$)Cr(CO)(NO)(PPh$_3$) [93] (0.58g, 1.33mmol) in CH$_2$Cl$_2$ (30mL). The solution immediately became dark green, and gas was evolved. Just enough chlorine was added to consume all the organometallic reactant, as monitored by the disappearance of its characteristic carbonyl absorption in the IR spectrum of the reaction mixture. The final green solution was concentrated under reduced pressure to a volume of 10mL and was filtered through a Florisil column (2x5cm) supported on a medium porosity frit. The column was washed with CH$_2$Cl$_2$ (60mL) until the washings were colourless. Hexanes (60mL) were added to the filtrate and the resulting solution was concentrated in vacuo to induce the crystallization of 0.34g (57% yield) of bright green, analytically pure ($\eta^5$-C$_5$H$_5$)Cr(NO)(PPh$_3$)Cl.

The analogous bromide and iodide complexes were prepared in a similar manner (in isolated yields of 43% and 41% respectively) by the dropwise addition of a solution of bromine in CH$_2$Cl$_2$ or by the addition of a stoichiometric amount of solid iodine to a CH$_2$Cl$_2$ solution of ($\eta^5$-C$_5$H$_5$)Cr(CO)(NO)(PPh$_3$).

For X=Cl: Anal. Calcd for C$_{23}$H$_{20}$NClCrOP: C, 62.10; H, 4.53; N, 3.15. Found: C, 61.90; H, 4.56; N, 3.09. IR (CH$_2$Cl$_2$): $\nu$(NO) 1664 cm$^{-1}$. Mp (in air) 157°C dec.

For X=Br: Anal. Calcd for C$_{23}$H$_{20}$NBrCrOP: C, 56.46; H,
4.12; N, 2.86. Found: C, 56.44; H, 4.19; N, 2.88. IR (CH₂Cl₂): ν(NO) 1664 cm⁻¹. Mp (in air) 162°C dec.

Reaction of (η⁵-C₅Me₅)Cr(CO)₂(NO) with I₂. Solid iodine (0.13g, 0.5mmol) was added to a stirred, red solution of (η⁵-C₅Me₅)Cr(CO)₂(NO) [62] (0.27g, 1.0mmol) in CH₂Cl₂ (25mL). Gas evolution occurred, and the solution became purple-red initially and then brown in colour. After being stirred for 24 hr, the solution was concentrated in vacuo to 1mL and was transferred by syringe to the top of a Florisil column (2x5cm) made up in CH₂Cl₂. Elution of the column with CH₂Cl₂ developed an orange-brown band which was eluted from the column and collected. Hexanes (70mL) were added to the eluate, and the resulting solution was concentrated to 20mL under reduced pressure whereupon a small amount of an orange-brown solid precipitated. The mixture was then gently warmed to redissolve this solid, and the warm solution was cooled overnight to -10°C to obtain golden-brown crystals of (η⁵-C₅Me₅)Cr(NO)₂I (0.08g, 42% yield based on NO).

Anal. Calcd for C₁₆H₁₈N₂CrIO₂: C, 32.10; H, 4.04; N, 7.49. Found: C, 31.83; H, 3.91; N, 7.19. IR (CH₂Cl₂): ν(NO) 1786,1687 cm⁻¹. ¹H-NMR (CDCl₃): δ 1.91(s). Mp (in air) 119°C dec. Mass spectrum m/z(Rel. Intensity): 374(39) [P]⁺, 344(19) [P-NO]⁺, 314(100) [P-2NO]⁺.
Reaction of $\left(\eta^5-C_5Me_5\right)Cr(CO)_2(NO)$ with $Br_2$ and NO. A solution of $Br_2$ in $CH_2Cl_2$ was added dropwise to a stirred red solution of $\left(\eta^5-C_5Me_5\right)Cr(CO)_2(NO)$ (0.55G, 2.0mmol) in $CH_2Cl_2$ (30mL). Gas was evolved and the solution became bright green in colour. The addition of bromine was monitored by the disappearance of the $\nu$(CO) absorptions of the organometallic reactant. When addition was complete the infrared spectrum of the reaction mixture exhibited three $\nu$(NO) bands (1784, 1730 and 1685 cm$^{-1}$). Even upon prolonged stirring (24 hrs) there was no change in the relative intensities of these bands. Treatment of the solution with NO gas for 15 mins caused a diminution of the band at 1730cm$^{-1}$, together with a concomitant increase in intensity of the other two bands. The solution, now golden—brown in colour, was chromatographed on a 2x6cm Florisil column using $CH_2Cl_2$ as eluant. A golden—brown band was eluted, collected, and the solution taken to dryness. Recrystallization from $CH_2Cl_2$/hexanes produced 0.29g (53% yield w.r.t. Cr) of golden microcrystalline $\left(\eta^5-C_5Me_5\right)Cr(NO)_2Br$.

Anal. Calcd for $C_{16}H_{15}N_2BrCrO_2$: C, 36.71; H, 4.62; N, 8.57. Found: C, 36.77; H, 4.84; N, 8.47. IR ($CH_2Cl_2$): $\nu$(NO) 1784, 1685 cm$^{-1}$. $^1H$-NMR (CDCl$_3$): $\delta$ 1.82(s). $^{13}C$-NMR (CDCl$_3$): $\delta$ 112.2(C—CH$_3$), 9.7(CH$_3$). Mp (in air) 149°C dec. Mass spectrum m/z(Rel. Intensity): 326(18) [P]+, 296(23) [P–NO]+, 266(100) [P–2NO]+.
Reactions of \((\eta^5-C_5Me_5)M(CO)_2(NO)\) (M=Mo or W) with I₂. These experiments were performed similarly; only the conversion involving M=Mo is described here in detail.

A stirred, red \(CH_2Cl_2\) solution (80mL) of \((\eta^5-C_5Me_5)Mo(CO)_2(NO)\) [62] (1.59g, 5.00mmol) was treated with solid iodine (1.17g, 4.61mmol). The solution became deep purple in colour, and rapid gas evolution occurred. Hexanes (80mL) were added after 1 hr, and the solution was concentrated under reduced pressure to induce the crystallization of 2.26g (88% yield) of purple \([(\eta^5-C_5Me_5)Mo(NO)I_2]_2\).

The tungsten congener was prepared in a similar manner, but the reaction mixture was slowly concentrated in vacuo so as to drive the reaction to completion (i.e. to decarbonylate completely the intermediate carbonyl–nitrosyl complex formed during this transformation). Recrystallization of the final residue from \(CH_2Cl_2/\)hexanes afforded green–brown microcrystals of \([(\eta^5-C_5Me_5)W(NO)I_2]_2\) in 78% yield.

For M=Mo: Anal. Calcd for \(C_{20}H_{30}N_2I_4Mo_2O_2\): C, 23.32; H, 2.94; N, 2.72; I, 49.28. Found: C, 23.55; H, 2.81; N, 2.59; I, 49.11. IR (\(CH_2Cl_2\)): \(\nu(NO)\) 1660 cm⁻¹. \(^1H–NMR\) (\(CDCl_3\)): \(\delta 2.05\) (s). \(^{13}C–NMR\) (\(CDCl_3\)): \(\delta 118.6(C–CH_3)\), 13.2(CH₃). Mp (in air) 164°C dec.

For M=W: Anal. Calcd for \(C_{20}H_{30}N_2I_4O_2W_2\): C, 19.91; H, 2.51; N, 2.32; I, 42.09. Found: C, 20.14; H, 2.45; N, 2.25; I,
41.91. IR (CH$_2$Cl$_2$): $\nu$(NO) 1629 cm$^{-1}$. $^1$H-NMR (CDCl$_3$): $\delta$ 2.18(s). $^{13}$C-NMR (CDCl$_3$): $\delta$ 117.5(C—CH$_3$), 12.8(CH$_3$). Mp (in air) 74°C dec.

Reactions of $[(\eta^5$-C$_5$Me$_5$)M(NO)$_2$]$_2$ (M=Mo or W) with Lewis Bases L (L=PPh$_3$ or P(OPh)$_3$). Addition of solid PPh$_3$ (0.26g, 1.0mmol) to a stirred purple solution of $[(\eta^5$-C$_5$Me$_5$)Mo(NO)$_2$]$_2$ (0.52g, 0.50mmol) in CH$_2$Cl$_2$ (30mL) resulted in the solution becoming red in colour. Hexanes (30mL) were added after 30 mins, and the solution was concentrated in vacuo to obtain 0.65g (84% yield) of $(\eta^5$-C$_5$Me$_5$)Mo(NO)(PPh$_3$)I$_2$ as a dark red solid.

The other complexes were prepared similarly in comparable yields (64—84%).

For M=Mo; L=PPh$_3$: Anal. Calcd for C$_{28}$H$_{30}$Ni$_2$MoOP: C, 43.27; H, 3.89; N, 1.80. Found: C, 42.98; H, 3.86; N, 1.67. IR (CH$_2$Cl$_2$): $\nu$(NO) 1658 cm$^{-1}$. $^1$H-NMR (CDCl$_3$): $\delta$ 7.36(m,15H,C$_6$H$_5$), 1.99(s,15H,CH$_3$). Mp 106° dec.

For M=Mo; L=P(OPh)$_3$: Anal. Calcd for C$_{28}$H$_{30}$Ni$_2$MoOP: C, 40.75; H, 3.66; N, 1.70. Found: C, 40.72; H, 3.69; N, 1.68. IR (CH$_2$Cl$_2$): $\nu$(NO) 1662 cm$^{-1}$. $^1$H-NMR (CDCl$_3$): $\delta$ 7.07(m,15H,C$_6$H$_5$), 2.05(s,15H,CH$_3$). $^{13}$C-NMR (CDCl$_3$): (see Table 2.9). Mp 118°C dec.

For M=W; L=PPh$_3$: Anal. Calcd for C$_{28}$H$_{30}$Ni$_2$OPW: C, 38.87; H, 3.50; N, 1.62. Found: C, 38.62; H, 3.44; N, 1.63. IR (CH$_2$Cl$_2$): $\nu$(NO) 1628 cm$^{-1}$. $^1$H-NMR (CDCl$_3$): $\delta$
7.38 (m, 15H, C₆H₅), 2.17 (s, 15H, CH₃). Mp 128°C dec.

For M=W; L=P(OPh)₃: Anal. Calcd for C₂₈H₃₀Ni₂O₄PW: C, 36.82; H, 3.31; N, 1.53. Found: C, 36.99; H, 3.44; N, 1.65.

IR (CH₂Cl₂): ν(NO) 1640 cm⁻¹. ¹H-NMR (CDCl₃): δ 7.21 (m, 15H, C₆H₅), 2.34 (s, 12H, CH₃), 2.18 (s, 3H, CH₃). ¹³C-NMR (CDCl₃): (see Table 2.9). Mp 133°C dec.
CHAPTER THREE

SYNTHESIS AND CHARACTERISATION OF NEW CYCLOPENTADIENYL AND DIENE COMPLEXES DERIVED FROM \( \left( \eta^5 - C_5H_5 \right) M(\text{NO})I_2 \) \( (M=\text{Mo OR W}) \).

(i) Introduction

The formation and chemistry of \( M-C \) bonds is the quintessence of organometallic chemistry. In organometallic nitrosyl chemistry there are only a few examples of complexes which contain organic groups (other than the ubiquitous cyclopentadienyl group), mainly because of a lack of general preparative routes. For example, commonly used nitrosylating agents such as \( \text{NO, NO}^+ \) or \( \text{NOCl} \) commonly displace the organic groups from complexes such as \( \left( C_6H_6 \right) \text{Fe(CO)}_3 \) [68] or \( \left( C_6H_6 \right) \text{W(CO)}_3 \) [64]. However, with the preparation of a series of Group VIA cyclopentadienyl nitrosyl halides, the requisite precursors are available for the formation of a new series of organometallic complexes. This chapter presents the results of two reactions which lead to the formation of \( M-C \) bonds:—

a) the reaction of \( \left( \eta^5 - C_5H_5 \right) W(\text{NO})I_2 \) \( (\text{with 2 or 4}) \)
equivalents of $\text{M(C}_5\text{H}_5\text{)}$ (M=Na or Tl) to give $(\text{C}_5\text{H}_5)_2\text{W(NO)I}$ or $(\text{C}_5\text{H}_5)_3\text{W(NO)}$, and

b) the reduction of $[(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)I}]_2$ and $[(\eta^5-\text{C}_5\text{H}_5)\text{M(NO)I}]_2$ (M=Mo or W) by Na/Hg in the presence of an excess of olefin or diene.

(ii) Results And Discussion

(a) Reaction Of $[(\eta^5-\text{C}_5\text{H}_5)\text{W(NO)I}]_2$ With $\text{M(C}_5\text{H}_5\text{)}$ (M=Na or Tl)

The reaction of $[(\eta^5-\text{C}_5\text{H}_5)\text{W(NO)I}]_2$ in THF with thallium or sodium cyclopentadienide in appropriate stoichiometries affords the novel complexes $(\text{C}_5\text{H}_5)_2\text{W(NO)I}$ and $(\text{C}_5\text{H}_5)_3\text{W(NO)}$.

$$[(\eta^5-\text{C}_5\text{H}_5)\text{W(NO)I}]_2 + 2\text{M(C}_5\text{H}_5\text{)} \rightarrow 2(\text{C}_5\text{H}_5)_2\text{W(NO)I} + 2\text{MI} \quad ... (3.1)$$

$$[(\eta^5-\text{C}_5\text{H}_5)\text{W(NO)I}]_2 + 4\text{M(C}_5\text{H}_5\text{)} \rightarrow 2(\text{C}_5\text{H}_5)_3\text{W(NO)} + 4\text{MI} \quad ... (3.2)$$

M=Tl or Na.

Analogous conversions involving $[(\eta^5-\text{C}_5\text{H}_5)\text{Mo(NO)I}]_2$ can only be effected with Tl($\text{C}_5\text{H}_5$) since Na($\text{C}_5\text{H}_5$) is too reactive and fails to form any cyclopentadienyl derivatives.
IR monitoring of reactions 3.1 and 3.2 indicates that the iodide ligands of the organometallic reactant (which may be present as the solvated monomer (η⁵-C₅H₅)W(NO)I₂(THF)) are replaced sequentially, and indeed the transformations

\[(C₅H₅)₂W(NO)I + M(C₅H₅) \rightarrow (C₅H₅)₃W(NO) + MI\] ...

M=Tl or Na

can be performed independently.

Golden-brown \((C₅H₅)₂W(NO)I\) and brick-red \((C₅H₅)₃W(NO)\) are diamagnetic, relatively air-stable solids which are freely soluble in common organic solvents (except paraffin hydrocarbons) to give air-sensitive solutions. Their low-resolution mass spectra confirm their monomeric natures (parent ions at m/z=471 and 409 respectively) and display fragmentation patterns corresponding to the stepwise loss of ligands from the metal centre. Solutions of both complexes in CH₂Cl₂ exhibit single, strong absorptions in their IR spectra in the range normally associated with linearly bonded, terminal NO ligands, the respective \(\nu\)(NO) values being 1622 and 1588 cm⁻¹ for \((C₅H₅)₂W(NO)I\) and \((C₅H₅)₃W(NO)\).

The variable temperature \(^1H\)-NMR spectra of both complexes in C₆D₅CD₃ resemble those displayed by their molybdenum congeners [59,94,95]. Thus, for \((C₅H₅)₂W(NO)I\), the spectrum consists of a single, sharp resonance (δ5.77 at 27°C) in the temperature range -90 to +30°C. For
(C\textsubscript{5}H\textsubscript{5})\textsubscript{3}W(NO), the single sharp resonance (δ5.64 at 27°C) due to all three rapidly interconverting cyclopentadienyl rings starts to broaden at 0°C (see Figure 3.1). At about -40°C, two new broad peaks begin to grow, indicating the presence of a slowly moving η\textsuperscript{1}-C\textsubscript{5}H\textsubscript{5} ring. Between -40°C and -80°C these two peaks sharpen considerably. The low-field resonance (δ6.92 at -80°C) shows some degree of coupling and may be attributed to the olefinic hydrogens, while the high-field resonance (δ4.32 at -80°C) can be assigned to the remaining hydrogen. (The lower field portion of the expected AA'BB' spectrum is not observable, presumably due to masking by the solvent resonance). The signal due to the other two cyclopentadienyl rings sharpens somewhat between -30°C and -50°C, but below -50°C it collapses, and by -90°C it has separated into two equally intense peaks (δ4.82 and 5.57).

Both molecules (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}W(NO)X (X=I or η\textsuperscript{1}-C\textsubscript{5}H\textsubscript{5}) are thus probably stereochemically nonrigid in solution at room temperature, undergoing rearrangement processes which rapidly interconvert and equilibrate the cyclopentadienyl rings. To maintain an 18-electron valence configuration at the central metal, their instantaneous molecular structures may involve two C\textsubscript{5}H\textsubscript{5} rings bonded in the same, grossly unsymmetrical manner as that found for (C\textsubscript{5}H\textsubscript{5})\textsubscript{3}Mo(NO) [96] and (C\textsubscript{5}H\textsubscript{5})\textsubscript{2}Mo(NO)CH\textsubscript{3} [97] in the solid state (Figure 3.2a). Alternatively, one ring may be bonded in a planar η\textsuperscript{5} fashion and the other in a bent η\textsuperscript{3} fashion in a manner analogous to
Figure 3.1 80MHz $^1$H-NMR Spectra Of $(\text{C}_5\text{H}_5)_2\text{W(NO)}$ In The Temperature Range $-95^\circ\text{C} \rightarrow 27^\circ\text{C}$.

(s=solvent, X=impurity)
that observed in the crystal structure of the valence isoelectronic \((\text{C}_5\text{H}_5)_2\text{W(CO)}_2\) \[98\] and \((\text{C}_9\text{H}_7)_2\text{W(CO)}_2\) \[99\] (Figure 3.2b). Recently, it has been suggested that the solution behaviour of the molybdenum complex \((\text{C}_5\text{H}_5)_2\text{Mo(NO)}_1\) may be explained if the molecule exists transitionally as \((\eta^5-\text{C}_5\text{H}_5)(\eta^1-\text{C}_5\text{H}_5)\text{Mo(NO)}_1\) (possibly solvated) with the \(\eta^1-\) and \(\eta^5-\text{C}_5\text{H}_5\) rings rapidly exchanging their electronic roles \[100\] (Figure 3.2c). A final, albeit less likely, structure would involve two planar \(\eta^5-\text{C}_5\text{H}_5\) rings and a bent \(M-\text{NO}\) linkage (Figure 3.2d). Unfortunately, all attempts to prepare single crystals of either tungsten complex have so far resulted in highly disordered or twinned crystals.

Finally, it may be noted that the analogous allyl complexes \((\eta^5-\text{C}_5\text{H}_5)\text{M(NO)}(\eta^3-\text{C}_3\text{H}_5)\) have been prepared \[61,101,102\]. These complexes contain a very asymmetric allyl ligand, a fact which is a manifestation of the electronic asymmetry at the metal centre. It is quite probable that the factors responsible for the \(\sigma,\pi\) distortion of the \(\eta^3-\text{C}_3\text{H}_5\) group in these compounds are also operative in the \((\text{C}_5\text{H}_5)_2\text{W(NO)}_X\) \((X=I\) or \(\eta^1-\text{C}_5\text{H}_5\)) species described above.
Figure 3.2 Possible Molecular Structures For The Complexes \((C_5H_5)_2M(NO)X\).

\(a\)

(b) **Synthesis And Characterisation Of** \((\eta^5-C_5H_5)Mo(NO)(\eta^4\text{-diene})\)

It was recently reported that the reduction of \(\text{ZrCl}_4(\text{dmpe})_2\) or \([\eta^5-C_5H_5]\text{CoI}_2]_2\) with a sodium amalgam in
the presence of excess diene afforded the complexes \((\eta^4\text{-diene})_2\text{Zr(dmpe)}_2(\text{dmpe})\) \([103]\) and \((\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4\text{-diene})\) \([104]\) respectively. In a similar vein, the reduction of \([(\eta^5\text{-C}_5\text{R}_5)\text{CoI}_2]_2\) \((R=H \text{ or CH}_3)\) with Na/Hg in the presence of ethylene results in the formation of \((\eta^5\text{-C}_5\text{R}_5)\text{Co(C}_2\text{H}_4)_2\) in good yields \([105]\). The molybdenum and tungsten dimers, \([(\eta^5\text{-C}_5\text{H}_5)\text{M(NO)}I_2]_2\) \((M=\text{Mo or W})\) are valence isoelectronic with the cobalt diiodide dimer \([(\eta^5\text{-C}_5\text{H}_5)\text{CoI}_2]_2\), and so the same reactions of the two complexes together with the new chromium complex, \([(\eta^5\text{-C}_5\text{H}_5)\text{Cr(NO)I}_2]_2\), were performed in an attempt to prepare derivatives of the type \((\eta^5\text{-C}_5\text{H}_5)\text{M(NO)}(\eta^4\text{-diene})\) or \((\eta^5\text{-C}_5\text{H}_5)\text{M(NO)(olefin)}_2\). Unfortunately, the only combination of reactants to produce an isolable organometallic nitrosyl complex was the reduction of the molybdenum dimer in the presence of non-cyclic conjugated dienes. (Other combinations which failed to produce isolable complexes were \([(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}I_2]_2\) / diene, \([(\eta^5\text{-C}_5\text{H}_5)\text{Cr(NO)I}_2]_2\) / diene, \([(\eta^5\text{-C}_5\text{H}_5)\text{Mo(NO)}I_2]_2\) / cycloheptatriene, \([(\eta^5\text{-C}_5\text{H}_5)\text{Mo(NO)}I_2]_2\) / 1,5-cyclooctadiene, \([(\eta^5\text{-C}_5\text{H}_5)\text{Mo(NO)}I_2]_2\) / ethylene and \([(\eta^5\text{-C}_5\text{H}_5)\text{Mo(NO)}I_2]_2\) / diphenylacetylene). In all reactions a 10% excess of sodium amalgam was used to carry out the reduction, the ligand being present in 10–20 fold excess, (A saturated solution was used for the ethylene reaction).

The reduction of a THF solution of \([(\eta^5\text{-C}_5\text{H}_5)\text{Mo(NO)}I_2]_2\)
with Na/Hg in the presence of a 10–20 fold excess of the non-cyclic conjugated diene results in the formation in low yield of yellow \((\eta^5-C_5H_5)Mo(NO)(\eta^4-diene)\) (diene=2-methylbutadiene \(_1\), 2,3-dimethylbutadiene \(_2\), or 2,5-dimethyl-2,4-hexadiene \(_3\)).

\[
[(\eta^5-C_5H_5)Mo(NO)I_2]_2 + 4Na/Hg + 2\text{diene} \rightarrow (\eta^5-C_5H_5)Mo(NO)(\eta^4-diene) + 4NaI \ldots (3.4)
\]

The complexes may be isolated from the reaction mixture by filtration through alumina, followed by extraction of the residue with hexanes. Concentration of this solution in vacuo gives analytically pure \(_1\); \(_2\) and \(_3\) could be obtained by cooling the hexane solutions to \(-10^\circ\text{C}\).

The complexes are thermally unstable and are best stored at or below \(0^\circ\text{C}\). They are also slightly air-sensitive, but they may be exposed to air for short periods of time (5–10 mins) without noticeable decomposition. They are soluble in all organic solvents to give yellow air-sensitive solutions. Their infrared spectra in CH\(_2\)Cl\(_2\) solution display strong absorptions in the range 1584–1591 cm\(^{-1}\), the \(\nu(\text{NO})\) values decreasing with increasing methyl substitution in the diene ligand. Although these values are quite low, they may be attributed to a linear nitrosyl ligand, rather than a bent or bridging NO. The first alternative may be ruled out by considering the
effective atomic number formalism, as this would leave the molybdenum atom with a 16-electron configuration, while the second alternative may be eliminated on the basis of the mass spectra of 1 and 3, which only reveal peaks containing one Mo atom.

The usual coordination mode for a conjugated diene is \( s\text{-cis} \) e.g. \((\eta^4-s\text{-cis-diene})\text{Fe(CO)}\), \([106,107]\), \((\eta^4-s\text{-cis-diene})_2\text{Fe(CO)}\) \([108]\), \((\eta^5-C_5\text{H}_5)\text{M(\eta^4-s\text{-cis-diene})}\) (M=Rh or Co) \([104,107]\), \([(\eta^5-C_5\text{H}_5)\text{MoL}_2(\eta^4-s\text{-cis-diene})]^+\) (L\(_2\)=(CO)\(_2\) \([109]\) or dppe \([110]\)) and \((\eta^4-s\text{-cis-diene})\text{Cr(CO)}_4\) \([111]\). However, the \(^1\text{H-NMR}\) and \(^{13}\text{C-NMR}\) spectra of the complexes (see Tables 3.1 and 3.2 and Figure 3.3) reveal that the much rarer \( s\text{-trans} \) coordination mode is favoured by these complexes.

Evidence that supports this conclusion is as follows:—

(a) The \(^1\text{H-NMR}\) spectra of the complexes which contain symmetrically substituted dienes, 2 and 3, reveal that
the two ends of the diene are chemically inequivalent. A similar result is found in the $^{13}$C-NMR spectrum of 2.

(b) The s-vicinal coupling constant $J(H_2,H_3)$ for 3 is in the range normally associated with trans coupling constants (10-14Hz), rather than cis couplings (4-9Hz).

(c) Compared to typical cis-coordinated dienes [106-111] the central protons ($H_{21},H_{31}$) resonate at higher field and the anti protons ($H_{12},H_{41}$) are significantly deshielded; the syn protons ($H_{11},H_{42}$) are relatively unaffected.

This last effect has also been observed for the s-trans isomer of $(\eta^5-C_5H_5)_2Zr(\eta^4$-diene) (s-cis and s-trans) [112]. This complex is one of only three previously reported s-trans coordinated diene complexes, the other two complexes involving the diene ligand bridging two metal atoms ($\text{Mn}_2\text{(CO)}_8(\mu_2-\eta^5$-s-trans-C$_4H_6$) [113] and Os$_3\text{(CO)}_{10}$-($\mu_2-\eta^5$-s-trans-C$_4H_6$) [114]).

The isoprene complex 1 exists as a 3:1 mixture of diastereomers, which presumably differ in the orientation of the methyl substituent. It seems likely, from purely steric arguments, that the major isomer involves the methyl group being directed away from the cyclopentadienyl group. At any rate, there appears to be no evidence for the existence of an s-cis-diene complex.

These results demonstrate that the coordination of a conjugated diene exclusively in the s-trans geometry does
Figure 3.3 400MHz $^1$H-NMR Spectrum Of $(\eta^5-C_5H_5)Mo(NO)(\eta^4-s$-trans-$C_5H_8)$ 1 (vinyl region)
Table 3.1 \(^1\text{H}-\text{NMR Chemical Shift Data (}\delta\text{ In CDCl}_3\text{)}\)

For The New Diene Complexes

<table>
<thead>
<tr>
<th>Assignment</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\eta^5-C_5H_5))</td>
<td>5.53</td>
<td>5.48</td>
<td>5.30</td>
</tr>
<tr>
<td>(H_{11})</td>
<td>3.45</td>
<td>3.61</td>
<td></td>
</tr>
<tr>
<td>(H_{12})</td>
<td>1.94</td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td>(H_{21})</td>
<td></td>
<td></td>
<td>3.34</td>
</tr>
<tr>
<td>(H_{31})</td>
<td>2.37</td>
<td></td>
<td>2.71</td>
</tr>
<tr>
<td>(H_{41})</td>
<td>2.88</td>
<td>2.66</td>
<td></td>
</tr>
<tr>
<td>(H_{42})</td>
<td>3.35</td>
<td>3.59</td>
<td></td>
</tr>
<tr>
<td>(CH_3)</td>
<td>1.53</td>
<td>1.56</td>
<td>2.09</td>
</tr>
</tbody>
</table>

\(a\) major isomer
\(b\) minor isomer

not require two metal centres. The complexes \((\eta^5-C_5H_5)\text{Mo(NO)}(\eta^8-s\text{-trans-diene})\) represent the first examples of monomeric diene coordination where the \(s\text{-trans}\) geometry is significantly favoured over the \(s\text{-cis}\) geometry. In contrast, the analogous zirconium complexes,
Table 3.2 Proton-proton Coupling Constants (in Hz) For
The New Diene Complexes

<table>
<thead>
<tr>
<th>Assignment</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J(H_1,H_2)$</td>
<td>3.1</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>$J(H_2,H_3)$</td>
<td>1.9</td>
<td></td>
<td>12.0</td>
</tr>
<tr>
<td>$J(H_3,H_4)$</td>
<td>14.4</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>$J(H_4,H_5)$</td>
<td>7.0</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>$J(H_5,H_6)$</td>
<td>2.8</td>
<td>3.6</td>
<td>3.7</td>
</tr>
</tbody>
</table>

a major isomer
b minor isomer

$(\eta^5-C_5H_5)_2Zr(\eta^4$-diene), exist in an equilibrium mixture of the two geometries. For most dienes, the $s$-cis isomer predominates but 1,4-substituted dienes do favour the $s$-trans conformation, possibly for steric reasons. In addition, it has been demonstrated that the $s$-trans isomer is the initial kinetic product in all cases, equilibrium only being established above $-10^\circ C$ [112]. It is possible that $(\eta^5-C_5H_5)Mo(\text{NO})(\eta^4$-$s$-trans-diene) is also the kinetic product, but has a much higher activation barrier towards isomerisation.
The reasons for these new complexes' preference for the s-trans geometry are not entirely obvious. There would appear to be no steric restriction to s-cis coordination as the much more sterically crowded complex \[[(\eta^5-C_5H_5)Mo(dppe)(\eta^4-diene)]^+\] adopts the endo-s-cis conformation. It is probable, therefore, that the cause is electronic in nature. However, confirmation of this would require a detailed molecular orbital analysis of the "(\eta^5-C_5H_5)M(NO)" fragment and its bonding capabilities.

(iii) **Experimental Section**

General procedures employed in this research were described in Chapter 2 section (iii).

**Reaction of \([(\eta^5-C_5H_5)W(NO)I_2]_2\) with Tl(C_5H_5).** To a green solution of \([(\eta^5-C_5H_5)W(NO)I_2]_2\) (0.42g, 0.39mmol) [57] in THF (40ml) was added solid Tl(C_5H_5)\(^1\) (0.21g, 0.78mmol). The reaction mixture was stirred at room temperature for 1 hr whereupon it gradually darkened to a deep red colour, and a yellow precipitate of TlI formed. The mixture was then taken to dryness in vacuo, and the residue was extracted with CH_2Cl_2 (3x15mL). The extracts were filtered through a Celite

\(^1\) **Warning:** Thallium and its compounds are extremely toxic and must be handled with care.
column (3x3cm) supported on a medium-porosity frit, and the filtrate was concentrated under reduced pressure to ca. 5mL. The addition of hexanes (60mL) to this solution induced the precipitation of golden-brown, microcrystalline \((\text{C}_5\text{H}_5)_2\text{W(NO)}\)I (0.22g, 60% yield).

Anal. Calcd for \(\text{C}_{10}\text{H}_{10}\text{NIOW}\): C, 25.48; H, 2.12; N, 2.97; I, 27.00. Found: C, 25.13; H, 2.01; N, 3.13; I, 27.00. IR (CH\(_2\)Cl\(_2\)): \(\nu(\text{NO})\) 1622 cm\(^{-1}\). \(^1\)H-NMR (CDCl\(_3\)): \(\delta\) 6.16(s). \(^{13}\)C-NMR (CDCl\(_3\)): \(\delta\) 109.5. Mp (under N\(_2\)): 127\(^\circ\)C dec. Mass spectrum m/z (Rel. Intensity): 471(21) [P]+, 441(100) [P-NO]+, 314(85) [P-NO-I]+.

When Na(\(\text{C}_5\text{H}_5\)) (0.78mmol in 10mL of THF) was employed instead of Tl(\(\text{C}_5\text{H}_5\)) in the above reaction, the final organometallic product was isolated in comparable yield.

Reactions of \([(\eta^5-\text{C}_5\text{H}_5)\text{W(NO)}\text{I}_2]_2\) and \((\text{C}_5\text{H}_5)_2\text{W(NO)}\)I with Tl(\(\text{C}_5\text{H}_5\)). Solid Tl(\(\text{C}_5\text{H}_5\)) (0.27g, 1.0mmol) was added to a brown solution of \((\text{C}_5\text{H}_5)_2\text{W(NO)}\)I (0.47g, 1.0mmol) in THF (30mL) at ambient temperature. The mixture was stirred for 1hr, during which time a yellow solid precipitated. The final reaction mixture was filtered through a Celite column (3x5cm) supported on a frit, and the deep red filtrate was taken to dryness in vacuo. The resulting residue was dissolved in benzene (8mL), and the solution was transferred to a short (3x5cm) column of silica. Initial elution of the column with benzene developed a pale yellow band which was
collected. Removal of solvent from this eluate under reduced pressure afforded a small amount of an air-sensitive, yellow solid whose identity remains to be ascertained. Further elution of the column with benzene–THF (3:1) resulted in the development of a single red band which was collected and taken to dryness in vacuo. Recrystallization of the tarry, red residue from CH₂Cl₂/hexanes produced brick-red microcrystals of (C₅H₅)₃W(NO) (0.10g, 24% yield).

Anal. Calcd for C₁₅H₁₅NOW: C, 44.01; H, 3.67; N, 3.42. Found: C, 43.71; H, 3.55; N, 3.45. IR (CH₂Cl₂): ν(NO) 1588 cm⁻¹. ¹H–NMR (CDCl₃): δ 5.73(s). ¹³C–NMR (CDCl₃): δ 110.6. Mass spectrum m/z (Rel. Intensity): 409(26) [P]+, 379(14) [P-NO]+, 344(44) [P-C₅H₅]+, 314(100) [P-NO-C₅H₅]+.

The complex may be isolated in comparable yields by the reaction of Na(C₅H₅) with (C₅H₅)₂W(NO)I or the addition of either Na(C₅H₅) or Tl(C₅H₅) to a THF solution of [(η⁵−C₅H₅)W(NO)I₂]₂.

Reaction of [(η⁵−C₅H₅)Mo(NO)I₂]₂ with Na/Hg/diene. A red solution of [(η⁵−C₅H₅)Mo(NO)I₂]₂ (2.00g, 2.25mmol) in THF (75mL) containing 2mL of diene was added to a Na amalgam (0.23g, 10mmol Na in 5mL Hg). An immediate reaction occurred, and the solution turned a yellow-brown colour. After being stirred for 15 min to ensure complete reaction, the reaction mixture was filtered through a 3x6cm alumina column. The column was washed with THF until the washings
were colourless. The yellow–orange eluate was the taken to dryness in vacuo. Extraction of the orange residue with hexanes (3×15mL) followed by filtration of the combined extracts through a 2×4cm Celite column produced a pale yellow filtrate. This filtrate was taken to dryness in vacuo to give a yellow solid. In the case of 1 this solid proved to be analytically pure. For the other two complexes analytically pure material could be obtained by recrystallization from hexanes at -10°C. The complexes, \((\eta^5-C_5H_5)Mo(NO)(\eta^4-s\text{-trans}\text{-diene})\) were isolated in 6–10% yield.

For diene=C\(_5\)H\(_8\): Anal. Calcd for C\(_{10}\)H\(_{13}\)NMoO: C, 46.34; H, 5.06; N, 5.41. Found: C, 46.41; H, 5.24; N, 5.16. IR (CH\(_2\)Cl\(_2\)): \(\nu\text{(NO)}\) 1591 cm\(^{-1}\). \(^1\)H–NMR (CDCl\(_3\)): (see Tables 3.1 and 3.2). \(^{13}\)C–NMR (CDCl\(_3\)): \(\delta\) 96.82(C\(_2\)), 95.29(C\(_5\)H\(_5\)), 80.42(C\(_3\)), 55.60(C\(_1\)), 50.84(C\(_4\)), 17.55(CH\(_3\)). Mass spectrum m/z: [P]\(^+\)=261 (based on \(^{98}\)Mo).

For diene=C\(_6\)H\(_8\uranium\): Anal. Calcd for C\(_{11}\)H\(_{15}\)NMoO: C, 48.36; H, 5.53; N, 5.13. Found: C, 48.94; H, 5.84; N, 4.54. IR (CH\(_2\)Cl\(_2\)): \(\nu\text{(NO)}\) 1590 cm\(^{-1}\). \(^1\)H–NMR(CDCl\(_3\)): (see Tables 3.1 and 3.2). \(^{13}\)C–NMR (CDCl\(_3\)): \(\delta\) 111.09, 104.68(C\(_2\) and C\(_3\)), 96.76(C\(_5\)H\(_5\)), 55.05, 54.08(C\(_1\) and C\(_4\)), 23.89, 20.96(CH\(_3\)).

For diene=C\(_6\)H\(_9\uranium\): Anal. Calcd for C\(_{13}\)H\(_{19}\)NMoO: C, 51.83; H, 6.36; N, 4.65. Found: C, 51.95; H, 6.44; N, 4.66. IR (CH\(_2\)Cl\(_2\)): \(\nu\text{(NO)}\) 1584 cm\(^{-1}\). \(^1\)H–NMR (CDCl\(_3\)): (see Tables 3.1 and 3.2). Mass spectrum m/z: [P]\(^+\)=303 (based on \(^{98}\)Mo).
CHAPTER FOUR

SOLVENT CONTROL OF THE REACTIONS OF DICYCLOPENTADIENYLIODO-
NITROSYLMOLYBDENUM WITH SOME SILVER (I) SALTS.

(i) Introduction

Since the first report of its existence in 1968 [59], \( \text{(C}_5\text{H}_5\text{)}_2\text{Mo(NO)I} \) has attracted considerable attention [100, 115]. In particular, the molecular structure of the complex in solution and the mode of attachment of the cyclopentadienyl rings to the metal centre have been the subjects of much speculation (see Chapter 3 (ii)). It is clear from the previous studies that not all of the available electron density on the cyclopentadienyl ligands is being utilised by the metal. Consequently, it should be possible to effect the iodide–abstraction reaction

\[
(\text{C}_5\text{H}_5\text{)}_2\text{Mo(NO)I} - I^- \rightarrow [\eta^5-\text{C}_5\text{H}_5\text{)}_2\text{Mo(NO)}]^+ \quad \text{(4.1)}
\]

a process that would be facilitated by the concommitant linkage of both \( \text{C}_5\text{H}_5 \) rings to the molybdenum atom in an \( \eta^5 \)-fashion in order that the metal centre may retain the
favoured 18-electron configuration.

One of the principal methods for accomplishing conversions of the type (4.1) involves treatment of the organometallic halide with various silver (I) salts. Generally, the cationic complexes thus produced are 18-electron species in which either a donor solvent (e.g., CH₃CN, THF, acetone etc.) or a ligated counterion (e.g., BF₄⁻, PF₆⁻, SbF₆⁻ etc.) has replaced the halide in the metals coordination sphere, the latter situation occurring in weakly coordinating solvents [81,116,117]. This chapter describes investigations into the reactions of (C₅H₅)₂Mo(NO)I with AgY (Y=BF₄ or SbF₆). These investigations reveal a more pronounced influence of the solvent on the outcome of these transformations.

(ii) Results And Discussion

(a) Reaction Of Silver (I) Salts With (C₅H₅)₂Mo(NO)I In Acetonitrile.

The addition of a stoichiometric amount of AgBF₄ or AgSbF₆ to a solution of (C₅H₅)₂Mo(NO)I in CH₃CN results in the rapid precipitation of silver iodide and the formation of the new organometallic cation [(C₅H₅)₂Mo(NO)(CH₃CN)]⁺.
\[(\text{C}_5\text{H}_5)_2\text{Mo(NO)}\text{I} + \text{CH}_3\text{CN} + \text{AgY} \rightarrow [(\text{C}_5\text{H}_5)_2\text{Mo(NO)}(\text{CH}_3\text{CN})]\text{Y} + \text{AgI} \ldots(4.2)\]

The organometallic products from these conversions can be isolated in good yields (71–85%). Their formation indicates that under these conditions the metal centre prefers to attain the 18–electron configuration by coordination of a molecule of the donor solvent rather than by altering the nature of its linkages to the C\(_5\)H\(_5\) rings from that which exists in the iodide reactant.

The black salts \([(\text{C}_5\text{H}_5)_2\text{Mo(NO)}(\text{CH}_3\text{CN})]\text{Y} (\text{Y}=\text{BF}_4 \text{ or SbF}_6)\) are diamagnetic solids that can be handled in air for short periods of time without the occurrence of noticeable decomposition. They are freely soluble in most polar organic solvents to produce red–black, air–sensitive, and moisture–sensitive solutions. Their spectral properties are consistent with the cation possessing a monomeric molecular structure. Thus, their Nujol mull infrared spectra exhibit single strong absorptions in the region normally associated with terminal nitrosyl ligands [68] (e.g., \(\nu(\text{NO})=1665 \text{ cm}^{-1}\) for \(\text{Y}=\text{SbF}_6\)) as well as weaker bands attributable to the coordinated acetonitrile ligand (e.g., \(\nu(\text{CN})=2320 \text{ and } 2298 \text{ cm}^{-1}\) for \(\text{Y}=\text{SbF}_6; \text{ cf. } 2298 \text{ and } 2258 \text{ cm}^{-1}\) for free acetonitrile). The presence of the CH\(_3\)CN ligand is also confirmed by the \(^1\text{H–NMR} \) spectra, those of the SbF\(_6\) salt being presented in Figure 4.1. The \(^1\text{H–NMR} \) spectrum of the
Figure 4.1 80MHz $^1$H–NMR Spectra Of

$[(\text{C}_5\text{H}_5)_2\text{Mo(NO)}(\text{CH}_3\text{CN})]\text{SbF}_6$.

(a) in CD$_3$NO$_2$

(b) in CD$_3$CN
salt in CD$_3$NO$_2$ displays a broad resonance at $\delta$ 6.4 due to the
cyclopentadienyl protons and a sharp singlet at $\delta$ 2.70 due to
the protons of the coordinated CH$_3$CN (cf. $\delta$ 2.00 for free
CH$_3$CN). In CD$_3$CN, the peak due to the C$_5$H$_5$ protons is a
sharp singlet while the resonance due to the coordinated
acetonitrile is superimposed on the residual solvent signal.

A $^{13}$C-NMR spectrum of [(C$_5$H$_5$)$_2$Mo(NO)(CH$_3$CN)]BF$_4$ in CD$_3$CN
only displays a single sharp resonance due to the C$_5$H$_5$
carbons at $\delta$ 14.6 and signals at $\delta$ 108.5 and 1.3 due to
CH$_3$CN.

The broadness of the cyclopentadienyl resonance in the
$^1$H-NMR spectrum of [(C$_5$H$_5$)$_2$Mo(NO)(CH$_3$CN)]SbF$_6$ in CD$_3$NO$_2$
probably reflects the existence of a fluxional process
analogous to that believed to occur for the parent
(C$_5$H$_5$)$_2$Mo(NO)I [100, 115]. However, the fact that this
resonance becomes sharp when the salt is dissolved in CD$_3$CN
indicates some dependence of the rearrangement processes on
the solvent. In addition, the $^1$H- and $^{13}$C-NMR spectra
recorded in CD$_3$CN indicate that in solution there is a rapid
chemical exchange (on the NMR time scale) between free and
coordinated CH$_3$CN.

$$ [(C_5H_5)_2Mo(NO)(CH_3CN)]^+ + CD_3CN \rightleftharpoons [(C_5H_5)_2Mo(NO)(CD_3CN)]^+ + CH_3CN \quad (4.3) $$
(b) In Aqueous Acetone

The initial reaction between AgY (Y=BF₄ or SbF₆) and an equimolar amount of \((C₅H₅)₂Mo(NO)I\) in aqueous acetone proceeds as in acetonitrile, precipitation of AgI and formation of a red–black solution occurring rapidly. However, over a period of several hours, the solution becomes bright orange; salts of the trimetallic cation \([(\eta^5-C₅H₅)₂Mo(NO)(OH)]₃O⁺\) can be isolated in moderate yields from the final reaction mixture. Since the same products result when acetone solutions of the \([(C₅H₅)₂Mo(NO)(CH₃CN)]Y\) compounds are treated with water, it seems likely that the first step in both conversions involves the formation of the aquo cation \([(C₅H₅)₂Mo(NO)(OH)]⁺\) (Scheme 4.1). Once isolated, the hexafluoroantimonate or tetrafluoroborate salts of \([(\eta^5-C₅H₅)₂Mo(NO)(OH)]₃O⁺\) can be converted to the tetraphenylborate salt by simple metathesis with NaB(C₆H₅)₄ in H₂O.

The tris[\(\eta^5\)-cyclopentadienyl]hydroxonitrosylmolybdenio]oxonium salts are yellow (Y=B(C₆H₅)₄) or orange (Y=BF₄ or SbF₆) air–stable solids that crystallize from solution with one or two molecules of the solvent of crystallization. Their trimetallic nature can be determined from elemental analyses and confirmed by careful integration of the \(^1\)H-NMR spectrum of the tetraphenylborate salt. They
are soluble in strongly solvating solvents to afford bright orange air-stable solutions. The spectral properties of the SbF$_6^-$ salt, isolable as the acetone solvate, are typical of this class of compounds. Its Nujol mull infrared spectrum exhibits a strong $\nu$(NO) at 1666 cm$^{-1}$ and a weaker $\nu$(OH) at 3510 cm$^{-1}$. Its $^1$H–NMR spectrum in CD$_3$CN consists of single sharp peaks at $\delta$6.17, 2.08 and 1.67 of relative intensity 5:2:1, which are assignable to the protons of the C$_5$H$_5$, (CH$_3$)$_2$CO and OH groups respectively. The addition of a small quantity of D$_2$O to this CD$_3$CN solution causes the resonance at $\delta$1.67 to shift downfield to $\delta$3.73, thereby indicating rapid H–D chemical exchange, a feature typical of hydroxyl
groups. The \(^1\)H–NMR spectra of the BF\(_4^-\) and B(C\(_6\)H\(_5\))\(_4^-\) salts (both diaquo solvates) in (CD\(_3\))\(_2\)CO display a resonance at \(\delta 2.77\), which integrates for seven protons (3 due to coordinated OH plus 4 due to solvated H\(_2\)O). Upon addition of D\(_2\)O, this signal also shifts to \(\delta 4.5\).

These properties are in accord with the trimetallic cation possessing the basic structure,

![Diagram of the trimetallic cation structure](image)

an arrangement having overall C\(_3\) symmetry. Alternatively, the OH groups may bridge the edges of the Mo\(_3\) triangle as in the structure below.
Both arrangements satisfy the effective atomic number rule, the capping oxygen atom functioning as a formal four-electron donor. This latter feature has ample precedence in the literature e.g. \[\{(\eta^5-C_5H_5)Mo(CO)_2\}_3- (\mu_3-O)\] \[^{118}\], \[\{(\eta^5-C_5H_5)Co\}_3(\mu_3-CO)(\mu_3-O)\] \[^{119}\], \[\{(OC)_3Re\}_3(\mu_2-H)(\mu_3-O)\]^2- \[^{120}\], \[\{(F_3W)_3(\mu_2-O)\}_3(\mu_3-O)\]^5- \[^{121}\] and \[Na\{Mo_3(CO)_6(NO)\}_3(\mu_2-OMe)(\mu_3-O)\] \[^{2}\] \[^{122}\]. The molybdenum complex \[\{(\eta^5-C_5H_5)Mo(CO)_2\}_3(\mu_3-O)\] is of particular relevance since it is valence isoelectronic with the hydroxonitrosyl cation. It can be synthesised by the reactions of \[\{(\eta^5-C_5H_5)Mo(CO)_3\}\] or \[\{(\eta^5-C_5H_5)Mo(CO)_3(C_3H_6O)\}\] with water via the intermediate aquo complex, \[\{(\eta^5-C_5H_5)Mo(CO)_3(OH_2)\}\] \[^{118}\]. By analogy, the formation of \[\{(\eta^5-C_5H_5)Mo(NO)(OH)\}_3\] could involve
the decomposition of the initially formed

\[ [(C_5H_5)_2Mo(NO)(OH_2)]^+ \] cation (cf. Scheme 4.1) by a series of

Lowrey-Bronsted acid-base equilibria (see Scheme 4.2) to
give \[ [(C_5H_5)_2Mo(NO)]^+ \] in a fashion similar to that

\[
\begin{align*}
A & \quad + \quad B \quad \xleftrightarrow{} \quad [(C_5H_5)_2Mo(NO)]_2OH]^+ \quad + \quad H_2O \\
C & \quad + \quad H_2O \quad \xleftrightarrow{} \quad [(C_5H_5)_2Mo(NO)]_2O \quad + \quad H_3O^+ \\
A & \quad + \quad D \quad \xleftrightarrow{} \quad [(C_5H_5)_2Mo(NO)]_3O]^+ \quad + \quad H_2O \\
E & \quad + \quad 3H_2O \quad \rightarrow \quad [(\eta^5-C_5H_5)Mo(NO)(OH)]_3O]^+ \quad + \quad 3C_5H_6
\end{align*}
\]

proposed for the carbonyl derivative. The final step to form
the observed product would then require an irreversible
hydrolysis of one of the cyclopentadienyl ligands. Support
for the involvement of such a mechanism is provided by the
fact that, whereas \([(C_5H_5)_2Mo(NO)(CH_3CN)]BF_4\) readily converts to \[\{(\eta^5-C_5H_5)Mo(NO)(OH)\}_3O\]BF_4 in aqueous acetone, it is stable to hydrolysis in CH_3CN where the bulk solvent competes as a ligand, thereby suppressing the formation of the requisite aquo cation.

(c) In Dichloromethane

Since iodide abstraction from \((C_5H_5)_2Mo(NO)I\) in coordinating solvents apparently leads to \[(C_5H_5)_2Mo(NO)(solvent)]^+ cations rather than \[(\eta^5-C_5H_5)_2Mo(NO)]^+\), reaction 4.1 was next attempted in CH_2Cl_2, a non-coordinating solvent. Under these conditions, the desired conversion again does not occur in the presence of silver (I) salts as the adducts \((C_5H_5)_2Mo(NO)I.AgY\) precipitate instead in high yields. The reaction proceeds similarly for the congeneric tungsten complex prepared in Chapter 3.

\[
(C_5H_5)_2M(NO)I + AgY \rightarrow (C_5H_5)_2M(NO)I.AgY \ldots (4.4)
\]

\[M=Mo \text{ or } W; \: Y=BF_4 \text{ or } SbF_6.\]

These adducts are red-brown, air-stable (but light-sensitive) solids, which only dissolve in solvents with which they react at varying rates. For instance, decomposition of \((C_5H_5)_2Mo(NO)I.AgBF_4\) in CH_3NO_2, as
evidenced by precipitation of AgI, is only significant after more than 10 mins. Nevertheless, its initial solubility in this solvent precludes its being a physical mixture of \([(\eta^5-C_5H_5)_2Mo(NO)]BF_4\) and AgI.

The Nujol mull infrared spectra of the adducts display broad absorptions attributable to terminal nitrosyl ligands in the range 1615–1660 cm\(^{-1}\) (Table 4.1). Furthermore, these spectra show strong absorptions due to the anions, which indicate some degree of coordination of these species. Thus instead of displaying the characteristic single \(\nu(BF)\) absorption at 984 cm\(^{-1}\) assignable to the T\(_2\) stretching mode of a free BF\(_4\) anion, the spectrum of \((C_5H_5)_2Mo(NO)I\).AgBF\(_4\) displays \(\nu(BF)\) bands at 1083, 1053, 1018 and 1003 cm\(^{-1}\). The appearance of these bands may be attributed to a lowering of the local symmetry of the BF\(_4\)\(^{-}\) anions from T\(_d\) to C\(_{2v}\), a change which produces four infrared−active vibrations due to the 2A\(_1\), B\(_1\) and B\(_2\) stretching modes [118]. Similarly, the infrared spectrum of \((C_5H_5)_2Mo(NO)I\).AgSbF\(_6\) exhibits two \(\nu(SbF)\) bands at 659 and 639 cm\(^{-1}\), a feature which indicates a lowering of the local symmetry of the hexafluoroantimonate anion from O\(_h\) to C\(_{4v}\) or C\(_{2v}\) [123].

The mull infrared spectra also provide some insight into the nature of the adducts produced by reaction (4.4). The reactant, \((C_5H_5)_2Mo(NO)I\), molecules contain four potential Lewis base sites with which the soft Lewis acid Ag\(^+\) may interact.
Table 4.1 Nitrosyl Stretching Frequencies Of Some Molybdenum And Tungsten Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>medium</th>
<th>(\nu(\text{NO}), \text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_5\text{H}_5)_2\text{Mo(NO)}\text{I})</td>
<td>CH(_2\text{Cl}_2) Nujol</td>
<td>1642 (\text{a}) 1621</td>
</tr>
<tr>
<td>((\eta^5-\text{C}_5\text{H}_5)\text{Mo(NO)}(\eta^3-\text{C}_3\text{H}_5)\text{I})</td>
<td>KBr</td>
<td>1651 (\text{b})</td>
</tr>
<tr>
<td>((\text{C}_5\text{H}_5)_2\text{Mo(NO)}\text{I}\cdot\text{AgBF}_4)</td>
<td>Nujol</td>
<td>1644</td>
</tr>
<tr>
<td>((\text{C}_5\text{H}_5)_2\text{Mo(NO)}\text{I}\cdot\text{AgSbf}_6)</td>
<td>Nujol</td>
<td>1658</td>
</tr>
<tr>
<td>((\text{C}_5\text{H}_5)_2\text{W(NO)}\text{I})</td>
<td>CH(_2\text{Cl}_2) Nujol</td>
<td>1622 (\text{c}) 1581</td>
</tr>
<tr>
<td>((\eta^5-\text{C}_5\text{H}_5)\text{W(NO)}(\eta^3-\text{C}_3\text{H}_5)\text{I})</td>
<td>CH(_2\text{Cl}_2)</td>
<td>1636 (\text{d})</td>
</tr>
<tr>
<td>((\text{C}_5\text{H}_5)_2\text{W(NO)}\text{I}\cdot\text{AgBF}_4)</td>
<td>Nujol</td>
<td>1618</td>
</tr>
<tr>
<td>((\text{C}_5\text{H}_5)_2\text{W(NO)}\text{I}\cdot\text{AgSbf}_6)</td>
<td>Nujol</td>
<td>1616</td>
</tr>
</tbody>
</table>

\(\text{a}\) Taken from ref. 59.  
\(\text{b}\) Taken from ref. 101.  
\(\text{c}\) See chapter 3.  
\(\text{d}\) Taken from ref. 61.
That sites (a) and (b) are not involved in linkages to Ag⁺ is indicated by the ν(NO) data presented in Table 4.1 which reveal a shift to higher frequency of 25–40 cm⁻¹ upon adduct formation. Typically, the formation of isonitrosyl linkages (site (a)) results in the diminution of ν(NO) by 100–200 cm⁻¹ [32,33,124], and studies with related carbonyl complexes [125] suggest that formation of a M–Ag bond should be reflected by an increase in ν(NO) of at least 100 cm⁻¹. However, the infrared data are not sufficient to permit a differentiation between the two other possible structures.

---

1 A study of the interaction of (η⁵-C₅H₅)M(CO)(NO)(PPh₃) (M=Mo or W) with AlCl₃ and SnCl₄ shows that both the carbonyl and nitrosyl absorptions increase by 120–170 cm⁻¹ upon adduct formation via the transition metal [32,124].
For both arrangements a slight increase in the nitrosyl stretching frequency from that displayed by the parent \((C_5H_5)_2M(NO)I\) complex is to be expected [32, 124].

The \(^1H\)-NMR spectra of the adducts do not provide any further insight as to their structures. For instance, the spectrum of \((C_5H_5)_2Mo(NO)I\cdot AgBF_4\), in CD\(_3\)NO\(_2\) contains multiple signals in the region \(δ 5.86-6.88\), which cannot be readily assigned. Consequently, definitive resolution of this
question will require a single-crystal X-ray diffraction analysis of one of the adducts.

As stated earlier, the molybdenum adducts react with the donor solvents in which they dissolve, the solvents being better Lewis bases than \((\text{C}_5\text{H}_5)_2\text{Mo(NO)I}\) and complexing the silver ion preferentially. Thus, in acetonitrile the adducts convert to the \([(\text{C}_5\text{H}_5)_2\text{Mo(NO)(CH}_3\text{CN})]^{+}\) cation and \(\text{AgI}\), and in aqueous acetone they transform to the metallooxonium salts \([\{(\eta^5-\text{C}_5\text{H}_5)\text{Mo(NO)(OH)}\}_3\text{O}\}]^+\). The interrelationship of these reactions and those described earlier in the Chapter is presented in Scheme 4.3. Clearly,

Scheme 4.3
the solvent exerts a pronounced influence on the outcome of these transformations. In a non-donor solvent, the silver cation acts as a Lewis acid and forms an adduct with the organometallic complex. However, in a donor solvent that is a stronger Lewis base than the complex, the Ag\(^+\) ion reverts to its more common mode of reactivity, namely, halide abstraction.

(d) Reaction Of AlCl\(_3\) With \((C_5H_5)_2Mo(NO)I\) In CH\(_2\)Cl\(_2\).

In view of the solvent control of the reactions of \((C_5H_5)_2Mo(NO)I\) with silver (I) salts (Scheme 4.3), it thus appears that reaction 4.1 cannot be effected when Ag\(^+\) is employed as the iodide acceptor. Mindful of these results, the desired conversion was therefore attempted with AlCl\(_3\) (a harder Lewis Acid than Ag\(^+\)) as the halide abstractor in CH\(_2\)Cl\(_2\), a non-coordinating solvent. When attempted in this manner, the anticipated conversion (equation 4.5) does indeed occur, albeit in low yields.

\[
(C_5H_5)_2Mo(NO)I + AlCl_3 \rightarrow [(\eta^5-C_5H_5)_2Mo(NO)]AlCl_3I
\]

...(4.5)

An excess of aluminum chloride is required to drive the reaction to completion, and the new organometallic salt isolated is a dark red, moisture-sensitive solid, which is
fairly soluble in polar organic solvents. An infrared spectrum of a dichloromethane solution of the complex exhibits a strong absorption at 1690 cm\(^{-1}\) attributable to the terminal nitrosyl ligand. This band is at significantly higher frequency than the corresponding absorptions of the \((\text{C}_5\text{H}_5)\_2\text{Mo(NO)}\) precursor (\(\nu(\text{NO})=1642\ \text{cm}^{-1}\)) and the \([\(\text{C}_5\text{H}_5\)]\_2\text{Mo(NO)(CH}_3\text{CN)}\)]\(^+\) cation (\(\nu(\text{NO})=1673\ \text{cm}^{-1}\) for the \text{SbF}_6^-\) salt in \text{CH}_2\text{Cl}_2). Not surprisingly, the \(^1\text{H}-\text{NMR}\) spectrum of the complex in \((\text{CD}_3)_2\text{CO}\) consists of a single sharp resonance at 66.27 due to the equivalent \(\eta^5-\text{C}_5\text{H}_5\) ligands. The molar conductance of \([\(\eta^5-\text{C}_5\text{H}_5\)]\_2\text{Mo(NO)}\)AlCl\(_3\)I in \text{CH}_3\text{NO}_2 is 57.5 \(\Omega^{-1}\text{cm}^2\text{mol}^{-1}\), a value which is in the range associated with 1:1 electrolytes [126]. Interestingly, the 18-electron \([\(\eta^5-\text{C}_5\text{H}_5\)]\_2\text{Mo(NO)}\)]\(^+\) cation retains its identity in \text{CH}_3\text{CN} (i.e., \(\nu(\text{NO})=1678\ \text{cm}^{-1}\)) and does not convert to the \([\(\text{C}_5\text{H}_5\)]\_2\text{Mo(NO)(CH}_3\text{CN)}\)]\(^+\) species (\(\nu(\text{NO})=1651\ \text{cm}^{-1}\) in \text{CH}_3\text{CN}). Both of these observations are consistent with the complex being an ionic species.
rather than a Lewis acid–base adduct via a Mo—I—>Al linkage. Furthermore, the second observation also indicates that [(η⁵-C₅H₅)₂Mo(NO)]⁺ is not an intermediate either during the formation of the acetonitrile cation by reaction 4.2 or during the exchange process shown in equation 4.3. Plausible mechanisms for these reactions are thus:

\[
(C₅H₅)₂Mo(NO)I + CH₃CN \rightarrow (\eta^5-C₅H₅)(\eta^1-C₅H₅)Mo(NO)(CH₃CN)I \quad (4.6)
\]

\[
(\eta^5-C₅H₅)(\eta^1-C₅H₅)Mo(NO)(CH₃CN)I + Ag⁺ \rightarrow [(C₅H₅)₂Mo(NO)(CH₃CN)]⁺ + AgI \quad (4.7)
\]

and
\[(\text{C}_5\text{H}_5)_2\text{Mo(NO)}(\text{CH}_3\text{CN})]^+ + \text{CD}_3\text{CN} \rightarrow \]
\[\[(\eta^5-\text{C}_5\text{H}_5)(\eta^1-\text{C}_5\text{H}_5)\text{Mo(NO)}(\text{CH}_3\text{CN})(\text{CD}_3\text{CN})]^+ \ldots (4.8)\]

\[\[(\eta^5-\text{C}_5\text{H}_5)(\eta^1-\text{C}_5\text{H}_5)\text{Mo(NO)}(\text{CH}_3\text{CN})(\text{CD}_3\text{CN})]^+ \rightarrow \]
\[\[(\text{C}_5\text{H}_5)_2\text{Mo(NO)}(\text{CD}_3\text{CN})]^+ + \text{CH}_3\text{CN} \ldots (4.9)\]

These sequences of steps are in accord with McCleverty's proposal concerning the transitional structure of \((\text{C}_5\text{H}_5)_2\text{Mo(NO)}\text{I}\) in solution \[100\].

(iii) **Experimental Section**

General procedures employed in this research were described in Chapter 2 section (iii).

**Reaction of \((\text{C}_5\text{H}_5)_2\text{Mo(NO)}\text{I}\) with \(\text{AgY (Y=BF}_3\) or \(\text{SbF}_6\) in \(\text{CH}_3\text{CN}.\)** To a rapidly stirred green—brown solution of \((\text{C}_5\text{H}_5)_2\text{Mo(NO)}\text{I} [59] \(0.77\text{g}, 2.0\text{mmol})\) in \(\text{CH}_3\text{CN} \(40\text{mL})\) was added solid \(\text{AgBF}_3\) \(0.39\text{g}, 2.0\text{mmol})\). A white precipitate formed immediately, and the supernatant became red—black. After being stirred for 1 hr to ensure completion of the reaction, the reaction mixture was filtered through a column of Celite \(3\times3\text{cm})\) supported on a medium porosity frit. The filtrate was concentrated under reduced pressure to a volume of \(10\text{mL.}\) Addition of diethyl ether \((40\text{mL})\) induced the crystallization of black \([(\text{C}_5\text{H}_5)_2\text{Mo(NO)}(\text{CH}_3\text{CN})]\text{BF}_4\): \(0.54\text{g},\)
71% yield).

Anal. Calcd for $C_{12}H_{13}N_2BF_4MoO$: C, 37.53; H, 3.41; N, 7.30. Found: C, 37.58; H, 3.43; N, 7.26. IR (Nujol mull): $\nu$(CN) 2319, 2297 cm$^{-1}$; $\nu$(NO) 1666 (br) cm$^{-1}$. IR (CH$_3$CN): $\nu$(NO) 1651 cm$^{-1}$. $^1$H-NMR (CD$_3$CN): $\delta$ 6.36 (s). $^1$H-NMR (CD$_3$NO$_2$): $\delta$ 6.34 (br, 10H, $C_5H_5$), 2.70 (s, 3H, CH$_3$). $^{13}$C-NMR (CD$_3$CN): $\delta$ 114.6. Mp 125°C dec.

Analytically pure [(C$_5$H$_5$)$_2$Mo(NO)(CH$_3$CN)]SbF$_6$ can be obtained similarly in 85% yield from (C$_5$H$_5$)$_2$Mo(NO)I and AgSbF$_6$.

Anal. Calcd for $C_{12}H_{13}N_2F_6MoSbO$: C, 27.04; H, 2.46; N, 5.26. Found: C, 27.14; H, 2.40; N, 5.20. IR (Nujol mull): $\nu$(CN) 2320, 2298 cm$^{-1}$; $\nu$(NO) 1665 cm$^{-1}$; $\nu$(SbF) 650 (br) cm$^{-1}$. IR(CH$_3$CN): $\nu$(NO) 1651 cm$^{-1}$; $\nu$(SbF) 663 cm$^{-1}$. $^1$H-NMR (CD$_3$CN): $\delta$ 6.37 (s). $^1$H-NMR (CD$_3$NO$_2$): $\delta$ 6.40 (br, 10H, $C_5H_5$), 2.70 (s, 3H, CH$_3$). Mp 117°C dec.

Reaction of (C$_5$H$_5$)$_2$Mo(NO)I with AgY (Y=BF$_4$ or SbF$_6$) in aqueous acetone. Solid AgBF$_4$ (0.59g, 3.0mmol) was added to a stirred dark green solution of (C$_5$H$_5$)$_2$Mo(NO)I (1.15g, 3.0mmol) in acetone (125mL) containing H$_2$O (2mL). Immediately the solution became red–black, and white AgI precipitated. The reaction mixture was stirred at ambient temperature for 3 hr, whereupon the solution gradually became bright orange. The final mixture was filtered through Celite (vide supra), and the volume of the filtrate was
reduced to ca. 25mL in vacuo. Diethyl ether (40mL) was then slowly added to induce the crystallization of 0.37g (48% yield) of orange, microcrystalline $\text{(\(\eta^5\)-C$_5$H$_5$)MO(NO)(OH)$_3$O)}$BF$_4$·2H$_2$O.

Anal. Calcd for C$_{15}$H$_{22}$N$_3$Mo$_3$BF$_4$O$_9$: C, 23.61; H, 2.91; N, 5.51; Mo, 37.72. Found: C, 23.60; H, 2.45; N, 5.06; Mo, 37.83. IR(Nujol mull): $\nu$(OH) 3460(br) cm$^{-1}$; $\nu$(NO) 1662 cm$^{-1}$; $\nu$(BF) 1082, 1049, 1020, 999 cm$^{-1}$. $^1$H–NMR ((CD$_3$)$_2$CO): $\delta$ 6.27(s, 15H, C$_5$H$_5$), 2.77(s, 7H, OH). $^{13}$C–NMR (D$_2$O): $\delta$ 112.3. Mp 192°C dec.

The reaction of (C$_5$H$_5$)$_2$Mo(NO)I with AgSbF$_6$ was effected similarly except that 15mL of H$_2$O was employed. The final orange filtrate was taken to dryness in vacuo, and the resulting residue recrystallized from acetone/diethyl ether to obtain $\text{(\(\eta^5\)-C$_5$H$_5$)MO(NO)(OH)$_3$O)}$SbF$_6$·(CH$_3$)$_2$CO as an orange solid in 18% yield.

Anal. Calcd for C$_{18}$H$_{24}$N$_3$F$_6$Mo$_3$Sb: C, 23.15; H, 2.59; N, 4.50. Found: C, 23.29; H, 2.64; N, 4.26. IR (Nujol mull): $\nu$(OH) 3510 cm$^{-1}$; $\nu$(NO) 1666(br) cm$^{-1}$; $\nu$(SbF) 655 cm$^{-1}$. IR (CH$_3$CN): $\nu$(NO) 1674 cm$^{-1}$. $^1$H–NMR (CD$_3$CN): $\delta$ 6.17(s, 15H, C$_5$H$_5$), 2.08(s, 6H, CH$_3$), 1.67(s, 3H, OH). Mp 203°C dec.

Preparation of $\text{(\(\eta^5\)-C$_5$H$_5$)MO(NO)(OH)$_3$O}$$B$C$_6$H$_5$)$_4$·2H$_2$O. A saturated solution of NaB(C$_6$H$_5$)$_4$ (0.2g) in H$_2$O (10mL) was added dropwise to an orange solution of
\[
[(\eta^5-C_5H_5)Mo(NO)(OH)]_3O\text{BF}_4.2H_2O \quad (0.15g, \ 0.20mmol) \text{ in } H_2O \ \text{(100mL). A yellow precipitate formed immediately, and the mixture was stirred for 0.5 hr to ensure complete precipitation. The solid was then collected by filtration and recrystallized from acetone/water to isolate 0.1g (50% yield) of } [(\eta^5-C_5H_5)Mo(NO)(OH)]_3O\text{B}(C_6H_5)_3.2H_2O \text{ as a yellow solid.}
\]

Anal. Calcd for C_{39}H_{52}N_{3}Mo_{3}B_{0}O_{3}: C,47.06; H,4.25; N,4.22; Mo, 28.92. Found: C,47.00; H,4.00; N,4.45; Mo, 29.50. IR (Nujol mull): \nu(NO) 1661(br) cm\(^{-1}\). IR (CH\(_3\)CN): \nu(NO) 1675 cm\(^{-1}\). \(1^H\)-NMR ((CD\(_3\))\(_2\)CO): \delta 7.00(m,20H,C\(_6\)H\(_5\)), 6.20(s,15H,C\(_5\)H\(_5\)), 2.77(s,7H,OH). Mp 176°C dec.

Reaction of \([(C_5H_5)_2Mo(NO)(CH_3CN)]\text{BF}_4 \text{ with } H_2O. \text{ To a stirred dark red solution of } [(C_5H_5)_2Mo(NO)(CH_3CN)]\text{BF}_4 \ (0.34g, \ 0.90mmol) \text{ in acetone (50mL) was added } H_2O \ (1mL). \text{ The mixture gradually became orange over a period of 2 hr. It was then concentrated under reduced pressure to a volume of 15mL, and diethyl ether (30mL) was added dropwise to induce the crystallization of 0.08g (35% yield) of orange } [(\eta^5-C_5H_5)Mo(NO)(OH)]_3O\text{BF}_4.2H_2O, \text{ which was identified by its characteristic physical properties (vide supra).}

Reaction of \((C_5H_5)_2M(NO)I \quad (M=Mo \text{ or } W) \text{ with } AgY \ (Y=BF_4 \text{ or } SbF_6) \text{ in } CH_2Cl_2. \text{ These experiments were all performed in the same manner. The procedure, using the reaction of}
with AgBF₄ as a typical example, was as follows.

Solid AgBF₄ (0.59g, 3.0mmol) was added to a dark green solution of (C₅H₅)₂Mo(NO)I (1.15g, 3.0mmol) in CH₂Cl₂ (100mL), and the reaction mixture was stirred for 16 hr. During this time the solution became red, and a dark red solid slowly precipitated. This solid was collected by filtration, washed thoroughly with CH₂Cl₂ (3x40mL) and dried in vacuo to obtain 1.30g (75% yield) of analytically pure (C₅H₅)₂Mo(NO)I·AgBF₄.

The other red-brown adducts were isolated analogously in yields of 60% (M=Mo, Y=SbF₆), 74% (M=W, Y=BF₄) and 95% (M=W, Y=SbF₆).

For M=Mo, Y=BF₄: Anal. Calcd for C₁₀H₁₀NAgIMoBF₄O:
C, 20.79; H, 1.74; N, 2.42; Ag, 18.68; I, 21.96; Mo, 16.61.
Found: C, 20.61; H, 1.98; N, 1.99; Ag, 18.50; I, 21.90; Mo, 16.28. IR (Nujol mull): ν(NO) 1644(br); ν(BF) 1083(sh), 1053(m), 1018(sh), 1003(sh) cm⁻¹. ¹H-NMR (CD₃NO₂): δ 5.86-6.88 (multiple signals). Mp 75°C dec.

For M=Mo, Y=SbF₆: Anal. Calcd for C₁₀H₁₀NIAgF₆MoOSb:
C, 16.53; H, 1.39; N, 1.93; I, 17.46. Found: C, 16.76; H, 1.60; N, 1.66; I, 17.29. IR (Nujol mull): ν(NO) 1658(br); ν(SbF) 659(s), 639(sh) cm⁻¹. ¹H-NMR (CD₃NO₂): δ 5.60-7.00 (multiple signals). Mp 58°C dec.

For M=W, Y=BF₄: Anal. Calcd for C₁₀H₁₀NIAgBF₄OW:
C, 18.02; H, 1.50; N, 2.10; I, 19.07. Found: C, 17.35; H, 1.70;
N, 1.99; I, 18.88. IR (Nujol mull): \( \nu(NO) \) 1618, \( \nu(BF) \) 1091(m), 1059(m), 1024(sh), 1009(sh) cm\(^{-1}\). Mp 61°C dec.

For \( M=W, \ Y=SbF_6 \): Anal. Calcd for \( C_{10}H_{10}NIAgF_6OSbW \): C, 14.72; H, 1.23; N, 1.72; I, 15.58. Found: C, 15.20; H, 1.51; N, 1.48; I, 15.26. IR (Nujol mull): \( \nu(NO) \) 1616 cm\(^{-1}\); \( \nu(SbF) \) 658(s) cm\(^{-1}\). Mp 58°C dec.

Reactions of \( \text{(C}_5\text{H}_5\text{)}_2\text{Mo(NO)}\text{IAgBF}_4 \) with donor solvents.

(a) with acetonitrile. \( \text{(C}_5\text{H}_5\text{)}_2\text{Mo(NO)}\text{IAgBF}_4 \) (100mg) was added to acetonitrile (5mL) with stirring to obtain a dark red-brown solution and a small amount of an off-white solid. An infrared spectrum of the supernatant solution displayed a \( \nu(NO) \) absorption at 1651 cm\(^{-1}\) characteristic of \( [(\text{C}_5\text{H}_5\text{)}_2\text{Mo(NO)}(\text{CH}_3\text{CN})]\text{BF}_4 \).

Repetition of the experiment with CD\(_3\)CN as solvent afforded a red-brown supernatant solution whose \(^1\text{H–NMR}\) spectrum exhibited a single strong resonance at \( \delta 6.36 \) in addition to several weak signals in the region \( \delta 6.0-6.6 \).

(b) with acetone/water Attempted dissolution of \( \text{(C}_5\text{H}_5\text{)}_2\text{Mo(NO)}\text{IAgBF}_4 \) (50mg) in 2:1 (CD\(_3\))\(_2\)CO/D\(_2\)O (2mL) produced an orange-brown solution and an off-white solid. A \(^1\text{H–NMR}\) spectrum of the orange-brown solution contained a strong signal at \( \delta 6.36 \) and weaker, sharp signals at \( \delta 6.48, 6.20 \) and 6.10. After 2 days, the resonance at 1446.36 was unaltered, but the less intense peaks had diminished in intensity by ca. 50%.
A $^1$H–NMR spectrum of an authentic sample of $\{[(\eta^5-C_5H_5)Mo(NO)(OH)]_3O\}BF_4 \cdot 2H_2O$ in the same solvent mixture displayed a sharp signal at 66.36.

**Reaction of (C$_5$H$_5$)$_2$Mo(NO)$_2$ with AlCl$_3$.** To a stirred dark green solution of (C$_5$H$_5$)$_2$Mo(NO)$_2$ (0.77g, 2.0mmol) in CH$_2$Cl$_2$ (40mL) was added an excess of solid AlCl$_3$ (0.54g, 4.0mmol). The solution became dark red immediately, and a brown precipitate formed. The reaction mixture was stirred at ambient temperature for 10 mins and was then filtered through a short Celite column (3x2cm) supported on a medium porosity frit. The filtrate was concentrated under reduced pressure to ca. 10mL and was filtered into a flask containing diethyl ether (100mL) to induce the precipitation of 0.13g (13% yield) of dark red $\left[(\eta^5-C_5H_5)Mo(NO)\right]AlCl_3I$.

Anal. Calcd for C$_{10}$H$_{10}$NCl$_3$IAlMoO: C,23.26; H,1.95; N,2.71; Cl, 20.60; I, 24.58. Found: C,23.34; H,2.12; N,2.66; Cl, 20.50; I, 24.33. IR (CH$_2$Cl$_2$): $\nu$(NO) 1690 cm$^{-1}$. IR (CH$_3$CN): $\nu$(NO) 1678 cm$^{-1}$. $^1$H–NMR ((CD$_3$)$_2$CO): $\delta$ 6.27(s). Mp 95°C dec. Am (CH$_3$NO$_2$): 57.5 $\Omega^{-1}$cm$^2$mol$^{-1}$. 
CHAPTER FIVE

ELECTROPHILE–INDUCED REDUCTION OF COORDINATED NITROGEN MONOXIDE. SEQUENTIAL CONVERSION OF A $\mu_3$–NO GROUP TO $\mu_3$–NOH AND $\mu_3$–NH LIGANDS

(i) Introduction

Much attention has been focussed on the activation of carbon monoxide, [127,128] in an attempt to understand better the heterogeneous reduction of CO [129,130] and to develop suitable homogeneous analogues [131]. The activation of nitrogen monoxide, however, has received considerably less attention [19,128], although, as discussed in Chapter 1, it has recently been recognised as a major source of acid rain and photochemical smog.

Initial studies with regard to possible activation of coordinated NO were focussed primarily on the behaviour of nucleophiles or electrophiles towards linear or bent M–NO linkages, respectively [19,31,35,132]. e.g.
More recent research has begun to examine the analogous reactivity patterns of transition-metal complexes containing doubly-bridging NO groups \[43,133,134\] e.g.

\[
[(\eta^5-C_5H_5)Cr(NO)_2]_2 + Me^- \rightarrow (\eta^5-C_5H_5)_2Cr_2(NO)_3(N=CH_2) \]

\[\text{...(5.5)}\]

\[
[Ru_3(CO)_{10}(NO)]^- + Me^+ \rightarrow Ru_3(CO)_5(NOCH_3) \]

\[\text{...(5.6)}\]

However, maximum reduction of the NO bond order (and hence optimum activation of the bound NO) should occur in \(M_3(\mu_3-\text{NO})\) systems. Accordingly, this Chapter describes the reactions of one such system, \((\eta^5-C_5H_5Me)_3Mn_3(\text{NO})_4\), with strong protonic acids.
(ii) Results And Discussion

The reaction of \((\eta^5-C_5H_4Me)_3Mn_3(NO)\) with the strong protonic acids HBF₄·OMe₂ or HPF₆(aq) results in the unprecedented sequential transformations

\[
M_3(\mu_3-\text{NO}) \xrightleftharpoons{H^+}{E+3N} [M_3(\mu_3-\text{NOH})]^+ \xrightarrow{2H^+}{2e^-} [M_3(\mu_3-\text{NH})]^+
\]

\[3H^+, 2e^-\]

where \(M = (\eta^5-C_5H_4Me)Mn(NO)\)

which involve an overall, formal reduction of the \(\mu_3-\text{NO}\) ligand.

Addition of one equivalent of acid [HBF₄·OMe₂ or HPF₆(aq)] to a CH₂Cl₂ solution of \((\eta^5-C_5H_4Me)_3Mn_3(NO)_4\) (1) results in the rapid formation of \([((\eta^5-C_5H_4Me)_3Mn_3(NO)_3(NOH))]_Y\) \((Y=BF_4, 2a; Y=PF_6, 2b)\) which may be isolated in 43–66% yield as black, relatively air-stable, microcrystalline solids. The reaction is reversible as evidenced by the fact that the reverse transformations 2→1
may be cleanly effected with a stoichiometric amount of $\text{Et}_3\text{N}$. Further treatment of 2a or 2b with two equivalents of acid affords $[(\eta^5-\text{C}_{5}\text{H}_5\text{Me})_3\text{Mn}_3(\text{NO})_3(\text{NH})]X$ ($X=\text{BF}_4$, 3a; $X=\text{PF}_6$, 3b), which are more conveniently obtained from the reaction of 1 with an excess of the appropriate acid in CH$_2$Cl$_2$. 3a or 3b may also be isolated from the reaction mixture as black microcrystalline solids in 13–14% yield.

Single-crystal X-ray crystallographic analyses of 2a$^1$ and 3b$^2$ confirmed the identities of the hydroxyimido- and imido-containing cations, respectively, and revealed their molecular structures (Figures 5.1–5.3)$^3$. The complexes, 2a and 3b represent the first structurally characterised examples of $\text{M}_3(\mu_3-\text{NOH})$ and $\text{M}_3(\mu_3-\text{NH})$ linkages [135], although recently the analogous complexes $\text{Ru}_3(\text{CO})_{10}(\mu_3-\text{NOH})$ [134] and $\text{Fe}_3(\text{CO})_{10}(\mu_3-\text{NH})$ [136] have been spectroscopically characterised. In both complexes, the central $(\eta^5-\text{C}_{5}\text{H}_5\text{Me})_3\text{Mn}_3(\text{NO})_3$ core is essentially the same as that found for $(\eta^5-\text{C}_{5}\text{H}_5)_3\text{Mn}_3(\text{NO})_4$ (1') [37], the cyclopentadienyl

$^1$Single crystals obtained by slow cooling of a 1:1 CH$_2$Cl$_2$–diethyl ether solution.

$^2$Single crystals obtained by slow cooling of a saturated CH$_2$Cl$_2$ solution.

$^3$The crystal structure determination was kindly performed by Dr. S. J. Rettig of this department. See Appendix 1 for X-ray diffraction data, and tables of fractional coordinates, bond lengths, bond angles and isotropic and anisotropic thermal parameters for 2a and 3b.
Figure 5.1 Stereoscopic Views Of 2a And 3b

(a)

(b)
Figure 5.2 Molecular Structure Of 2a.
Figure 5.3 Molecular Structure of 3b
analogue of \( \text{J}_1 \). The most chemically interesting features of both structures involve the unique apical ligands. Both ligands are attached closer to the equilateral Mn\(_3\) triangle than the triply-bridging nitrosyl ligand in \( \text{J}'_1 \) (i.e. Mn–N(4)(av)=1.872(3)\( \text{Å} \) for 2a or 1.873(3) for 3b vs. 1.929(11)\( \text{Å} \) for \( \text{J}'_1 \)). Also, the N–O bond length of the NOH ligand in 2a (i.e. 1.393(4)\( \text{Å} \)) is considerably longer than that of the \( \mu_3\)-NO ligand in \( \text{J}'_1 \) (i.e. 1.247(5)\( \text{Å} \)). These two structural features are indicative of the relatively greater electron-accepting abilities of the \( \mu_3\)-NOH and \( \mu_3\)-NH groups. Both the hydroxyimido and the imido ligands in 2a and 3b, respectively, are also linked by hydrogen bonds to the counter anions. This hydrogen bonding in 2a (H–F=1.91(6)\( \text{Å} \)) produces a pronounced distortion of the BF\(_4^–\) anion to local \( C_{3v} \) symmetry, but in 3b (H–F=2.24(4)\( \text{Å} \)) it is not sufficiently strong to result in a unique P–F bond length in the PF\(_6^–\) anion. This feature is in agreement with both the known hydrogen-bonding capabilities of NH vs. OH [137] and the documented donor capacity of the anion (BF\(_4^–\)>PF\(_6^–\)) [138].

The spectroscopic properties (see Table 5.1) of the trimetallic cationic complexes can be readily understood in terms of their solid-state molecular structures, thus confirming that the basic structural units also persist in solution. The IR absorptions attributable to the \( \mu_2\)-NO groups in both 2 and 3 occur some 40 cm\(^{-1}\) higher in energy than in \( \text{J}_1 \), thereby indicating diminished electron density on
Table 5.1 Spectroscopic Properties Of The New Hydroxyimido And Imido Complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>IR(CH₂Cl₂) in cm⁻¹</th>
<th>'H-NMR δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>ν(OH) 3270</td>
<td>5.34(s,12H,C₅H₆Me) a</td>
</tr>
<tr>
<td></td>
<td>ν(NO) 1582,1523</td>
<td>1.86(s,9H,C₅H₆Me)</td>
</tr>
<tr>
<td></td>
<td>ν(NOH) 1030</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ν(BF) 1096(E), 968(A₁)</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>ν(OH) 3408</td>
<td>5.32(s,12H,C₅H₆Me) a</td>
</tr>
<tr>
<td></td>
<td>ν(NO) 1581,1524</td>
<td>1.86(s,9H,C₅H₆Me)</td>
</tr>
<tr>
<td></td>
<td>ν(NOH) 1035</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>ν(NH) 3275</td>
<td>5.26(s,6H,C₅H₆Me) b</td>
</tr>
<tr>
<td></td>
<td>ν(NO) 1579,1521</td>
<td>5.18(s,6H,C₅H₆Me)</td>
</tr>
<tr>
<td></td>
<td>ν(BF) 1068</td>
<td>1.80(s,9H,C₅H₆Me)</td>
</tr>
<tr>
<td>3b</td>
<td>ν(NH) 3326</td>
<td>21.95(t,1H,J(¹⁴N⁻¹H)=61Hz,NH)</td>
</tr>
<tr>
<td></td>
<td>ν(NO) 1581,1525</td>
<td>5.28(s,6H,C₅H₆Me) b</td>
</tr>
<tr>
<td></td>
<td>ν(PF) 847</td>
<td>5.17(s,6H,C₅H₆Me)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.82(s,9H,C₅H₆Me)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.53(t,1H,J(¹⁴N⁻¹H)=60.5Hz,NH)</td>
</tr>
</tbody>
</table>

a in (CD₃)₂CO  
b in CD₂Cl₂

the Mn₃(μ₂–NO)₃ framework in the former species. The distortion of the BF₄⁻ anion in 2a is also detectable by IR spectroscopy both in the solid state (Nujol mull) and in weakly–coordinating solvents such as CH₂Cl₂. Thus, for example, instead of a single strong absorption at 984 cm⁻¹
due to the T_2 stretching mode of the BF_4^- anion, the complex exhibits two absorptions at 1098 and 974 cm^{-1} due to the E and A_1 modes of a C_{3v} symmetry anion. Analogous effects of hydrogen bonding are not observable in the IR spectra of the other complexes. The spectra of both 2a and 2b also exhibit medium intensity absorptions at 1030 and 1035 cm^{-1} respectively, which may be assigned to the ν(NO) stretch of the hydroxyimido ligand (cf. Ru_3(CO)_10(NOH), ν(NO)=1120 cm^{-1} [134]). All four complexes give rise to fairly weak absorptions in the range 3200–3500 cm^{-1} due to the OH and NH groups. Again, the difference in the energy of these absorptions, due to the anions, may be explained by the expected hydrogen–bond strengths (BF_4^->PF_6 [138])

The ^1H-NMR spectra of 3a (Figure 5.4) and 3b in CD_2Cl_2 verify that the imido hydrogen remains attached to the μ_3-N atom (i.e. for 3a, δ 21.95 (t, 1H, J(1^4N-^1H)=61 Hz); for 3b, δ 21.53 (t, 1H, J(1^4N-^1H)=60.5 Hz)). In addition the spectra reveal the expected resonances due to the coordinated methylcyclopentadienyl ligand. Similar spectra of 2a and 2b in (CD_3)_2CO also display signals due to the methylcyclopentadienyl ligand, but, do not, however, reveal signals due to the μ_3-NOH in the range δ=+30->-35 ppm, a

^1X-H bonds which are involved in hydrogen bonding absorb at lower frequencies, as the hydrogen bonding tends to reduce the X-H bond strength [139].
Figure 5.4 80MHz $^1$H-NMR Spectrum Of 3a In CD$_2$Cl$_2$. 

61Hz

25 20 15 10 5 0 ppm δ
probable consequence of the hydrogen bonding.

The proton induced transformations $1\rightarrow 2\rightarrow 3$ represent two steps of a possible process for the reduction of NO to NH$_3$.

$$\begin{align*}
M_3(\mu_3\text{-NO}) & \xrightarrow{H^+} \underset{Et_3N}{\text{[M}_3(\mu_3\text{-NOH})]^+} \xrightarrow{2H^+/2e^-} \text{[M}_3(\mu_3\text{-NH})]^+ \\
3H^+, 2e^- & \end{align*}$$

where $M = (\eta^5-C_5H_4Me)Mn(NO)$

The two electrons required in the second step are most likely provided intermolecularly by the manganese atoms of the cluster. In this sense, the process is analogous to that described by Shriver and co-workers for the conversion of coordinated CO to CH$_4$ by strong acids [140]. However, there are two major differences in the trimetallic manganese nitrosyl system:—

(a) activation of the N–O bond does not require binding of the oxygen atom to form an $\eta^2$–NO linkage as in the Fe$_4$(CO) case (see Scheme 5.1) and
Scheme 5.1

\[
\begin{align*}
CO + CH_4 + Fe^{2+} & \rightarrow \text{Scheme 5.1 intermediates} \\
& \rightarrow CO + CH_4 + Fe^{2+}
\end{align*}
\]
(b) the final imido complex is stable to excess acid. Recently, it was reported that the ruthenium nitrosyl complex \([\text{Ru(trpy)(bpy)(NO)}]^{3+}\) could be reversibly electrochemically reduced in acid media to the corresponding ammonia complex \([141]\).

\[
\text{[Ru(trpy)(bpy)(NO)]}^{3+} + 6e^- + 5H^+ \rightarrow \text{[Ru(trpy)(bpy)(NH3)]}^{2+} + H_2O \ldots(5.7)
\]

However, in this system, the original nitrosyl reactant is stable to acid alone, the reaction proceeding via 2 one-electron reductions to give \([\text{Ru(trpy)(bpy)(NO)}]^+\). This reduced species, which presumably contains a bent Ru–NO linkage, is then rapidly protonated (Scheme 5.2).

The initial protonation in the ruthenium system is therefore at the nitrogen atom of a bent nitrosyl ligand, whereas reaction of the trimetallic manganese complex with acid is at oxygen, resulting in the first characterised example of the alternate NOH connectivity. Further protonation of \([\text{(trpy)(bpy)Ru(HNO)}]^2+\) results in the cleavage of the N=O bond, probably via the hydroxyamido complex \([\text{(trpy)(bpy)Ru(NHOH)}]^3+\) followed by elimination of \(H_2O\). (Analogous complexes of both ligands have previously been reported \([31,35,132]\)). Interestingly, further protonation of 2 should also occur at the lone pair of the oxygen atom to give \([\eta^5–C_5H_4Me)_3Mn_3(NO)_3(NOH_2)]^{2+}\), which
probably would rapidly lose water to give the nitride [(\(\eta^5\)-C\(_5\)H\(_4\)Me),Mn\(_3\)(NO)\(_3\)N]\(^{2+}\). Reduction is presumed to occur at this point to give the neutral nitride, which is then protonated to give the ultimate imido product, 3 (Scheme
Scheme 5.3

\[
\begin{align*}
\left[ \text{Mn}_3 \text{N-O}^- \text{H} \right]^+ & \quad + \text{H}^+ \\
& \rightarrow \\
\left[ \text{Mn}_3 \text{N-O}^+ \text{H} \right]^{2+} \\
& \quad + \text{2e}^- \quad - \text{H}_2 \text{O} \\
\left[ \text{Mn}_3 \text{NH} \right]^+ & \quad + \text{H}^+ \\
& \rightarrow \\
\text{Mn}_3 \text{N} \\
\end{align*}
\]

(iii) Experimental Section

General procedures employed in this research were described in Chapter 2 section (iii). \([(\eta^5-\text{C}_5\text{H}_5\text{Me})\text{Mn(CO)(NO)}]_2\) and \((\eta^5-\text{C}_5\text{H}_5\text{Me})_3\text{Mn}_3(\text{NO})_4\) were prepared by a modification of the literature procedures [56a,74].
Preparation of \[([\eta^5-C_5H_4Me]Mn(CO)(NO)]_2\). A suspension of \([([\eta^5-C_5H_4Me]Mn(CO)(NO)]PF_6\) (14g, 38mmol) in H\(_2\)O (60mL)/toluene (120mL) was treated dropwise over a period of about 30 mins with a solution of NaBH\(_4\) (2g, 52mmol) in H\(_2\)O (30mL). Reaction occurred as evidenced by gas evolution and a darkening of the reaction mixture. After 2 hrs the toluene layer was filtered through a Celite column (3x5cm) supported on a coarse porosity frit. The aqueous fraction was further extracted with toluene (3x20mL) and the combined extracts were concentrated in vacuo, to yield a deep red solid. The crude product was purified by chromatography on a short alumina column (5x6cm) using benzene as eluant. Concentration of the eluate in vacuo resulted in 5.56g (75% yield) of \([([\eta^5-C_5H_4Me]Mn(CO)(NO)]_2\).

Preparation of \([\eta^5-C_5H_4Me]_3Mn_3(NO)_4\). 2.0g (5.2mmol) of \([([\eta^5-C_5H_4Me]Mn(CO)(NO)]_2) was dissolved in THF (120mL) and heated at reflux for 18 hr. The resulting dark green reaction mixture was cooled to room temperature and concentrated in vacuo to 20mL, whereupon it was filtered through Florisil (2x3cm). The remaining solid residue was extracted with THF (3x15mL) and the combined filtrates were taken to dryness in vacuo. Recrystallization of the crude solid from CH\(_2\)Cl\(_2\)/hexanes resulted in 0.78g (57% w.r.t. NO) of black microcrystalline \([\eta^5-C_5H_4Me]_3Mn_3(NO)_4\).
Reaction of \( \eta^5-C_5H_4Me \)_3Mn_3(NO)_4 with one equivalent of acid. To a rapidly stirred dark green solution of \( \eta^5-C_5H_4Me \)_3Mn_3(NO)_4 (0.30g, 0.57mmol) in CH_2Cl_2 (20mL) was added HBF_4·OMe_2 (0.6mmol). Immediate reaction occurred, the colour darkened a little, and a small amount of solid precipitated from solution. After being stirred for 2 hrs, the reaction mixture was filtered through Celite (2x3cm), and the reaction residue extracted with CH_2Cl_2 (3x5mL). The combined filtrates were concentrated in vacuo to ca. 10mL and Et_2O (25mL) was added to induce the crystallization of black \( \{(\eta^5-C_5H_4Me)_3Mn_3(NO)_3(NOH)\}BF_4 \). (0.23g, 66% yield).

Anal. Calcd for C_{18}H_{22}N_3BF_4Mn_3O_4: C, 35.44; H, 3.64; N, 9.19. Found: C, 35.07; H, 3.61; N, 8.98. IR (Nujol mull): \( \nu(OH) 3270\text{ (br) cm}^{-1}\); \( \nu(NO) 1581, 1514, 1034 \text{ cm}^{-1}\); \( \nu(BF) 1098\text{ (E)}, 974(A), 713(A) \text{ cm}^{-1}\). IR (CH_2Cl_2): \( \nu(NO) 1582, 1523 \text{ cm}^{-1}\); \( \nu(BF) 1096\text{ (E)}, 968(A) \text{ cm}^{-1}\). \(^1\text{H-NMR ((CD}_3)_2CO): \delta 5.34(\text{s,12H,C}_5H_6), 1.86(\text{s,9H,CH}_3)\).

The hexafluorophosphate salt was prepared similarly in 43% yield by using aqueous HPF_6 as the strong acid.

Anal. Calcd for C_{18}H_{22}N_3F_6Mn_3O_4P: C, 32.35; H, 3.32; N, 8.39. Found: C, 32.38; H, 3.36; N, 8.24. IR (CH_2Cl_2): \( \nu(OH) 3408\text{ (br) cm}^{-1}\); \( \nu(NO) 1581, 1524, 1035 \text{ cm}^{-1}\); \( \nu(PF) 848 \text{ cm}^{-1}\). \(^1\text{H-NMR ((CD}_3)_2CO): \delta 5.32(\text{s,12H,C}_5H_6), 1.86(\text{s,9H,CH}_3)\).

Reaction of \( \{(\eta^5-C_5H_4Me)_3Mn_3(NO)_3(NOH)\}BF_4 \) with NEt_3. A solution of \( \{(\eta^5-C_5H_4Me)_3Mn_3(NO)_3(NOH)\}BF_4 \) (0.06g, 0.1mmol)
in CH₂Cl₂ (3mL) was treated with NEt₃ (0.014mL, 0.1mmol). A small amount of a white solid precipitated from solution and an infrared spectrum of the supermatant solution indicated essentially quantitative formation of (η⁵-C₅H₄Me)₃Mn₃(NO)₄.

Reaction of (η⁵-C₅H₄Me)₃Mn₃(NO)₄ with excess acid. To a rapidly stirred dark green solution of (η⁵-C₅H₄Me)₃Mn₃(NO)₄ (0.30g, 0.57mmol) in CH₂Cl₂ (10mL) was added 0.5mL HBF₄·OMe₂ in several aliquots. The solution lightened a little in colour and a red oily solid precipitated. After 1 hr, the reaction was quenched with water (60mL), and then concentrated in vacuo to remove the CH₂Cl₂. The resulting black–green solid was collected on a Celite column (2x3cm) supported on a medium porosity frit, and dried for 6 hrs under high vacuum. Extraction of the Celite bed with CH₂Cl₂ (3x10mL) resulted in a dark green solution which was concentrated to 5mLs. Addition of Et₂O (25mL) caused the crystallization of black microcrystalline [(η⁵-C₅H₄Me)₃Mn₃(NO)₃(NH)]BF₄ (0.06g, 17% yield).

Anal. Calcd for C₁₈H₂₄N₄BF₄Mn₃O₃: C, 36.39; H, 3.73; N, 9.43. Found: C, 36.18; H, 3.74; N, 9.18. IR (CH₂Cl₂): ν(NH) 3275 cm⁻¹; ν(NO) 1579, 1551 cm⁻¹; ν(BF) 1068 cm⁻¹. 'H–NMR (CD₂Cl₂): δ 21.95(t, 1H, J(¹⁴N–¹H)=61Hz, NH), 5.26(s, 6H, C₅H₄), 5.18(s, 6H, C₅H₄), 1.80(s, 9H, CH₃).

The hexafluorophosphate salt was prepared similarly in 13% yield by addition of an excess of aqueous HPF₆ to
$(\eta^5-C_5H_4Me)_3Mn_3(NO)_8$.

IR (CH$_2$Cl$_2$): $\nu$(NH) 3326 cm$^{-1}$; $\nu$(NO) 1581, 1525 cm$^{-1}$; $\nu$(PF) 847 cm$^{-1}$.

'H-NMR (CD$_2$Cl$_2$): $\delta$

21.53(t, 1H, J($^1$H-$^1$H)=60.5Hz, NH), 5.28(s, 6H, C$_5$H$_4$),
5.17(s, 6H, C$_5$H$_4$), 1.82(s, 9H, CH$_3$).
(i) Introduction

The preparation and characterisation of the bimetallic cations \([(\eta^5-C_5H_5)M(NO)_2]^{+} \text{ (M=Mo or W)} [55b]\) and \([(\eta^5-C_5H_5)_2Re(NO)_2]^+ [142]\) were recently reported. Salts containing these cations were synthesised in good yields by treatment of the monomeric hydrides \((\eta^5-C_5H_5)M(NO)H\) (M=Mo or W) and \((\eta^5-C_5H_5)Re(NO)H\), with hydride-abstracting carbocations in non-donor solvents, e.g.

\[ 2(\eta^5-C_5H_5)W(NO)_2H + \text{Ph}_3\text{CBF}_4 \longrightarrow [(\eta^5-C_5H_5)_2W_2(NO)_4]^{+} \text{BF}_4^- + \text{Ph}_3\text{CH} \ldots (6.1) \]

While the rhenium complex could be readily deprotonated to yield \([(\eta^5-C_5H_5)Re(CO)(NO)]_2\), the group VI bimetallic cations only result in the monomeric products \((\eta^5-C_5H_5)M(NO)_2H\) and \([(\eta^5-C_5H_5)M(NO)_2(B)]^{+} \text{ (B=base)}\) when treated with a variety of bases. Furthermore, while
protonation of \([\eta^5-C_5H_5]Fe(CO)_2\)_2 results in the analogous hydrido-bridged cations \([\eta^5-C_5H_5]Fe_2(CO)_4H]^+ [143]\), reaction of \([\eta^5-C_5H_5]Cr(NO)_2\)_2 with strong acids only results in the oxidative cleavage of the Cr-Cr bond and formation of \([\eta^5-C_5H_5]Cr(NO)_2]^+ [144]\).

\[
\text{\([\eta^5-C_5H_5]Fe(CO)_2\)_2 + H}^+ \rightarrow \text{\([\eta^5-C_5H_5]Fe_2(CO)_4H]^+ \quad \ldots (6.2)}
\]

\[
\text{\([\eta^5-C_5H_5]Cr(NO)_2\)_2 + 2H}^+ \rightarrow 2\text{\([\eta^5-C_5H_5]Cr(NO)_2]^+ + H}_2 \quad \ldots (6.3)}
\]

In order to attempt to rationalise these results, the reactions of the manganese dimers \([\eta^5-C_5H_4R]Mn(CO)(NO)]_2\) (R=H or Me) with HBF₄⋅OMe₂ have been performed. These reactions result in a complex mixture of products, two of which result from electrophile-induced reduction of a coordinated nitrosyl ligand. This Chapter describes these reactions in detail, and proposes a unifying rationale for the apparently disparate reactivities of the isoelectronic complexes \([\eta^5-C_5H_5]M(LO)_2\)_2 (M=Cr, Mn, Fe; L=N, C).
(ii) Results And Discussion

Treatment of red-violet \([\eta^5-C_5H_4R]Mn(CO)(NO)]_2\) (R=H or Me) with HBF₄·OMe₂ in CH₂Cl₂ results in an immediate reaction, the mixture becoming brown in colour. As for the reaction of the isoelectronic \([\eta^5-C_5H_5]Cr(NO)_2]_2\), two equivalents of acid are required to consume completely the dimeric reactants. However, unlike the analogous chromium and iron complexes, these reactions involving the manganese dimers afford a complex mixture of products. Fortunately, most of the organometallic products may be separated by virtue of their differing solubility properties in the manner summarised in Scheme 6.1. Careful monitoring of the progress of the original reaction verifies that the nitrosyl-containing complexes indicated in the Scheme, as well as \([\eta^5-C_5H_4R]Mn(CO)_2(NO)]_2\) (R=H or Me) which probably ends up as a component of the yellow solid, are formed initially and not during subsequent work-up procedures. Unfortunately, the dicarbonyl-nitrosyl cation can not be separated from the other components of the yellow solid.

The protonation of \([\eta^5-C_5H_4R]Mn(CO)(NO)]_2\) (R=H or Me) thus produces ultimately two well-known and two novel organometallic nitrosyl complexes of manganese in each case. The familiar \([\eta^5-C_5H_4R]Mn(CO)_2(NO)]_2\) cations [74,145] (IR (CH₂Cl₂): R=H, \(\nu(CO)\ 2125, 2075\ cm^{-1}; \nu(NO)\ 1840\ cm^{-1}\); R=Me, \(\nu(CO)\ 2116, 2075\ cm^{-1}; \nu(NO)\ 1846\ cm^{-1}\) have been
Scheme 6.1

**final reaction mixture**

- add H$_2$O
- remove CH$_2$Cl$_2$

Red-brown solution

- NaBPh$_4$

Brown solid

- extract with CH$_2$Cl$_2$

Brown solution

- add Et$_2$O

Yellow solid

- [(η$^5$-C$_5$H$_4$R)$_2$Mn$_2$(NO)$_3$(CO)(NH$_2$)]BPh$_4$

Black solid

- extract with toluene

Brown solution

- concentrate in vacuo

- crystallize from CH$_2$Cl$_2$-toluene

- (η$^5$-C$_5$H$_4$R)$_2$Mn$_2$(NO)$_3$(NO$_2$)

- [(η$^5$-C$_5$H$_4$R)$_3$Mn$_3$(NO)$_3$NH]BF$_4$

synthesised by the high-yield reaction

(η$^5$-C$_5$H$_4$R)Mn(CO)$_3$ + NO$^+$ $\longrightarrow$ [(η$^5$-C$_5$H$_4$R)Mn(CO)$_2$(NO)]$^+$ + CO  

...(6.4)

and the subsequent conversion of these cations to

(η$^5$-C$_5$H$_4$R)$_2$Mn$_2$(NO)$_3$(NO$_2$) (IR (CH$_2$Cl$_2$): R=H, $\nu$(NO) 1754, 1532 cm$^{-1}$; R=Me, $\nu$(NO) 1744, 1536 cm$^{-1}$) in moderate yields has recently been reported [67], i.e.

[(η$^5$-C$_5$H$_4$R)Mn(CO)$_2$(NO)]$^+$ + NO$_2^-$ $\longrightarrow$

(η$^5$-C$_5$H$_4$R)$_2$Mn$_2$(NO)$_3$(NO$_2$)  

...(6.5)
The trimetallic imido complexes were described in the previous Chapter for the case \( R=\text{Me} \) and the perhydrocyclopentadienyl derivative \( (R=\text{H}) \) exhibits very similar physical properties (i.e. IR \((\text{CH}_2\text{Cl}_2)\): \( \nu(\text{NO}) 1586, 1532 \text{ cm}^{-1} \). \( ^{1}H-\text{NMR} \) \( ((\text{CD}_3)_2\text{CO}) \): \( \delta 22.52(t,1H,J(^{14}N-^{1}H)=62.5\text{Hz},\text{NH}), 5.59(s,15H,\text{C}_5\text{H}_5) \).

The previously unreported bimetallic amido complexes, 
\[
[(\eta^5-\text{C}_5\text{H}_4\text{R})_2\text{Mn}_2(\text{NO})_2(\text{CO})(\text{NH}_2)]\text{BPh}_4,
\]
are obtainable in 15\% yield from the original protonation reaction (see Scheme 6.1), the cyclopentadienyl complex crystallizing from CH\(_2\)Cl\(_2\)/Et\(_2\)O as the CH\(_2\)Cl\(_2\) hemi-solvate. The compounds are brown, microcrystalline solids which dissolve in polar organic solvents to produce air-sensitive solutions. Their spectroscopic properties are consistent with the cations existing in solutions as a mixture of the diastereomers.
the trans form being predominant in less polar solvents and the cis isomer (an enantiomeric pair) becoming relatively more abundant in more polar solvents. Thus, their CH₂Cl₂ solutions display IR absorptions attributable to bridging NH₂ groups (R=H, ν(NH) 3330, 3259 cm⁻¹; R=Me, ν(NH) 3336, 3272 cm⁻¹), bridging carbonyl (R=H, ν(CO) 1855 cm⁻¹, R=Me, ν(CO) 1856 cm⁻¹) and terminal nitrosyl ligands (R=H, ν(NO) 1764 cm⁻¹; R=Me, ν(NO) 1754 cm⁻¹). However, when dissolved in the more polar CH₃CN, the complexes exhibit two IR absorptions due to the NO groups (R=H, ν(NO) 1785(m), 1759(s) cm⁻¹; R=Me, ν(NO) 1785(m), 1754(s) cm⁻¹), the higher

'It has previously been established that the cis/trans isomer ratio of the related (η⁵-C₅H₅R)₂Mn₂(NO)₃X complexes increases in more polar solvents [67].
energy bands being assignable to the cis isomer (as they do not appear in less polar solvents). The $^1$H-NMR spectrum of the cyclopentadienyl complex in $(CD_3)_2CO$ (a solvent of intermediate polarity) reveals the presence of the CH$_2$Cl$_2$ of solvation and tetraphenylborate anion, but does not contain detectable signals due to the NH$_2$ group. Furthermore, it displays two sharp resonances in the cyclopentadienyl region at δ5.81 and 5.58 of relative intensity 9:1 which may be assigned to the trans and cis isomers, respectively. The analogous spectrum of the methylcyclopentadienyl compound is more complex, exhibiting six distinct signals for the ring protons and two separate signals for the methyl protons in addition to the complex multiplet due to the BPh$_4^-$ anion. While the exact assignment of these resonances due to the $\eta^5$-C$_5$H$_5$Me ligands is not possible, this complexity is nevertheless indicative of each methylcyclopentadienyl ligand being bound to an asymmetric manganese centre [67].

It is clear from the preceding results that treatment of the $[(\eta^5$-C$_5$H$_5$R)M(LO)$_2$]$_2$ (M=Cr, Mn or Fe; L=C or N; R=H or Me) dimers with HBF$_4$.OMe$_2$ in CH$_2$Cl$_2$ results in markedly different types of products. A possible explanation for these varied experimental observations is that entirely different pathways are being followed during the various conversions. For instance, one pathway might involve initial proton transfer (protonation), i.e.
whereas another might have electron transfer (oxidative cleavage) as the first step, i.e.

\[
[(\eta^5-C_5H_4R)M(LO)]_2 + H^+ \rightarrow [(\eta^5-C_5H_4R)_2M_2(LO)_4H]^+ 
\]

\[(\eta^5-C_5H_4R)M(LO)]_2 + 2H^+ \rightarrow 2[(\eta^5-C_5H_4R)M(LO)]^+ + H_2
\]

In other words, it is possible that the differing chemical behaviour of the organometallic dimers towards H\(^+\) may simply be a manifestation of their intrinsically differing tendencies to undergo oxidation. This view seems to be supported at first glance by previously documented chemistry of \([(\eta^5-C_5H_5)Fe(CO)_2]_2\) and \([(\eta^5-C_5H_5)Cr(NO)_2]_2\) which indicates that the Cr–Cr bond in the chromium dimer is more readily cleaved by electrophiles. Thus while the reaction

\[
[(\eta^5-C_5H_5)Cr(NO)_2]_2 + PbCl_2 \rightarrow 2(\eta^5-C_5H_5)Cr(NO)_2Cl + Pb
\]

proceeds cleanly, the iron dimer apparently does not react with PbCl\(_2\) [56]. In similar fashion, the chromium complex dehalogenates vicinal or benzylic organic halides whereas the iron complex does not [56]. Furthermore, \([(\eta^5-C_5H_5)Cr(NO)_2]_2\) is oxidised rapidly (10 mins) by two
equivalents of Ph₃CBF₄, i.e.

\[ \text{[(η⁵-C₅H₅)Cr(NO)₂]₂ + 2Ph₃C⁺} \quad \rightarrow \quad 2[\text{[(η⁵-C₅H₅)Cr(NO)₂]⁺}] \quad + \quad 2\text{Ph₃C}^- \quad \text{(6.9)} \]

wheras when \[ \text{[(η⁵-C₅H₅)Fe(CO)₂]₂} \] in CH₂Cl₂ is treated with approximately three equivalents of Ph₃CBF₄, the dimer is only slowly consumed in 45 hr [146]

Preliminary electrochemical measurements [147] indicate, however, that this interpretation is too simplistic. Thus, the iron complex exhibits a reversible oxidation (E =+0.68V vs SCE), while the chromium complex is oxidised irreversibly (E =+0.85V vs SCE). Although a direct comparison of E values cannot be made, it is clear that the iron complex is more prone to oxidation and thus, in the context of the protonation reactions, if H⁺ is sufficiently strong an oxidant to oxidise \[ \text{[(η⁵-C₅H₅)Cr(NO)₂]₂} \] according to equation 6.7, then it should also be sufficiently potent to effect the oxidation of the iron complex.

On the basis of the currently available data, a more

---

1 It is tempting to formulate the organometallic product formed in this reaction as (η⁵-C₅H₅)Fe(CO)₂BF₄. However, the IR data reported [146] do not agree with those displayed by authentic (η⁵-C₅H₅)Fe(CO)₂BF₄, recently isolated by Mattson and Graham [117].
unified rationale of the reactions of the dimers with H⁺ may be proposed. The first step consists of adduct formation to produce the cationic [(η⁵−C₅H₅R)₂M₂(NO)₄H]⁺ species as summarised in equation 6.6. This adduct may prove to be sufficiently stable to be isolable (as in the case of M=Fe). Alternatively, the adduct may undergo unsymmetrical dissociation. For instance, in the case of M=Cr, such dissociation, i.e.

\[
[(\eta^5-C_5H_5)_2Cr(NO)_4H]^+ \rightarrow [(\eta^5-C_5H_5)Cr(NO)_2]^+ + (\eta^5-C_5H_5)Cr(NO)_2H \quad \text{(6.10)}
\]

would afford the ultimate [(\eta^5-C_5H_5)Cr(NO)_2]^+ product and the neutral hydrido complex, (\eta^5-C_5H_5)Cr(NO)_2H. However, this latter compound is thermally unstable [45] and reverts to the original dimeric reactant via

\[
2(\eta^5-C_5H_5)Cr(NO)_2H \rightarrow [(\eta^5-C_5H_5)Cr(NO)_2]_2 + H_2 \quad \text{(6.11)}
\]

Sequential recycling of conversions 6.6, 6.10 and 6.11 finally results in the net transformation 6.3. Evidence in support of this interpretation comes from the observed chemistry of the isolable [(\eta^5-C_5H_5)_2M'M²(NO)_4H]^⁺ (M¹=M²=Mo or W; M¹=Mo, M²=W) cations. Dissolution of a 1:1 mixture of the Mo₂ and W₂ cations or the pure MoW cation results in the same equilibrium mixture [55b].
This reaction suggests that the bimetallic cations exist in equilibrium with their monometallic components e.g.

\[
[(\eta^5-C_5H_5)_2M_2(NO)_6]^{+} \leftrightarrow [(\eta^5-C_5H_5)_2M(NO)_2]^{+} + (\eta^5-C_5H_5)_2M(NO)_2H \quad \ldots (6.13)
\]

The molybdenum and tungsten hydrides have reasonable thermal stability in solution. However, the congenic chromium complex is unknown, all attempts at preparing it in a similar reaction to that used to synthesize the Mo and W species resulting in the \([(\eta^5-C_5H_5)Cr(NO)_2]_2\) dimer. Thus, for \(M=Cr\) the equilibrium 6.13 would be driven to the right by the thermal instability of the hydride.

In a similar manner when \(M=Mn\), the initial \([(\eta^5-C_5H_5R)_2Mn_2(CO)_2(NO)_2H]^{+}\) adduct could cleave in a number of ways. One such unsymmetrical cleavage would produce the observed \([(\eta^5-C_5H_5R)Mn(CO)_2(NO)]^{+}\) cations and "\((\eta^5-C_5H_5R)Mn(NO)H\)".

\[
[(\eta^5-C_5H_5R)_2Mn_2(CO)_2(NO)_2H]^{+} \rightarrow [(\eta^5-C_5H_5R)Mn(CO)_2(NO)]^{+} + "(\eta^5-C_5H_5R)Mn(NO)H" \quad \ldots (6.14)
\]

Since the coordinatively saturated manganese hydride...
(η⁵-C₅H₆Me)Mn(NO)(PPh₃)H readily loses PPh₃ in solution to give the trimetallic cluster (η⁵-C₅H₆Me)₃Mn₃(NO), the coordinatively unsaturated hydride complex would be expected to spontaneously trimerise. As discussed in Chapter 5, the trimetallic nitrosyl cluster reacts with excess acid to produce the cationic imido complex [(η⁵-C₅H₆R)₃Mn₃(NO)₃(NH)]⁺. The origins of the bimetallic nitrosyl products presented in Scheme 6.1 remain to be ascertained, reactions 6.4 and 6.5 being unlikely in this system. However, the formation of the amide complex does represent a second example of the proton–induced reduction of coordinated NO.

One final point merits mention. In principle, the initial cationic adducts formed via reaction 6.6 could also undergo inner–sphere electron transfer processes, i.e.

$$2[(\eta^5-C_5H_6R)_2M_2(LO)H]^+ \longrightarrow 2[(\eta^5-C_5H_6R)Mn(LO)]_2^+ + H_2$$

...(6.15)

the net result being formation of the radical bimetallic monocations. No direct physical evidence for the existence of such bimetallic species has been found for any of the iron, chromium or manganese systems. Interestingly, however, this is the principal mode of reaction when [(η⁵-C₅H₅)Co(NO)]₂ is treated with a slight excess of HBF₄·OME₂ in CH₂Cl₂, i.e.
2[(η⁵-C₅H₅)Co(NO)]₂ + 2H⁺ → 2[(η⁵-C₅H₅)Co(NO)]₂⁺ + H₂

...(6.16)

The previously reported [148], paramagnetic [(η⁵-C₅H₅)Co(NO)]₂BF₄ may be easily isolated as a purple microcrystalline solid in 73% yield from the final reaction mixture.

(iii) Experimental Section

General procedures employed during this work were described in Chapter 2 section (iii).

Reaction of [(η⁵-C₅H₅)Mn(CO)(NO)]₂ with HBF₄·OMe₂.

Typically, 13.6M HBF₄·OMe₂ (0.29mL, 4.0mmol) was added to a stirred, red-violet solution of [(η⁵-C₅H₅)Mn(CO)(NO)]₂ (0.71g, 2.0mmol) in CH₂Cl₂ (30mL). The solution became brown in colour immediately, and a brown solid precipitated. After being stirred for 2 hr to ensure complete reaction, H₂O (60mL) was added, and the mixture was concentrated in vacuo to remove the CH₂Cl₂. At this stage, the reaction mixture, which consisted of a black solid and a red-brown aqueous solution, was filtered through Celite (2x3cm), and the collected solid was washed with H₂O (4x20mL). The black solid and the combined red-brown filtrates were then worked up separately in the manner described below.
Work-up of the black solid. The collected solid was first dried for 2 hrs at room temperature and 5 x 10^{-3} mm Hg pressure. It was then removed from the Celite column with CH₂Cl₂ (3x15mL), a process that afforded a dark green solution which in turn was taken to dryness under reduced pressure. Extraction of this residue with toluene (3x2mL) produced a brown solution which upon slow concentration in vacuo deposited a small amount of a brown solid. This solid was tentatively identified as \((\eta^5-\text{C}_5\text{H}_5)_2\text{Mn}_2(\text{NO})_3(\text{NO}_2)\) by IR spectroscopy (IR (CH₂Cl₂): \(\nu(\text{NO})\) 1754, 1532 cm⁻¹) [67].

Further extraction of the residue with CH₂Cl₂ (3x10mL) afforded a dark green solution. Addition of toluene (10mL) to this solution and careful concentration of the resulting solution under reduced pressure caused the crystallization of 80mg (10% yield) of black \([(\eta^5-\text{C}_5\text{H}_5)_3\text{Mn}_3(\text{NO})_3(\text{NH})]\text{BF}_4\), which was collected by filtration (IR (CH₂Cl₂): \(\nu(\text{NO})\) 1586, 1532 cm⁻¹). \(^1\text{H}-\text{NMR}\) ((CD₃)₂CO): \(\delta\) 22.52(t,1H,\(J(1^\text{H}-1^\text{H})=62.5\text{Hz, NH}\)), 5.59(s,15H,\text{C}_5\text{H}_5).

Work-up of the red-brown aqueous solution. The original combined filtrates were treated with a saturated aqueous solution of NaBPh₄ (1.03g, 3.00mmol) whereupon a brown solid precipitated, leaving an essentially colourless supernatant solution. The brown solid was collected by filtration, washed with H₂O (3x20mL), and dried for 2 hr at room temperature under high vacuum. Extraction of the dried solid with CH₂Cl₂ (3x20mL) produced a brown solution which was
concentrated to ca. 10mL under reduced pressure. Dropwise addition of Et₂O (40mL) to this solution caused the precipitation of a brown, microcrystalline solid in 15% yield with respect to Mn. This solid was identified as 

\[ (\eta^5-C_5H_5)\text{Mn}_2(\text{NO})_2(\text{CO})(\text{NH}_2) \text{BPh}_4\cdot 0.5\text{CH}_2\text{Cl}_2. \]

Anal. Calcd for C₃₃₅H₃₃N₉BClMn₂O₃: C, 60.41; H, 4.71; N, 5.96. Found: C, 60.69; H, 4.85; N, 6.25. IR (CH₂Cl₂): ν(NH) 3330(w), 3259(w) cm⁻¹; ν(CO) 1855(m) cm⁻¹; ν(NO) 1764(s) cm⁻¹. IR (CH₃CN): ν(CO) 1864(m) cm⁻¹; ν(NO) 1785(m), 1759(s) cm⁻¹. ¹H-NMR ((CD₃)₂CO): δ 7.35-6.75(m, 20H, C₆H₅), 5.81(s, 9H, C₅H₅), 5.62(s, 1H, CH₂Cl₂), 5.58(s, 1H, C₅H₅).

When [(η⁵-C₅H₅Me)Mn(CO)(NO)]₂ was subjected to the identical experimental procedure, methylcyclopentadienyl analogues of the products desired above were obtained in comparable yields. The spectroscopic properties of the C₅H₅Me-containing complexes are presented below:

\[ (\eta^5-C_5H_5Me)\text{Mn}_2(\text{NO})_2(\text{CO})\text{BPh}_4. \]

IR (CH₂Cl₂): ν(NO) 1744, 1536 cm⁻¹ [67].

\[ [(\eta^5-C_5H_5Me)\text{Mn}_2(\text{NO})_2(\text{CO})(\text{NH}_2)]\text{BPh}_4. \]

IR (CH₂Cl₂): ν(NH) 3336(w), 3272(w) cm⁻¹; ν(CO) 1856(m) cm⁻¹; ν(NO) 1754(s) cm⁻¹. IR (CH₃CN): ν(CO) 1864(m) cm⁻¹; ν(NO) 1785(m), 1754(s) cm⁻¹. ¹H-NMR ((CD₃)₂CO): δ 7.35-6.76(m, 20H, C₆H₅), 5.96(s, 2H, C₅H₅Me), 5.72(s, 1H, C₅H₅Me), 5.59(s, 1H, C₅H₅Me), 5.34(s, 1H, C₅H₅Me), 5.19(s, 2H, C₅H₅Me), 4.99(s, 1H, C₅H₅Me), 2.38(s, 3H, C₅H₅Me), 2.26(s, 3H, C₅H₅Me).
Reaction of \([\eta^5\text{-C}_5\text{H}_5\text{Co(NO)}]_2\) with \(\text{HBF}_4\cdot\text{OMe}_2\). A rapidly stirred brown solution of \([\eta^5\text{-C}_5\text{H}_5\text{Co(NO)}]_2\) \([26]\) (0.55g, 1.8mmol) in \(\text{CH}_2\text{Cl}_2\) (30mL) was treated with 13.6M \(\text{HBF}_4\cdot\text{OMe}_2\) (0.26mL, 3.5mmol). The solution became red–violet, and a small amount of a dark solid precipitated. After being stirred for 30 mins, the reaction mixture was filtered through a Celite column (2x3cm) supported on a medium porosity frit. The column was then washed with \(\text{CH}_2\text{Cl}_2\) (3x15mL) and the combined filtrates were concentrated under reduced pressure to a volume of 15mL. Dropwise addition of \(\text{Et}_2\text{O}\) (50mL) to this solution induced the precipitation of 0.51g (73% yield) of purple, microcrystalline \([\eta^5\text{-C}_5\text{H}_5\text{Co(NO)}]_2\text{BF}_4\) which was collected by filtration.

Anal. Calcd for \(\text{C}_{10}\text{H}_{10}\text{N}_2\text{BCo}_2\text{F}_4\text{O}_2\): C, 30.42; H, 2.55; N, 7.10. Found: C, 30.59; H, 2.75; N, 6.95. IR (\(\text{CH}_2\text{Cl}_2\)): \(\nu(\text{NO}) 1622\text{ cm}^{-1}\); \(\nu(\text{BF}) 1057, 1034\text{ cm}^{-1}\).
At the outset of the research described herein, the prevailing point of view was that a coordinated nitrogen monoxide is largely unreactive. It is certainly true that other ligands in the metal's coordination sphere are often attacked preferentially. However, the results described in Chapters 5 and 6 demonstrate that, in the absence of other reactive sites, bridging nitrosyl ligands can be converted into $\mu_3\text{NOH}$, $\mu_3\text{NH}$ and $\mu_2\text{NH}_2$ groups. While the objectives outlined in the introduction have been accomplished, it is obvious that much further work will be required to find systems which can be used industrially to convert NO to useful products.

With regard to the particular system studied, an external source of electrons must be found so that the conversions may be performed in much higher yields. In addition, the chemistry of the hydroxyimido and imido complexes should be investigated in order to find ways of releasing the nitrogen-containing groups. Since it appears that the binding of the NO ligand to 3 metallic centres activates it and stabilises the products, a separate line of
research worth investigating is the reactivity of the original reactant, \((\eta^5-C_5H_5R)_3Mn_3(NO)_4\) \((R=H\text{ or } Me)\), towards nucleophiles, such as \(H^-\) or \(R^-\).

The results described in chapters 2, 3 and 4 show that the nitrosyl ligand can also impart some unique chemical properties to some other ligand in the metal's coordination sphere, or to the molecule as a whole. For example, the nitrosyl ligand seems to favour the formation of paramagnetic monomers in the system, \((\eta^5-C_5H_5)Cr(NO)LX\), rather than diamagnetic dimers. In addition, the presence of the NO ligand may be the reason behind the preference for s–trans coordination of the diene in \((\eta^5-C_5H_5)Mo(NO)(\eta^4\text{-diene})\). In conclusion, it is becoming increasingly clear that considerable caution should be exercised when predicting the properties of organometallic nitrosyl complexes on the basis of the much more fully–developed and better–understood carbonyl chemistry.
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APPENDIX 1

X-RAY DIFFRACTION DATA

Diffractometer: Enraf-Nonius CAD4
Radiation: MoK (λ=0.71073 Å)
All atoms refined, including H atoms.

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<th>3b Triclinic</th>
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<td>P1</td>
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</tr>
<tr>
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Error in observation:

of unit weight.
Table A1 Final Positional (fractional x 10^4, Mn x 10^5, H x10^3) And Isotropic Thermal Parameters (U x 10^3 A^2) For 2 a .

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Table A2 Final Anisotropic Thermal Parameters ($U_{ij} \times 10^3$; Mn $\times 10^4$) For 2a

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*The anisotropic thermal parameters employed in the refinement are $U_{ij}$ in the expression:

$$f = f^0 \exp(-2\pi^2 \sum U_{ij} h_i h_j a_i^* a_j^*)$$
Table A3  Bond Lengths (Å) For 2a With Estimated Standard Deviations In Parentheses.

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Table A4 Bond Angles (deg) For 2a With Estimated Standard Deviations In Parentheses.

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H(NO)-F(1)-B     112(2)
Table A5 Final Positional (fractional \( \times 10^8 \), Mn And P \( \times 10^8 \), H \( \times 10^3 \)) And Isotropic Thermal Parameters (U \( \times 10^3 \) A\(^2\)) For 3b.

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*The anisotropic thermal parameters employed in the refinement are U_{ij} in the expression:

\[ f = f_0 \exp(-2\pi^2\Sigma U_{ij} h_i h_j a_i^* a_j^*) \]
Table A7 Bond Lengths (Å) For 3b With Estimated Standard Deviations In Parentheses.

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### Table A8 Bond Angles (deg) For 3b With Estimated Standard Deviations In Parentheses.

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**Also**  
N(4)-H-F(1)  
165(3)
APPENDIX 2

INFRA-RED, $^1$H–NMR, $^{13}$C–NMR AND ESR SPECTRA OF THE NEW COMPLEXES PREPARED IN THIS RESEARCH
$[(\eta^5-C_5H_5)Cr(NO)I]_2$, IR (CH$_2$Cl$_2$):

$[(\eta^5-C_5H_5)Cr(NO)(OEt)]_2$, IR(CH$_2$Cl$_2$):

$[(\eta^5-C_5H_5)Cr(NO)(OMe)]_2$, IR (CH$_2$Cl$_2$):
(η⁵-C₅H₅)Cr(NO)(PPh₃)Cl.

IR (CH₂Cl₂):

EPR (Toluene):
\((\eta^5-C_5H_5)Cr(NO)(PPh_3)Br\).

**IR \((CH_2Cl_2)\):**

![IR spectrum graph](image)

**EPR (Toluene):**

![EPR spectrum graph](image)
(η⁵-C₅H₅)Cr(NO)(PPh₃)I.

IR (CH₂Cl₂):

EPR (Toluene):
$(\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}\{(\text{OPh})_3\}I$.

IR ($\text{CH}_2\text{Cl}_2$):

EPR (Toluene):
\((\eta^5-\text{C}_5\text{H}_5)\text{Cr(NO)}\{\text{P(OEt)}_3\})\text{I.}\)

IR (CH\(_2\text{Cl}_2\)):

EPR (Toluene):

\[ \alpha^{31}\text{P}, \quad g_{\text{iso}} \]

\[ \text{20G} \]
(η⁵-C₅Me₅)Cr(NO)₂Br.

IR (CH₂Cl₂):

'H-NMR (CDCl₃):
$(\eta^5-\text{C}_5\text{Me}_5)\text{Cr(NO)}_2\text{I}$.

IR (CH$_2$Cl$_2$):

$^1$H-NMR (CDCl$_3$):
\[ ([\eta^5-C_5\text{Me}_5]\text{Mo(NO)}\text{I}_2]\text{)_2.} \]

IR (CH\textsubscript{2}Cl\textsubscript{2}): 

\[ \text{WAVENUMBER (CM}^{-1}\text{) WAVENUMBER (CM}^{-1}\text{)} \]

\[ \text{'H-NMR (CDCl}_3): \]

\[ 8 \quad 6 \quad 4 \quad 2 \quad 0 \delta \]
\[(\eta^5-C_5Me_5)W(NO)_2I_2\]

IR (CH\_2Cl\_2):

\(^1\text{H-NMR (CDCl}_3\):
$^{13}$C-NMR (CDCl$_3$):
$(\eta^5-C_5\text{Me}_5)\text{Mo(NO)}(\text{PPh}_3)\text{I}_2$.

IR (CH$_2$Cl$_2$):

$^1$H-NMR (CDCl$_3$):
$(\eta^5$-C$_5$Me$_5$)Mo(NO){P(OPh)$_3$}I$_2$. 

IR (CH$_2$C$_2$):

$^1$H-NMR (CDCl$_3$):

![IR spectrum](image1.png)

![$^1$H-NMR spectrum](image2.png)
$^{13}$C-NMR (CDCl$_3$):
(η^5-C₅Me₅)W(NO)(PPh₃)I₂.

IR (CH₂Cl₂):

^1H-NMR (CDCl₃):
(η⁵-C⁵Me₅)W(NO){P(OPh)₃}I₂.

IR (CH₂Cl₂):

¹H-NMR (CDCl₃):
(C₅H₅)₂W(NO)I.

IR (CH₂Cl₂):

'H-NMR (CDCl₃):
$^{13}$C-NMR (CDCl$_3$):
(η⁵-C₅H₅)Mo(NO)(η⁶-s-trans-C₅H₅).

IR (CH₂Cl₂):

'H-NMR (CDCl₃):
$^{13}\text{C-NMR} \ (\text{CDCl}_3)$
\((\eta^5-C_5H_5)\text{Mo(NO)(\eta^8-s\text{-}trans-C_6H_{10})}\).

\textbf{IR (CH}_2\text{Cl}_2\text{):}

\textbf{\textsuperscript{1}H-NMR (CDCl}_3\text{):}
\((\eta^5-C_5H_5)Mo(NO)(\eta^8-s\text{-}trans-C_6H_14)\).

IR \((CH_2Cl_2)\):

\(^1H\)-NMR \((CDCl_3)\):
\[(\text{C}_5\text{H}_5)_2\text{Mo(NO)(CH}_3\text{CN)}\text{]}\text{BF}_4.\]

IR (Nujol mull):

\[\text{^1H-NMR (CD}_3\text{NO}_2):\]
IR (CH$_3$CN):

$^1$H-NMR (CD$_3$CN):
$^{13}$C-NMR (CD$_3$CN):
\[ [(\text{C}_5\text{H}_5)_2\text{Mo(NO)}(\text{CH}_3\text{CN})]\text{SbF}_6. \]

IR (Nujol mull):

\[ '\text{H}-\text{NMR } (\text{CD}_3\text{NO}_2): \]
IR($\text{CH}_3\text{CN}$):

'H-NMR ($\text{CD}_3\text{CN}$):
\[
\{(\eta^5-\text{C}_5\text{H}_5)\text{Mo(NO)(OH)}\}_3\text{O}\}\text{BF}_3 \cdot 2\text{H}_2\text{O}.
\]

**IR (Nujol mull):**

![IR spectrum image]

**\(^1\text{H-NMR ((CD}_3)_2\text{CO):**

![NMR spectrum image]
$^{13}\text{C-NMR (D}_2\text{O):}$
\[
\left\{\left[\eta^5-C_5H_5\right]Mo(NO)(OH)_{3}O\right\}_3O\text{SbF}_6\cdot(CH_3)_2CO.
\]

**IR (CH\textsubscript{3}CN):**

\[\text{WAVENUMBER (cm}^{-1}\text{)}\]

\[\text{NO}\]

\[\text{OH}\]

\[\text{SbF}_6\]

\[\text{(CH}_3\text{)}_2\text{CO}\]

**\textsuperscript{1}H-NMR (CD}_3\text{CN):**

\[\text{WAVENUMBER (cm}^{-1}\text{)}\]

\[\text{8} \quad 6 \quad 4 \quad 2 \quad 0\]
\[ \{[\eta^5-C_5H_5]Mo(NO)(OH)\}_3O\]BF_4 \cdot 2H_2O.

IR (Nujol mull):

'H-NMR (CD_3CN):

[Diagram of IR spectrum]

[Diagram of 'H-NMR spectrum]
(C₅H₅)₂M(NO)₁.AgY.

(a) M=Mo, Y=BF₄. IR (Nujol mull):  (b) IR (CH₃CN):

(c) M=Mo, Y=SbF₆. IR (Nujol mull):
(d) \( \text{M} = \text{Mo}, \ \text{Y} = \text{SbF}_6 \). IR(CH\(_3\)CN):

(e) \( \text{M} = \text{W}, \ \text{Y} = \text{BF}_4 \). IR (Nujol mull):

(f) \( \text{M} = \text{W}, \ \text{Y} = \text{SbF}_6 \). IR (Nujol mull):
\[ \left( \eta^5-C_5H_5 \right)_2 Mo(No) \] AlCl_3 I.

IR (CH_2Cl_2):

\[ \text{H-NMR } (\text{CD}_3)_2 CO: \]

\[ \text{H-NMR } (\text{CD}_3)_2 CO: \]
\([\eta^5-C_5H_{12}Me)_3Mn_3(NO)_3(NOH)]BF_4\).

IR (Nujol mull):

'\text{H}-\text{NMR (CD}_3\text{)}_2\text{CO}':
\[(\eta^5-C_5H_4Me)_3Mn_3(NO)_3(NOH))]PF_6.\]

IR (CH$_2$Cl$_2$):

$^1$H–NMR ((CD$_3$)$_2$CO):

8  6  ppm  4  2  0δ
\[(\eta^5-C_5H_4Me)_3Mn_3(NO)_3(NH)\]BF_4.

IR (CH_2Cl_2):

'\textsuperscript{1}H-NMR (CD_2Cl_2):
\[ \left( \eta^5-C_5H_5Me \right)_3Mn_3(NO)_3(NH) \] PF$_6$.

**IR (CH$_2$Cl$_2$):**

![IR Spectrum Graph]

**$^1$H-NMR (CD$_2$Cl$_2$):**

![NMR Spectrum Graph]
\[
[(\eta^5-C_5H_5)_2Mn_2(NO)_2(CO)(NH_2)]BPh_4 \cdot 0.5\text{CH}_2\text{Cl}_2.
\]

**IR (CH\textsubscript{2}Cl\textsubscript{2}):**

**\textsuperscript{1}H-NMR ((CD\textsubscript{3})_2CO):**
IR (CH$_3$CN):

![IR Spectrum of $\text{[(η}-C_5H_6\text{Me})_2\text{Mn}_2\text{(NO)}_2\text{(CO)}\text{(NH}_2\text{]}\text{BPh}_8$.}]

IR (CH$_2$Cl$_2$):
IR (CH$_3$CN):

$^1$H-NMR (CD$_3$)$_2$CO:
PUBLICATIONS


Legzdins, P.; Martin, D.T.; Nurse, C.R.; Wassink, B. Organometallic Nitrosyl Chemistry, 19. Protonation vs. Oxidative Cleavage of the Isoelectronic Complexes \( [(n^5-C_5H_5R)M(LO)]_2 \) (\( M = \text{Cr, Mn, Fe} \); \( L = \text{C or N} \); \( R = \text{H or Me} \)) by HBF\(_4\). *Organometallics*, in press.