STUDIES ON TRANSITION METAL NITROSYL CHEMISTRY

by

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ABSTRACT

The reactions of nitrosyl chloride with a variety of anionic and neutral metal carbonyl and \( n^5 \)-cyclopentadienylmetal carbonyl compounds of Cr, Mo, W, Mn, Re, Fe and Co are described. In most cases nitrosyl-containing complexes are formed in reasonable yields. The advantages and limitations of nitrosyl chloride as a general synthetic reagent for the preparation of transition metal nitrosyl complexes are discussed.

The high yield syntheses of \( \text{CpM(CO)}_2 \text{(NO)} \) \((\text{M} = \text{Cr, Mo or W}) \) from \( \text{Na[CpM(CO)}_3 \) and Diazald are detailed. Subsequent reaction of the dicarbonylnitrosyl species with nitrosyl chloride affords the corresponding \( \text{CpM(NO)}_2 \text{Cl} \) complexes in excellent yields. The \( \text{CpM(NO)}_2 \text{R} \) \((\text{M} = \text{Cr or Mo; R = Me, Et, i-Bu or Ph; M = W; R = Me or Ph}) \) complexes are obtained in the reactions of \( \text{CpM(NO)}_2 \text{Cl} \) with alkyl- or arylaluminum reagents. Some further derivatives of the \( \text{CpM(NO)}_2 \text{Cl} \) complexes and the high yield preparation of \( \text{[CpCr(NO)}_2 \text{Cl]}_2 \) are also described. Previously unreported compounds are characterized by infrared and nuclear magnetic resonance spectroscopy and by mass spectrometry.
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ABBREVIATIONS AND COMMON NAMES

The following abbreviations and common names, some of which are presently used in the scientific literature, are employed throughout this thesis.

Å : Angstrom
AlR₃ : trialkyl(or aryl)aluminum
Amt. : amount
Bu : butyl
n-Bu₂0 : di-n-butyl ether
calcd. : calculated
cm⁻¹ : wave numbers in reciprocal centimeters
compd. : compound
Cp : pentahapto-cyclopentadienyl, n⁵-C₅H₅
dec. : decomposes
Diazald : N-methyl-N-nitroso-p-toluenesulfonamide
diglyme : bis(2-methoxyethyl)ether
DME : 1,2-dimethoxyethane
Et : ethyl
Et₂O : diethyl ether
EtOAc : ethyl acetate
EtOH : ethanol
h : hour(s)
Hz : Herz, cycles per second
IR : infrared
J : magnetic resonance coupling constant in cycles per second
3,4-lutidine: 3,4-dimethylpyridine
m : medium
Me : methyl
m/e : mass to charge ratio
min. : minute(s)
mm : millimeters of mercury
abbreviations and common names (cont'd)

NMR : nuclear magnetic resonance
4-picoline : 4-methylpyridine
Ph : phenyl
PPh₃ : triphenylphosphine
pz : pyrazoyl
R : alkyl or aryl
R_f : perfluoroalkyl
s : strong
Temp. : temperature
THF : tetrahydrofuran
w : weak
η³ : trihapto-
η⁵ : pentahapto-
ν : stretching frequency
τ : NMR chemical shift in parts per million
CHAPTER I

GENERAL INTRODUCTION

Numerous transition metal nitrosyl compounds are known and the development of their chemistry, which has been the subject of several reviews (1, 2, 3), has closely paralleled that of the metal carbonyl complexes. Consequently, it has been recognized for some time that nitric oxide can bond to metals in a manner quite different from carbon monoxide. The structures of a number of nitrosyl compounds (4) strikingly demonstrate the variable nature of the metal-nitrosyl bond, which has also received considerable attention from a theoretical point of view (5). In particular, two bonding modes have been observed which are best represented by the Lewis structures I and II. Structure I is characterized by a linear M-N=O bond and an M-N bond distance which

\[
\begin{align*}
\text{I} & : \text{M-N=O} \\
\text{II} & : \text{M-N}.
\end{align*}
\]

strongly suggests the existence of multiple bond character. In this instance the nitric oxide ligand formally behaves as a three-electron donor. This type of bonding is by far the most common among the complexes studied to date. In structure II the nitrosoyl group formally acts as
a one-electron donor and the M-N-O bond angle is 120°. Although the M-N bond is longer than in the linear bonding mode, it is still somewhat shorter than the expected single M-N σ-bond distance. While both of these limiting structures have been observed, most of the complexes have M-N-O bond angles which range from 120° to 180°.

The use of metal nitrosyl complexes as specific homogeneous catalysts has generated much recent interest. For example, Fe(CO)₂(NO)₂ catalytically dimerizes butadiene to 4-vinylcyclohex-1-ene, and isoprene to a mixture of 1,4-dimethyl-4-vinyl- and 1,5-dimethyl-5-vinylcyclohex-1-ene (6). Interestingly, both of these dimerizations occur even in the presence of other olefins, Lewis acids, or Lewis bases. Furthermore, the Rh(NO)(PPh₃)₃ complex has been found to catalytically hydrogenate both terminal and cyclic olefins under ambient conditions (7). If this hydrogenation is performed in the absence of peroxides or O₂, accompanying olefin isomerization does not occur and the catalyst may be recovered unchanged.

Metal nitrosyl complexes find their greatest application in the field of olefin disproportionation (8). Most commonly used are the M(NO)₂X₂L₂ (M = Mo or W; X = Cl, Br or I; L = phosphines, phosphites, arsines and amines) complexes in conjunction with an organoaluminum cocatalyst such as Me₃Al₂Cl₃ or AlCl₃.

Bearing in mind the interesting bonding, structural, catalytic and reactivity properties of metal nitrosyl complexes, the development of new synthetic routes to these compounds must surely be welcomed. A
perusal of a review article (9) which deals exclusively with the preparation of metal nitrosyl compounds reveals the obvious lack of a general preparative route. This fact in itself is not surprising since a large variety of metals is encompassed. Unfortunately, many of the existing synthetic routes produce the desired product in low yield and/or with much expenditure of effort. The work in this thesis is presented in the spirit of developing new synthetic techniques which, in addition to yielding existing compounds more conveniently, may also be applied to the synthesis of new metal nitrosyl complexes. The studies presented in Chapter II and III are exploratory in nature. For instance, the scope of the reaction of nitrosyl chloride with a variety of anionic and neutral organometallic complexes is outlined. Chapter IV describes in detail the successful application of this and other synthetic methods during the preparation of a variety of halo-, alkyl- and aryl-(cyclopentadienyl)nitrosyl complexes of chromium, molybdenum and tungsten.
CHAPTER II

THE REACTION OF NITROSYL CHLORIDE WITH SOME TRANSITION METAL CARBONYL ANIONS

2.1 Introduction

The first and only reported reaction of nitrosyl chloride with a transition metal carbonyl anion involves the synthesis of \((\text{RB(pz)}_3)\text{M(CO)}_2(\text{NO})\) from \([\{(\text{RB(pz)}_3)\text{M(CO)}_3\}]^-\) \((\text{RB(pz)}_3 = \text{tris(pyrazoyl)}-)\)-borate; \(R = \text{H or pz}; M = \text{Cr, Mo or W}\) \((10)\). In spite of the large number of readily obtainable metal carbonyl anions \((11)\), this type of reaction has been completely ignored. A study to determine the extent to which nitrosyl chloride can be employed as a general reagent for the synthesis of neutral nitrosyl complexes, from the corresponding carbonyl anions, was therefore undertaken. The generality of this synthetic approach as well as its limitations, are herein clearly delineated. In many instances, this new route affords the desired nitrosyl complexes more conveniently and in higher yields than was previously possible. Furthermore, the need for organometallic anions which are soluble in non-donor solvents has led, during the course of this work, to the efficient and high yield synthesis of \((\text{PPh}_3)_2\text{NX}\) and \((\text{PPh}_3)_2\text{NW(CO)}_5\text{X}\) \((X = \text{Cl, Br or I})\).
Specifically, this chapter describes the reactions of nitrosyl chloride with the following species: \((\text{PPh}_3)_2\text{NMn(CO)}_5\), \(\text{Na}[\text{Re(CO)}_5]\), \(\text{Ph}_3\text{SnRe(CO)}_5\), \(\text{Na}_2[\text{Fe(CO)}_4]\), \(\text{Na}[\text{CpFe(CO)}_2]\), \(\text{CpFe(CO)}_2\text{SnPh}_3\), \(\text{Na}[\text{CpM(CO)}_3]\) (\(M = \text{Cr, Mo or W}\)) and \(\text{A}[\text{W(CO)}_5\text{X}]\) (\(A = (\text{PPh}_3)_2\text{N}; \text{X} = \text{Cl, Br or I}; \text{A} = \text{Et}_4\text{N}; \text{X} = \text{Cl or Me}\)). The chemical and physical properties of the products in the above reactions are considered where appropriate.

2.2 Experimental

All chemicals used were of reagent grade or comparable purity and were either purchased from commercial suppliers or prepared according to reported procedures. Their purity was ascertained from elemental analyses and/or melting point determinations. The uncorrected melting points were taken in capillaries in air or under prepurified nitrogen using a Gallenkamp Melting Point Apparatus. All solvents were dried according to known methods (12) and thoroughly purged with prepurified nitrogen prior to use. All manipulations, unless otherwise stated, were performed on the bench (using conventional techniques for handling air sensitive compounds (13)) or in a Vacuum Atmospheres Corporation Dri-Lab model HE-43-2 dry box filled with prepurified nitrogen.

Infrared spectra were recorded on Perkin Elmer 457 or 710A spectrophotometers and calibrated with the 1601 cm\(^{-1}\) absorption band of a polystyrene film. Proton magnetic resonance spectra were recorded on a Varian Associates T-60 spectrometer using tetramethylsilane as an
internal standard. The low-resolution mass spectra were taken at 70 eV on an Atlas CH4B spectrometer and the high-resolution mass spectrum was obtained on an Associated Electrical Industries MS902 spectrometer with the assistance of Dr. G. Eigendorf and Mr. G. Gunn. Elemental analyses were performed by Mr. P. Borda of this Department.

Two reagents used frequently throughout this work were nitrosyl chloride (C1NO) and the bis(triphenylphosphine)iminium halides ((PPh₃)₂NX; X = Cl, Br or I). Their syntheses are described below.

2.2a Preparation of nitrosyl chloride.

Nitrosyl chloride was prepared in the following manner, the procedure employed being a modification of an earlier report (14). A 100 ml three-necked flask was equipped with a nitrogen inlet, a dropping funnel and a drying tower (2 x 20 cm) packed from top to bottom with equal volumes of anhydrous CaCl₂, KCl and NaNO₂. The top of the tower was fitted with a 5 ml graduated cold trap equipped with a stopcock on the trap inlet, as shown in Figure 1 [C1NO is a highly corrosive substance which necessitates the use of apparatus constructed exclusively from glass]. The trap outlet was connected to a 100 ml two-necked flask equipped with a nitrogen inlet secured with a silica-gel drying tube. After flushing the entire apparatus with nitrogen, the reaction flask was charged with concentrated aqueous HCl (32 ml). An aqueous solution (10 ml) of NaNO₂ (5.54 g) was added dropwise to the rapidly stirred acid solution at room temperature. The gaseous C1NO which formed instantly was carried by a slow stream of N₂ (ca. 20 ml min⁻¹)
FIG 1 APPARATUS FOR PURIFYING NITROSYL CHLORIDE
into the cold trap held at -78°C. In this manner, 2.5 ml (50 mmol) of ClNO were generated. This was distilled under vacuum into the 100 ml flask and 50 ml of CH₂Cl₂, THF or Et₂O were added to the cold ClNO to yield deep red solutions which were found to be thermally stable at 20°C. The chemical and physical properties of ClNO have been extensively described (15).

All subsequent reactions involving ClNO were performed by the dropwise addition of one of these solutions to the appropriate reaction mixture while monitoring the course of the reaction by infrared spectroscopy.

2.2b Preparation of bis(triphenylphosphine)iminium chloride, bromide and iodide, (PPh₃)₂NX (X = Cl, Br or I).

The compounds (PPh₃)₂NX (X = Cl, Br or I) were synthesized according to a modification of a published procedure (16).

2.2b1 Preparation of (PPh₃)₂NCl.

A three-necked 300 ml flask was equipped with a nitrogen inlet, a gas inlet, a magnetic stirrer and a Dry-ice reflux condenser secured with a silica gel drying tube. The flask was charged with PPh₃ (76.8 g, 293 mmol; Matheson Coleman and Bell) and 1,1,2,2-tetrachloroethane (100 ml; Fisher reagent). The resultant solution was cooled to -78° in a Dry-ice-isopropanol bath and chlorine (14.2 g, 200 mmol; Matheson of Canada) was bubbled through the reaction mixture
over a period of 10 min. The gas inlet was replaced with a stopper and the Dry-ice condenser with a water-cooled reflux condenser. 

NH_{2}OH·HCl (6.9 g, 100 mmol; Mallinckrodt analytical reagent grade) was added and the mixture was allowed to warm to room temperature. Finally, the reaction mixture was heated under reflux until the evolution of HCl(g) ceased (about 6 h) and then was allowed to cool to room temperature. [Subsequent manipulations were performed in air.]

The orange solution was poured into EtOAc (400 ml) whereupon a large quantity of tan crystals formed over a period of 18 h. The crystals were collected by suction filtration, recrystallized from boiling water and dried in a vacuum desiccator. The solid was dissolved in CH_{2}Cl_{2} (260 ml) and Et_{2}O (500 ml) was added, thereby producing the white crystalline product which was collected by suction filtration. Final drying \textit{in vacuo} (5 x 10^{-3} \text{mm}) at 125°C for 70 h afforded 49.1 g (85.5 mmol, 85% yield) of (PPh_{3})_{2}NCl.

\textbf{Anal. Calcd. for [P(C_{6}H_{5})_{3}]_{2}NC1:} C, 75.32; H, 5.27; N, 2.44.
\textbf{Found:} C, 75.56; H, 5.42; N, 2.22. m.p. (under N\textsubscript{2}): 275.5-276.5°C.
Proton NMR, \textit{\tau}(in CDCl\textsubscript{3}), -C\textsuperscript{H\textsubscript{5}}: 2.33(m).

2.2b2 Preparation of (PPh\textsubscript{3})\textsubscript{2}NBr.

The (PPh\textsubscript{3})\textsubscript{2}NBr was prepared in a manner comparable to that described above for (PPh\textsubscript{3})\textsubscript{2}NCl. The required amount of bromine (Fisher reagent grade) was dissolved in CHCl\textsubscript{2}CHCl\textsubscript{2} (20 ml) and added dropwise, over a period of 1 h, to the vigorously stirred reaction mixture cooled in an ice-water bath. The initial crude product was
obtained by pouring the cooled reaction mixture into Et₂O (600 ml) and was recrystallized from boiling water (750 ml). The product was finally recrystallized by the addition of EtOAc (500 ml) to a CH₂Cl₂ solution (150 ml) of the salt. Drying in vacuo (5 x 10⁻³ mm) for 70 h at 125°C produced 51.0 g (83 mmol, 83% yield) of the analytically pure (PPh₃)₂NBr.


2.2b3 Preparation of (PPh₃)₂NI.

[The following manipulations were performed in air.] To a solution of (PPh₃)₂NCl (18.8 g, 32.8 mmol) in EtOH (200 ml, "100%" not further purified) was added finely pulverized NaI (15.0 g, 100 mmol; Mallinckrodt analytical reagent). The mixture was stirred rapidly for 1 h at room temperature and then taken to dryness in vacuo. The product was extracted into a total of 200 ml of CH₂Cl₂ and the extract was reduced to ca. 100 ml in vacuo.

The addition of Et₂O (300 ml) produced the white crystalline product which was collected by suction filtration and dried at 125°C (5 x 10⁻³ mm) for 70 h. This procedure produced 20.6 g (31.0 mmol, 95% yield) of analytically pure (PPh₃)₂NI.

Anal. Calcd. for [P(C₆H₅)₃]₂NI: C, 64.97; H, 4.53; N, 2.10. Found: C, 65.09; H, 4.67; N, 2.17. m.p. (under N₂) 251.0-252.3°C. Proton NMR, τ (in CDCl₃), -C₆H₅: 2.50(m).
The (PPh$_3$)$_2$NX ($X = \text{Cl, Br or I}$) compounds are white solids which are soluble in CH$_2$Cl$_2$, CHCl$_2$CHCl$_2$, EtOH and boiling water, but insoluble in EtOAc, Et$_2$O, THF, benzene and hexanes. Although stable in dry air indefinitely, these compounds are hygroscopic and are therefore best stored in a desiccator.

2.2c Preparation of bis(triphenylphosphine)iminium pentacarbonylhalo-
tungstates, (PPh$_3$)$_2$NW(CO)$_5$X ($X = \text{Cl, Br or I}$).

These complexes were conveniently prepared by the reaction of W(CO)$_6$ with the appropriate (PPh$_3$)$_2$NX salt. The experimental procedure, using the iodide complex as a representative example, was as follows.

A DME (90 ml) solution containing W(CO)$_6$ (7.39 g, 21.0 mmol; Pressure Chemical Co.) and (PPh$_3$)$_2$NI (13.3 g, 20.0 mmol) was heated under reflux for 6 h. The resultant clear yellow solution was allowed to cool to room temperature and the volume reduced in vacuo until the first traces of crystals appeared. Slow addition of hexanes (120 ml) produced yellow crystals which were collected by suction filtration and washed with hexanes (2 x 40 ml). The product was dried at 60°C (5 x 10$^{-3}$ mm) for 18 h. A quantitative yield of analytically pure (PPh$_3$)$_2$NW(CO)$_5$I was thus obtained (Table I).

The (PPh$_3$)$_2$NW(CO)$_5$X ($X = \text{Cl or Br}$) complexes were similarly obtained in greater than 95% yields and their elemental analyses and physical properties are compiled in Table I.
Table I. Elemental Analyses and Physical Properties of (PPh$_3$)$_2$NW(CO)$_5$X (X = Cl, Br or I).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>Mp., °C (under N$_2$)</th>
<th>Analyses, %</th>
<th>Proton NMR, $\tau$(in CDCl$_3$)</th>
<th>$\nu$(CO), cm$^{-1}$ (in CH$_2$Cl$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PPh$_3$)$_2$NW(CO)$_5$Cl</td>
<td>Yellow</td>
<td>145(dec)</td>
<td>Calcd: 54.84 3.37 1.56</td>
<td>2.52(m)</td>
<td>2065(w), 1915(s), 1837(m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found: 54.44 3.51 1.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PPh$_3$)$_2$NW(CO)$_5$Br</td>
<td>Yellow</td>
<td>150(dec)</td>
<td>Calcd: 52.25 3.21 1.49</td>
<td>2.50(m)</td>
<td>2065(w), 1915(s), 1842(m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found: 52.04 3.31 1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PPh$_3$)$_2$NW(CO)$_5$I</td>
<td>Yellow</td>
<td>178(dec)</td>
<td>Calcd: 49.77 3.06 1.42</td>
<td>2.51(m)</td>
<td>2063(w), 1918(s), 1850(m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found: 49.74 3.20 1.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
All three complexes are yellow solids which may be exposed to air for several days without noticeable decomposition but are best stored under nitrogen. They are very soluble in CH$_2$Cl$_2$, diglyme and DME, less soluble in Et$_2$O, THF and EtOAc and insoluble in hexanes. The solubility increases markedly with increasing atomic weight of the halogen.

2.2d Reactions of nitrosyl chloride with some anionic and neutral complexes of manganese, rhenium and iron. Reaction with bis(triphenylphosphine)iminium pentacarbonylmanganate, (PPh$_3$)$_2$NMn(CO)$_5$.

To a light yellow solution of (PPh$_3$)$_2$NMn(CO)$_5$ (17) (0.81 g, 1.1 mmol) in CH$_2$Cl$_2$ (30 ml) was added dropwise with stirring at room temperature a solution of ClNO in CH$_2$Cl$_2$. Immediately, the reaction solution became deep red and gas was evolved. After the addition of ClNO was complete, the solution was stirred for an additional 10 min. Distillation in vacuo yielded a CH$_2$Cl$_2$ solution containing only Mn(CO)$_4$(NO) which was identified by its infrared spectrum (18). The yield was estimated to be 70% from the relative intensities of the carbonyl absorptions in the reactant and product infrared spectra.

The reactions of ClNO with some organometallic complexes of rhenium and iron were performed similarly and the experimental procedures are summarized in Table II.
Table II. Reaction of Nitrosyl Chloride with some Complexes of Rhenium and Iron.

<table>
<thead>
<tr>
<th>Transition metal compd. (mmol)</th>
<th>Amnt. of CINO (mmol)</th>
<th>Solvent (ml)</th>
<th>Temp. and reaction time</th>
<th>Products (yields)</th>
<th>Isolation and Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na[Re(CO)₅]₁⁹(4.0)</td>
<td>4.0</td>
<td>THF(50)</td>
<td>0°, 15 min.</td>
<td>Re₂(CO)₁₀</td>
<td>Sublimation at 40-60° (5x10⁻³ mm); infrared spectrum a</td>
</tr>
<tr>
<td>Ph₃SnRe(CO)₅²₀(1.5)</td>
<td>2.0</td>
<td>CH₂Cl₂(10)</td>
<td>20°, 15 min.</td>
<td>Re(CO)₅SnClₓPh₃₋ₓ (x = 0,1,2,3)</td>
<td>Sublimation at 60° (5x10⁻³ mm); infrared spectrum b</td>
</tr>
<tr>
<td>Na₂[Fe(CO)₄]²¹,²²(10)</td>
<td>20</td>
<td>Et₂O(150)</td>
<td>-78°, 30 min.</td>
<td>Fe(CO)₂(NO)₂(30%)</td>
<td>Vacuum distillation; infrared spectrum²³</td>
</tr>
<tr>
<td>Na[CpFe(CO)₂]²⁴(14)</td>
<td>14</td>
<td>THF(50)</td>
<td>0°, 20 min.</td>
<td>[CpFe(CO)₂]₂(90%)</td>
<td>Identification in solution by infrared spectroscopy a</td>
</tr>
<tr>
<td>CpFe(CO)₂SnPh₃²⁴(2.0)</td>
<td>3.0</td>
<td>CH₂Cl₂(15)</td>
<td>20°, 15 min.</td>
<td>CpFe(CO)₂-SnClₓPh₃₋ₓ (x = 0,1,2,3)</td>
<td>THF extracts; infrared spectrum²⁵</td>
</tr>
</tbody>
</table>

a. By comparison with the infrared spectrum of the authentic compound.
b. Inferred from the characteristic shift of the carbonyl absorptions to higher wave numbers.
2.2e Reactions of nitrosyl chloride with tricarbonyl($n^5$-cyclopentadienyl) anions of chromium, molybdenum and tungsten, $[\text{CpM(CO)}_3]^-$
(M = Cr, Mo or W).

A THF solution of ClNO was added dropwise, with rapid stirring at room temperature to Na[CpCr(CO)$_3$] (27) (4.89 g, 22.0 mmol) in THF (120 ml). Gas was evolved and a dark solid precipitated during the course of the reaction. The addition of ClNO was continued until the starting anion was completely consumed. The infrared spectrum of the final reaction mixture revealed the presence of CpCr(CO)$_2$(NO) (1) and [CpCr(CO)$_3$]$^2$ (28) as the major carbonyl-containing compounds. The mixture was taken to dryness in vacuo and sublimation of the residue at 60° (5 x 10$^{-3}$ mm) onto a water-cooled probe produced 1.01 g (5.0 mmol, 23% yield) of CpCr(CO)$_2$(NO) which was identified by its infrared spectrum. The reactions of the molybdenum and tungsten containing anions proceeded similarly. If an excess of ClNO was employed in the above syntheses, significant amounts of CpM(NO)$_2$Cl and attendant decomposition products were formed. The physical and chemical properties of the CpM(CO)$_2$(NO) complexes have been previously described (28).

2.2f Reaction of sodium nitrite and acetic acid with sodium tricarbonyl-($n^5$-cyclopentadienyl)tungstate, Na[CpW(CO)$_3$].

To a solution of Na[CpW(CO)$_3$] (27) (1.80 g, 5.1 mmol) and NaNO$_2$ (0.35 g, 5.1 mmol) in nitrogen-saturated water (30 ml) was added dropwise with stirring an aqueous solution (10 ml) of acetic acid (5 mmol). Immediately, gas was evolved and a dark yellow solid formed. The reaction
mixture was further stirred for 0.5 h and then filtered. The resultant solid was dried \textit{in vacuo} and sublimed at 60°C (5 \times 10^{-3} \text{ mm}) onto a water-cooled probe producing 1.01 g of a mixture of CpW(CO)$_2$(NO) and CpW(CO)$_3$H which were identified by their infrared spectra (1, 27, 29).

**2.2g** Reactions of nitrosyl chloride with bis(triphenylphosphine)iminium pentacarbonylhalotungstates, (PPh$_3$)$_2$NW(CO)$_5$X (X = Cl, Br or I), and with tetraethylammonium pentacarbonylchloro (or methyl) tungstate, Et$_4$NW(CO)$_5$X (X = Cl or Me).

A CH$_2$Cl$_2$ solution of ClNO was added dropwise with stirring to (PPh$_3$)$_2$NW(CO)$_5$Br (5.5 g, 5.8 mmol) in CH$_2$Cl$_2$ (50 ml) at -78°C. Gas was evolved and the addition of ClNO was continued until the carbonyl infrared absorptions due to the starting material disappeared. The mixture was taken to dryness \textit{in vacuo}. Sublimation of the residue at 45°C (5 \times 10^{-3} \text{ mm}) onto a water-cooled probe produced 0.82 g (2.0 mmol, 35% yield) of W(CO)$_4$(NO)Br which was identified by its infrared spectrum (30).

The reactions of ClNO with the remaining tungsten complexes were performed similarly and the experimental details are presented in Table III.

**2.2h** Reactions of tetracarbonylhalonitrosyltungstens, W(CO)$_4$(NO)X (X = Cl or Br), with tetrahydrofuran.

A THF solution (20 ml) containing W(CO)$_4$(NO)Cl (0.50 g, 1.4 mmol) was stirred at room temperature until the infrared absorptions
<table>
<thead>
<tr>
<th>Metal Complex (mmol)</th>
<th>Solvent (ml)</th>
<th>Reaction temp.</th>
<th>Products (yields)</th>
<th>Isolation and Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PPh$_3$)$_2$NW(CO)$_5$Cl (5.1)</td>
<td>CH$_2$Cl$_2$ (50)</td>
<td>-78°</td>
<td>W(CO)$_4$(NO)Cl (25%)</td>
<td>A</td>
</tr>
<tr>
<td>(PPh$_3$)$_2$NW(CO)$_5$Br (5.8)</td>
<td>CH$_2$Cl$_2$ (50)</td>
<td>-78°</td>
<td>W(CO)$_4$(NO)Br (35%)</td>
<td>A</td>
</tr>
<tr>
<td>(PPh$_3$)$_2$NW(CO)$_5$I (9.0)</td>
<td>CH$_2$Cl$_2$ (50)</td>
<td>-78°</td>
<td>W(CO)$_4$(NO)I (25%)</td>
<td>A</td>
</tr>
<tr>
<td>Et$_4$NW(CO)$_5$Cl$_3$ (7.7)</td>
<td>THF (75) or CH$_2$Cl$_2$ (100)</td>
<td>-78°</td>
<td>W(CO)$_6$ and W(CO)$_4$(NO)Cl (~8%)</td>
<td>A</td>
</tr>
<tr>
<td>Et$_4$NW(CO)$_5$CH$_3$ (3.6)</td>
<td>CH$_2$Cl$_2$ (50)</td>
<td>-78° or 25°</td>
<td>W(CO)$_6$, W(CO)$_4$(NO)Cl, Et$_4$NW(CO)$_5$I</td>
<td>B</td>
</tr>
</tbody>
</table>

A  Sublimation at 45°C ($5 \times 10^{-3}$ mm), infrared spectrum.\textsuperscript{30}

B  Identification in solution by infrared spectroscopy.\textsuperscript{30, 31}
due to the initial reactant disappeared (ca. 24 h). The solution was taken to dryness in vacuo (5 x 10^{-3} mm) to give a quantitative yield of an orange complex identified as [W(CO)₂(NO)(THF)Cl]₂.

**Anal. Calcd. for W(CO)₂(NO)Cl(C₄H₈O): C, 19.10; H, 2.12; N, 3.71; Cl, 9.39. Found: C, 19.20; H, 2.11; N, 3.56; Cl, 9.64.**

ν(CO) cm⁻¹ (in THF): 2020(s); 1907(s). ν(NO) cm⁻¹ (in THF): 1636(s). Proton NMR, τ (in C₆D₆), THF: 5.60(m); 7.85(m).

Similarly, W(CO)₄(NO)Br was quantitatively converted to [W(CO)₂(NO)(THF)Br]₂ as evidenced by the similarity of its infrared spectrum with that of [W(CO)₂(NO)(THF)Cl]₂.

ν(CO) cm⁻¹ (in THF): 2010(s); 1905(s). ν(NO) cm⁻¹ (in THF): 1635(s).

The [W(CO)₂(NO)(THF)X]₂ (X = Cl or Br) complexes are yellow-orange solids which are stable in air for at least 10 h but are best stored under nitrogen. They are soluble in THF, CH₂Cl₂ and benzene and insoluble in hexanes. However, solutions containing these compounds decompose rapidly upon exposure to air.

### 2.3 Results and Discussion

#### 2.3a Bis(triphenylphosphine)iminium chloride, bromide and iodide,

(PPh₃)₂NX (X = Cl, Br or I).

The (PPh₃)₂NX (X = Cl or Br) compounds can best be prepared in high yields according to eq. 1.
This synthesis has been previously utilized only in the preparation of \((\text{PPh}_3)_2\text{NCl}\) (16), but we have subsequently found that the above reaction can also be directly applied to the high yield synthesis of \((\text{PPh}_3)_2\text{NBr}\). This method, however, fails for the preparation of \((\text{PPh}_3)_2\text{NI}\). The latter compound is conveniently obtained quantitatively by the disproportionation reaction between \((\text{PPh}_3)_2\text{NCl}\) and NaI in ethanol according to the equation

\[
(\text{PPh}_3)_2\text{NCl} + \text{Na}^+ + \text{I}^- \rightarrow (\text{PPh}_3)_2\text{NI} + \text{NaCl}(s)
\]

in which the equilibrium lies well to the side of \((\text{PPh}_3)_2\text{NI}\) by virtue of the low solubility of NaCl in ethanol. The syntheses of \((\text{PPh}_3)_2\text{NX}\) \((X = \text{Br or I})\) have been previously reported although a cumbersome and inefficient method was used (16).

The \((\text{PPh}_3)_2\text{NX}\) compounds are stable indefinitely in air and water. However, contrary to a previous report (16), we find them to be quite hygroscopic as shown by elemental analyses and proton NMR spectroscopic investigations. Consequently, if the presence of water is detrimental in subsequent reactions involving these salts, they must be stored in a desiccator. The compounds are thermally stable even at their relatively high melting points which are in excess of 250°C. Their chemical and physical properties are not unlike those of tetraethylammonium salts except that, surprisingly, the \((\text{PPh}_3)_2\text{NX}\) compounds are very soluble in chlorinated solvents. The geometric and electronic
structures of the \([\text{(PPh}_3\text{)}_2\text{N}]^+\) cation have been the subjects of considerable study and both a bent and linear arrangement of P-N-P atoms have been found (33, 34).

The use of \([\text{(PPh}_3\text{)}_2\text{N}]^+\) as a counterion in the isolation of transition metal carbonyl anions is of immense value. Not only are crystalline samples of the carbonyl anions readily obtainable, but these salts are often air stable in the solid state for many hours. Also, unlike the alkali metal salts of carbonyl anions, the \([\text{(PPh}_3\text{)}_2\text{N}]^+\) derivatives are very soluble and stable in chlorinated solvents. In fact, this enhanced stability has been highly beneficial in the x-ray structural determinations of many interesting mono- and poly-nuclear metal carbonyl complexes (33).

2.3b Bis(triphenylphosphine)iminium pentacarbonylhalotungstates,
\((\text{PPh}_3\text{)}_2\text{NW(CO)}_5\text{X} \ (X = \text{Cl, Br or I}).\)

The \((\text{PPh}_3\text{)}_2\text{NX} \ (X = \text{Cl, Br or I})\) salts react with \(\text{W(CO)}_6\) in refluxing DME with the evolution of gas to give virtually quantitative yields of the \((\text{PPh}_3\text{)}_2\text{NW(CO)}_5\text{X}\) complexes, as in eq. 3.

\[(\text{PPh}_3\text{)}_2\text{NX} + \text{W(CO)}_6 \rightarrow (\text{PPh}_3\text{)}_2\text{NW(CO)}_5\text{X} + \text{CO} \quad 3.\]

These syntheses are comparable to those reported for the preparation of the \(\text{Et}_4\text{NW(CO)}_5\text{X}\) complexes in diglyme at 120°C (31). However, the reactions reported here are performed with great facility at 85°C and are complete in six hours. The lower reaction temperature and the shorter reaction
time serve to eliminate any accompanying decomposition products which may arise from the pyrolysis of the desired materials.

Unlike the $\text{Et}_4\text{NW(CO)}_5\text{X}$ compounds, the $[(\text{PPh}_3)_2\text{N}]^+$ derivatives are not photolytically decomposed by ordinary lighting, and they are also more stable toward atmospheric oxidation. In fact, as solids they are stable in air for several days and their solutions may be exposed to air for a short period of time without noticeable decomposition. In contrast, the $[\text{Et}_4\text{N}]^+$ containing compounds are so unstable in solution that the acquisition of consistently accurate infrared data is difficult.

The solution infrared spectra of the $(\text{PPh}_3)_2\text{NW(CO)}_5\text{X}$ complexes display the expected three-band pattern similar to the isostructural neutral compounds Mn(CO)$_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br} \text{ or I}$) (35) and W(CO)$_5\text{L}$ ($\text{L} = \text{amine or phosphine}$) (36). Of course, the C-0 stretching frequencies of the ionic species occur at much lower frequencies due to the enhanced metal-carbonyl backbonding.

Because of their greater solubility in common organic solvents, the $[(\text{PPh}_3)_2\text{N}]^+$ salts are more useful than the $[\text{Et}_4\text{N}]^+$ analogs as reactive synthetic precursors (17, 37-40). In particular, they can be readily converted to the W(CO)$_4$(NO)$_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br} \text{ or I}$) complexes as described subsequently. In summary it should be noted that a wide variety of $(\text{PPh}_3)_2\text{NM(CO)}_5\text{X}$ complexes, where $\text{X}$ is a halogen or pseudo-halogen, have been previously prepared by diverse means (37-41). However, the preparative methods described in this thesis are far superior simply because the desired products are obtained much more
conveniently and in quantitative yields.

2.3c Reactions of nitrosyl chloride with metal carbonyl anions.

It is a well known fact that transition metal carbonyl anions are sufficiently nucleophilic to displace a halide from both organic and inorganic halides according to the general reaction scheme

\[ [\text{Cp}_m\text{M(CO)}_n^-] + RX \rightarrow \text{Cp}_m\text{M(CO)}_nR + X^- \]

where \( m = 0 \) or 1; \( n = 1-5 \) depending on M (11). The success of the above reaction is dependent, among other variables, on the nucleophilicity of the anion, and the rate of such a reaction has been used as a measure of the nucleophilic strength of some metal carbonyl anions (42).

In a conversion analogous to the above reaction we find that some of these anions will also displace the chloride from nitrosyl chloride thereby providing a convenient synthetic route to neutral nitrosoyl compounds. The method can also be applied to the di-anionic complex, \([\text{Fe(CO)}_4]^{2-}\). Except for the preparation of \((\text{RB(pz)}_3)^-\text{M(CO)}_2(\text{NO})\) \((\text{RB(pz)}_3 = \text{tris(pyrazoyl)borate}; \text{R} = \text{H or pz}; \text{M} = \text{Cr, Mo or W})\) from \([((\text{RB(pz)}_3)^-\text{M(CO)}_3])^-\) (10), this class of reactions has largely been ignored. Typical examples of such reactions are summarized in eq. 5-8.

\[ (\text{PPh}_3)_2\text{NMn(CO)}_5 + \text{CINO} \xrightarrow{\text{CH}_2\text{Cl}_2} \text{Mn(CO)}_4(\text{NO}) \] 5.

\[ \text{Na}_2[\text{Fe(CO)}_4] + 2\text{CINO} \xrightarrow{\text{Et}_2\text{O}} \text{Fe(CO)}_2(\text{NO})_2 \] 6.

\[ \text{Na}[\text{CpM(CO)}_3] + \text{CINO} \xrightarrow{\text{THF}} \text{CpM(CO)}_2(\text{NO}) \]

\((\text{M} = \text{Cr, Mo or W})\) 7.
\[ A[W(CO)_5X] + ClNO \xrightarrow{\text{THF or CH}_2\text{Cl}_2} W(CO)_4(NO)X \] (8.

\( A = (\text{PPh}_3)_2\text{N}; \ X = \text{Cl, Br or I}; \ A = \text{Et}_4\text{N}; \ X = \text{Cl or Me} \)

All these conversions are accompanied by gas evolution and they proceed readily in reasonable yields. The attendant formation of an inorganic chloride undoubtedly provides a strong thermodynamic driving force for these reactions.

It appears that nitrosyl chloride behaves as a nitrosonium salt in its reactions with anions even though the molecule itself is bent and the N-Cl bond is largely covalent. For instance, microwave spectroscopy of isotopically labelled ClNO molecules shows the O-N-Cl angle to be 113.3° (43), and an N-O bond order of 1.9 is obtained from force constant calculations utilizing infrared data (15). Furthermore, the N-O stretching frequency of ClNO in a dichloromethane solution occurs at 1845 cm\(^{-1}\) while in nitrosonium salts, which contain the triply bonded nitrosonium cation, the values fall within the 2150-2400 cm\(^{-1}\) range (44). These observations therefore suggest that the nitrosyl chloride molecule is mainly covalent containing an sp\(^2\) hybridized nitrogen atom and an N-O double bond. Nevertheless, the anomalously large N-Cl distance of 1.975 ± 0.005 Å (43) has been explained in terms of the contribution of ionic resonance forms such as

\[ \overset{\cdot}{\underset{\cdot}{\overset{\cdot}{\underset{\cdot}{O=N^+}}} \overset{Cl^-}}{\text{Cl}} \]
In the gaseous state, at 20°C, nitrosyl chloride disproportionates to NO and Cl\textsubscript{2} to the extent of about 0.5% (44). Although the extent of this equilibrium in solutions of dichloromethane or tetrahydrofuran is not known, evidence for it is presented in Chapter IV. Chemically, nitrosyl chloride often behaves as a strong oxidizing agent, being reduced to Cl\textsuperscript{-} and NO or N\textsubscript{2} (15, 45, 46).

2.3c1 Reactions of nitrosyl chloride with organometallic anions of manganese, rhenium and iron.

The reaction of nitrosyl chloride with (PPh\textsubscript{3})\textsubscript{2}NMn(CO)\textsubscript{5} in dichloromethane proceeds smoothly and cleanly at room temperature to give Mn(CO)\textsubscript{4}(NO) in good yields. However, the analogous reaction involving Na[Re(CO)\textsubscript{5}] affords Re\textsubscript{2}(CO)\textsubscript{10} as the only carbonyl containing compound. It appears that the [Re(CO)\textsubscript{5}]\textsuperscript{-} anion is oxidized to the dimer by nitrosyl chloride according to eq. 9.

\[
\text{Na[Re(CO)\textsubscript{5}]} + \text{ClNO} \rightarrow \frac{1}{2}\text{Re\textsubscript{2}(CO)\textsubscript{10}} + \text{NaCl} + \text{NO} \quad 9.
\]

In this connection the use of nitrosyl chloride as an oxidant has already been mentioned and indeed, nitrosonium salts have been used previously in the oxidation of organometallic anions. An example of such an oxidation is the formation of the paramagnetic Cr(CO)\textsubscript{5}I complex as indicated in eq. 10 (45).

\[
\text{[Cr(CO)\textsubscript{5}I]}^- + \text{NOPF\textsubscript{6}} \rightarrow \text{Cr(CO)\textsubscript{5}I} + \text{PF\textsubscript{6}^-} + \text{NO} \quad 10.
\]
The dianionic Na$_2$[Fe(CO)$_4$] complex reacts with nitrosyl chloride to form Fe(CO)$_2$(NO)$_2$ as the only nitrosyl containing species. The possibility that this reaction proceeds through the well known [Fe(CO)$_3$(NO)]$^-$ anion was not investigated in our work. However, the infrared spectrum of the final reaction mixture confirms the presence of small amounts of Fe$_3$(CO)$_{12}$, likely produced by the nitrosyl chloride oxidation of [Fe(CO)$_4$]$^{2-}$. This is not surprising in light of the fact that a similar oxidation of [HFe(CO)$_4$]$^-$ by manganese dioxide constitutes an important synthetic route to Fe$_3$(CO)$_{12}$ (29, 47, 48).

The relative nucleophilicities of a variety of metal carbonyl and cyclopentadienylmetal carbonyl anions, in the presence of Bu$_4$NCIO$_4$, have been compiled and the factors which determine nucleophilic character have been discussed (42). The reactions of nitrosyl chloride with the anions described in this chapter suggest a relationship between the reaction products and the nucleophilicity of the anions. Hence, the mildly nucleophilic [Mn(CO)$_5$]$^-$ anion readily yields Mn(CO)$_4$(NO) while the more nucleophilic [Re(CO)$_5$]$^-$ anion simply gives the oxidation product, Re$_2$(CO)$_{10}$. Not surprisingly therefore, the most nucleophilic anion thus far investigated, [CpFe(CO)$_2$]$^-$, is oxidized nearly quantitatively to [CpFe(CO)$_2$]$_2$.

In an effort to reduce the nucleophilic behavior of [Re(CO)$_5$]$^-$ and [CpFe(CO)$_2$]$^-$ the Ph$_3$Sn derivatives of these anions were prepared. Generally, complexes of the type Ph$_3$SnM, where M is a transition metal carbonyl moiety, contain a predominantly covalent tin-metal bond. Consequently, it is not unreasonable that the transition metal carbonyl
group will possess a greatly reduced nucleophilicity. However, the subsequent reactions of nitrosyl chloride with $\text{Ph}_3\text{SnRe(CO)}_5$ and $\text{CpFe(CO)}_2\text{SnPh}_3$ in dichloromethane yield only the mixed $\text{Re(CO)}_5\text{SnCl}_x\text{Ph}_{3-x}$ and $\text{CpFe(CO)}_2\text{SnCl}_x\text{Ph}_{3-x}$ complexes, where $x = 1, 2$ or $3$. The cleavage of the tin-carbon bond rather than the tin-metal bond parallels the reactions of halogens and hydrogen halides with $\text{Ph}_3\text{SnMn(CO)}_5$, $\text{Ph}_3\text{SnRe(CO)}_5$, and $\text{CpFe(CO)}_2\text{SnPh}_3$ (24, 49-51).

The success of the reaction of nitrosyl chloride with $\text{(PPh}_3\text{)}^2\text{NMn(CO)}_5$ prompted the attempted isolation of the $[\text{Re(CO)}_5]^-$ and $[\text{CpFe(CO)}_2]^-$ anions as their $[(\text{PPh}_3)_2\text{N}]^+$ salts. Unfortunately, all efforts were thwarted by the persistent formation of $\text{Re}_2(\text{CO})_{10}$, $[\text{CpFe(CO)}_2]_2$ and attendant decomposition products. Even though $[\text{Mn(CO)}_5]^-$ and $\text{HMn(CO)}_5$ react with Diazald to yield $\text{Mn(CO)}_4(\text{NO})$ (18), the same reaction could not be effected with either $[\text{Re(CO)}_5]^-$ and $[\text{CpFe(CO)}_2]^-$ or their respective hydrido derivatives. While there is no a priori reason for their inherent instability under ambient conditions, the $\text{Re(CO)}_4(\text{NO})$ and $\text{CpFe(CO)}(\text{NO})$ complexes still remain unknown.

2.3c2 Reactions of nitrosyl chloride with tricarbonyl($n^5$-cyclopentadienyl) anions of chromium, molybdenum and tungsten, $[\text{CpM(CO)}_3]^-$

$\text{(M = Cr, Mo or W)}.$

Treatment of $\text{Na[CpM(CO)}_3]$ with nitrosyl chloride in tetrahydrofuran yields a mixture of the $\text{CpM(CO)}_2(\text{NO})$, $\text{CpM(NO)}_2\text{Cl}$ and $[\text{CpM(CO)}_3]_2$ compounds. Even though the anions of chromium and molybdenum are slightly
less nucleophilic than \([\text{Mn(CO)}_5]^-\) (42), a significant amount of oxidation to \([\text{CpM(CO)}_3]_2\) occurs. The formation of \(\text{CpM(NO)}_2\text{Cl}\) arises from the oxidative substitution of nitrosyl chloride on the initial \(\text{CpM(CO)}_2(\text{NO})\) products according to eq. 11.

\[
\text{CpM(CO)}_2(\text{NO}) + \text{ClNO} \xrightarrow{-} \text{CpM(NO)}_2\text{Cl} + 2\text{CO}
\]  

(M = Cr, Mo or W)

This is a particular example of the broad class of reactions between nitrosyl chloride and neutral metal carbonyl complexes to be discussed in Chapters III and IV.

The preparation of \(\text{Fe(CO)}_2(\text{NO})_2\) by the treatment of \(\text{Na[Fe(CO)}_3\text{NO]}\) or \(\text{Na[Fe(CO)}_4\text{H]}\) with aqueous sodium nitrite and acetic acid has been previously reported (52, 53). The reaction of \(\text{Na[CpW(CO)}_3\text{]}\) with these reagents proceeds analogously whereupon a mixture of \(\text{CpW(CO)}_2(\text{NO)}\) and \(\text{CpW(CO)}_3\text{H}\) is formed. The latter complex is undoubtedly produced by the direct protonation of \([\text{CpW(CO)}_3]\) by acetic acid, a well known synthesis (27). However, difficulty in separating these two products renders this synthetic route impractical. The very high yield syntheses of all three \(\text{CpM(CO)}_2(\text{NO})\) complexes developed during the course of this work are detailed in Chapter IV.
2.3c3 Reactions of nitrosyl chloride with bis(triphenylphosphine)-iminium pentacarbonylhalotungstates, \((\text{PPh}_3)_2\text{NW(CO)}_5\text{X} \ (\text{X} = \text{Cl, Br or I})\) and tetraethylammonium pentacarbonylchloro (or methyl) tungstate, \(\text{Et}_4\text{NW(CO)}_5\text{X} \ (\text{X} = \text{Cl or Me})\).

All three \((\text{PPh}_3)_2\text{NW(CO)}_5\text{X}\) complexes react with nitrosyl chloride in dichloromethane at \(-78^\circ\text{C}\) to give moderate yields of \(\text{W(CO)}_4(\text{NO})\text{X}\) according to eq. 12. If excess nitrosyl chloride is used,

\[
(\text{PPh}_3)_2\text{NW(CO)}_5\text{X} + \text{ClNO} \rightarrow \text{W(CO)}_4(\text{NO})\text{X} + (\text{PPh}_3)_2\text{NCI} + \text{CO}
\]

or if the reaction is attempted at room temperature, the yields of the desired products are reduced markedly.

The \(\text{W(CO)}_4(\text{NO})\text{X}\) complexes have been previously synthesized by the action of p-toluenesulphonic acid and pentyl nitrite, or nitrosonium hydrogen sulfate acid on \(\text{Et}_4\text{NW(CO)}_5\text{X}\) (30). Our repeated attempts to obtain the desired products in yields which even approximate those reported met with failure. Another reported route to the chloride and iodide containing compounds involves the treatment of \(\text{HW}_2(\text{CO})_9(\text{NO})\) with nitrosyl chloride and iodine respectively (54). However, the required \(\text{HW}_2(\text{CO})_9(\text{NO})\) complex can be obtained from a two-step synthesis in yields of only 40% (55, 56).

Unlike all of the previous syntheses discussed above, the present reactions of nitrosyl chloride with \((\text{PPh}_3)_2\text{NW(CO)}_5\text{X}\) afford the \(\text{W(CO)}_4(\text{NO})\text{X}\) complexes without the attendant formation of \(\text{W(CO)}_6\). Thus, the difficult task of separating the physically similar \(\text{W(CO)}_4(\text{NO})\text{X}\) and \(\text{W(CO)}_6\) compounds is avoided. Also, since the \((\text{PPh}_3)_2\text{NW(CO)}_5\text{X}\)
complexes are readily obtained in quantitative yield, as discussed earlier in this chapter, this preparative route is indeed attractive.

Interestingly, the choice of countercation in the reactions between the \([W(CO)_5X]^-\) salts and nitrosyl chloride has a profound effect on product distribution. Unlike the \([(PPh_3)_2N]^+\) salts, the \(Et_4NW(CO)_5X\) compounds readily yield \(W(CO)_6\) as the major product regardless of the solvent employed.

\(Et_4NW(CO)_5Me\), when treated with nitrosyl chloride in dichloromethane, produces a mixture of \(W(CO)_4(NO)Cl\), \(W(CO)_6\) and \(Et_4NW(CO)_5Cl\). The latter compound is likely formed in a manner similar to the reaction of hydrogen chloride with \(Me_4NW(CO)_5R\), where \(R = Me\) or \(CH_2Ph\). For example, treatment of \(Me_4NW(CO)_5CH_2Ph\) with a slight excess of hydrogen chloride yields toluene (94%) and \(Me_4NW(CO)_5Cl\) (32). Once the primary product, \(Et_4NW(CO)_5Cl\), is formed, subsequent reaction with nitrosyl chloride produces \(W(CO)_4(NO)Cl\) and \(W(CO)_6\) as previously described. In support of this reaction pathway it was found that an excess of nitrosyl chloride simultaneously reduced the final yield of \(Et_4NW(CO)_5Cl\) and increased the yields of \(W(CO)_4(NO)Cl\) and \(W(CO)_6\). The anticipated product from the reaction between nitrosyl chloride and \(Et_4NW(CO)_5Me\) was the as yet unknown \(W(CO)_4(NO)Me\) complex. This type of conversion is not without precedent since the anions \([R_3M'M(CO)_5]^-\) (\(M = Mo\) or \(W\); \(M' = Si, Ge, Sn\) or \(Pb\); \(R = Me\) or \(Ph\)) react with \(NOPF_6\) to give \(R_3M'M(CO)_4(NO)\) in yields ranging from 7 to 74% (46i). Our attempts to prepare \(W(CO)_4(NO)Me\) by the action of methyl Grignard reagents, methyllithium and trimethylaluminum on \(W(CO)_4(NO)X\) complexes
failed, probably due to the great lability of the carbon monoxide ligand in the halo-containing reactant.

2.3d Reactions of tetracarbonylhalonitrosyltungstens, $W(CO)_4(NO)X$ ($X = Cl$ or $Br$), with tetrahydrofuran.

The facile substitution of either one or two carbonyl ligands in $W(CO)_4(NO)X$ ($X = Cl$, $Br$ or $I$) has been amply demonstrated (57, 58). For example, reaction with stoichiometric quantities of either $PPh_3$ or $AsPh_3$ in refluxing chloroform yields $\text{mer-}W(CO)_3(NO)(L)X$, whereas excess ligand produces $\text{cis-}W(CO)_2(NO)(L)_2X$. If carbonyl substitution is effected using bis(diphenylarsino)methane (dam) only the monodentate $\text{mer-}W(CO)_3(NO)(\text{dam})X$ and $\text{cis-}W(CO)_2(NO)(\text{dam})_2X$ complexes are formed. However, when half the stoichiometric amount of dam is employed, the product obtained is $[W(CO)_2(NO)X]_{2}\text{dam}$, which is believed to contain both halide and dam bridges (58).

We discovered that stirring a tetrahydrofuran solution of $W(CO)_4(NO)X$ ($X = Cl$ or $Br$) for 24 hours resulted in the quantitative formation of the corresponding $[W(CO)_2(NO)(\text{THF})X]_2$ complexes. The presence of tetrahydrofuran in these compounds was confirmed by elemental analyses and proton NMR spectroscopy which displayed the characteristic proton resonances at $\tau5.60(m)$ and $\tau7.85(m)$. As expected, these values are somewhat lower than the corresponding values of uncomplexed tetrahydrofuran. The electron donation from the THF oxygen atom to the central metal is expected to deshield the protons on the $\alpha$-carbon more than those on the $\beta$-carbon atoms. In agreement with this
expectation, the α-carbon proton resonances do indeed experience the greater downfield shift.

The \([\text{W(CO)}_2(\text{NO})(\text{THF})X]_2\) complexes are believed to be dimeric with structures similar to that proposed for \([\text{W(CO)}_2(\text{NO})X]_2\) dam except that the bridging dam is replaced by two terminally bonded tetrahydrofuran ligands, as shown by two possible structures A and B. Consistent with this belief, both the tetrahydrofuran and dam containing compounds display similar infrared spectra which are characterized by two carbonyl and one nitrosyl stretching absorptions (58). In compliance with the "18-electron rule", the dimers presumably are held together by halide bridges without the aid of a metal-metal bond.
CHAPTER III

REACTIONS OF NITROSYL CHLORIDE WITH NEUTRAL METAL CARBONYL COMPLEXES

3.1 Introduction

As described in the previous chapter the reactions of nitrosyl halides with metal carbonyl or n5-cyclopentadienylmetal carbonyl anions had received virtually no attention until this study. On the other hand, their reactions with neutral complexes have been previously investigated, although by no means exhaustively (9). Because the nitrosyl halides are powerful oxidants, strict attention must be given to the reaction conditions which are, by and large, empirically determined. Thus the temperature, the solvent, the phase and especially the stoichiometry of the reaction are crucial in determining the reaction products. Reactive substrates include non-carbonyl as well as carbonyl containing compounds. In the former category, the nitrosyl halides usually add oxidatively to the metal complex with or without ligand displacement. However, the majority of the published reports describe the reactions of nitrosyl halides with transition metal complexes which contain one or more carbonyl ligands, and only these are considered here.
At this point a clear distinction must be made between the nitrosyl halides and various nitrosonium salts. The latter reagents invariably form cationic nitrosyl complexes, as shown in eq. 13,

\[
\text{Cp}\text{M(CO)}_n + \text{NO}^+\text{A}^- \rightarrow [\text{Cp}\text{M(CO)}_{n-1}(\text{NO})]^+\text{A}^- + \text{CO}
\]  

(\text{m} = 0 \text{ or } 1 \text{ and } n = 2-6 \text{ depending on M})

since anions, A\text{--}, such as PF$_6$\text{--} and BF$_4$\text{--} show a remarkable propensity to remain uncoordinated. Only one mole equivalent of carbon monoxide is displaced and the product formed is a 1:1 electrolyte. Any remaining coordinated carbonyl ligands are usually quite susceptible to displacement by even weakly nucleophilic neutral or anionic molecules such as acetone or halide anions (59, 60). The weakened metal-carbon bond in cationic carbonyl compounds is consistent with current bonding theories, and the resultant enhanced lability of the CO ligand can be advantageously exploited in the synthesis of both cationic and neutral carbonyl compounds.

On the other hand, the nitrosyl halides almost always react with metal carbonyls to form products which contain a coordinated halide ligand. However, two cases of cationic products similar to those obtained with the nitrosonium salts have been reported (61, 72a). For instance, both ClNO and BrNO react with Fe(CO)$_3$(PPh$_3$)$_2$ in acetonitrile to give [Fe(CO)$_2$(NO)(PPh$_3$)$_2$]$^+X^-$. By far the most common mode of reaction is that depicted in
equation 14

\[ \text{Cp}_m \text{M(CO)}_n + \text{XNO} \rightarrow \text{Cp}_m \text{M(CO)}_{n-2} \text{(NO)}X + 2\text{CO} \] 14.

\[(m = 1 \text{ or } 2 \text{ and } n = 2-6 \text{ depending on } M)\]

which involves the coordination of one mole of XNO for every two moles of CO displaced. Since NO is a stronger \(\pi\)-acceptor than CO, it effectively competes with CO in the extent of \(\pi\)-backbonding with the central metal, thereby resulting in a weaker metal-carbon bond. Any remaining carbonyl ligand in the initial product is now sufficiently labile to be displaced even by a chlorine atom which is already coordinated to a transition metal. The result is the formation of dimers, or polymers of indeterminate length, which contain chlorine bridges. These general principles are exemplified in the following syntheses.

\[ \text{Re(CO)}_4(L)\text{Cl} + \text{ClNO} \rightarrow \text{Re(CO)}_2(\text{NO})\text{LCl}_2 + 2\text{CO} \] 63

\[(L = \text{C}_5\text{H}_5\text{N}, \text{C}_5\text{H}_5\text{NO}, \text{C}_4\text{H}_8\text{S}, \text{Bu}_3\text{P}, \text{Ph}_3\text{PO}, \text{4-picoline or 3,4-lutidine})\]

\[ \text{M(CO)}_6 + 2\text{ClNO} \rightarrow [\text{M(NO)}_2\text{Cl}_2]_n + 6\text{CO} \] 64

\[(M = \text{Mo or W})\]

\[ \text{Mo(CO)}_4(\text{PPh}_3)_2 + 2\text{BrNO} \rightarrow \text{Mo(NO)}_2\text{Br}_2(\text{PPh}_3)_2 + 4\text{CO} \] 65

\[ \text{LM(CO)}_2(\text{N}_2\text{Ph}) + \text{ClNO} \rightarrow \text{LM(NO)(N}_2\text{Ph})\text{Cl} + 2\text{CO} \] 66

\[(M = \text{Mo or W}; L = \text{HB}(pz)_3; M = \text{Mo}; L = \text{Cp})\]
\[
RB(pz)_3M(CO)_2(NO) + ClNO \rightarrow RB(pz)_3M(NO)_2Cl + 2CO \tag{10}
\]

\( (M = Mo; R = H \text{ or } pz; M = W; R = H) \)

\[
HB(3,5-Me_2pz)_3Mo(CO)_2(NO) + ClNO \rightarrow HB(3,5-Me_2pz)_3Mo(NO)_2Cl + 2CO
\tag{10}
\]

The last two of these reactions have a counterpart in the cyclopentadienyl derivatives, \( \text{CpM(CO)}_2(NO) \) (\( M = \text{Cr, Mo or W} \)), and the reaction of ClNO with these complexes has been developed into a high yield synthetic route to the \( \text{CpM(NO)}_2Cl \) compounds, as described in Chapter IV. In this chapter the reactions of ClNO with \( \text{Fe(CO)}_5 \), \( \text{Fe(CO)}_2(NO)_2 \), \([\text{CpFe(CO)}_2]_2 \), \( \text{Co(CO)}_3(NO) \) and \( \text{CpCo(CO)}_2 \) are described.

### 3.2 Experimental

All experimental procedures described here were performed under the same general conditions detailed in section 2.2.

**Reactions of nitrosyl chloride with neutral complexes of iron and cobalt.**

To a vigorously stirred solution of \( \text{Fe(CO)}_5 \) (7.5 ml, 58 mmol) in \( \text{CH}_2\text{Cl}_2 \) (30 ml) was added at room temperature a \( \text{CH}_2\text{Cl}_2 \) (50 ml) solution containing ClNO (7.37 g, 112 mmol). Gas was rapidly evolved and the reaction mixture became violet-black. The final mixture was taken to dryness and the residue was extracted into hexanes (150 ml). The extract was cooled to \(-78^\circ\text{C}\) thereby precipitating a dark red-brown solid which
Table IV. Reactions of Nitrosyl Chloride with some Neutral Complexes of Iron and Cobalt.

<table>
<thead>
<tr>
<th>Transition metal compd. (mmol)</th>
<th>Amt. of ClNO (mmol)</th>
<th>Solvent (ml)</th>
<th>Temp.</th>
<th>Products (yields)</th>
<th>Isolation and Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CO)$_2$(NO)$_2$ (28.8)</td>
<td>40</td>
<td>Pentane(20)</td>
<td>25°</td>
<td>Fe(NO)$_3$Cl (31%)</td>
<td>Precipitated from pentane at -78°; infrared spectrum$^{2,69,70}$</td>
</tr>
<tr>
<td>[CpFe(CO)$_2$]$_2$ (1.4)</td>
<td>4.0</td>
<td>CH$_2$Cl$_2$(30)</td>
<td>25°</td>
<td>CpFe(CO)$_2$Cl (51%)</td>
<td>Sublimation at 50-60° ($5\times10^{-3}$mm); infrared spectrum$^68$</td>
</tr>
<tr>
<td>Co(CO)$_3$(NO)$_2$ (4)</td>
<td>a</td>
<td>CH$_2$Cl$_2$(60)</td>
<td>-78°</td>
<td>[Co(NO)$_2$Cl]$_2$</td>
<td>Identification in solution by infrared spectroscopy$^{2,69,70}$</td>
</tr>
<tr>
<td>CpCo(CO)$_2$ (10)</td>
<td>a</td>
<td>CH$_2$Cl$_2$(50)</td>
<td>-78°</td>
<td>[Co(NO)$_2$Cl]$_2$</td>
<td>Sublimation at 90-100° ($5\times10^{-3}$mm); infrared spectrum$^{2,69,70}$, elemental analysis.</td>
</tr>
</tbody>
</table>

a A CH$_2$Cl$_2$ solution of ClNO was added until the disappearance of the infrared absorptions due to the initial reactant.
was collected by suction filtration. In this manner 3.0 g (17 mmol, 29% yield) of Fe(NO)₃Cl, identified by infrared spectroscopy (2), was isolated. Fe(NO)₃Cl is unstable at 25°C readily liberating nitric oxide, especially under vacuum, so that an acceptable elemental analysis for this compound could not be obtained.

The reactions of ClNO with other neutral complexes of iron and cobalt were performed similarly and the experimental details are summarized in Table IV.

3.3 Results and Discussion

3.3a Reaction of nitrosyl chloride with pentacarbonyliron, Fe(CO)₅.

When a dichloromethane solution of Fe(CO)₅ is treated with nitrosyl chloride vigorous gas evolution occurs and the reaction mixture becomes violet-black. The only nitrosyl containing product, Fe(NO)₃Cl, is subsequently isolated in 29% yield and identified by its characteristic infrared spectrum (69, 70). Optimum yields are obtained when the ratio of nitrosyl chloride to Fe(CO)₅ is 2:1, and ratios larger than this result in a rapidly diminishing yield of Fe(NO)₃Cl. In view of the high oxidizing property of nitrosyl chloride, FeCl₃ is likely a byproduct of this reaction, although this compound was not isolated and identified.

No infrared spectral evidence was obtained for the possible formation of Fe(CO)₂(NO)₂ as an intermediate. However, treatment of Fe(CO)₂(NO)₂ with nitrosyl chloride under similar experimental conditions did produce Fe(NO)₃Cl in comparable yield. This preparative route to Fe(NO)₃Cl utilizing Fe(CO)₅ is much more convenient than the previously reported procedure (71).
Fe(NO)$_3$Cl is a dark red-brown solid which is soluble in common organic solvents including hexanes. The complex loses nitric oxide at room temperature even under nitrogen. Sublimation under vacuum is possible but only with extensive attendant decomposition. This substantial thermal instability thwarts all attempts to obtain an acceptable elemental analysis for this compound.

Previous investigations of the reactions of ClNO with Fe(CO)$_5$ demonstrate that different products may be obtained depending on reaction conditions. In liquid hydrogen chloride the isolable product is [Fe(CO)$_5$(NO)]$^+$Cl$^-$ which rapidly dissociates to ClNO and Fe(CO)$_5$ at room temperature (72a). The surprisingly low N-O stretching frequency of 1610 cm$^{-1}$ displayed by this compound is indicative of a nitrosyl ligand coordinated as NO$^-$, i.e. a bent M-N-O geometry. Apart from the difference in the metal-nitrosyl bonding modes, the equilibrium behaviour of ClNO with Fe(CO)$_5$ bears resemblance to the coordination reaction of ClNO with a variety of metal halides, as exemplified by eq. 15 (15).

$$
\text{ClNO} + \text{FeCl}_3 \rightarrow \text{ClNO} \cdot \text{FeCl}_3 \rightarrow \text{NO}^+ + \text{FeCl}_4^-
$$

15.

In contrast, other workers have found that nitrosyl chloride and Fe(CO)$_5$, in a ratio of 1.5:1, react at room temperature in a steel bomb to give a mixture of Fe(CO)$_2$(NO)$_2$ and Fe(CO)$_5$ (72b). As the ratio increases, lower yields of Fe(CO)$_2$(NO)$_2$ are obtained until, at the ratio of 2.7:1, only a mixture of carbon monoxide and oxides of nitrogen is found. Unfortunately, the reaction residue has not been examined for the possible
presence of Fe(NO)$_3$Cl. If the reaction is repeated in pentane under ambient temperature and pressure, only a mixture of Fe(CO)$_2$(NO)$_2$ and Fe(CO)$_5$ is obtained.

3.3b Reaction of nitrosyl chloride with bis[dicarbonyl($\eta^5$-cyclopentadienyl)iron], [CpFe(CO)$_2$]$_2$.

Nitrosyl chloride reacts with dimeric metal carbonyl complexes to produce monomeric, dimeric or polymeric nitrosyl compounds as shown in eq. 16-18 (3, 63, 73).

\[
[CpRu(CO)$_2$]_2 + CINO \rightarrow CpRu(NO)Cl_2 \quad 16.
\]

\[
[Re(CO)$_4$Cl]_2 + CINO \rightarrow [Re(CO)$_2$(NO)Cl]_2 \quad 17.
\]

\[
[M(CO)$_4$Cl]_2 + CINO \rightarrow [M(NO)Cl$_3$]_n + [M(NO)$_2$Cl$_2$]_2 \quad 18.
\]

(M = Mo or W)

In contrast to the reaction depicted in eq. 16 we find that [CpFe(CO)$_2$]$_2$ is cleaved by CINO without the formation of a nitrosyl compound. The resultant CpFe(CO)$_2$Cl complex may be formed according to the plausible reaction scheme

\[
[CpFe(CO)$_2$]_2 + CINO \rightarrow CpFe(CO)$_2$Cl + [CpFe(CO)$_2$]$^- + NO^+
\]

followed by

\[
[CpFe(CO)$_2$]$^- + NO^+ \rightarrow \frac{1}{2}[CpFe(CO)$_2$]_2 + NO
\]
with the second step being identical to the oxidation of \([\text{CpFe(CO)}_2]^-\) by \text{ClNO}\ as described in Chapter II. This transformation parallels the known air oxidation of \([\text{CpFe(CO)}_2]_2\) in the presence of \text{HCl}\ (68), for which the following reaction sequence may be surmised.

\[
[\text{CpFe(CO)}_2]_2 + \text{HCl} \xrightarrow{\Delta} \text{CpFe(CO)}_2\text{Cl} + \text{CpFe(CO)}_2\text{H}
\]

\[
2\text{CpFe(CO)}_2\text{H} \xrightarrow{\text{O}_2} [\text{CpFe(CO)}_2]_2 + \text{H}_2\text{O}
\]

The hydrido complex is known to undergo air oxidation to give the initial reactant dimer. In a similar manner, the \(M_2(\text{CO})_{10}\) (\(M = \text{Mn}\) or \(\text{Re}\)) compounds are cleaved by \text{ClNO}\ to afford only the \(M(\text{CO})_5\text{Cl}\) species (74). The formation of the metal halide complexes reported here does not comprise a useful synthetic method since better yields are more conveniently obtained according to existing procedures (68, 75).

3.3c Reactions of nitrosyl chloride with tricarbonylnitrosylcobalt, \(\text{Co(CO)}_3(\text{NO})\), and dicarbonyl(\(\eta^5\)-cyclopentadienyl)cobalt, \(\text{CpCo(CO)}_2\).

Both \(\text{Co(CO)}_3(\text{NO})\) and \(\text{CpCo(CO)}_2\) react with nitrosyl chloride to give \([\text{Co(NO)}_2\text{Cl}]_2\) in moderate yields. The reaction is rapid even at \(-78^\circ\text{C}\) and the use of excess nitrosyl chloride results in extensive decomposition. The dimeric \([\text{Co(NO)}_2\text{Cl}]_2\) was previously prepared in a manner similar to the preparation of \(\text{Fe(NO)}_3\text{Cl}\) (76). The displacement of olefinic ligands by nitrosyl chloride is not unknown (3), but the displacement of the cyclopentadienyl ligand has not been previously
reported. Thus, the formation of \([\text{Co(NO)}_2\text{Cl}]_2\) from \(\text{CpCo(CO)}_2\) and \(\text{ClNO}\) is unprecedented. Similarly, the \(n^5\)-cyclopentadienyl ligand in \(\text{CpRe(CO)}_3\) has been shown to undergo a similar displacement to yield the \([\text{Re(CO)}_2(\text{NO})\text{Cl}_2]\_2\) dimer (74), which has been previously reported (63).
CHAPTER IV

CYCLOPENTADIENYLNITROSYL COMPLEXES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

4.1 Introduction

The number of cyclopentadienyl nitrosyl complexes of the group VI transition metals has grown steadily in the past two decades. Both mono- and dinuclear species are known, and most display a rich and varied chemistry. The CpM(CO)\(_2\)(NO) (M = Mo or W) compounds have been obtained in very low yields by the treatment of aqueous solutions of Na[CpM(CO)\(_3\)] with nitric oxide (77). Since these nucleophilic anions react with protic solvents to form the hydrido complexes, CpM(CO)\(_3\)H, the synthesis likely occurs by attack of nitric oxide on these hydrido intermediates. The cleavage of the weak metal-metal bond of [CpCr(CO)\(_3\)]\(_2\) with nitric oxide affords the chromium carbonylnitrosyl analog in good yields (78). However, since the dimeric precursor can be obtained only in low yields and with much expenditure of effort (79), this synthetic route is not practical. Although a number of polynuclear carbonyl complexes react with nitric oxide to produce mononuclear nitrosyl derivatives, the metal-metal bonds in [CpM(CO)\(_3\)]\(_2\) (M = Mo or W) are too strong to be cleaved by nitric oxide. A more general nitrosylating agent
is Diazald, which converts CpM(CO)₃H (M = Mo or W) to CpM(CO)₂(NO) in reasonable yields (27, 80). However, it was recently found that the hydrido precursors are not necessary and the synthesis can be performed directly with the anions [CpM(CO)₃]⁻ (M = Cr, Mo or W) (81) thereby eliminating an unnecessary synthetic procedure. A number of substituted complexes CpM(CO)(NO)L containing a variety of donor ligands has been reported (28).

Another series of related compounds can be represented by the general formula CpM(NO)₂Cl, of which the chromium derivative is the most studied. It may be obtained in modest yield when a mixture of CrCl₃ and NaC₅H₅ is treated with nitric oxide (27, 29, 82). The corresponding molybdenum compound is obtained in poor yields by the reaction of TiC₅H₅ with [Mo(NO)₂Cl₂]₂ₙ (83), or by the reaction of NaN₃ with [CpMo(CO)₃NH₃]Cl in hydrochloric acid (84). The previously unknown tungsten analog, obtained by the treatment of [CpW(NO)₂(CO)]PF₆ with NaCl (59), was reported shortly after our synthesis of this complex. A number of compounds derived from CpCr(NO)₂Cl, such as CpCr(NO)₂X (X = F, Br, I, CN, NCS, NO₂ and NCSe) (82, 85), [CpCr(NO)₂L]Cl, [CpCr(NO)L₂]Cl and CpCr(NO)(L)Cl (86) has already been obtained. However, no derivatives of the molybdenum and tungsten chloro complexes were known when this research was undertaken.

Prior to this work, five dinuclear chromium species, [CpCr(NO)L]₂ (L = NMe₂, SPh and SMe) (87, 88), Cp₂Cr₂(NO)₃NH₂ (89), and [CpCr(NO)₂]₂ (90) had been characterized, and all these complexes contain bridging NO and/or L ligands (91-94). The molybdenum dimers,
[CpMo(NO)L]₂ (L = I, SPh and SCH₂Ph), [CpMo(NO)L₂]₂ (L = I, SPh, SCH₂Ph and CO₂R₆) and [CpMo(NO)(SCH₂Ph)I]₂ have all been derived from [CpMo(NO)I₂]₂ rather than from CpMo(NO)₂Cl (95-97). The treatment of [CpMo(NO)I₂]₂ with PPh₃, P(OPh)₃ and C₅H₅N yields CpMo(NO)(L)I₂ (96).

Until now, the only known alkyl and aryl compounds of the type CpM(NO)₂R were the Me, Et, Ph and σ-C₅H₅ derivatives of chromium (27, 98). The first three are obtained in 60, 5, and 0.5% yields, respectively, by the reaction of the corresponding Grignard reagent with either CpCr(NO)₂Br or CpCr(NO)₂I. In general, the chloronitrosyl complex gives the poorest yields, and when THF is substituted for Et₂O as solvent, the CpCr(NO)₂Me complex is obtained in only 1% yield. Interestingly, diazomethane inserts into the Cr-Cl bond of CpCr(NO)₂Cl to afford CpCr(NO)₂CH₂Cl in 3% yield, a reaction similar to the insertion into CpM(CO)₃H (M = Mo or W) and CpW(CO)₃CH₃ to give the corresponding methyl and ethyl derivatives (27, 99). The σ-C₅H₅ derivative is obtained by the reaction of NaC₅H₅ or TlC₅H₅ with the halonitrosyl compound (18, 98).

Recently, an interesting series of complexes (C₅H₅)₂Mo(NO)X (X = I, Me and σ-C₅H₅) has been prepared. Thus, the treatment of [CpMo(NO)I₂]₂ with 2TlC₅H₅ and 4TlC₅H₅ yields (C₅H₅)₂Mo(NO)I (83) and (C₅H₅)₂Mo(NO)(σ-C₅H₅)(100), and the reaction of the former product with MeMgBr produces (C₅H₅)₂Mo(NO)Me (83). At room temperature, the NMR spectrum of each of the three (C₅H₅)₂Mo(NO)X complexes exhibits only one sharp cyclopentadienyl proton resonance. In order to satisfy the "18-electron rule", an instantaneous structure containing rapidly
interchanging $n^5$- and $n^3$-$C_5H_5$ rings was proposed (83). However, the x-ray structures of $(C_5H_5)_2Mo(NO)(n^5C_5H_5)$ (101) and $(C_5H_5)_2Mo(NO)Me$ (102) show that the non-$n^1-C_5H_5$ rings, though magnetically non-equivalent, are equivalent with respect to the central metal atom. Assuming similar structures in solution, the NMR behavior over a wide temperature range then does not require the $n^5-C_5H_5 \leftrightarrow n^3-C_5H_5$ fluxionality. Moreover, the complexes $(C_5H_5)_2Mo(NO)S_2CNMe_2$ and $[PPh_4][((C_5H_5)_2Mo(NO)S_2CC(CN)_2]$, which have the chelating $S_2CNMe_2$ and $S_2C_2(CN)_2$ ligands, contain both $n^1-C_5H_5$ and $n^5-C_5H_5$ rings which become equivalent at 70°C due to rapid $n^1-C_5H_5 \leftrightarrow n^5-C_5H_5$ interchange (103).

This chapter describes the chain of events which subsequently leads to the acquisition of the $\text{CpM(NO)}_2R$ complexes, where $M = \text{Cr, Mo or W; } R = \text{alkyl or aryl.}$ The synthetic route, which is generally applicable to all three metals, begins with the commercially available metal hexacarbonyl compounds, as in the scheme:

$$M(\text{CO})_6 \rightarrow \text{Na}[\text{CpM(\text{CO})}_3] \rightarrow \text{CpM(\text{CO})}_2(\text{NO}) \rightarrow \text{CpM(\text{NO})}_2\text{Cl} \rightarrow \text{CpM(\text{NO})}_2R$$

The success of this preparative method is largely due to the high yield synthesis of each intermediate compound, as described herein. Although the $\text{CpM(\text{CO})}_2(\text{NO})$ species have been previously characterized, the $\text{CpM(\text{NO})}_2\text{Cl}$ and $\text{CpM(\text{NO})}_2R$ compounds have not been thoroughly studied either because of the difficulty in their preparation or simply because they were previously unknown. Therefore, not only are the syntheses of $\text{CpMo(\text{CO})}_2(\text{NO})$, $\text{CpM(\text{NO})}_2X$ and $\text{CpM(\text{NO})}_2R$ described, but the chemical and physical properties of some further derivarives of $\text{CpM(\text{NO})}_2X$ are reported.
4.2 Experimental

All experimental procedures described here were performed under the same general conditions detailed in section 2.2.

4.2a Preparation of dicarbonyl($n^5$-cyclopentadienyl)nitrosyl complexes of chromium, molybdenum and tungsten, CpM(CO)$_2$(NO) (M = Cr, Mo or W).

The success of the high yield syntheses of the CpM(CO)$_2$(NO) complexes depends on the availability of the Na[CpM(CO)$_3$] anions uncontaminated by any NaC$_5$H$_5$. The molybdenum and tungsten salts were obtained according to a published procedure (27), although a 5% mole excess of the M(CO)$_6$ compounds was used to improve the yields of the desired anions. Also, the tungsten reaction was allowed to continue for 70 h in order to ensure more complete conversion. The chromium salt was efficiently prepared in the following manner. A THF solution containing NaC$_5$H$_5$ (27) (4.18 g, 47.5 mmol) was concentrated in vacuo just until a slurry formed (approx. 20 ml). n-Butyl ether (100 ml; Eastman Kodak practical grade) and Cr(CO)$_6$ (11.0 g, 50.0 mmol; Pressure Chemical Co.) were added and the mixture was heated under gentle reflux for 12 h with vigorous stirring. The final mixture was allowed to cool to room temperature and filtered. The pale yellow solid thus collected was washed with n-butyl ether (3 x 30 ml) and once with hexanes (30 ml), and dried at 25°C (5 x 10$^{-3}$ mm) for 18 h. The Na[CpM(CO)$_3$] complexes of molybdenum and tungsten were freed of any unreacted M(CO)$_6$ by simply taking the final reaction mixture to dryness in vacuo and heating.
the residue to 60° (5 x 10^{-3} mm) for 12 h. All three salts were used without further purification.

The three CpM(CO)$_2$(NO) complexes were prepared similarly and the experimental procedure using the molybdenum complex as a typical example, was as follows.

To a rapidly stirred THF solution (120 ml) containing Na[CpMo(CO)$_3$] (13.0 g, 48.7 mmol) was added dropwise at room temperature a solution of Diazald (10.4 g, 48.6 mmol; Eastman Kodak reagent grade) in THF (50 ml). Gas was evolved and an orange solid precipitated. The final reaction mixture was taken to dryness in vacuo and sublimation of the residue at 60°C (5 x 10^{-3} mm) onto a water-cooled probe for 18 h produced 11.2 g (45.3 mmol, 93% yield) of analytically pure CpMo(CO)$_2$(NO). The chromium and tungsten compounds were obtained in yields of 82 and 84% respectively.

**Anal. Calcd. for C$_5$H$_5$Cr(CO)$_2$(NO):** C, 41.39; H, 2.48; N, 6.90.
**Found:** C, 41.40; H, 2.60; N, 6.70. $\nu$(CO) cm$^{-1}$ (in CH$_2$Cl$_2$): 2020(s); 1945(s). $\nu$(NO) cm$^{-1}$ (in CH$_2$Cl$_2$): 1680(s).

**Calcd. for C$_5$H$_5$Mo(CO)$_2$(NO):** C, 34.03; H, 2.04; N, 5.67.
**Found:** C, 34.28; H, 2.24; N, 5.54. $\nu$(CO) cm$^{-1}$ (in CH$_2$Cl$_2$): 2020(s); 1937(s). $\nu$(NO) cm$^{-1}$ (in CH$_2$Cl$_2$): 1663(s).

**Calcd. for C$_5$H$_5$W(CO)$_2$(NO):** C, 25.10; H, 1.50; N, 4.18.
**Found:** C, 25.29; H, 1.70; N, 4.13. $\nu$(CO) cm$^{-1}$ (in CH$_2$Cl$_2$): 2010(s); 1925(s). $\nu$(NO) cm$^{-1}$ (in CH$_2$Cl$_2$): 1655(s).
4.2b Preparation of chloro(\(n^5\)-cyclopentadienyl)dinitrosyl complexes of chromium, molybdenum and tungsten, CpM(NO)\(_2\)Cl (M = Cr, Mo or W).

All three CpM(NO)\(_2\)Cl compounds were prepared in a similar manner. The yields of the chromium and tungsten complexes were optimized by performing the reactions at -78°C. The molybdenum compound was obtained in excellent yields even at room temperature and a typical synthesis was as follows.

A CH\(_2\)Cl\(_2\) solution (100 ml) containing CpMo(CO)\(_2\)(NO) (6.5 g, 26 mmol) was treated dropwise with rapid stirring at room temperature with a solution of ClNO in CH\(_2\)Cl\(_2\). Gas evolution occurred and the initial orange solution became dark green. The course of the reaction was followed by infrared spectroscopy and ClNO was added just until the carbonyl absorptions due to the reactant disappeared. (Great care was taken not to add excessive amounts of ClNO since this resulted in a significant reduction in the yield of the desired product. Conversely if insufficient ClNO was employed, then some difficulty was encountered in the separation of the unreacted CpM(CO)\(_2\)(NO) from the desired product.) The final reaction mixture was concentrated in vacuo to ca. 30 ml and filtered through a short (3 x 5 cm) Florisil column. The column was washed with CH\(_2\)Cl\(_2\) until the washings were colorless, and the combined filtrates were taken to dryness to give 6.0 g (2.3 mmol, 90% yield) of analytically pure CpMo(NO)\(_2\)Cl. The chromium and tungsten complexes were obtained in yields of 77 and 72% respectively.
Table V. Elemental Analyses and Physical Properties of CpM(NO)$_2$X ($M = Cr$, Mo or W; $X = Cl$ or I).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>Mp, °C (under N$_2$)</th>
<th>Analyses, %</th>
<th>Proton NMR, $\tau$ (in C$_6$D$_6$)</th>
<th>$\nu$(NO) cm$^{-1}$ (in CH$_2$Cl$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpCr(NO)$_2$Cl</td>
<td>gold</td>
<td>144 (dec)</td>
<td>calcd: 28.26 2.37 13.18 16.68</td>
<td>5.22(s) 1816(s), 1711(s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found: 28.29 2.55 12.86 16.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpMo(NO)$_2$Cl</td>
<td>green</td>
<td>116</td>
<td>calcd: 23.42 1.96 10.92</td>
<td>4.93(s) 1759(s), 1665(s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found: 23.53 1.90 10.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpW(NO)$_2$Cl</td>
<td>green</td>
<td>127 (dec)</td>
<td>calcd: 17.44 1.46 8.13 10.29</td>
<td>5.02(s) 1733(s), 1650(s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found: 17.68 1.62 8.10 10.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpCr(NO)$_2$I</td>
<td>dark gold</td>
<td>146 (dec)</td>
<td>calcd: 19.75 1.66 9.22</td>
<td>5.28(s) 1808(s), 1718(s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found: 19.71 1.76 9.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpMo(NO)$_2$I</td>
<td>olive green</td>
<td>114 (dec)</td>
<td>calcd: 17.26 1.45 8.05</td>
<td>5.00(s) 1764(s), 1677(s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found: 17.33 1.40 7.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CpW(NO)$_2$I</td>
<td>olive green</td>
<td>129 (dec)</td>
<td>calcd: 13.78 1.16 6.43</td>
<td>4.94(s) 1740(s), 1657(s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found: 13.78 1.17 6.36</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The complexes, along with their elemental analyses and physical properties, are listed in Table V.

4.2c Preparation of ($\eta^5$-cyclopentadienyl)iododinitrosyl complexes of chromium, molybdenum and tungsten, CpM(NO)$_2$I (M = Cr, Mo or W).

All the CpM(NO)$_2$I complexes were prepared in a similar manner and the customary procedure for the synthesis of the CpCr(NO)$_2$I compound was as follows.

A THF solution (150 ml) containing CpCr(NO)$_2$Cl (2.54 g, 12.0 mmol) and NaI (9.0 g, 60 mmol; Mallinckrodt reagent grade) was stirred at room temperature for 18 h. The reaction mixture became a very dark yellow-brown in color and a white solid formed. The final mixture was taken to dryness in vacuo and the resultant residue extracted into CH$_2$Cl$_2$ (150 ml). The extract was filtered through a short (3 x 5 cm) Florisil column and taken to dryness in vacuo (5 x 10$^{-3}$ mm) thereby affording a virtually quantitative yield of the analytically pure CpCr(NO)$_2$I complex. The elemental analyses and physical properties of all three CpM(NO)$_2$I compounds are given in Table V.

4.2d Preparation of bis[(-$\eta^5$-cyclopentadienyl)ethoxonitrosylchromium], [CpCr(NO)(OEt)]$_2$.

A solution of CpCr(NO)$_2$Cl (2.13 g, 10.0 mmol) in EtOH (120 ml) was treated with NaOEt (0.80 g, 12.0 mmol) at room temperature. Immediately, the mixture became yellow-red and a fine white solid formed.
The mixture was stirred for 0.5 h and the infrared spectrum of the supernatant liquid displayed absorptions at 1792 cm\(^{-1}\) (s) and 1685 cm\(^{-1}\) (s) indicative of the CpCr(NO)\(_2\)(OEt) complex (cf. infrared spectrum of CpCr(NO)\(_2\)Cl, \(\nu\)(NO) cm\(^{-1}\) (in EtOH): 1812(s); 1708(s)). The solvent was removed in vacuo yielding a red oil. During final drying at 25°C (5 x 10\(^{-3}\) mm) for 0.5 h, the red oil was transformed to a green solid. This product was extracted into CH\(_2\)Cl\(_2\) (25 ml) and chromatographed through a Florisil column (2.5 x 8 cm) with CH\(_2\)Cl\(_2\) as eluent. The eluate was taken to dryness in vacuo (5 x 10\(^{-3}\) mm) yielding 0.64 g (3.3 mmol, 33% yield) of the olive-green [CpCr(NO)(OEt)\(_2\)] compound.

**Anal.** Calcd. for \([C_5H_5Cr(NO)(OEt)]_2\): C, 43.58; H, 5.21; N, 7.40. Found: C, 43.78; H, 5.26; N, 7.29. \(\nu\)(NO) cm\(^{-1}\) (in CH\(_2\)Cl\(_2\)): 1660. Mp. (under N\(_2\)): 233°C (dec).

The CpM(NO)\(_2\)Cl (M = Mo or W) complexes reacted with LiOEt in THF producing yellow-red solutions which, when taken to dryness, yielded yellow-red oils. These oils remained unchanged even after heating at 95°C (5 x 10\(^{-3}\) mm) for 2 h. Their infrared spectra suggested that the products were CpMo(NO)\(_2\)Et (\(\nu\)(NO) cm\(^{-1}\) (in CH\(_2\)Cl\(_2\)): 1740(s); 1630(s)) and CpW(NO)\(_2\)Et (\(\nu\)(NO) cm\(^{-1}\) (in CH\(_2\)Cl\(_2\)): 1710(s); 1610(s)).

**4.2e Preparation of bis[chloro(n\(^5\)-cyclopentadienyl)nitrosylchromium], [CpCr(NO)Cl]\(_2\).**

A sample of [CpCr(NO)\(_2\)(OEt)\(_2\)] (0.19 g, 1.0 mmol) was dissolved in benzene (30 ml) and dry HCl(g) was bubbled through the solution. Immediately, the off-green reaction mixture became a very intense green
in color. Enough HCl(g) was added to just completely consume the initial reactant (monitored by infrared spectroscopy). The mixture was taken to dryness in vacuo and the product crystallized from CH$_2$Cl$_2$ (20 ml) by the addition of hexanes (50 ml). The solid was collected by filtration and dried at 25°C (5 × 10$^{-3}$mm) to give 0.16 g (0.88 mmol, 88% yield) of the green [CpCr(NO)Cl]$_2$ complex.

**Anal. Calcd. for [C$_5$H$_5$Cr(NO)Cl]$_2$:** C, 32.90; H, 2.76; N, 7.67. Found: C, 32.50; H, 2.61; N, 7.66. v(NO) cm$^{-1}$ (in CH$_2$Cl$_2$): 1678.

Mp. (under N$_2$): 140 (dec).

### 4.2f Preparation of alkyl- and aryl-(n$^5$-cyclopentadienyl)dinitrosyl complexes of chromium, molybdenum and tungsten, CpM(NO)$_2$R

(M = Cr, Mo or W; R = alkyl or aryl).

Since the various alkyl and aryl derivatives were similarly prepared, two representative syntheses are described below. Table VI summarizes the particular experimental details.

#### 4.2fl Preparation of (n$^5$-cyclopentadienyl)methyldinitrosyltungsten, CpW(NO)$_2$Me.

A benzene solution (12 ml) containing Me$_3$Al (0.22 g, 3.1 mmol; Texas Alkyls) was added dropwise at room temperature to a stirred solution of CpW(NO)$_2$Cl (1.0 g, 2.9 mmol) in benzene (25 ml). The green solution was allowed to stir for 48 h during which time a red-brown oily solid deposited on the walls of the reaction flask. (The reaction was followed
Table VI. Reaction Conditions and Purification Methods for \( \text{CpM(NO)}_2 \text{R} \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Alkylation or Arylation Agent</th>
<th>Reaction time (hours)</th>
<th>Purification methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CpCr(NO)}_2 \text{C}_6\text{H}_5 )</td>
<td>((\text{C}_6\text{H}_5)_3\text{Al} )</td>
<td>0.5</td>
<td>AB</td>
</tr>
<tr>
<td>( \text{CpCr(NO)}_2 \text{CH}_3 )</td>
<td>((\text{CH}_3)_3\text{Al} )</td>
<td>0.5</td>
<td>AB</td>
</tr>
<tr>
<td>( \text{CpCr(NO)}_2 \text{C}_2\text{H}_5 )</td>
<td>((\text{C}_2\text{H}_5)_3\text{Al} )</td>
<td>0.5</td>
<td>A</td>
</tr>
<tr>
<td>( \text{CpCr(NO)}_2 \text{i-C}_4\text{H}_9 )</td>
<td>((\text{i-C}_4\text{H}_9)_2\text{AlH} )</td>
<td>0.5</td>
<td>A</td>
</tr>
<tr>
<td>( \text{CpMo(NO)}_2 \text{C}_6\text{H}_5 )</td>
<td>((\text{C}_6\text{H}_5)_3\text{Al} )</td>
<td>1.5</td>
<td>AA</td>
</tr>
<tr>
<td>( \text{CpMo(NO)}_2 \text{CH}_3 )</td>
<td>((\text{CH}_3)_3\text{Al} )</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>( \text{CpMo(NO)}_2 \text{C}_2\text{H}_5 )</td>
<td>((\text{C}_2\text{H}_5)_3\text{Al} )</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>( \text{CpMo(NO)}_2 \text{i-C}_4\text{H}_9 )</td>
<td>((\text{i-C}_4\text{H}_9)_2\text{AlH} )</td>
<td>0.5</td>
<td>A</td>
</tr>
<tr>
<td>( \text{CpW(NO)}_2 \text{C}_6\text{H}_5 )</td>
<td>((\text{C}_6\text{H}_5)_3\text{Al} )</td>
<td>1</td>
<td>AB</td>
</tr>
<tr>
<td>( \text{CpW(NO)}_2 \text{CH}_3 )</td>
<td>((\text{CH}_3)_3\text{Al} )</td>
<td>48</td>
<td>AB</td>
</tr>
</tbody>
</table>

\( ^\dagger \text{A} - \text{chromatographic separation on alumina using benzene as the eluant.} \)

\( \text{B} - \text{sublimation in vacuum} \)
by infrared spectroscopy and such monitoring of several experiments showed these to be the optimum stoichiometry and reaction time.

Judging from the relative $v$(NO) band intensities of the final reaction mixture, the CpW(NO)$_2$Me product and unreacted CpW(NO)$_2$Cl were present in ca. equimolar quantities. The reaction mixture was concentrated in vacuo to ca. 15 ml and the supernatant liquid chromatographed in a short (3 x 7 cm) column of alumina (Woelm neutral grade 1) with benzene as eluent. The eluate was taken to dryness in vacuo and the resultant solid sublimed at 30°C (5 x 10$^{-3}$ mm) onto a water-cooled probe affording 0.20 g (0.62 mmol, 20% yield) of analytically pure CpW(NO)$_2$Me.

4.2f2 Preparation of [n$^5$-cyclopentadienyl)dinitrosylphenylmolybdenum, CpMo(NO)$_2$Ph.

A solution of Ph$_3$Al (28) (0.35 g, 1.4 mmol) in benzene (70 ml) was added dropwise to a solution of CpMo(NO)$_2$Cl (1.0 g, 3.9 mmol) in the same solvent (30 ml). A red-brown solid formed and the mixture was further stirred for 1 h at which point the infrared spectrum of the supernatant liquid confirmed the depletion of the initial reactant. The final reaction mixture was concentrated in vacuo to ca. 20 ml and the supernatant liquid was chromatographed on an alumina column. The product was eluted with benzene and only the main portion of the green product band was collected. The solvent was removed from the eluate and the residue was dried at room temperature in vacuo (5 x 10$^{-3}$ mm) for 4 h thus providing 0.65 g (2.2 mmol, 56% yield) of CpMo(NO)$_2$Ph as an analytically pure olive-green oil.
All the other complexes in Table VII were obtained in yields of 30-50%. Their elemental analyses and physical properties are given in Tables VII and VIII. All the complexes are stable in air for short periods of time but are best stored under nitrogen and below 0°C. They are very soluble in common organic solvents including hexanes.

4.2g Preparation of bis[(n^5-cyclopentadienyl)dinitrosylchromium], \([\text{CpCr(NO)}_2\text{]}_2\).

To an amalgam made from sodium (0.5 g, 20 mmol) and mercury metal (20 ml) was added a solution of \(\text{CpCr(NO)}_2\text{Cl}\) (1.06 g, 5.00 mmol) in benzene (120 ml). This reaction mixture was stirred vigorously at room temperature until the infrared spectrum of the supernatant liquid contained no absorption bands due to the initial reactant (ca. 1.5 h). [Reaction beyond this point led to decomposition of the desired product.]

During the course of the reaction a grey solid was deposited and the solution became red-purple in color. The supernatant liquid was syringed from the amalgam and concentrated in vacuo to ca. 20 ml. This solution was transferred to a short (2 x 5 cm) column of alumina (Woelm neutral grade 1) and the column was eluted with benzene until the washings were colorless (ca. 120 ml). Solvent was removed from the eluate in vacuo and the remaining purple-black solid was dried at room temperature under high vacuum \((5 \times 10^{-3} \text{mm})\) for 2 h. In this manner 0.68 g (1.9 mmol, 77% yield) of the analytically pure \([\text{CpCr(NO)}_2\text{]}_2\) complex was obtained.

Anal. Calcd. for \(\left[(\text{C}_5\text{H}_5)\text{Cr(NO)}_2\right]_2\): C, 33.91; H, 2.85; N, 15.82. Found: C, 33.78; H, 2.75; N, 15.82. \(\nu(\text{NO}) \text{ cm}^{-1}\) (in \(\text{CH}_2\text{Cl}_2\)): 1667(s); 1512(m). Mp. (in air): 147°C (dec).
Table VII. Elemental Analyses and Physical Properties of CpM(NO)$_2$R.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>$\text{Mp,}^\circ\text{C (in air)}$</th>
<th>Analyses, % calculated</th>
<th>Analyses, % found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>CpCr(NO)$_2$C$_6$H$_5$</td>
<td>dark green</td>
<td>48-48.5</td>
<td>51.97</td>
<td>3.97</td>
</tr>
<tr>
<td>CpCr(NO)$_2$CH$_3$</td>
<td>dark green</td>
<td>80.5-81.0</td>
<td>37.51</td>
<td>4.20</td>
</tr>
<tr>
<td>CpCr(NO)$_2$C$_2$H$_5$</td>
<td>green</td>
<td>oil</td>
<td>40.70</td>
<td>4.89</td>
</tr>
<tr>
<td>CpCr(NO)$_2$i-C$_4$H$_9$</td>
<td>green</td>
<td>oil</td>
<td>46.15</td>
<td>6.03</td>
</tr>
<tr>
<td>CpMo(NO)$_2$C$_6$H$_5$</td>
<td>olive green</td>
<td>oil</td>
<td>44.31</td>
<td>3.38</td>
</tr>
<tr>
<td>CpMo(NO)$_2$CH$_3$</td>
<td>green</td>
<td>61.5-62.0</td>
<td>30.53</td>
<td>3.42</td>
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<tr>
<td>CpMo(NO)$_2$C$_2$H$_5$</td>
<td>green</td>
<td>oil</td>
<td>33.52</td>
<td>4.03</td>
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<td>CpMo(NO)$_2$i-C$_4$H$_9$</td>
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<td>38.86</td>
<td>5.07</td>
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<td>109-110</td>
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<tr>
<td>CpW(NO)$_2$CH$_3$</td>
<td>pale green</td>
<td>75-76</td>
<td>22.24</td>
<td>2.49</td>
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Table VIII. IR and $^1$H NMR Data for CpM(NO)$_2$R.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR$^a$</th>
<th>$^1$H NMR $\tau$(in C$_6$D$_6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu$(NO) cm$^{-1}$</td>
<td>$^3$C$_5$H$_5$</td>
</tr>
<tr>
<td>CpCr(NO)$_2$Cl</td>
<td>1815(s)</td>
<td>1710(vs)$^b$</td>
</tr>
<tr>
<td>CpCr(NO)$_2$C$_6$H$_5$</td>
<td>1792</td>
<td>1690</td>
</tr>
<tr>
<td>CpCr(NO)$_2$CH$_3$</td>
<td>1780</td>
<td>1675</td>
</tr>
<tr>
<td>CpCr(NO)$_2$C$_2$H$_5$</td>
<td>1772</td>
<td>1670</td>
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<tr>
<td>CpCr(NO)$_2$i-C$_4$H$_9$</td>
<td>1775</td>
<td>1675</td>
</tr>
<tr>
<td>CpMo(NO)$_2$Cl</td>
<td>1758</td>
<td>1665$^b$</td>
</tr>
<tr>
<td>CpMo(NO)$_2$C$_6$H$_5$</td>
<td>1745</td>
<td>1658</td>
</tr>
<tr>
<td>CpMo(NO)$_2$CH$_3$</td>
<td>1728</td>
<td>1640</td>
</tr>
<tr>
<td>CpMo(NO)$_2$C$_2$H$_5$</td>
<td>1735</td>
<td>1643</td>
</tr>
<tr>
<td>CpMo(NO)$_2$i-C$_4$H$_9$</td>
<td>1725</td>
<td>1638</td>
</tr>
<tr>
<td>CpW(NO)$_2$Cl</td>
<td>1733</td>
<td>1650$^b$</td>
</tr>
<tr>
<td>CpW(NO)$_2$C$_6$H$_5$</td>
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<td>1630</td>
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<tr>
<td>CpW(NO)$_2$CH$_3$</td>
<td>1705</td>
<td>1620</td>
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</table>

$^a$ Hexane solution unless indicated otherwise.

$^b$ Dichloromethane solution.

$^c$ Approximate centroid of complex multiplet (m).
4.3 Results and Discussion

4.3a The dicarbonyl(n^5-cyclopentadienyl)nitrosyl complexes of chromium, molybdenum and tungsten, CpM(CO)₂(NO) (M = Cr, Mo or W).

All three CpM(CO)₂(NO) compounds were obtained according to the following sequence of reactions:

\[
\text{NaC}_5\text{H}_5 + M\text{(CO)}_6 \rightarrow \text{Na}[\text{CpM(CO)}_3] + 3\text{CO}
\]

\[
\text{Na}[\text{CpM(CO)}_3] + p-\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N(NO)}\text{CH}_3 \rightarrow \text{THF} \rightarrow \text{CpM(CO)}_2\text{(NO)} + \text{CO} + p-\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N(CH}_3\text{)}\text{Na}
\]

The success of this synthetic route depends critically on the availability of the corresponding Na[CpM(CO)_3] salts which are free of any unreacted NaC_5H_5. The presence of this contaminant is immediately evident upon subsequent reaction with Diazald since a brown-black, rather than the expected orange-red, reaction mixture is obtained. Furthermore, the yield of the desired carbonylnitrosyl is drastically reduced. However, once the sufficiently pure anions are obtained, their reaction with Diazald in THF produces the CpM(CO)_2(NO) complexes in excellent, reproducible yields ranging from 82-93%, depending on M. Also, these syntheses can be easily scaled to produce the desired products in quantities as large as 30 g while still maintaining the same high yields. Undoubtedly, the experimental procedures described for the preparation of these complexes are the most convenient thus far developed (27, 77, 78, 80, 81).
The Na[CpM(CO)₃] (M = Mo or W) salts can be readily obtained, in THF under reflux, according to a published procedure (27). However, to ensure complete conversion important modifications have been necessarily made. Thus, the syntheses are performed with NaCp as the limiting reagent and the reaction involving the tungsten compound is allowed to continue for the extended period of 72 hours. Unfortunately, under the same conditions, Cr(CO)₆ and NaC₅H₅ react very slowly and the conversion after seven days of reaction is still relatively low. Although diglyme has been previously employed in the preparation of Na[CpCr(CO)₃] (79), its strong solvating characteristics renders its use impractical. However, if Cr(CO)₆ and NaC₅H₅ are allowed to react in n-Bu₂O under reflux for 18 hours, a virtually quantitative yield of the desired product is obtained. The Na[CpCr(CO)₃], insoluble in n-Bu₂O, precipitates as a crystalline pale yellow solid during the course of the reaction. Subsequent purification, to remove excess M(CO)₆, of the Na[CpM(CO)₃] compounds is easily performed as described in the Experimental section.

The properties of the CpM(NO)₂(NO) compounds have been previously described (2, 3, 28). The complexes are orange to orange-red solids readily soluble in organic solvent and stable in air for short periods of time. However, they may be stored indefinitely under nitrogen at room temperature.

4.3b The chloro(η⁵-cyclopentadienyl)dinitrosyl complexes of chromium, molybdenum and tungsten, CpM(NO)₂Cl (M = Cr, Mo or W).

The high yield syntheses of all three complexes are effected by
the treatment of \( \text{CpM(CO)}_2(\text{NO}) \) with \( \text{ClNO} \) in \( \text{CH}_2\text{Cl}_2 \), according to eq. 19.

\[
\text{CpM(CO)}_2(\text{NO}) + \text{ClNO} \rightarrow \text{CpM(NO)}_2\text{Cl} + 2\text{CO} \tag{19}
\]

\( M = \text{Cr, Mo or W} \)

In order to maximize yields, the transformations involving the chromium and tungsten containing compounds must be performed at \(-78^\circ\text{C}\), while the molybdenum complex can be obtained in excellent yields at room temperature. The latter reaction is accompanied by the formation of a small amount of \( [\text{CpMo(NO)}\text{Cl}_2]_2 \), identified by elemental analysis and its characteristic infrared spectrum (104). Since this byproduct can also be formed by the direct treatment of \( \text{CpM(CO)}_2(\text{NO}) \) with \( \text{Cl}_2 \) (104), its appearance simply reflects the fact that \( \text{ClNO} \) exists in solution as part of the equilibrium

\[
2\text{ClNO} \rightarrow 2\text{NO} + \text{Cl}_2
\]

As in most reactions between the nitrosyl halides and metal carbonyls, special attention must be taken to avoid excess nitrosyl halide. Typically, the above conversions are followed by infrared spectroscopy and enough \( \text{ClNO} \) is added until the carbonyl absorptions of the reactant have just disappeared. In this manner, the further reaction of the desired products is effectively prevented. In any case, the general applicability of the reaction given by eq. 19, utilizing the now readily available starting materials, makes this high yield preparative route superior to all others thus far reported (27, 29, 59, 83, 84, 105).
The CpM(NO)₂Cl complexes, along with some of their physical properties, are presented in Table V. They are crystalline solids which have low solubility in hexanes but are very soluble in most other organic solvents. Contrary to a previous report (83), CpMo(NO)₂Cl, as well as the chromium and tungsten derivatives, are stable indefinitely under nitrogen at room temperature, and all three can be exposed to air for short periods of time without noticeable decomposition. Furthermore, the molybdenum complex melts at 116°C without decomposition and all three compounds may be sublimed at 40-50°C (5 x 10⁻³ mm) although some decomposition occurs with the chromium and tungsten species. Chemically, the CpM(NO)₂Cl compounds are useful precursors for the synthesis of a wide variety of stable alkyl and aryl complexes, CpM(NO)₂R, as discussed subsequently.

All three CpM(NO)₂I complexes are obtained in quantitative yields by the disproportionation reaction between NaI and the corresponding chloro complexes in THF. Their physical (Table V) and chemical properties are very similar to those of the chloro compounds. The molybdenum and tungsten complexes have not been previously reported.

The x-ray crystal structure of CpCr(NO)₂Cl indicates a pseudotetrahedral ("piano stool") arrangement of ligands about the chromium atom (106) as in C. The C₅H₅ ring randomly occupies one of two coplanar
orientations in which all the Cr-C distances are approximately equal, the average distance being 2.20 Å.

The Cr-NO bond distances of 1.717 (0.012) and 1.704 (0.013) Å, which are virtually identical to the value of 1.716 (0.003) found in CpCr(NO)$_2$(NCO) (107), are about 0.4 Å shorter than the expected Cr-N(sp) bond length. In fact, the Cr-N bond order is estimated to be 1.7, indicating the nitrosyl is bonded as NO$^+$ with appreciable electron donation from the Cr(d) to the N(pπ*) orbitals. The Cr-N-O fragments in both the chloro and isocyanato compounds depart from linearity by about 10°. This is ascribed to electrostatic repulsion between the oxygen atom of the nitrosyl ligand and the chloride or isocyanate ligand rather than to crystal packing forces.

The mass spectral data for the CpM(NO)$_2$Cl complexes, given in Tables IX and X, exhibit the expected fragmentation patterns. The presence of MCp$^+$ and MCpCl$^+$ and the concurrent absence of M(NO)$^+$ and M(NO)Cl$^+$ fragments can be attributed to the fact that the M-Cp linkage is stronger than the M-NO bond. The mass spectrum of CpMo(CO)$_2$(NO) displays a similar behavior (108). Furthermore, as is found in the cases of CpFe(CO)$_2$Cl (108) and CpMo(CO)$_3$Cl (109), the M-Cp and M-Cl bonds in the CpM(NO)$_2$Cl complexes are ruptured with about equal difficulty. The [MC$_3$H$_3$]$^+$ fragments, which occur frequently in the mass spectra of Cp-containing complexes, are not observed for the chromium compound but become increasingly abundant for the molybdenum and tungsten analogs. In addition, the relative abundance of fragments containing the nitrosyl group suggest a M-NO bond strength which increases as Mo ≤ Cr < W,
Table IX. High Resolution Mass Spectral Data for CpCr(NO)$_2$Cl.

<table>
<thead>
<tr>
<th>m/e measured</th>
<th>m/e calculated</th>
<th>relative abundance</th>
<th>assignment</th>
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<tbody>
<tr>
<td>213.9423</td>
<td>213.9414</td>
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<tr>
<td>211.9440</td>
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<td>32.6</td>
<td>C$_5$H$_5$Cr(NO)$_2^{35}$Cl$^+$</td>
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<tr>
<td>183.9447</td>
<td>183.9434</td>
<td>13.8</td>
<td>C$_5$H$<em>5$Cr(NO)$</em>{37}$Cl$^+$</td>
</tr>
<tr>
<td>181.9476</td>
<td>181.9464</td>
<td>36.6</td>
<td>C$_5$H$<em>5$Cr(NO)$</em>{35}$Cl$^+$</td>
</tr>
<tr>
<td>153.9459</td>
<td>153.9455</td>
<td>36.6</td>
<td>C$_5$H$<em>5$Cr$</em>{37}$Cl$^+$</td>
</tr>
<tr>
<td>151.9481</td>
<td>151.9484</td>
<td>100</td>
<td>C$_5$H$<em>5$Cr$</em>{35}$Cl$^+$</td>
</tr>
<tr>
<td>176.9796</td>
<td>176.9756</td>
<td>5.3</td>
<td>C$_5$H$<em>5$Cr(NO)$</em>{2}^+$</td>
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<tr>
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<tr>
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<tr>
<td>86.9089</td>
<td>86.9093</td>
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<td>65.0396</td>
<td>65.0391</td>
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<tr>
<td>51.9412</td>
<td>51.9404</td>
<td>13.8</td>
<td>Cr$^+$</td>
</tr>
</tbody>
</table>
Table X. Low Resolution Mass Spectral Data for CpM(NO)$_2$Cl$^a$.

(M = Mo or W)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Abundance</th>
<th>Assignment</th>
<th>m/e</th>
<th>Relative Abundance</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>258</td>
<td>43.7</td>
<td>C$_5$H$_5$Mo(NO)$_2$Cl$^+$</td>
<td>344</td>
<td>100</td>
<td>C$_5$H$_5$W(NO)$_2$Cl$^+$</td>
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<tr>
<td>228</td>
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<tr>
<td>198</td>
<td>100</td>
<td>C$_5$H$_5$MoCl$^+$</td>
<td>284</td>
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<td>C$_5$H$_5$WC1$^+$</td>
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<tr>
<td>172</td>
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<tr>
<td>163</td>
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<td>137</td>
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<tr>
<td>133</td>
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<td>MoCl$^+$</td>
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<tr>
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<td>W$^+$</td>
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<td>C$_5$H$_5^+$</td>
<td>65</td>
<td>6.8</td>
<td>C$_5$H$_5^+$</td>
</tr>
</tbody>
</table>

$^a$ The assignments involve the most abundant naturally occurring isotopes, i.e. $^{98}$Mo, $^{184}$W and $^{35}$Cl, in each fragment.
similar to the ordering of the M-CO bond strengths in the CpM(CO)₃Cl compounds (28).

A wide variety of derivatives of the type CpCr(NO)₂X (X = F, Br, I, CN, NCS, NO₂ (82), and NCSe (85)) have been obtained by the treatment of an aqueous solution of [CpCr(NO)₂]⁺, generated from CpCr(NO)₂Cl and AgNO₃, with NaX or KX. The isoselenocyanato complex decomposes readily in solution to give CpCr(NO)₂CN and elemental selenium. Also, CpCr(NO)₂SCF₃ is formed when the chloro compound is allowed to react with AgSCF₃ in acetone (110). In the above reactions, the intermediary nitrate salt has not been previously isolated. However, we find that treatment of CpCr(NO)₂Cl with AgNO₃ or AgBF₄ in water produces a precipitate of AgCl and a dark green supernatant solution. Subsequent extraction of the dried reaction mixture into CH₂Cl₂ followed by crystallization from CH₂Cl₂/hexanes yields the CpCr(NO)₂NO₃ and CpCr(NO)₂BF₄ compounds as stable green solids which are soluble in most organic solvents except hydrocarbons. Their infrared spectra in CH₂Cl₂ display nitrosyl stretching absorptions at 1841 and 1738 cm⁻¹, and at 1848 and 1744 cm⁻¹ for the NO₃⁻ and BF₄⁻ salts respectively. These absorptions are similar to those displayed by [CpCr(NO)₂]⁺[AlCl₄]⁻ (111) and are consistent with reduced Cr(dπ) to N(pπ*) donation. However, present attempts to perform the same reaction with the molybdenum complex proceeded with gas evolution and attendant decomposition.
4.3c Bis[(n⁵-cyclopentadieny1)ethoxonitrosylchromium], [CpCr(NO)(OEt)]₂, and bis[chloro(n⁵-cyclopentadieny1)nitrosylchromium, [CpCr(NO)Cl]₂.

When CpCr(NO)₂Cl is treated with NaOEt in EtOH or with LiOEt in THF, the CpCr(NO)₂OEt can be isolated as an unstable red oil. Its infrared spectrum in EtOH displays absorptions at 1792 and 1685 cm⁻¹, which are significantly lower than those of the chloro complex (i.e. 1812 and 1708 cm⁻¹ in EtOH) due to the greater electron donating ability of the alkoxide ligand. Upon exposure to high vacuum at room temperature, CpCr(NO)₂(OEt) spontaneously loses nitric oxide to form the new olive green solid, [CpCr(NO)(OEt)]₂, according to eq. 20. This same transformation can be effected by the elution of a CH₂Cl₂ solution of the dinitrosyl compound through an alumina column. The dimeric species, identified by elemental analysis and mass spectrometry, contains in its infrared spectrum a single terminal nitrosyl absorption at 1660 cm⁻¹ in CH₂Cl₂, similar to the previously reported [CpCr(NO)L]₂ (L = NMe₂, SPh and SMe) compounds (87, 88). The [CpCr(NO)(OEt)] complex is soluble in most organic solvents and can be handled in air for short periods of time without noticeable decomposition. It decomposes without melting at 233°C, under nitrogen.

On the other hand, the similar reactions of the molybdenum and tungsten chloro compounds with the above reagents yield only reddish oils similar in appearance to CpCr(NO)₂(OEt). A comparison of their infrared
spectra with those of the starting chloro complexes, given in the Experimental section and in Table V, suggests that these compounds can be formulated as CpM(NO)$_2$(OEt). They possess a remarkable thermal stability since heating to 95°C under vacuum for two hours effects no change. Also, the attempted dimerization on an alumina column resulted only in complete decomposition, and analytically pure samples of the dinitrosyls cannot be obtained. The CpM(NO)$_2$L (L = SbBu, NPh$_2$ and NH$_2$) complexes are prepared similarly and they exhibit a behavior similar to the ethoxide derivatives. A variety of [CpMo(NO)L]$_2$ and [CpMo(NO)L$_2$]$_2$ (L = I, SPh, SCH$_2$Ph and CO$_2$R$_p$) have been reported but they are obtained from [CpMo(NO)I]$_2$ rather than CpMo(NO)$_2$Cl (95-97).

The reaction of [CpCr(NO)(OEt)]$_2$ with gaseous HCl in benzene affords the novel green [CpCr(NO)Cl]$_2$ complex in high yield, according to eq. 21. Without making any implications as to the mechanism, this conversion

$$[\text{CpCr(NO)(OEt)}]_2 + 2\text{HCl} \rightarrow [\text{CpCr(NO)Cl}]_2 + 2\text{EtOH}$$  21.

can be considered as an acid-base reaction between H$^+$ and OEt$^-$, and in principle, a similar transformation should occur with any acid stronger than EtOH. As expected, the substitution of the ethoxide group by the chloride anion causes the terminal nitrosyl stretching frequency to increase from 1660 to 1678 cm$^{-1}$. Like [CpCr(NO)(OEt)]$_2$, the chloro derivative is very soluble in common organic solvents except hexanes and, though stable in air for short periods of time, is best stored under nitrogen.

The structures of [CpCr(NO)(OEt)]$_2$ and [CpCr(NO)Cl]$_2$ are expected to be similar to those of [CpCr(NO)(SPh)]$_2$ (91) and
[CpCr(NO)(NMe₂)]₂ (92), which are characterized by symmetrically bridging SPh and NMe₂ ligands and by a distinct metal-metal bond. Both the trans and cis forms, D and E, can be isolated. Also, the structure of

![Diagram of D and E complexes]

Cp₂Cr₂(NO)₂(NH₂) shows a trans arrangement containing both nitrosyl and amido bridges (94). The Cr-N linkages of the terminally coordinated nitrosyl groups have considerable double bond character, while the Cr-N-O bond angles are approximately 170°, as they are also in CpCr(NO)₂Cl and CpCr(NO)₂(NCO) (106, 107).

The dimeric nature of [CpCr(NO)(OEt)]₂ and [CpCr(NO)Cl]₂ is confirmed by their mass spectral data, shown in Table XI. The fragmentation patterns, indicating the loss of NO, ethyl, ethoxo, chloro and C₅H₅ fragments, are similar to those found in the mass spectra of [CpMo(NO)I]₂ and [CpMo(NO)(SCH₂Ph)]₂, in which the parent ions are also relatively abundant (95). In the mass spectra of both the chloro and ethoxo complexes the intensity pattern at m/e = 182 is indicative of [Cp₂Cr]⁺ rather than the [(C₅H₅)₂Cr₂]⁺ or [CpCr(NO)Cl]⁺ fragments. The same assignment has been made in the cases of [CpCr(NO)(SMe)]₂ (88) and Cp₂Cr₂(NO)₃(NH₂) (89), where [Cp₂Cr]⁺ is thought to arise from the
Table XI. Low Resolution Mass Spectral Data for \([\text{CpCr(NO)}X]_2\)^a.

<table>
<thead>
<tr>
<th>m/e</th>
<th>[\text{CpCr(NO)(OEt)}]_2 Relative Abundance</th>
<th>Assignment</th>
<th>m/e</th>
<th>[\text{CpCr(NO)Cl}]_2 Relative Abundance</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>384</td>
<td>0.6</td>
<td>(\text{Cp}_2\text{Cr}_2(\text{OEt})_2(\text{NO})^+)</td>
<td>364</td>
<td>0.4</td>
<td>(\text{Cp}_2\text{Cr}_2\text{Cl}_2(\text{NO})^+)</td>
</tr>
<tr>
<td>354</td>
<td>6.8</td>
<td>(\text{Cp}_2\text{Cr}_2(\text{OEt})_2(\text{NO})^+)</td>
<td>334</td>
<td>3.3</td>
<td>(\text{Cp}_2\text{Cr}_2\text{Cl}_2(\text{NO})^+)</td>
</tr>
<tr>
<td>324</td>
<td>10.0</td>
<td>(\text{Cp}_2\text{Cr}_2(\text{OEt})^+)</td>
<td>304</td>
<td>3.4</td>
<td>(\text{Cp}_2\text{Cr}_2\text{Cl}_2^+)</td>
</tr>
<tr>
<td>295</td>
<td>1.5</td>
<td>(\text{Cp}_2\text{Cr}_2(\text{OEt})^+)</td>
<td>182</td>
<td>10.0</td>
<td>(\text{Cp}_2\text{Cr}^+)</td>
</tr>
<tr>
<td>279</td>
<td>1.7</td>
<td>(\text{Cp}_2\text{Cr}_2(\text{OEt})^+)</td>
<td>152</td>
<td>2.9</td>
<td>(\text{CpCrCl}^+)</td>
</tr>
<tr>
<td>250</td>
<td>2.1</td>
<td>(\text{Cp}_2\text{Cr}_2^+)</td>
<td>117</td>
<td>3.1</td>
<td>(\text{CpCr}^+)</td>
</tr>
<tr>
<td>182</td>
<td>6.4</td>
<td>(\text{Cp}_2\text{Cr}^+)</td>
<td>52</td>
<td>2.3</td>
<td>(\text{C}^+)</td>
</tr>
<tr>
<td>162</td>
<td>1.4</td>
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<tr>
<td>117</td>
<td>0.9</td>
<td>(\text{CpCr}^+)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>1.4</td>
<td>(\text{C}^+)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a The assignments involve the most common naturally occurring isotopes, i.e. \(^{52}\text{Cr}\) and \(^{35}\text{Cl}\).*
fragmentation of the metastable \([\text{Cp}_2\text{Cr}_2S_2]^+\) and \([\text{Cp}_2\text{Cr}_2(\text{NH}_2)]^+\) species respectively.

4.3d The alkyl- and aryl-(\(\eta^5\)-cyclopentadienyl)dinitrosyl complexes of chromium, molybdenum and tungsten, \(\text{Cp}_2\text{M}(\text{NO})_2R\) \((M = \text{Cr}, \text{Mo} \text{or} W; R = \text{alkyl} \text{or} \text{aryl})\).

These complexes are obtained in reasonable yields by the reaction of the corresponding \(\text{Cp}_2\text{M}(\text{NO})_2\text{Cl}\) compounds with the appropriate organo-aluminum reagent according to the general eq. 21,

\[
\text{Cp}_2\text{M}(\text{NO})_2\text{Cl} + \text{R-Al} \xrightarrow{\text{benzene}} \text{Cp}_2\text{M}(\text{NO})_2\text{R} + \text{Cl-Al}
\]

where \(M = \text{Cr}, \text{Mo} \text{or} W\) and \(R = \text{alkyl} \text{or} \text{aryl}\). During the course of the reaction an oily red-brown solid of undetermined composition is deposited, and the exact nature of the aluminum byproduct remains to be ascertained. This synthetic procedure appears to be quite general for the chromium and molybdenum compounds and is limited only by the availability of the appropriate AlR₃ reagent. However, in the case of tungsten, only the phenyl and methyl derivatives are obtained, the latter only after a prolonged reaction time. Treatment of \(\text{Cp}_2\text{W}(\text{NO})_2\text{Cl}\) with \(\text{Et}_3\text{Al}\) or \(\text{AlH}(\text{i-Bu})_2\) under various reaction conditions fails to give the expected alkylated products. Interestingly, in the reactions involving \(\text{AlH}(\text{i-Bu})_2\) only the i-Bu group, rather than the hydride, is transferred to the metal. The Me, Et and Ph derivatives of chromium were previously reported (27) but are obtained here in better yields. The remaining alkyl
and aryl complexes were unknown prior to this work. The physical properties of these complexes are summarized in Tables VII and VIII.

All the complexes are very soluble in organic solvents, including hexanes, and may be exposed to air for short periods of time without decomposition. Those compounds which are solids at room temperature sublime readily at 30-40°C (5 x 10⁻³ mm) without decomposition and are, indeed, best purified in this manner. However, the ones which are liquids at room temperature decompose slowly under nitrogen but may be stored for many months at -5°C or lower. The methyl and phenyl derivatives, especially those of chromium, are the most thermally stable and melt without decomposition.

The infrared spectra (Table VIII) of all the complexes display two strong absorptions, similar to those in CpM(NO)₂Cl, due to terminal nitrosyl N-O stretchings. As expected, these stretching frequencies decrease in the order Cl > Ph > alkyl which parallels the ability of these ligands to withdraw electronic charge from the central metal.

The proton NMR spectra (Table VIII) exhibit a sharp singlet for the C₅H₅ protons as well as the expected patterns and integration ratios for the alkyl and aryl protons. Not too surprisingly, the position of the Cp resonance remains nearly independent of the chloro, alkyl or aryl substituent present for any given metal. Any electronic perturbation about the central metal is buffered by the presence of the strong π-accepting nitrosyl ligands. In fact, the N-O stretching frequencies do vary significantly, as mentioned, and hence provide a more sensitive measure for detecting changes in electronic distribution around the central
Figure 2. $^1$H NMR of $(\eta^5-C_5H_5)Mo(NO)_2CH_2CH_3$

A

Experimental spectrum

B

Computer fitted spectrum with parameters: $\tau(CH_2) 8.10$, $\tau(CH_3) 8.26$, $J(CH_2CH_3) 7.54$
metal. The presence of the σ-bonded ethyl group in CpMo(NO)$_2$Et is unequivocally demonstrated by the computer fitting of the $A_2B_3$ multiplet due to the alkyl proton resonance, from which the following parameters can be extracted (Figure 2): $\tau(CH_2) 8.10, \tau(CH_3) 8.26, J(CH_2, CH_3)$ 7.54 Hz$^\dagger$.

The mass spectral data for each complex in Table XII exhibit the molecular ion as the highest-mass fragment. The fragmentation patterns for the Et and i-Bu derivatives of molybdenum are similar, but assignments are complicated by concomitant fragmentation of the alkyl groups and by the large number of molybdenum isotopes. The most striking difference between the phenyl and methyl complexes is the systematic absence of the [CpM(NO)]$^+$ and [CpM(NO)$_2$]$^+$ fragments in the phenyl compounds, and the absence of [(C$_3$H$_3$)MR]$^+$ and [CpMR]$^+$ in the methyl derivatives. These data strongly suggest that the metal-carbon bond is stronger in the phenyl than in the methyl compounds, and that the trend is independent of the metal. The major difference among the metals is that the chromium-containing complexes show an abundance of Cr$^+$ and [CpCr]$^+$ fragments whereas, for the molybdenum- and tungsten-containing analogs, the corresponding fragments are much less abundant.

The two most general preparative routes to σ-bonded alkyl and aryl complexes involve the nucleophilic displacement of the halide from either the transition metal complex, eq. 22, or from an alkyl or aryl halide,

$^\dagger$ We thank Ms. V. Gibb for assistance in obtaining these spectra.
Table XII. Mass Spectral Fragmentation Data for CpM(NO)$_2$R.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M$^+$</th>
<th>C$_5$H$_5$M$^+$</th>
<th>C$_5$H$_5$M(NO)$^+$</th>
<th>C$_5$H$_5$M(NO)$_2$$^+$</th>
<th>ion$^b$</th>
<th>C$_3$H$_3$MR$^+$</th>
<th>C$_5$H$_5$MR$^+$</th>
<th>C$_5$H$_5$M(NO)R$^+$</th>
<th>C$_5$H$_5$M(NO)$_2$R$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpCr(NO)$_2$C$_6$H$_5$</td>
<td>10.0</td>
<td>8.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
<td>7.5</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>CpMo(NO)$_2$C$_6$H$_5$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.7</td>
<td>3.6</td>
<td>8.2</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>CpW(NO)$_2$C$_6$H$_5$</td>
<td>-</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>4.2</td>
<td>7.2</td>
<td>10.0</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>CpCr(NO)$_2$CH$_3$</td>
<td>10.0</td>
<td>8.4</td>
<td>2.7</td>
<td>1.2</td>
<td>-</td>
<td>2.1</td>
<td>7.2</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>CpMo(NO)$_2$CH$_3$</td>
<td>5.7</td>
<td>3.6</td>
<td>10.0</td>
<td>6.2</td>
<td>-</td>
<td>-</td>
<td>6.2</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>CpW(NO)$_2$CH$_3$</td>
<td>0.4</td>
<td>-</td>
<td>2.9</td>
<td>3.4</td>
<td>-</td>
<td>-</td>
<td>4.6</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>CpCr(NO)$_2$Et</td>
<td>10.0</td>
<td>2.7</td>
<td>1.9</td>
<td>2.0</td>
<td>-</td>
<td>1.9</td>
<td>5.6</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>CpCr(NO)$_2$i-Bu</td>
<td>10.0</td>
<td>9.9</td>
<td>3.5</td>
<td>4.1</td>
<td>7.2</td>
<td>-</td>
<td>9.9</td>
<td>2.9</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Entries in this table are relative ion intensities with the most intense metal containing ion assigned an arbitrary value of 10.0. Relative intensities were evaluated by measuring peak heights corresponding to the most abundant isotope of each metal: $^{52}$Cr, $^{98}$Mo and $^{184}$W.

$^b$ Only unambiguously assignable ions are given; for the polyisotopic molybdenum and tungsten overlapping of some medium to strong intensity peaks in the lower mass range made assignments difficult. Selected compounds were run on the MS902 high resolution instrument which measured exact masses of all major peaks; calculated and measured values were in good agreement.
The synthetic route given by eq. 23 cannot be exploited in this instance since all attempts to obtain the \([\text{CpM(NO)}]^-\) anions have thus far failed. Indeed, the only well characterized organometallic nitrosyl anion which has been successfully used as a synthetic precursor is \([\text{Fe(CO)}_3(\text{NO})]^-\) (53, 113, 114). While eq. 22 has been applied with modest success in the preparation of \(\text{CpCr(NO)}_2\)\(\text{R}\) (\(\text{R} = \text{Me}, \text{Et or Ph}\)) (27), the similar reactions of \(\text{CpM(NO)}_2\text{Cl}\) (\(\text{M} = \text{Mo or W}\)) with various alkyllithium and Grignard reagents fail to yield even spectroscopically detectable quantities of the corresponding alkyl or aryl derivatives. These reagents are not sufficiently selective in the nucleophilic displacement of the halide and they appear to attack other functional groups. In contrast, we find the organoaluminum reagents to be particularly mild and selective in their reactions with \(\text{CpM(NO)}_2\text{Cl}\) complexes. This feature is also illustrated by the exclusive monoalkylation of some dichloro compounds of ruthenium even when an excess of the organoaluminum reagent is used at elevated temperatures (115).

Organaloaluminum compounds are relatively strong Lewis acids which are known to coordinate to the oxygen end of carbonyl ligands in a variety of neutral (116) and anionic (117) \(\text{n}^5\)-cyclopentadienylmetal carbonyl complexes. Non-bonding electron pairs localized on the metal atom may also
serve as a Lewis base site and a number of 1:1 adducts containing the M-Al bond have been isolated (118). However, no infrared spectroscopic evidence was obtained in support of any similar Lewis acid-base adducts during our preparation of the CpM(NO)₂R complexes.

Although useful in the syntheses of main group metal alkyl and aryl compounds (119), the organoaluminum reagents have received very little attention in the formation of transition metal-carbon bonds (112). The general reaction of organoaluminum compounds with metal halides (eq. 24)

\[ R-Al + M-X \rightarrow Al-X + M-R \]  

is favored when M is substantially electropositive and X is electronegative. The conversion does not likely take place by a dissociative and reassociative ionic pathway since the organoaluminum compounds are largely covalent. Also, the reactions are typically performed in solvents which do not support ionization and, indeed, the use of coordinating solvents or the presence of Lewis bases retard the reaction. Consistent with the above facts, the present alkylation reactions can be considered to occur via a Lewis acid-base intermediate as in III or IV, where M is an organometallic residue.
If M is sufficiently electropositive, as is the case with the alkali metals, III and IV are formed as stable products rather than intermediates (119). Since the CpM(NO)₂Cl complexes display a certain inclination to form the cationic [CpM(NO)₂]⁺ species, the benzene insoluble byproduct deposited during the syntheses of CpM(NO)₂R may reasonably be formulated as [CpM(NO)₂]⁺ [AlR₃Cl]⁻. However, this possibility was not investigated.

In contrast to the numerous CpCr(NO)₂R complexes, the only known isoelectronic tricarbonyl analog is the thermally unstable CpCr(CO)₃Me compound. However, the CpM(CO)₃R (M = Mo or W) compounds are more abundant and have been the subject of considerable study. Notably, these complexes undergo a thermal transformation to yield [CpM(CO)₃]₂ (120, 121) or, when R = Et, Ph or CH₂Ph, [RC₅H₄M(CO)₃]₂ (121, 122). Our attempts to obtain similarly the analogous, but as yet unknown, [CpM(NO)₂]₂ (M = Mo or W) dimers by the thermolysis of the alkyl- or arylidinitrosyl complexes have been unsuccessful. Moreover, the nitrosyl complexes are understandably more inert toward substitution than the isoelectronic CpM(CO)₃R analogs, and no reaction parallel to carbonyl "insertion" has yet been found.

On the other hand, both CpCr(NO)₂R and CpM(CO)₃R undergo insertion of SO₂ affording derivatives which contain the S-sulfinate linkage, M-S-R (123-125). The rates of insertion into the nitrosyl containing complexes are, by far, the greatest among the variety of compounds studied (126). Infrared spectroscopic evidence (127) and kinetic studies (126) indicate that SO₂ insertion occurs with the initial
formation of the O-sulfinate linkage M-OSR followed by rearrangement to the S-sulfinate compound. Similarly, (CN)$_2$C=CC(CN)$_2$ reacts with the above carbonyl and nitrosyl complexes to give the direct insertion product, MC(CN)$_2$CC(CN)$_2$R, and the keteniminato derivative, MN=C=CC(CN)$_2$C(CN)$_2$R (124, 128).

Stannous chloride and bromide insert into the metal-carbon bond of a variety of alkylcarbonyl(n$_5$-cyclopentadienyl)metal complexes (M-R) to yield MSnRX$_2$, MSnX$_3$ and MX, depending on reaction conditions (129). We find that reaction of SnCl$_2$ with CpMo(NO)$_2$-Bu results in the formation of CpMo(NO)$_2$Cl exclusively. However, SnCl$_2$ does insert into the metal-chlorine bond of CpCr(NO)$_2$Cl according to the solvent dependent equilibrium, eq. 25. In donor solvents such as THF the left hand side of eq. 25 is

$$\text{CpCr(NO)$_2$Cl} + \text{SnCl}_2 \rightleftharpoons \text{CpCr(NO)$_2$SnCl}_3$$

favored probably due to Lewis acid-base interaction between SnCl$_2$ and the solvent, whereas CH$_2$Cl$_2$ and benzene shift the equilibrium to the side of CpCr(NO)$_2$SnCl$_3$. The infrared nitrosyl stretching frequencies (1733 and 1825 cm$^{-1}$ in CH$_2$Cl$_2$) of CpCr(NO)$_2$SnCl$_3$ are approximately 20 cm$^{-1}$ higher than those of CpCr(NO)$_2$Cl, which we attribute to the previously demonstrated poorer $\sigma$-donating and stronger $\pi$-accepting properties of the SnCl$_3$ entity (26a).

4.3e Bis[(n$5$-cyclopentadienyl)dinitrosylchromium], [CpCr(NO)$_2$]$_2$.

When a benzene solution containing CpCr(NO)$_2$Cl is allowed to stir over a sodium amalgam, [CpCr(NO)$_2$]$_2$ is obtained in over 60% yield.
This synthetic route is far superior to the one previously reported in which the desired product is extracted in only 5% yield (90). The same conversion can be effected by using a zinc amalgam and, to a lesser extent, with finely divided magnesium or ytterbium metal although a much longer reaction time is necessary. In these latter reactions no evidence is obtained for the existence of activated species (105) such as "CpCr(NO)₂MgCl". When finely divided zinc metal is employed, no reaction occurs and the use of a magnesium amalgam in THF causes immediate decomposition of the starting chloro complex. Correspondingly, the attempted reduction of the CpM(NO)₂Cl (M = Mo or W) compounds using a wide variety of reaction conditions fails to yield the still unknown [CpM(NO)₂]₂ (M = Mo or W) complexes.

The original synthesis of [CpCr(NO)₂]₂ from CpCr(NO)₂Cl and NaBH₄ is believed to occur through the formation of CpCr(NO)₂H although no evidence for this hydrido intermediate was obtained (90). However, we find that CpMo(NO)₂Cl reacts with NaBH₄ in MeOH or EtOH at -30°C to yield a volatile pale-green solid which decomposes rapidly at room temperature. Its infrared spectrum (1740 and 1645 cm⁻¹ in EtOH) bears a striking resemblance to those of the alkyl and aryl derivatives, and on this basis the complex is formulated as CpMo(NO)₂H. The thermal or oxidative degradation of this species, either in solution or in the solid, fails to provide the [CpMo(NO)₂]₂ compound.

The infrared spectrum of [CpCr(NO)₂]₂ exhibits two strong nitrosyl absorptions at 1667 and 1512 cm⁻¹ in CH₂Cl₂, indicative of both terminal and bridging nitrosyl ligands. In CDCl₃ solutions the dimer exists in both the cis and trans forms, F and G, as evidenced by its
room temperature proton NMR which contains two sharp singlets at τ5.20 and τ5.00 in the ratio of 1:20 (93). In the solid state, \([\text{CpCr(NO)}_2\]_2\) (93), is isostructural with trans-[\text{CpFe(CO)}_2\]_2 (130), trans-\([\text{CpCr(NO)}(\text{SPh})]_2\) (91) and trans-[\text{CpCr(NO)}(\text{NH}_2)]_2 (92). The metal-metal distance of 2.615 Å in the dinitrosyl dimer is significantly shorter than those of the SPh (2.90 Å) and NH\(_2\) (2.67 Å) containing species. While the terminal Cr-N-O bond angles in the SPh and NH\(_2\) compounds deviate from linearity by about 10°, the corresponding angle in the dinitrosyl species is virtually linear (176.6°), possibly as a result of reduced electron density on the metal atoms of the nitrosyl bridged compound. The terminal Cr-N bond lengths for all three dimers fall within the range of 1.64-1.69 Å and are not much different from the value of 1.71 Å in the CpCr(NO)\(_2\)Cl compound (106). As expected, the Cr-N distance (1.960 Å) in the symmetrically-bridging nitrosyl ligands is considerably longer than the terminal Cr-N bonds.

The mass spectrum of \([\text{CpCr(NO)}_2\]_2\) (Table XIII) displays the molecular ion peak and is consistent with the dimeric formulation. Since no \([\text{CpCr(NO)}_n]^\dagger\) or \([\text{C}_3\text{H}_3\text{Cr(NO)}_n]^\dagger\) (n = 1 or 2) fragments are formed, it
Table XIII. Low Resolution Mass Spectral Data for [CpCr(NO)$_2$]$_2$.

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Abundance</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>354</td>
<td>3.1</td>
<td>Cp$_2$Cr$_2$(NO)$_4$^+</td>
</tr>
<tr>
<td>324</td>
<td>2.2</td>
<td>Cp$_2$Cr$_2$(NO)$_3$^+</td>
</tr>
<tr>
<td>294</td>
<td>0.3</td>
<td>Cp$_2$Cr$_2$(NO)$_2$^+</td>
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<td>264</td>
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<td>Cp$_2$Cr$_2$(NO)^+</td>
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<tr>
<td>182</td>
<td>6.1</td>
<td>(C$_3$H$_3$)$_2$Cr$_2$^+</td>
</tr>
<tr>
<td>117</td>
<td>2.3</td>
<td>CpCr^+</td>
</tr>
<tr>
<td>52</td>
<td>4.2</td>
<td>Cr^+</td>
</tr>
</tbody>
</table>

^a The assignments involve the most common naturally occurring isotope, i.e. $^{52}$Cr.
appears that fragmentation prefers to occur without rupture of the metal-metal bond. In contrast, the isoelectronic non-bridged [CpCr(CO)₃]₂ dimer does not display a molecular ion peak and, indeed, only mononuclear fragments are found (131). Unlike [CpCr(NO)(OEt)]₂ or [CpCr(NO)Cl]₂, and contrary to a previous report (89), we find that the mass spectrum of [CpCr(NO)₂]₂ does not contain a peak which may be assigned to the [Cp₂Cr]⁺ fragment. Instead we assign the peak at m/e = 182 to the dinuclear [(C₃H₅)₂Cr₂]⁺ fragment. Furthermore, the greater abundance of dinuclear species in the mass spectrum of [CpCr(NO)₂]₂ suggests that the nitrosyl ligand forms a stronger bridge than do the OEt or Cl ligands in related compounds.
Conclusion

It should be stressed that while metal-nitrosyl bonds may be formed by a variety of synthetic methods, none of these preparative routes has general applicability. In contrast, this work has shown nitrosyl chloride to be the single most versatile synthetic reagent available for the formation of M-NO linkages. The direct formation of chloronitrosyl complexes from neutral carbonyl compounds is of particular interest. As discussed in this thesis, the former compounds, which contain a very reactive metal-chlorine bond, serve as useful precursors in the preparation of further nitrosyl derivatives. For example, the metal-halide bond may be converted to a large variety of metal-heteroatom \( \sigma \)-bonds containing elements from Groups IVA, VA and VIA.

Obviously, the behavior of nitrosyl chloride with many more neutral and anionic metal carbonyl complexes remains to be investigated. Most importantly, such studies should be undertaken with the aim of developing convenient synthetic routes to nitrosyl complexes, and not simply as a study of the chemistry of nitrosyl chloride.

The scarcity of anionic nitrosyl complexes is surprising, especially in view of the multitude of anionic carbonyl compounds which
has been characterized. While attempts to effect the chemical reduction of various nitrosyl compounds have so far been unsuccessful, nitrosyl-containing anions might be obtained by electrochemical reduction at a controlled potential. Further work in this direction is currently in progress.

While numerous nitrosyl compounds are known, many, which are expected to be stable under ambient conditions, are simply nonexistent at present. For instance, in the "pseudo iron-carbonyl" series, Fe(CO)$_5$, Mn(CO)$_4$(NO), Cr(CO)$_3$(NO)$_2$ and V(CO)$_2$(NO)$_3$, the last two compounds have yet to be reported. The synthesis of such unknown species should be endeavored in order to enhance our knowledge of potentially useful nitrosyl complexes. Specifically, the preparation of these compounds should not be viewed as an end in itself. Rather, future studies should be directed at establishing the comparative chemistry between similar nitrosyl and carbonyl compounds and the practical application of nitrosyl complexes in various organic syntheses.
REFERENCES

   (b) J.A.J. Thompson and W.A.G. Graham, ibid., 6, 1875 (1967).
   (b) B.J. Hathaway, D.G. Holah and A.E. Underhill, ibid., 2444 (1962).
   (g) N.G. Connelly and J.D. Davis, ibid., 38, 385 (1972).
53. F. Steel, ibid., 269, 40 (1952).
   (b) B.F.G. Johnson, S. Bhaduri and N.G. Connelly, ibid., 40, C36 (1972).
   (d) M. Green and S.H. Tayler, ibid., 2629 (1972).
   (e) N.G. Connelly, ibid., 2183 (1973).
74. J.K. Hoyano, unpublished results.
    (1941).
77. E.O. Fischer, O. Beckert, W. Hafner and H.O. Stahl, Z. Naturforsch.,
    10b, 598 (1955).
    (1973).
    23b, 106 (1968).
(c) A.E. Crease, Ph.D. Thesis (1973).


(c) F. Calderazzo, Pure Appl. Chem., 33, 453 (1973).


