

SOME CHEMISTRY OF ORGANOMETALLIC NITROSYL COMPLEXES OF

Cr, Mo and W

By

TEEN TEEN CHIN

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Department of CHEMISTRY

The University of British Columbia  
Vancouver, Canada

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## Abstract

While cationic nitrosyl complexes containing the " $\text{Cp}'\text{M}(\text{NO})_2$ " ( $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$  ( $\text{Cp}$ ) or  $\eta^5\text{-C}_5\text{Me}_5$  ( $\text{Cp}^*$ );  $\text{M} = \text{Cr}, \text{Mo}$  and  $\text{W}$ ) fragment are well-known, cationic nitrosyl complexes containing the " $\text{Cp}'\text{M}(\text{NO})$ " fragment are rarely encountered. The preparation of a series of cationic nitrosyl complexes containing the latter fragment resulting from the treatment of  $[\text{Cp}'\text{M}(\text{NO})\text{X}_m]_n$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $\text{X} = \text{I}, \text{Br}$  or  $\text{Cl}$ ;  $m = 2$ ;  $n = 1$  or  $2$ ;  $\text{M} = \text{Cr}$ ;  $\text{X} = \text{I}$ ;  $m = 1$ ;  $n = 2$ ) with nitrosonium,  $[\text{NO}]^+$ , or silver(I),  $[\text{Ag}]^+$ , salts in  $\text{CH}_3\text{CN}$  is described. Treatment of the  $\text{Mo}$  and  $\text{W}$  dihalo nitrosyl complexes,  $[\text{Cp}'\text{M}(\text{NO})\text{X}_2]_n$ , with one equivalent of  $[\text{NO}]^+$  or  $[\text{Ag}]^+$  salts in  $\text{CH}_3\text{CN}$  affords the diamagnetic monocations  $[\text{Cp}'\text{M}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$ . In a special case, the treatment of  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  with one equivalent of  $[\text{NO}]^+$  in  $\text{CH}_3\text{CN}$  affords the unprecedented dication  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3]^{2+}$ . These diamagnetic cations have been characterized by their elemental analyses, IR and NMR data and single-crystal X-ray structural determinations of  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2][\text{BF}_4]$  and  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ . Extension of this chemistry to  $[\text{CpCr}(\text{NO})\text{I}]_2$  results in the isolation of a new paramagnetic cationic complex,  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2][\text{PF}_6]$ . The chromium complex (also isolated as its  $\text{BPh}_4^-$  salt) is characterized by its elemental analysis, IR and ESR data as well as a single crystal X-ray structure

determination. Upon treatment of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2][\text{PF}_6]$  with NaOMe, the bimetallic  $[\text{CpCr}(\text{NO})(\text{OMe})]_2$  complex is obtained.

The synthesis and characterization of the dinitrosyl dimers  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) is described. They are prepared in moderate yields by the reduction of  $\text{Cp}^*\text{M}(\text{NO})_2\text{Cl}$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) with zinc amalgam in THF. The molybdenum dimer  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$ , reacts with  $\text{SnCl}_2$  to form the chloro complex,  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$ .

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## Lists of Abbreviations

Å	-	angstrom
cm <sup>-1</sup>	-	wavenumber
bpy	-	2,2'-bipyridine
Cp	-	η <sup>5</sup> -cyclopentadienyl
Cp <sup>*</sup>	-	η <sup>5</sup> -pentamethylcyclopentadienyl
calcd	-	calculated
DMF	-	N,N'-dimethylformamide
deg	-	degree
e.s.d.	-	estimated standard deviation
g	-	gram
h	-	hour
[HB(Me <sub>2</sub> pyz) <sub>3</sub> ] <sup>-</sup>	-	tris(3,5-dimethylpyrazolyl)borate
Me	-	CH <sub>3</sub> , methyl
Ph	-	C <sub>6</sub> H <sub>5</sub> , phenyl
phen	-	1,10-phenanthroline
ESR	-	electron spin resonance
IR	-	infrared
NMR	-	nuclear magnetic resonance
[NO] <sup>+</sup>	-	nitrosonium ion
THF	-	tetrahydrofuran
X	-	I, Br or Cl ligand

$\nu_{\text{NO}}$	-	nitrosyl stretching frequency
$\nu_{\text{CO}}$	-	carbonyl stretching frequency
ppm	-	parts per million
$^{13}\text{C}\{^1\text{H}\}$	-	proton-decoupled carbon 13
$m/z$	-	mass-to-charge ratio (in the mass spectrum)
$[\text{P}]^+$	-	parent molecular ion (in the mass spectrum)

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Lastly, I want to express my gratitude to my parents for their support throughout this work.

## **Chapter 1**

### **General Introduction**

Coordination of small molecules to transition metals has always been of interest to organometallic chemists. The incorporation of the gaseous molecules into transition-metal complexes may alter the chemistry of the bound small molecule from that of the free species. This allows the reactivity of the coordinated molecules to be exploited. One of the most important small molecules to be exploited to date is carbon monoxide, CO, and volumes of information have been published on the chemistry of transition-metal carbonyl complexes.<sup>1</sup> The chemistry of transition-metal nitrosyl complexes (compounds containing the NO ligand), however, is less well developed. But, with the interest in the synthesis and reactivity of nitrosyl complexes over the last two decades,<sup>2</sup> it is clear that the extent of chemistry exhibited by these nitrosyl complexes may be as broad as that displayed by their carbonyl counterparts.

A major thrust in the investigations of transition-metal nitrosyl complexes derives from the considerable interest in :<sup>3,4</sup>

(i) the conversion of NO gas, a major pollutant emitted from the combustion of fossil fuels, to less harmful products such as N<sub>2</sub> and NH<sub>3</sub>. The first step is to trap the NO on a transition-metal center to form a nitrosyl complex. Once

this is obtained, the reactivity of the coordinated NO ligand can be exploited to attain the desired objective.

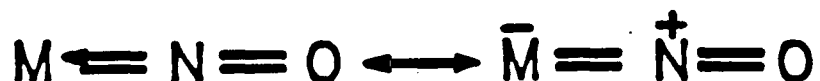
(ii) the utilization of transition-metal nitrosyl complexes in organic synthesis; e.g. to study the transformations and reactions of the coordinated NO ligand with various organic substrates to yield N-bonded organic compounds.

The electronic structures of NO and CO are very similar except that NO has one more electron which occupies the  $\pi^*$  orbital. The presence of this extra electron allows the NO ligand to behave in a fashion unobserved for a carbonyl group, i.e. to form a bent M-N-O bond. Thus, the different bonding modes of the NO group may be described as follows :<sup>5,6</sup>

- a) terminal, linear M-NO ,
- b) terminal, bent M-NO , and
- c) bridging.

a) Terminal, Linear M-NO Bond

The terminal, linear bonding mode of nitrosyl ligands is the most common, especially for organometallic compounds. In its terminal, linear form, as illustrated by the resonance structures below, the nitrosyl ligand

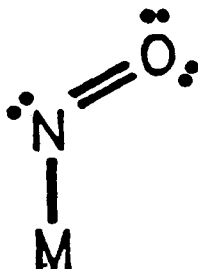




functions as a three-electron donor. The idealized MNO angle is  $180^\circ$ , but this angle is usually between  $165^\circ$  to  $180^\circ$ . The bonding involves a synergic combination of  $\sigma$ -donation from the nitrosyl ligand and  $M\pi \rightarrow NO\pi^*$  backdonation. The degree of the metal  $\pi$ -donation is dependent on the electron richness of the metal center. Traditionally, the linear nitrosyl ligand is considered to be bound formally as  $NO^+$ , which is isoelectronic to CO.

b) Terminal, Bent M-NO Bond

The terminal, bent bonding mode of NO is not as common as the terminal, linear bonding mode in organometallic compounds. This type of bonding is often observed for late transition-metal nitrosyl coordination complexes, but is rare in organometallic nitrosyl complexes. In this form, the nitrosyl ligand functions as a one-electron donor (formally  $NO^-$ ), i.e.



Although the idealized MNO angle is  $120^\circ$ , the observed MNO

angles can range between  $120^\circ$  to  $140^\circ$ , depending on the extent of the interaction of the nitrogen lone pair with the metal. Bent nitrosyl groups are generally found at the apical position of square pyramidal complexes.

An ideal example of a transition-metal nitrosyl complex representing the two types of M-NO coordination geometries (linear M-NO and bent M-NO) described earlier is shown in Figure 1.1.<sup>7</sup> The Ru-NO bond angle of the axial NO ligand

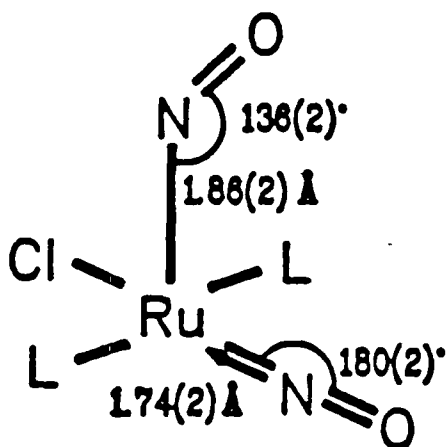


Figure 1.1 Structure of  $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2(\text{Cl})]^+$

is much smaller than that of the basal NO ligand. Also, the Ru-N bond distance in the bent NO ligand is longer than in the linear NO ligand. These structural features are consistent with the simple bonding description described in the preceding paragraphs.

c) Bridging NO group

Complexes containing the bridging NO ligand are known although they are much less common than the terminal NO derivatives. Both doubly and triply bridging NO groups are known. An example of a complex containing the doubly and triply bridging forms is shown in Figure 1.2.<sup>8</sup> In the doubly bridging mode, the NO ligand donates two electrons to one metal and one electron to the other metal. The triply bridged NO ligand is considered to be a one-electron donor to each metal centre.

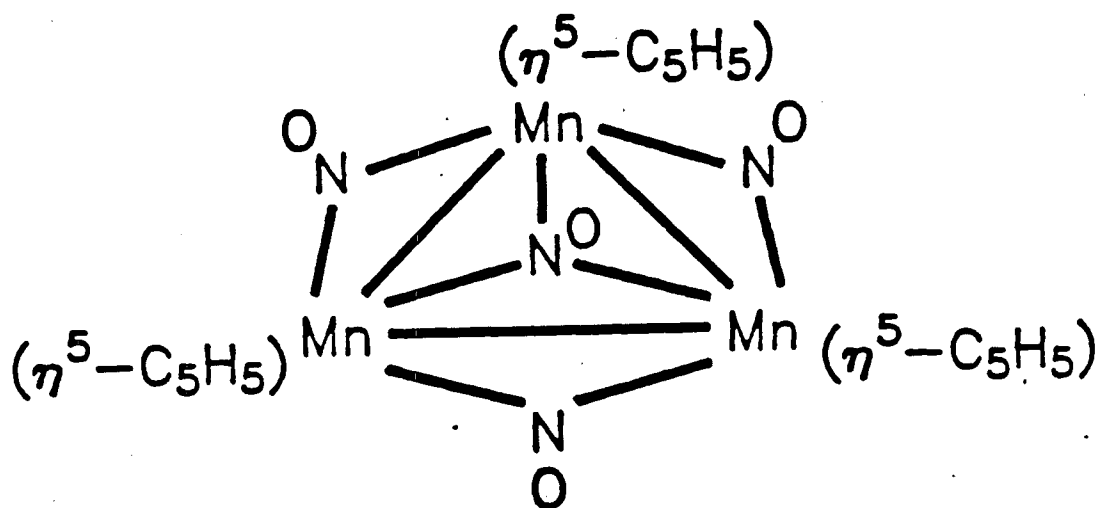
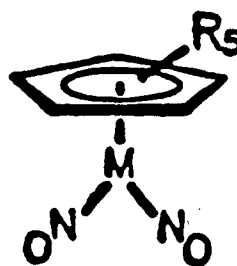
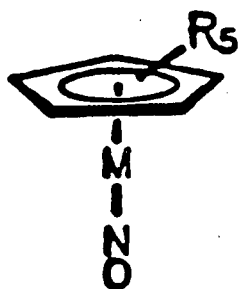


Figure 1.2 Structure of  $\text{Cp}_3\text{Mn}_3(\text{NO})_4$

One of the most distinctive physical properties of the NO ligand is the infrared  $\nu_{\text{NO}}$  band. Terminal NO complexes exhibit strong  $\nu_{\text{NO}}$  bands ranging from  $1900\text{ cm}^{-1}$  (in cationic

complexes) to as low as  $1455\text{ cm}^{-1}$  (in anionic complexes). The  $\nu_{\text{NO}}$  frequencies of bent MNO groups are usually lower than the  $\nu_{\text{NO}}$  frequencies of linear MNO groups but their ranges overlap such that the  $\nu_{\text{NO}}$  frequency is not a reliable criterion for assigning structures. Bridging NO groups generally exhibit lower  $\nu_{\text{NO}}$  frequencies than terminal NO groups in their IR spectra.

The major objective at the outset of this research was to determine the effect of NO ligands on the characteristic chemistry of organometallic nitrosyl complexes. Specifically, the work presented in this thesis deals primarily with the synthesis and reactivity of some Group 6 organometallic nitrosyl complexes containing the  $\text{Cp}'\text{M}(\text{NO})$  or  $\text{Cp}'\text{M}(\text{NO})_2$  fragments ( $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$  (Cp) or  $\eta^5\text{-C}_5\text{Me}_5$  ( $\text{Cp}^*$ );  $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ), i.e.



( $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ;  $\text{R} = \text{H}$  or  $\text{Me}$ )

The complexes that contain these fragments possess piano stool molecular structures and the M-NO linkages are essentially linear. In this connection, Chapter 2 of this thesis describes the reactions of the complexes,  $[\text{Cp}'\text{M}(\text{NO})\text{X}_2]_n$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $n = 1$  or  $2$ ;  $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ ) and  $[\text{CpCr}(\text{NO})\text{I}]_2$ , with  $[\text{Ag}]^+$  or  $[\text{NO}]^+$  salts in acetonitrile. This study has led to the syntheses of a series of novel diamagnetic cationic complexes  $[\text{Cp}'\text{M}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ ) and  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3]^{2+}$ . Also, the synthesis, characterization and reactivity of a paramagnetic radical cation  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]^{\cdot+}$  are presented.

Chapter Three deals with the reduction chemistry of the dinitrosyl compounds  $\text{Cp}^*\text{M}(\text{NO})_2\text{Cl}$  ( $\text{M} = \text{Cr}$ ,  $\text{Mo}$ ,  $\text{W}$ ). This study has led to the isolation of the new dinitrosyl dimers  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$  ( $\text{M} = \text{Cr}$  and  $\text{Mo}$ ). The preparation and chemical properties of these dimers is described and compared with their valence isoelectronic carbonyl analogues  $[\text{Cp}'\text{M}(\text{CO})_2]_2$  ( $\text{Cp}' = \text{Cp}$  or  $\text{Cp}^*$ ;  $\text{M} = \text{Fe}$ ,  $\text{Ru}$ ).

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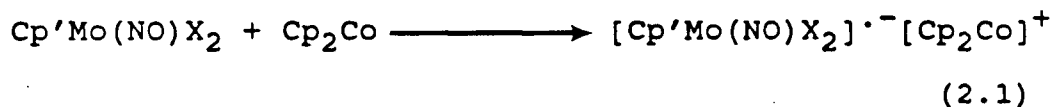
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**Chapter 2**

**New Organometallic Cationic Nitrosyl Complexes of  
Cr, Mo and W**

## Introduction

An electrochemical study on the series of dihalo nitrosyl complexes,  $[\text{Cp}'\text{Mo}(\text{NO})\text{X}_2]_n$  [ $\text{Cp}' = \text{Cp}$  or  $\text{Cp}^*$ ;  $\text{X} = \text{I}$ ,  $\text{Br}$  or  $\text{Cl}$ ;  $n = 1$  or  $2$ ], was initiated in our laboratory by G. B. Richter-Addo a few years ago.<sup>1</sup> In general, these complexes undergo reversible one-electron reductions (by cyclic voltammetry). The electrochemically observed reductions can be effected on a preparative scale by employing  $\text{Cp}_2\text{Co}$  as the chemical reductant, i.e.



These unusual radical anionic complexes are isolable in good yields and have been fully characterized.<sup>2</sup>

In this connection, it has also been observed that these dihalo nitrosyl complexes exhibit irreversible oxidation behaviour. Accordingly, the chemical behaviour of the  $\text{Cp}'\text{Mo}(\text{NO})\text{X}_2$  complexes under oxidizing conditions becomes of interest. In this chapter, the reactions of these nitrosyl complexes with two different chemical oxidants ( $[\text{NO}]\text{PF}_6$  and  $[\text{Ag}]\text{Y}$  ( $\text{Y} = \text{BF}_4$  or  $\text{PF}_6$ )) in  $\text{CH}_3\text{CN}$  are presented. This study has also been extended to encompass the diiodo complexes of



tungsten,  $[\text{Cp}'\text{W}(\text{NO})\text{I}_2]_n$  ( $n = 1$  or  $2$ ), and the related monoiodo chromium complex,  $[\text{CpCr}(\text{NO})\text{I}]_2$ .

This investigation has led to the synthesis of a new series of diamagnetic monocationic nitrosyl complexes  $[\text{Cp}'\text{M}(\text{NO})\text{X}(\text{NCCH}_3)_2][\text{Y}]$  ( $\text{Cp}' = \text{Cp}$  or  $\text{Cp}^*$ ;  $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $\text{X} = \text{I}$ ,  $\text{Br}$  or  $\text{Cl}$ ;  $\text{Y} = \text{BF}_4$  or  $\text{PF}_6$ ) and a dicationic complex  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ . Extension of this investigation to the related chromium complex,  $[\text{CpCr}(\text{NO})\text{I}]_2$ , has resulted in the isolation of a novel paramagnetic cationic complex  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2][\text{PF}_6]$ . In this chapter, the synthesis and characterization of these cationic complexes is presented. Some reactivity of the paramagnetic cationic chromium complex  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2][\text{PF}_6]$  is also described.

### Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions using conventional Schlenk techniques<sup>3</sup> or in a Vacuum Atmospheres Corp. Dri-Lab Model He-43-2 drybox. The halo nitrosyl reagents,  $[\text{CpMo}(\text{NO})\text{Br}_2]_2$ <sup>4</sup>,  $\text{Cp}^*\text{W}(\text{NO})\text{I}_2$ <sup>5</sup> and  $[\text{CpCr}(\text{NO})\text{I}]_2$ <sup>6</sup>, were prepared by published procedures. The permethylated  $\text{Cp}^*\text{Mo}(\text{NO})\text{X}_2$  (X = Br, I) analogues were prepared by treating  $\text{Cp}^*\text{Mo}(\text{CO})_2(\text{NO})$  and  $\text{X}_2$  in a manner similar to that employed for the preparation of their Cp analogues. Both  $[\text{Cp}'\text{Mo}(\text{NO})\text{Cl}_2]_2$  ( $\text{Cp}' = \text{Cp}$  or  $\text{Cp}^*$ )<sup>7</sup> complexes were prepared by treating the corresponding  $\text{Cp}'\text{Mo}(\text{CO})_2(\text{NO})$  species with an equimolar amount of  $\text{PCl}_5$  in  $\text{Et}_2\text{O}$ . The  $[\text{Cp}'\text{Mo}(\text{NO})\text{Cl}_2]_2$  complexes that precipitated from  $\text{Et}_2\text{O}$  were isolated by filtration of the reaction mixture and subsequently dried in vacuo. The purity of the halo nitrosyl complexes was ascertained by elemental analyses and conventional spectroscopic techniques. All other reagents used were of reagent grade or of comparable purity and were purchased from commercial suppliers. Acetonitrile, hexanes, and diethyl ether were dried with  $\text{CaH}_2$ , nitromethane with  $\text{CaSO}_4$ , THF with sodium/benzophenone ketyl, toluene and benzene with sodium, and  $\text{CH}_2\text{Cl}_2$  with  $\text{P}_2\text{O}_5$ . The solvents were distilled from their respective drying agents and purged with

dry  $N_2$  prior to use. All reactions described below were performed at ambient temperatures.

Infrared spectra were obtained with a Nicolet 5DX FT-IR instrument (internally calibrated with a He/Ne laser). Proton NMR spectra were obtained on a Bruker WP-80 or Varian XL-300 spectrometer with reference to the residual proton signal of the deuterated solvent employed, and are reported in ppm downfield from  $Me_4Si$ . Carbon-13 NMR spectra were recorded on a Varian XL-300 spectrometer operated by the staff of the departmental NMR laboratory headed by Dr. S.O. Chan. The ESR spectra were recorded using a spectrometer and interfaced computer system<sup>8</sup> operated by Dr. F.G. Herring. Low resolution mass spectra were recorded with a Kratos MS50 instrument, at 70 eV, by the staff of the mass-spectrometry laboratory headed by Dr. G.K. Eigendorf. Elemental analyses were performed by Mr. P. Borda.

**Preparation of  $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ , 1.** A stirred solution of  $Cp^*Mo(NO)I_2$  (1.18 g, 2.29 mmol) in  $CH_3CN$  (60 mL) was treated dropwise at room temperature with a solution of  $[NO]PF_6$  (0.401 g, 2.29 mmol) in  $CH_3CN$  (15 mL). The reaction mixture was allowed to stir for 40 min during which time the colour of the solution changed from dark reddish-brown to light brown. The progress of the reaction

was monitored by IR spectroscopy which revealed that the intensity of the  $\nu_{\text{NO}}$  of  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  ( $1660\text{ cm}^{-1}$ ) gradually decreased with the concomitant growth of a new nitrosyl band at  $1680\text{ cm}^{-1}$ . The volume of the solvent in the final reaction mixture was then reduced to 10 mL in vacuo. Addition of diethyl ether (120 mL) precipitated  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ , complex 1, as an air-stable, yellow, microcrystalline solid (0.617 g, 0.915 mmol, 40% yield). The analytical, IR and NMR data for this compound and the other new compounds synthesized in this work are collected in Tables 2.1, 2.2 and 2.3 presented on pages 25, 26, and 27, respectively.

The dicationic complex 1 could also be obtained in similar yield by treating  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  with two equivalents of  $[\text{Ag}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$ . The final reaction mixture was filtered through a column (2 x 2 cm) of Celite supported on a frit. Workup of the resulting yellow filtrate was as described above.

Large oval shaped crystals of  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$  1 suitable for X-ray crystallographic analysis were grown by maintaining a saturated  $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$  solution of complex 1 at  $0^\circ\text{C}$  for 7 days.

**Preparation of  $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6$ , 2.** Solid  $[\text{Ag}]\text{PF}_6$  (0.256 g, 1.01 mmol) was added to a stirred  $\text{CH}_3\text{CN}$

solution (20 mL) of  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  (0.520 g, 1.01 mmol). The colour of the reaction mixture changed from dark reddish-brown to dark yellow and a yellow-white precipitate formed. After 30 min, a IR spectrum of the supernatant solution revealed the complete consumption of the starting organometallic complex ( $\nu_{\text{NO}}$  1660  $\text{cm}^{-1}$ ) and the formation of a new nitrosyl-containing compound ( $\nu_{\text{NO}}$  1684  $\text{cm}^{-1}$ ). The final reaction mixture was filtered through a column (2 x 3 cm) of Celite supported on a medium porosity glass frit. The resulting dark yellow filtrate was concentrated to 5 mL, layered with  $\text{Et}_2\text{O}$  (40 mL) and cooled to 0°C for 12 h. The microcrystalline solid that deposited was collected and dried in vacuo ( $5 \times 10^{-3}$  mm) for 5-6 h. This procedure afforded 0.21 g (0.34 mmol, 34% yield) of  $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6$ , complex 2, as an analytically pure, dark yellow microcrystalline solid.

**Preparation of  $[\text{CpMo}(\text{NO})\text{Br}(\text{NCCH}_3)_2]\text{BF}_4$ , 3.** To a stirred  $\text{CH}_3\text{CN}$  solution (40 mL) of  $\text{CpMo}(\text{NO})\text{Br}_2$  (1.22 g, 3.47 mmol) was added solid  $[\text{Ag}]\text{BF}_4$  (0.67 g, 3.4 mmol). The colour of the solution instantaneously changed from light brown to dark orange and a creamy, light yellow solid precipitated. After 30 min, an IR spectrum of the supernatant solution revealed the complete consumption of  $\text{CpMo}(\text{NO})\text{Br}_2$  ( $\nu_{\text{NO}}$  1686  $\text{cm}^{-1}$ ) and the formation of a new product ( $\nu_{\text{NO}}$  1709  $\text{cm}^{-1}$ ).

Subsequent workup of the reaction mixture was as described for the preparation of the cationic complex 2. This procedure afforded 0.92 g (2.1 mmol, 61% yield) of  $[\text{CpMo}(\text{NO})\text{Br}(\text{NCCH}_3)_2]\text{BF}_4$ , complex 3, as a light brown, microcrystalline solid.

$[\text{CpMo}(\text{NO})\text{Br}(\text{NCCH}_3)_2]\text{PF}_6$  could also be synthesized by treatment of  $\text{CpMo}(\text{NO})\text{Br}_2$  with an equimolar amount of  $[\text{NO}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  but the transformation did not proceed cleanly and the final cationic product was obtained in very low isolated yield (5%).

**Preparation of  $[\text{Cp}^*\text{Mo}(\text{NO})\text{Br}(\text{NCCH}_3)_2]\text{PF}_6$ , 4.** A stirred  $\text{CH}_3\text{CN}$  solution (40 mL) of  $\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2$  (0.26 g, 0.62 mmol) was treated dropwise with a solution of  $[\text{NO}]\text{PF}_6$  (0.107 g, 0.611 mmol) in  $\text{CH}_3\text{CN}$  (10 mL), and the progress of the reaction was monitored by IR spectroscopy. The intensity of the nitrosyl band due to  $\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2$  ( $\nu_{\text{NO}}$  1659  $\text{cm}^{-1}$ ) slowly decreased with an increase in the intensity of a new nitrosyl band at 1684  $\text{cm}^{-1}$ . After 2 h, the reaction mixture was treated in a manner similar to that described for the preparation of complex 1. By this procedure, the complex 4,  $[\text{Cp}^*\text{Mo}(\text{NO})\text{Br}(\text{NCCH}_3)_2]\text{PF}_6$ , was isolated as a dark yellow microcrystalline solid in 68% yield (0.24 g, 0.42 mmol).

Preparation of  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{BF}_4$ , 5. Solid  $[\text{Ag}]\text{BF}_4$  (0.280 g, 1.44 mmol) was added to a stirred  $\text{CH}_3\text{CN}$  solution (30 mL) of  $\text{CpMo}(\text{NO})\text{Cl}_2$  (0.38 g, 1.4 mmol). The colour of the reaction mixture changed from dark orange-brown to dark yellow and a white solid precipitated. After 30 min, an IR spectrum of the solution mixture revealed the complete consumption of  $\text{CpMo}(\text{NO})\text{Cl}_2$  ( $\nu_{\text{NO}}$  1680  $\text{cm}^{-1}$ ) and the formation of a new product ( $\nu_{\text{NO}}$  1707  $\text{cm}^{-1}$ ). Subsequent workup of the reaction mixture was as described above for the preparation of complex 2. By this method, 0.22 g (0.56 mmol, 38% yield) of analytically pure, yellow-orange crystals of  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{BF}_4$ , complex 5, were obtained.

$[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{PF}_6$  could also be obtained by the treatment of  $\text{CpMo}(\text{NO})\text{Cl}_2$  with  $[\text{NO}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  but this route afforded the cation in very low isolated yield (5%).

Large crystals of  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{BF}_4$  suitable for X-ray crystallographic analysis were obtained by maintaining a  $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$  solution of the salt at  $-25^\circ\text{C}$  for 7 days.

Preparation of  $[\text{Cp}^*\text{Mo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{PF}_6$ , 6. A  $\text{CH}_3\text{CN}$  solution (10 mL) of  $[\text{NO}]\text{PF}_6$  (0.208 g, 1.19 mmol) was added dropwise to a stirred solution of  $\text{Cp}^*\text{Mo}(\text{NO})\text{Cl}_2$  (0.380 g, 1.24 mmol) in  $\text{CH}_3\text{CN}$  (30 mL). The colour of the reaction

mixture gradually changed from light brown to a lighter brown. The progress of the reaction was monitored by IR spectroscopy which revealed that the intensity of the  $\nu_{\text{NO}}$  of  $\text{Cp}^*\text{Mo}(\text{NO})\text{Cl}_2$  ( $1652\text{ cm}^{-1}$ ) gradually decreased with the concomitant growth of a new nitrosyl band at  $1680\text{ cm}^{-1}$ . After 2.5 h, the resulting reaction mixture was treated as described earlier for the preparation of complex 1. This method afforded analytically pure, light brown-orange crystals of  $[\text{Cp}^*\text{Mo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{PF}_6$ , complex 6, (0.11 g, 0.22 mmol, 20% yield).

**Preparation of  $[\text{CpW}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6$ , 7.** A stirred  $\text{CH}_3\text{CN}$  solution (60 mL) of  $\text{CpW}(\text{NO})\text{I}_2$  (0.67 g, 1.26 mmol) was treated dropwise at room temperature with a solution of  $[\text{NO}]\text{PF}_6$  (0.21 g, 1.20 mmol) in  $\text{CH}_3\text{CN}$  (15 mL). The reaction mixture was allowed to stir for 6 h during which time the colour of the solution changed from light brownish-orange to light brownish-green. Subsequent workup of the reaction mixture was as described for the preparation of complex 1. This procedure afforded 0.12 g (0.20 mmol, 15% yield) of analytically pure yellowish-green crystals of  $[\text{CpW}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6$ , 7.

**Preparation of  $[\text{Cp}^*\text{W}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{BF}_4$ , 8.** To a stirred  $\text{CH}_3\text{CN}$  solution (30 mL) of  $\text{Cp}^*\text{W}(\text{NO})\text{I}_2$  (0.750 g, 1.24



mmol) was added  $[\text{Ag}]\text{BF}_4$  (0.242 g, 1.24 mmol). The colour of the solution immediately changed from dark orange-red to dark yellow with the concomitant formation of a creamy yellow precipitate. After 30 min, an IR spectrum of the supernatant solution revealed the complete consumption of  $\text{Cp}^*\text{W}(\text{NO})\text{I}_2$  ( $\nu_{\text{NO}}$  1638  $\text{cm}^{-1}$ ) and the formation of a new product ( $\nu_{\text{NO}}$  1661  $\text{cm}^{-1}$ ). The reaction mixture was filtered through a column (2 x 2 cm) of Celite supported on a frit, and the filtrate was concentrated to 10 mL. Addition of  $\text{Et}_2\text{O}$  (40 mL) resulted in the precipitation of a dark yellow solid which was collected and washed with  $\text{Et}_2\text{O}$  (2 x 10 mL). The dark yellow solid was then dried in vacuo for 5-6 h. This procedure produced 0.58 g (0.89 mmol, 72% yield) of  $[\text{Cp}^*\text{W}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{BF}_4$ , **8**.

**Preparation of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ , **9**.** To a stirred solution containing  $[\text{CpCr}(\text{NO})\text{I}]_2$  (0.780 g, 1.42 mmol) in acetonitrile (30 mL) was added  $[\text{Ag}]\text{PF}_6$  (0.720 g, 2.80 mmol). The colour of the solution immediately changed from dark olive green to bright green, a change that was accompanied by the formation of a yellow-white precipitate. After the reaction mixture had been stirred for 30 min at room temperature, an IR spectrum of the solution indicated the complete consumption of the starting organometallic reactant ( $\nu_{\text{NO}}$  1680(s)  $\text{cm}^{-1}$ ) and the formation of a new nitrosyl-

containing compound ( $\nu_{\text{NO}}$  1710(s)  $\text{cm}^{-1}$ ). The reaction mixture was filtered through a column of Celite (2 x 2 cm) supported on a medium porosity glass frit. The bright green filtrate was concentrated to approximately 5 mL in vacuo. Addition of diethyl ether (20 mL) afforded a green microcrystalline solid that was collected by filtration and washed with diethyl ether (2 x 20 mL). The bright green solid was dried in vacuo ( $5 \times 10^{-3}$  mm) at room temperature for 12 hours. This procedure afforded  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ , complex 9, (0.50 g, 1.40 mmol, 49% yield) as an elementally pure, microcrystalline green solid.

Large crystals of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ , complex 9, suitable for X-ray crystallographic analysis were obtained by maintaining a  $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$  solution of complex 9 at  $-25^\circ\text{C}$  for 2 weeks.

A DMF solution of complex 9 used for ESR measurement was prepared as follows. The DMF solvent was first dried over anhydrous BaO for 24 h, filtered through Celite and then purged with  $\text{N}_2$ . In a glove box, a weighed amount of complex 9 was dissolved in enough DMF to make up a  $5 \times 10^{-5}$  M solution. A small portion of the resulting green solution was then transferred into a melting point capillary tube via a disposable syringe. The capillary tube was then sealed with Dow-Corning High Vacuum grease.

Reaction of  $[\text{CpCr}(\text{NO})\text{I}]_2$  with  $[\text{Ag}]\text{BF}_4$  in  $\text{CH}_2\text{Cl}_2$ . A stirred  $\text{CH}_2\text{Cl}_2$  solution (20 mL) of  $[\text{CpCr}(\text{NO})\text{I}]_2$  (0.400 g, 0.730 mmol) was treated with solid  $[\text{Ag}]\text{BF}_4$  (0.285 g, 1.46 mmol). The colour of the reaction mixture changed from dark green to darker olive green and a creamy white solid precipitated. After 30 min, an IR spectrum of the supernatant solution indicated the complete consumption of the starting organometallic reactant ( $\nu_{\text{NO}}$  1676(s)  $\text{cm}^{-1}$ ), and two new strong nitrosyl absorptions had grown in at 1842 and 1740  $\text{cm}^{-1}$ . The final reaction mixture was filtered through a column of Celite (2 x 3 cm) supported on a medium porosity glass frit. The olive green filtrate was treated dropwise with a  $\text{CH}_2\text{Cl}_2$  solution of  $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$  until the latter absorptions in its IR spectrum were completely replaced by bands at 1819(s) and 1713(vs)  $\text{cm}^{-1}$ . The resulting green brown solution was filtered through a short Florisil column (2 x 4 cm) supported on a frit. The golden-brown filtrate was concentrated to 5 mL and addition of hexanes (50 mL) afforded  $\text{CpCr}(\text{NO})_2\text{Cl}$  (0.020 g, 13% yield) which was collected and dried in vacuo. The organometallic compound was readily identified by its characteristic spectral properties.<sup>9</sup> : IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{NO}}$  1819(s), 1713(s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  4.77 (s, 5H); low

resolution mass spectrum (probe temperature 150°C),  $m/z$  212  $[P^+]$ .

**Some Reactivity of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ , 9.**

**a) Reaction of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  with  $\text{Na}[\text{BPh}_4]$ .**

To a  $\text{CH}_2\text{Cl}_2$  solution (20 mL) of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  (0.10 g, 0.27 mmol) was added solid  $\text{Na}[\text{BPh}_4]$  (0.090 g, 0.27 mmol). The resulting mixture was stirred at room temperature for 1 h, during which time the color of the solution changed from bright green to a slightly darker green, and a white solid precipitated. An IR spectrum of the solution exhibited only one strong nitrosyl band at 1718(s)  $\text{cm}^{-1}$ . The final mixture was filtered through a column of Celite (2 x 2 cm) supported on a glass frit, and the green filtrate was taken to dryness in vacuo. The resulting green solid was redissolved in  $\text{CH}_3\text{CN}$  (5 mL) and layered with  $\text{Et}_2\text{O}$  (30 mL). This mixture was cooled to -25°C overnight. This procedure afforded  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{BPh}_4 \cdot 1/2\text{CH}_3\text{CN}$  (0.0300 g, 20.3% yield) as an analytically pure microcrystalline green solid.

Anal. Calcd. for  $\text{C}_{33}\text{H}_{31}\text{N}_3\text{OBCr}$  : C, 71.77; H, 5.72; N, 8.62. Found: C, 71.30; H, 5.70; N, 8.35. IR (Nujol mull)  $\nu_{\text{NO}}$  1696(s)  $\text{cm}^{-1}$ ;  $\nu_{\text{CN}}$  2320(w), 2292(w), 2253(vw)  $\text{cm}^{-1}$ .

b) Reaction of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  with NaOMe.

Excess NaOMe (0.080 g, 1.5 mmol) was added to a stirred  $\text{CH}_2\text{Cl}_2$  solution (20 mL) of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  (0.10 g, 0.27 mmol). The colour of the reaction mixture gradually changed from bright green to dark olive green over the course of 30 min and a white precipitate was observed. An IR spectrum of the supernatant solution displayed a new nitrosyl band at  $1661(\text{s}) \text{ cm}^{-1}$ , and the nitrosyl band of the starting organometallic reactant ( $\nu_{\text{NO}} 1715 \text{ cm}^{-1}$ ) had completely disappeared. The final mixture was filtered through a Florisil column (2 x 4 cm), and the column was washed with  $\text{CH}_2\text{Cl}_2/\text{THF}$  (1:1) until the washings were colourless. The resulting olive green filtrate was taken to dryness in vacuo. The green solid was redissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL), layered with hexanes (15 mL) and cooled to  $-25^\circ\text{C}$  overnight. This procedure yielded  $[\text{CpCr}(\text{NO})(\text{OMe})]_2$  (0.012 g, 25% yield) which was readily identified by its characteristic spectroscopic properties.<sup>6</sup> IR( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{NO}} 1661(\text{s}) \text{ cm}^{-1}$ . Mass spectrum (probe temperature  $150^\circ\text{C}$ )  $m/z$  326  $[\text{P} - \text{NO}]^+$ .

Table 2.1. Physical and Analytical Data<sup>(a)</sup> for the Complexes 1 - 9.

Complex		Yield(%)	C	H	N
[Cp <sup>*</sup> Mo(NO)(NCCH <sub>3</sub> ) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	1	40	28.75 (29.26)	3.53 (3.66)	8.30 (8.54)
[Cp <sup>*</sup> Mo(NO)I(NCCH <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	2	34	26.89 (27.32)	3.34 (3.41)	6.42 (6.83)
[CpMo(NO)Br(NCCH <sub>3</sub> ) <sub>2</sub> ]BF <sub>4</sub>	3	61	24.86 (24.54)	2.60 (2.27)	9.25 (9.54)
[Cp <sup>*</sup> Mo(NO)Br(NCCH <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	4	68	29.75 (29.58)	3.79 (3.70)	7.36 (7.39)
[CpMo(NO)Cl(NCCH <sub>3</sub> ) <sub>2</sub> ]BF <sub>4</sub>	5	38	27.22 (27.31)	2.91 (2.78)	10.62 (10.62)
[Cp <sup>*</sup> Mo(NO)Cl(NCCH <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	6	20	32.25 (32.09)	4.06 (4.01)	8.20 (8.02)
[CpW(NO)I(NCCH <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	7	15	17.07 (17.06)	2.11 (1.74)	6.82 (6.63)
[Cp <sup>*</sup> W(NO)I(NCCH <sub>3</sub> ) <sub>2</sub> ]BF <sub>4</sub>	8	72	26.41 (26.05)	3.32 (3.26)	6.81 (6.51)
[CpCr(NO)(NCCH <sub>3</sub> ) <sub>2</sub> ]PF <sub>6</sub>	9	48	28.88 (28.88)	2.94 (2.93)	11.23 (11.13)

(a) Calculated values in parentheses.

Table 2.2. Infrared Data for the Complexes 1-9. (a)

Complex		Nujol mull		In CH <sub>3</sub> CN	Nujol mull
		$\nu_{\text{NO}}$ (cm <sup>-1</sup> )			$\nu_{\text{CN}}$ (cm <sup>-1</sup> )
[Cp <sup>+</sup> Mo(NO)(NCCH <sub>3</sub> ) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	1	1718	(1645)	1680 (1660)	2320, 2292(w)
[Cp <sup>+</sup> Mo(NO)I(NCCH <sub>3</sub> ) <sub>2</sub> ][PF <sub>6</sub> ]	2	1686	(1645)	1684 (1660)	2326, 2295(w)
[CpMo(NO)Br(NCCH <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ]	3	1701	(1668)	1709 (1686)	2326, 2297(w)
[Cp <sup>+</sup> Mo(NO)Br(NCCH <sub>3</sub> ) <sub>2</sub> ][PF <sub>6</sub> ]	4	1678	(1649)	1684 (1659)	2322, 2295(w)
[CpMo(NO)Cl(NCCH <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ]	5	1705	(1659)	1707 (1680)	2328, 2299(w)
[Cp <sup>+</sup> Mo(NO)Cl(NCCH <sub>3</sub> ) <sub>2</sub> ][PF <sub>6</sub> ]	6	1668	(1648)	1680 (1652)	2326, 2297(w)
[CpW(NO)I(NCCH <sub>3</sub> ) <sub>2</sub> ][PF <sub>6</sub> ]	7	1686	(1640)	1676 (1657)	2328, 2299(w)
[Cp <sup>+</sup> W(NO)I(NCCH <sub>3</sub> ) <sub>2</sub> ][BF <sub>4</sub> ]	8	1653	(1627)	1661 (1638)	2324, 2293(w)
[CpCr(NO)(NCCH <sub>3</sub> ) <sub>2</sub> ][PF <sub>6</sub> ]	9	1709	(1663)	1710 (1680)	2326, 2297(w)

(a) Nitrosyl stretching frequencies of the neutral precursors are given in parentheses.

Table 2.3.  $^1\text{H}$  NMR and  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR data (a) for the Complexes 1 - 8.

	$^1\text{H}$ NMR( $\delta$ )	$^{13}\text{C}$ ( $^1\text{H}$ ) NMR( $\delta$ )
$[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ 1	2.74 (s, 9H, $\text{CH}_3\text{CN}$ )	140.30 (s, $\text{CH}_3\text{CN}$ )
	2.18 (s, 15H, $\text{C}_5(\text{CH}_3)_5$ )	125.03 (s, $\text{C}_5(\text{CH}_3)_5$ )
		10.61 (s, $\text{C}_5(\text{CH}_3)_5$ )
		4.84 (s, $\text{CH}_3\text{CN}$ )
$[\text{Cp}^*\text{Mo}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6$ 2	2.65 (s, 6H, $\text{CH}_3\text{CN}$ )	140.89 (s, $\text{CH}_3\text{CN}$ )
	2.09 (s, 15H, $\text{C}_5(\text{CH}_3)_5$ )	122.63 (s, $\text{C}_5(\text{CH}_3)_5$ )
		11.20 (s, $\text{C}_5(\text{CH}_3)_5$ )
		4.89 (s, $\text{CH}_3\text{CN}$ )
$[\text{CpMo}(\text{NO})\text{Br}(\text{NCCH}_3)_2]\text{BF}_4$ 3	6.52 (s, 5H, $\text{C}_5\text{H}_5$ )	139.10 (s, $\text{CH}_3\text{CN}$ )
	2.56 (s, 6H, $\text{CH}_3\text{CN}$ )	112.20 (s, $\text{C}_5\text{H}_5$ )
		4.63 (s, $\text{CH}_3\text{CN}$ )
$[\text{Cp}^*\text{Mo}(\text{NO})\text{Br}(\text{NCCH}_3)_2]\text{PF}_6$ 4	2.67 (s, 6H, $\text{CH}_3\text{CN}$ )	n.o.
	2.08 (s, 15H, $\text{C}_5(\text{CH}_3)_5$ )	
$[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{BF}_4$ 8	6.51 (s, 5H, $\text{C}_5\text{H}_5$ )	137.63 (s, $\text{CH}_3\text{CN}$ )
	2.54 (s, 6H, $\text{CH}_3\text{CN}$ )	112.52 (s, $\text{C}_5\text{H}_5$ )
		4.46 (s, $\text{CH}_3\text{CN}$ )



Table 2.3 (Cont'd)

$[\text{Cp}^*\text{Mo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{PF}_6$ 6	2.65 (s, 6H, $\text{CH}_3\text{CN}$ )	137.11 (s, $\text{CH}_3\text{CN}$ )
	2.07 (s, 15H, $\text{C}_5(\text{CH}_3)_5$ )	123.33 (s, $\text{C}_5(\text{CH}_3)_5$ )
		10.68 (s, $\text{C}_5(\text{CH}_3)_5$ )
		4.48 (s, $\text{CH}_3\text{CN}$ )
$[\text{Cp}^*\text{W}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6$ <sup>(b)</sup> 7	6.45 (s, 5H, $\text{C}_5\text{H}_5$ )	n.o.
	1.96 (s, 6H, $\text{CH}_3\text{CN}$ )	
$[\text{Cp}^*\text{W}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{BF}_4$ 8	2.74 (s, 6H, $\text{CH}_3\text{CN}$ )	139.93 (s, $\text{CH}_3\text{CN}$ )
	2.21 (s, 15H, $\text{C}_5(\text{CH}_3)_5$ )	118.37 (s, $\text{C}_5(\text{CH}_3)_5$ )
		10.76 (s, $\text{C}_5(\text{CH}_3)_5$ )
		5.16 (s, $\text{CH}_3\text{CN}$ )

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(a) NMR spectra are recorded in  $\text{CD}_3\text{NO}_2$ .

(b) NMR spectrum is recorded in  $\text{CD}_3\text{CN}$ .

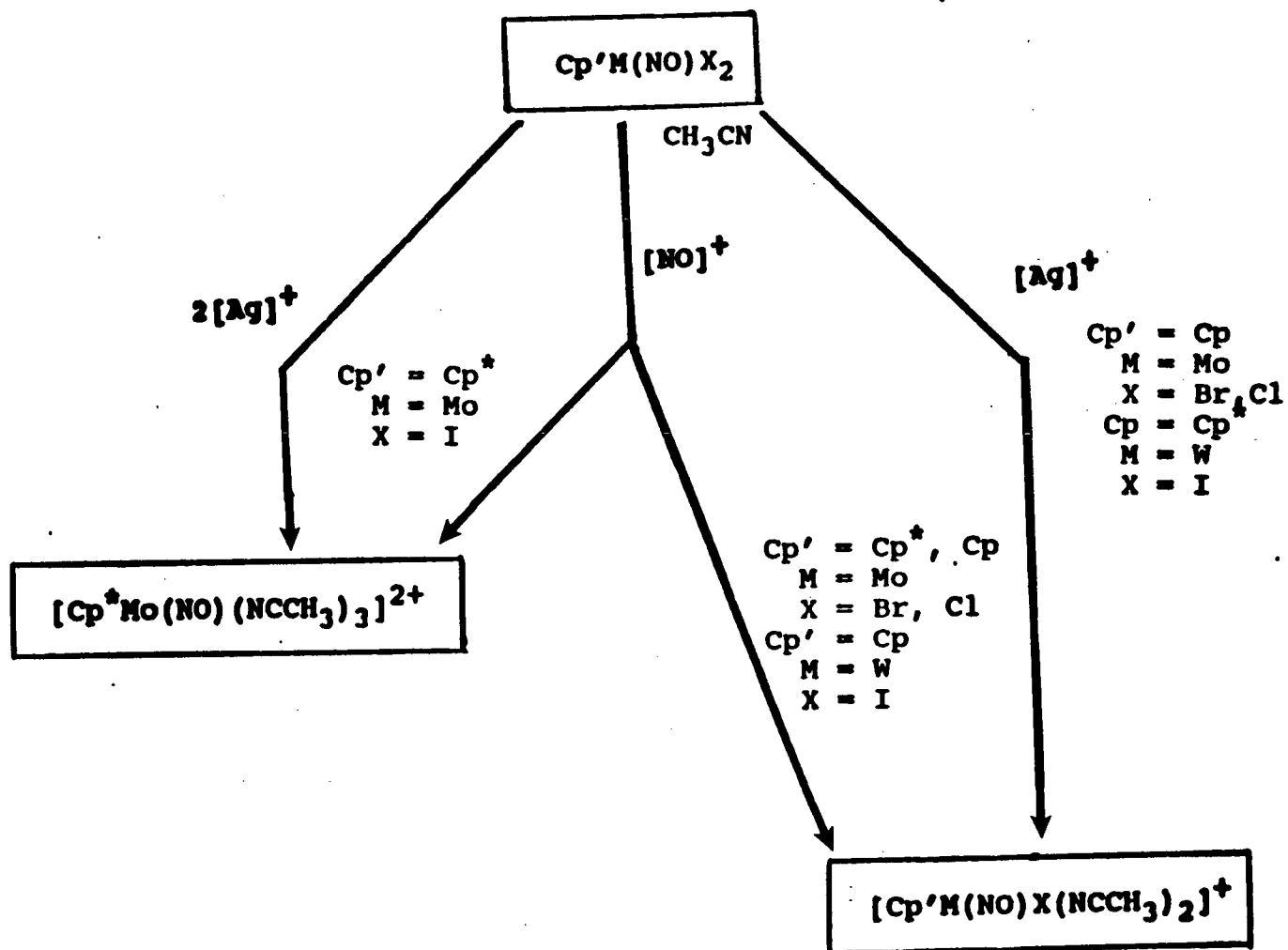
(c) n.o. = not obtained.

## Results and Discussion

The preparation and characterization of the diamagnetic complexes 1 - 8 will be discussed in Part (I). The preparation, characterization and subsequent chemical reactivity of the paramagnetic complex 9 will be considered in Part (II).

### (I) The Syntheses and Characterization of the Diamagnetic Cationic Complexes 1 - 8.

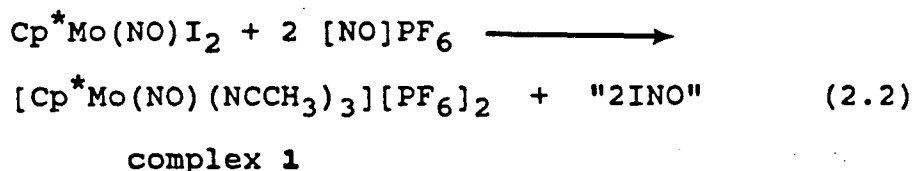
The cationic complexes 1 - 8 obtained during this work were prepared by the treatment of the  $\text{Cp}'\text{M}(\text{NO})\text{X}_2$  complexes with either  $[\text{NO}]^+$  or  $[\text{Ag}]^+$  salts in  $\text{CH}_3\text{CN}$ . The transformations involved are summarized in Scheme 2.1. The progress of the reactions was conveniently monitored by IR spectroscopy. All the complexes 1 - 8 were purified by fractional crystallization from their respective  $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$  solutions. The physical data (yields, elemental analyses, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra) of complexes 1 - 8 are collected in Tables 2.1 - 2.3. The preparations and physical properties of each of these cationic complexes will now be considered in turn.



Scheme 2.1

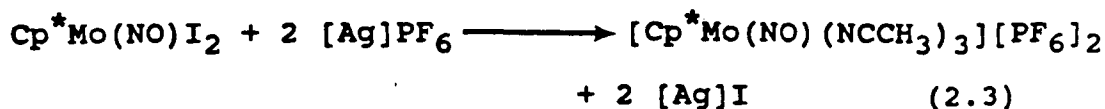
(I-A)  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ , complex 1.

Treatment of  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  with one equivalent of  $[\text{NO}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  affords  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$  1 (as in eq 2.2) in moderate yield. The same complex is obtained regardless whether one or two equivalents of  $[\text{NO}]\text{PF}_6$  are used. In eq 2.2, the stoichiometric ratio of  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  to  $[\text{NO}]\text{PF}_6$  is written as 1 : 2 for the sake of balancing the equation.



In order to obtain uncontaminated  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$  in respectable yield, it is important that the  $[\text{NO}]\text{PF}_6$  reagent (dissolved in  $\text{CH}_3\text{CN}$ ) be added slowly in a dropwise manner to the  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  complex, otherwise the reaction is often accompanied by the formation of many nitrosyl-containing byproducts, a feature which lowers the isolated yield of the desired product substantially.

Alternatively, the dicationic complex 1 can also be synthesized by treating  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  with two equivalents of  $[\text{Ag}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$ , i.e.,

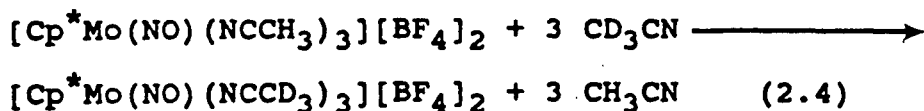


Pure  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$  is a yellow microcrystalline solid which is thermally stable at room temperature in the solid state under  $\text{N}_2$  for several months. As a solid, it can be handled in air for several hours without any noticeable decomposition. The complex is sparingly soluble in THF and quite soluble in acetone, acetonitrile and nitromethane to yield air-sensitive yellow solutions.

The infrared spectra of  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ , complex 1, either as a Nujol mull or as a  $\text{CH}_3\text{CN}$  solution, exhibit strong absorptions attributable to the terminal nitrosyl ligand. The nitrosyl-stretching frequency of complex 1 ( $1718\text{ cm}^{-1}$  as a Nujol mull) occurs at a much higher frequency than that of its neutral precursor  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  ( $1645\text{ cm}^{-1}$ ) indicative of a substantial decrease in backbonding to the nitrosyl ligand. In addition to the nitrosyl-stretching frequency, the IR spectrum (Nujol mull) of complex 1 also exhibit two weak bands at  $2320$  and  $2292\text{ cm}^{-1}$  attributable to the  $\nu_{\text{CN}}$  of the coordinated acetonitrile ligands.<sup>10</sup> These observed  $\nu_{\text{CN}}$  bands are comparable to those observed for the dicationic complex  $[\text{Cp}_2\text{Ti}(\text{NCCH}_3)_2][\text{PF}_6]_2$  ( $\nu_{\text{CN}}$   $2325$  and  $2288\text{ cm}^{-1}$ ).<sup>11</sup>

The  $^1\text{H}$  NMR spectrum of complex 1 in  $\text{CD}_3\text{NO}_2$  exhibits a singlet at  $\delta$  2.74 corresponding to the three equivalent

CH<sub>3</sub>CN ligands as well as a singlet due to the Cp\* ligand at  $\delta$  2.18. The proton resonance of the CH<sub>3</sub>CN ligands is shifted 0.74 ppm downfield to that of free CH<sub>3</sub>CN ( $\delta$  2.00 in CD<sub>3</sub>NO<sub>2</sub>). The downfield shift which accompanies the coordination of the CH<sub>3</sub>CN to the metal centre has also been observed in other cationic metal-acetonitrile complexes.<sup>11,12</sup> The three CH<sub>3</sub>CN ligands in complex 1 show considerable lability in solution at 25°C as demonstrated by <sup>1</sup>H NMR spectroscopy. Thus, the <sup>1</sup>H NMR spectrum of a freshly prepared solution of [Cp\*Mo(NO)(NCCH<sub>3</sub>)<sub>3</sub>][BF<sub>4</sub>]<sub>2</sub> in CD<sub>3</sub>CN exhibits a resonance at  $\delta$  1.93 due to the protons of free CH<sub>3</sub>CN along with another peak at  $\delta$  2.58 for the coordinated CH<sub>3</sub>CN. When the sample is left standing at room temperature for several hours, the signal at  $\delta$  2.58 disappears completely together with an increase in the intensity of the resonance at 1.93 ppm. These observations are indicative of an exchange between the coordinated CH<sub>3</sub>CN and free CD<sub>3</sub>CN molecules, i.e.,



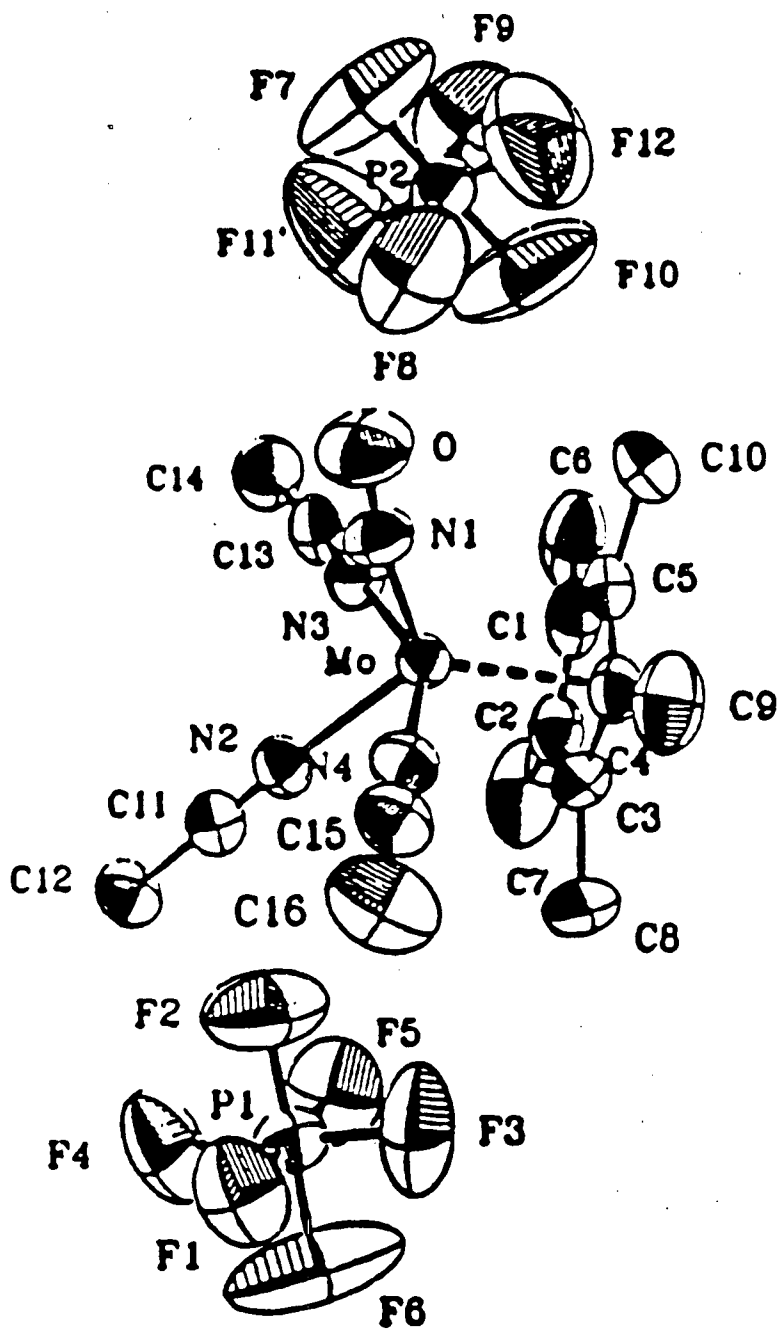
This is certainly an important feature since it has been previously demonstrated that the ability of some cationic transition metal nitrosyl complexes (with coordinated

acetonitrile ligands) to catalyze the oligomerization and polymerization of olefins is due to the electrophilic nature of the cation as well as to the lability of the acetonitrile ligands in solution. This feature will be discussed in more detail later in this chapter.

In order to remove any possible ambiguities about the true nature of  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ , the structure of this complex has been determined crystallographically. (The X-ray analyses discussed in this work were done by Ms. Vivien Yee and Dr. James Trotter of this department. Details of the data collection and refinement will be reported elsewhere). The solid state molecular structure of  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$  is shown in Figure 2.1. Lists of selected bond lengths and bond angles are presented in Tables 2.4 and 2.5 respectively. The crystal structure of  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$  consists of discrete  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3]^{2+}$  cations and  $\text{PF}_6^-$  anions. As may be observed, the molybdenum atom is coordinated to a  $\text{Cp}^*$  ring, to a nitrosyl ligand and to the nitrogen of the three acetonitrile ligands. The coordination geometry about the central Mo atom is that of a four-legged piano stool. A comparison of the structural parameters between complex 1 and other cationic complexes containing the " $\text{Cp}^*\text{Mo}(\text{NO})$ " fragment cannot be made since reports on the structural determinations

of cationic complexes containing this particular unit are lacking in the chemical literature. Nevertheless, the structural features in complex 1 can be compared to the closely related cationic complex,  $[\{(\text{C}_5\text{H}_7\text{N}_2)_3\text{BH}\}\text{Mo}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ ,<sup>13</sup> as well as the neutral carbonyl complex,  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$ ,<sup>14</sup> and they are discussed in more detail below. The distance of the Mo atom to the plane of the  $\text{Cp}^*$  ring in complex 1 is 2.027 Å, which is in reasonable agreement to that found for  $\text{Cp}^*\text{Mo}(\text{CO})_3\text{H}$  (2.016 Å). The MoNO angle in complex 1 is essentially linear, although slightly more bent than in  $[\{(\text{C}_5\text{H}_7\text{N}_2)_3\text{BH}\}\text{Mo}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  ( $170.5(6)^\circ$  vs.  $173.4(8)^\circ$ ). The Mo-NO bond (1.803 Å) is longer and the N-O bond (1.16 Å) is shorter compared to the respective bond lengths in  $[\{(\text{C}_5\text{H}_7\text{N}_2)_3\text{BH}\}\text{Mo}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ . The three acetonitrile ligands are N-bonded to the Mo centre in a linear fashion and the Mo-N bond lengths (2.173(5) Å, 2.142(6) Å and 2.131(6) Å) are in reasonable agreement to that found for  $[\{(\text{C}_5\text{H}_7\text{N}_2)_3\text{BH}\}\text{Mo}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  (2.139(9) Å and 2.145(9) Å). The acetonitrile ligand which is trans to the nitrosyl ligand exhibits a longer Mo-N bond (2.173(5) Å) compared to the other two acetonitrile ligands, a feature which is in accord with its less successful competition for the available electrons on the metal centre being trans to the strongly electron-withdrawing NO ligand.





**Figure 2.1.** Solid-state molecular structure of  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$  complex 1.

**Table 2.4.** Selected Bond Lengths (Å) for  
 $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ , Complex 1.

Bond	Length(a)
Mo - Cp*	2.027(3)
Mo - N1	1.803(5)
Mo - N2	2.173(5)
Mo - N3	2.142(6)
Mo - N4	2.131(6)
O - N1	1.161(7)
N2 - C11	1.122(7)
N3 - C13	1.121(8)
N4 - C15	1.121(9)
C11 - C12	1.451(8)
C13 - C14	1.462(11)
C15 - C16	1.481(11)

(a) E.s.d.'s are in parentheses.

Table 2.5. Selected Bond Angles (deg) for  
 $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ , Complex 1.

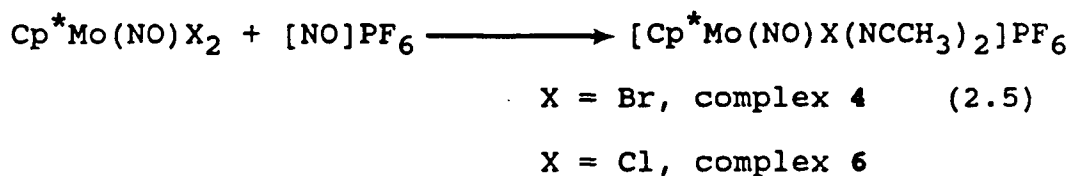
Bond	Angle (a)
N1 - Mo - Cp*	121.3(2)
N2 - Mo - Cp*	126.81(17)
N3 - Mo - Cp*	103.32(17)
N4 - Mo - Cp*	104.40(17)
Mo - N1 - O	170.5(6)
Mo - N2 - C11	175.7(6)
Mo - N3 - C13	174.2(6)
Mo - N4 - C15	177.8(6)
N1 - Mo - N2	111.9(2)
N1 - Mo - N3	87.0(2)
N1 - Mo - N4	85.6(2)
N2 - Mo - N3	78.1(2)
N2 - Mo - N4	78.8(2)
N2 - C11 - C12	178.2(7)
N3 - C13 - C14	178.9(8)
N4 - C15 - C16	177.9(9)

(a) E.s.d.'s are in parentheses.

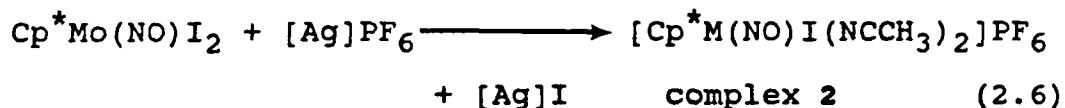
(I-B) The Complexes  $[\text{Cp}^*\text{Mo}(\text{NO})\text{X}(\text{NCCH}_3)_2][\text{PF}_6]$

(X = I, Br, Cl), Complexes 2, 4 and 6.

Interestingly enough, treatment of the bromo and chloro analogues  $\text{Cp}^*\text{Mo}(\text{NO})\text{X}_2$  (X = Br, Cl) with one equivalent of  $[\text{NO}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  under the same conditions as for the iodo complex does not afford a dicationic compound. Instead, these reactions afford organometallic monocationic complexes i.e.,



However, the iodo analogue,  $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6$ , cannot be prepared by this route. Rather, this complex can be prepared by the treatment of  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  with one equivalent of  $[\text{Ag}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  (eq 2.6).



In their pure form, these three cationic complexes are thermally stable dark yellow to orange solids that can be handled in air for short periods of time with no noticeable decomposition occurring. If they are obtained in an impure

form, they are prone to undergo decomposition to light brown oils when exposed to air. The complexes are soluble in polar organic solvents (similar solubility properties as complex 1) to give air-sensitive light orange solutions.

Their IR spectra (as Nujol mulls) display  $\nu_{\text{NO}}$ 's in the region 1668-1686  $\text{cm}^{-1}$  (Table 2.2), attributable to the terminal nitrosyl ligands. Again, these  $\nu_{\text{NO}}$  values are shifted to a higher frequency as compared to their neutral dihalo nitrosyl precursors indicative of reduced backbonding from the metal centre to the NO ligand in the cationic complexes. An interesting feature that can be observed in this series  $[\text{Cp}^*\text{Mo}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$ , is that the nitrosyl stretching frequencies (in the solid state) decreases in the order  $\text{I} > \text{Br} > \text{Cl}$ . An increase in  $\nu_{\text{NO}}$  is usually attributed to a decrease in electron density at the metal centre thereby permitting less backbonding into the  $\text{NO } \pi^*$  orbital. Since the electronegativity of the halide group decreases in the order  $\text{Cl} > \text{Br} > \text{I}$ , one would anticipate the electron density available for backbonding to decrease in the order  $\text{Cl} > \text{Br} > \text{I}$  as well. However, the observed increase in the  $\nu_{\text{NO}}$  values is opposite to expectations (based on electronegativity arguments). The exact reason for the observation of this opposite trend is not clear. This trend is also observed in the series  $\text{CpW}(\text{NO})_2\text{X}$  ( $\text{X} = \text{I}, \text{Br}, \text{Cl}$ ).<sup>15</sup> In addition to the NO

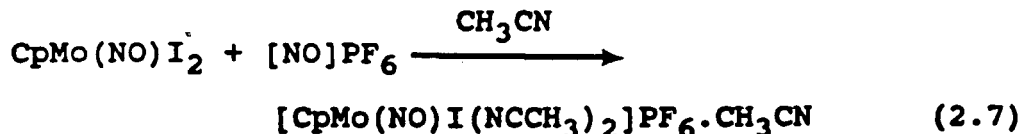
bands, weak absorptions attributable to the coordinated  $\text{CH}_3\text{CN}$  ligands ( $\nu_{\text{CN}}$ ) are observable in the region  $2322\text{--}2295\text{ cm}^{-1}$  in their IR spectra. By analogy to the structurally characterized complex 1 already discussed in the preceding paragraphs, the  $\text{CH}_3\text{CN}$  ligands are probably coordinated to the metal centre via the N atom in a linear fashion. The  $^1\text{H}$  NMR spectra of these complexes exhibit the expected resonances for the coordinated  $\text{CH}_3\text{CN}$  as well as the  $\text{Cp}^*$  ligands. The positions of the  $\text{Cp}^*$  resonances in the NMR spectra are in close agreement to that observed for the better known  $[\text{Cp}^*\text{Mo}(\text{CO})_2\text{L}_2]\text{PF}_6$  ( $\text{L}$  = nitriles or phosphines) complexes.<sup>16</sup> Unlike the positions of the  $\nu_{\text{NO}}$  frequencies in the IR spectra, the positions of the  $\text{Cp}^*$  resonances in the NMR spectra do not exhibit any trends with respect to the electronegativity differences of the halide group. Complexes 2, 4 and 6 probably possess the familiar four-legged piano stool molecular structures. However, further discussion on their molecular geometries will be deferred until the properties of several related complexes are discussed.

(I-C)  $[\text{CpMo}(\text{NO})\text{X}(\text{NCCH}_3)_2][\text{BF}_4]$  ( $\text{X} = \text{Br}, \text{Cl}$ ),

Complexes 3 and 5.

It has been observed<sup>1</sup> that the treatment of  $\text{CpMo}(\text{NO})\text{I}_2$  with  $[\text{NO}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  affords

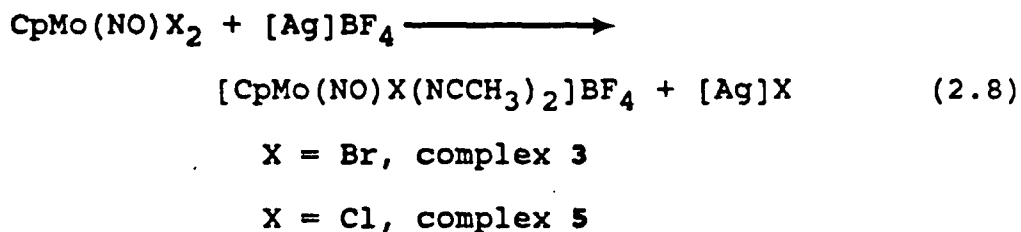
$[\text{CpMo}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6 \cdot \text{CH}_3\text{CN}$ , as summarized in eq. 2.7, in good yield.



However the treatment of the bromo and chloro analogues,  $\text{CpMo}(\text{NO})\text{X}_2$  ( $\text{X} = \text{Br}, \text{Cl}$ ), with  $[\text{NO}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  under the same conditions yields the corresponding  $[\text{CpMo}(\text{NO})\text{X}(\text{NCCH}_3)_2]\text{PF}_6$  complexes in extremely low yields (5%). These low isolated yields are probably due to several factors. Firstly, the long reaction times involved (4 to 5 h) may allow the thermal decomposition of the cationic products to occur. Secondly, in addition to the products of interest, many other nitrosyl-containing byproducts (observable in the IR spectra during the course of the reaction) are also formed during the reaction thus making the final isolation of the cationic complexes difficult. Thirdly, the final cationic products are often contaminated with unreacted starting materials thus requiring repeated fractional crystallizations in the purification procedure which lowers the isolated yields.

Although the  $[\text{CpMo}(\text{NO})\text{X}(\text{NCCH}_3)_2]\text{PF}_6$  ( $\text{X} = \text{Br}, \text{Cl}$ ) complexes can be obtained by the treatment of  $\text{CpMo}(\text{NO})\text{X}_2$  with  $[\text{NO}]^+$  in  $\text{CH}_3\text{CN}$ , the low isolated yields do not allow their characteristic chemistry to be studied conveniently. To

obtain these cationic complexes in better yields, I next attempted the reaction of  $\text{CpMo}(\text{NO})\text{X}_2$  with  $[\text{Ag}]\text{BF}_4$  in  $\text{CH}_3\text{CN}$ . Indeed, the treatment of the  $\text{CpMo}(\text{NO})\text{X}_2$  ( $\text{X} = \text{Br}, \text{Cl}$ ) complexes with one equivalent of the  $[\text{Ag}]^+$  salt in  $\text{CH}_3\text{CN}$  affords the cations in much higher yields (as in eq 2.8).

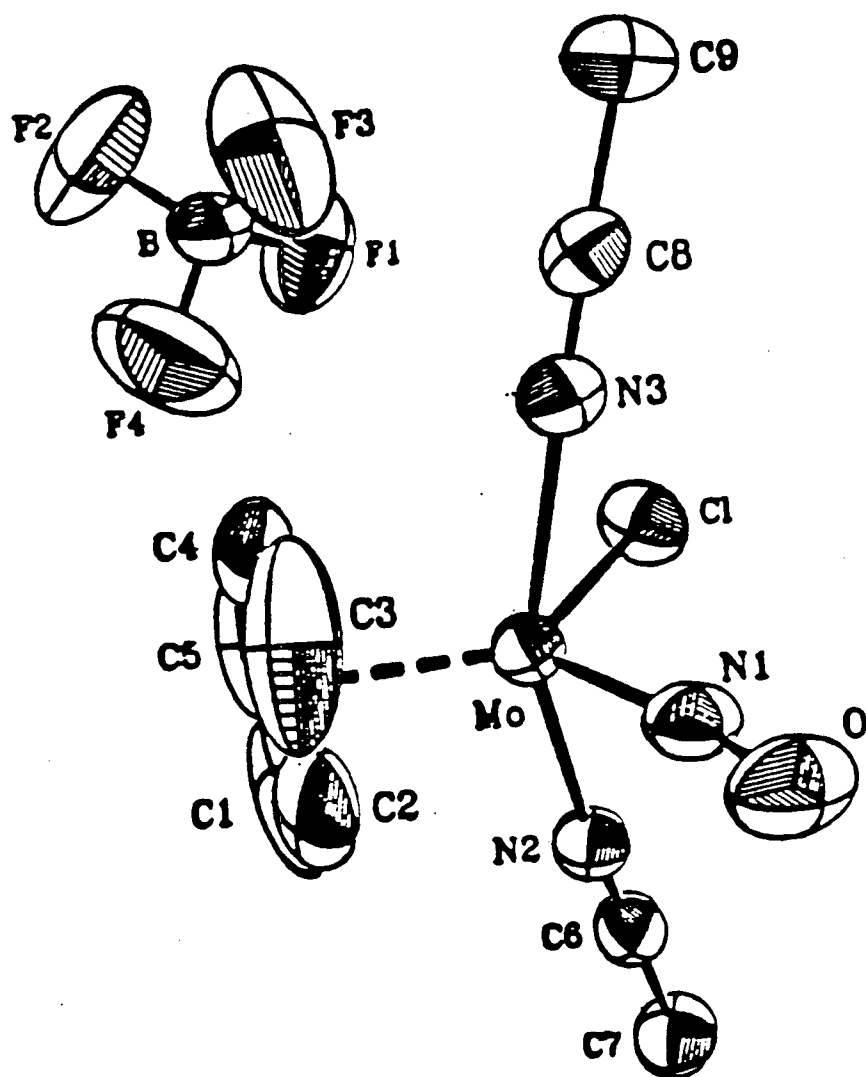


The physical properties of the new complexes 3 and 5 are quite similar to those of their  $\text{Cp}^*$  analogues. Their IR spectra exhibit nitrosyl absorptions in the region 1705-1709  $\text{cm}^{-1}$ , which are approximately 20-35  $\text{cm}^{-1}$  higher in energy than those exhibited by their  $\text{Cp}^*$  analogues. This is simply a reflection of the better electron-donating abilities of the  $\text{Cp}^*$  ligand as compared to the Cp ligand. In addition, the  $\nu_{\text{CN}}$  bands which are due to the coordinated  $\text{CH}_3\text{CN}$  ligands are observable in the region 2299-2326  $\text{cm}^{-1}$ .

The solid-state molecular structure of complex 5 is shown in Figure 2.2. Lists of selected bond lengths and bond angles are presented in Tables 2.6 and 2.7, respectively. The crystal structure of complex 5 consists of discrete  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]^+$  cations and  $\text{BF}_4^-$  anions. As may be



observed, 5 also possesses the familiar four-legged piano stool molecular geometry. The overall structural parameters about the Mo atom exhibit normal values and some comparisons can be made with the corresponding values observed for related cationic Mo complexes. The average distance of the Mo atom to the plane of the Cp ring (2.032 Å) in 5 is slightly longer than that observed for  $[\text{Cp}_2\text{MoI}(\text{NCCH}_3)]\text{PF}_6$ <sup>17</sup> (1.986 Å and 1.965 Å). The Mo-Cl distance (2.415 Å) in 5 is slightly shorter than the corresponding distance observed in  $\text{Cp}_2\text{MoCl}(\text{C}_2\text{H}_5)$ <sup>18</sup> (2.502 Å). The Mo-NO bond (1.790 Å) is shorter and the N-O bond (1.183 Å) is longer than the respective bond lengths in complex 1. The MoNO group (169.8°) is also essentially linear although it is just slightly more bent than that in complex 1. The two  $\text{CH}_3\text{CN}$  ligands (in a trans orientation to each other) are also N-bonded to the Mo center in a linear fashion and the Mo-N bond lengths (2.160 Å and 2.141 Å) are in reasonable agreement with the corresponding bond lengths observed in complex 1. By comparison, the closely related  $[\text{CpMo}(\text{NO})\text{I}(\text{PMe}_3)_2]^+$  complex has been formulated as having trans  $\text{PMe}_3$  ligands.<sup>19</sup>



**Figure 2.2.** Solid-state molecular structure of  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{BF}_4$  complex 5

Table 2.6. Selected Bond Lengths (Å)  
for  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2][\text{BF}_4]$  Complex 5.

Bond	Length <sup>(a)</sup>
Mo - Cp	2.032(5)
Mo - N1	1.790(12)
Mo - N2	2.160(3)
Mo - N3	2.141(3)
O - N1	1.183(5)
Mo - Cl	2.415(12)
N2 - C6	1.119(5)
N3 - C8	1.129(5)
C6 - C7	1.448(6)
C8 - C9	1.448(6)

(a) E.s.d.'s are in parentheses.

Table 2.7. Selected Bond Angles (deg) for  
 $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2][\text{BF}_4]$  Complex 5.

Bond	Angle (a)
Cl - Mo - N1	110.31(14)
Cl - Mo - N2	78.73(11)
Cl - Mo - N3	78.55(10)
Cl - Mo - Cp	129.43(14)
N1 - Mo - N2	87.75(15)
N1 - Mo - N3	87.58(15)
N1 - Mo - Cp	120.23(19)
N2 - Mo - N3	153.54(14)
N2 - Mo - Cp	103.75(17)
N2 - Mo - Cp	101.09(18)
Mo - N1 - O	169.8(4)
Mo - N2 - C6	175.6(4)
Mo - N3 - C8	177.6(4)

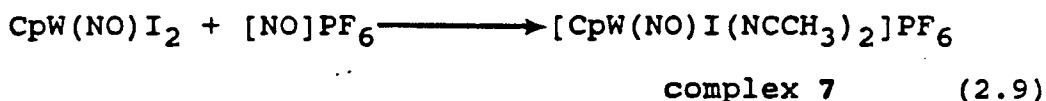
(a) E.s.d.'s are in parentheses.

(I-D)  $[\text{Cp}'\text{W}(\text{NO})\text{I}(\text{NCCH}_3)][\text{Y}]$  ( $\text{Y} = \text{PF}_6$  or  $\text{BF}_4$ ),

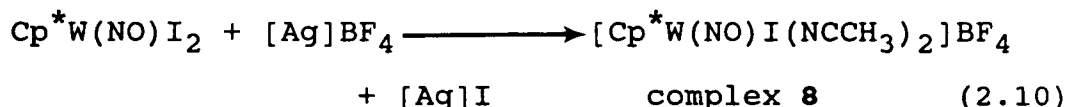
Complexes 7 and 8.

It has been previously observed<sup>20</sup> that under certain reducing conditions, the  $\text{Cp}'\text{W}(\text{NO})\text{I}_2$  complexes exhibit different chemical behaviour compared to the molybdenum analogues,  $\text{Cp}'\text{Mo}(\text{NO})\text{I}_2$ . Therefore, it is of interest to determine if the dihalo nitrosyl complexes of tungsten will behave differently than the corresponding molybdenum complexes under the oxidizing conditions studied in this work. Thus, the reactions of the  $\text{Cp}'\text{W}(\text{NO})\text{I}_2$  complexes with  $[\text{NO}]\text{PF}_6$  and  $[\text{Ag}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  have also been investigated.

Treatment of  $\text{CpW}(\text{NO})\text{I}_2$  with one equivalent of  $[\text{NO}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  affords the analogous  $[\text{CpW}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6$ , complex 7, i.e.



Unfortunately, extending reaction 2.9 to the  $\text{Cp}^*$  analogue,  $\text{Cp}^*\text{W}(\text{NO})\text{I}_2$ , results in the formation of a mixture of several nitrosyl-containing products (observable in the IR spectrum during the course of the reaction). To obtain the  $\text{Cp}^*$  analogue of complex 7, the reaction between  $\text{Cp}^*\text{W}(\text{NO})\text{I}_2$  and  $[\text{Ag}]\text{BF}_4$  was next attempted. Indeed, this reaction (eq 2.10) affords the complex  $[\text{Cp}^*\text{W}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{BF}_4$ , 8 in good yield.



In their pure form, these two compounds 7 and 8 are slightly more air-sensitive than their molybdenum congeners but can still be handled in air for short periods of time with no noticeable decomposition occurring. Their solubility properties are similar to those of their Mo analogues although the tungsten cationic complexes are more air-sensitive in solution. As anticipated, the IR spectra of complexes 7 and 8 exhibit  $\nu_{\text{NO}}$ 's in the region 1653-1686  $\text{cm}^{-1}$  attributable to the terminal nitrosyl ligands and weak  $\nu_{\text{CN}}$ 's in the region 2299-2324  $\text{cm}^{-1}$  due to the coordinated acetonitrile ligands. A comparison of the nitrosyl stretching frequencies of  $[\text{Cp}^*\text{W}(\text{NO})\text{I}(\text{NCCH}_3)_2]^+$  and its corresponding Mo congener reveals that the  $\nu_{\text{NO}}$  of the W complex is approximately 30  $\text{cm}^{-1}$  lower in energy than that of the Mo complex. This trend is in accord with that previously observed for the  $[\text{CpM}(\text{NO})\text{I}(\text{PMe}_3)_2]^+$  complexes ( $\text{M} = \text{Mo}$ ,  $\nu_{\text{NO}}$  1668  $\text{cm}^{-1}$ ;  $\text{M} = \text{W}$ ,  $\nu_{\text{NO}}$  1645  $\text{cm}^{-1}$ ).<sup>19</sup> The  $^1\text{H}$  NMR spectra (Table 2.3) of complexes 7 and 8 exhibit the expected resonances for the coordinated  $\text{CH}_3\text{CN}$  ligands as well as the Cp or  $\text{Cp}^*$  rings.

(I-E) Probable Molecular Structures of the Monocationic Complexes.

By analogy to complex 5, the rest of the cationic complexes  $[\text{Cp}'\text{M}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$  described in this work can be proposed to possess the four-legged piano stool molecular geometries in the solid state with the  $\text{CH}_3\text{CN}$  ligands trans to each other (Figure 2.3). This proposal is based on the similarities in their spectroscopic properties to those of the structurally characterized complex 5.

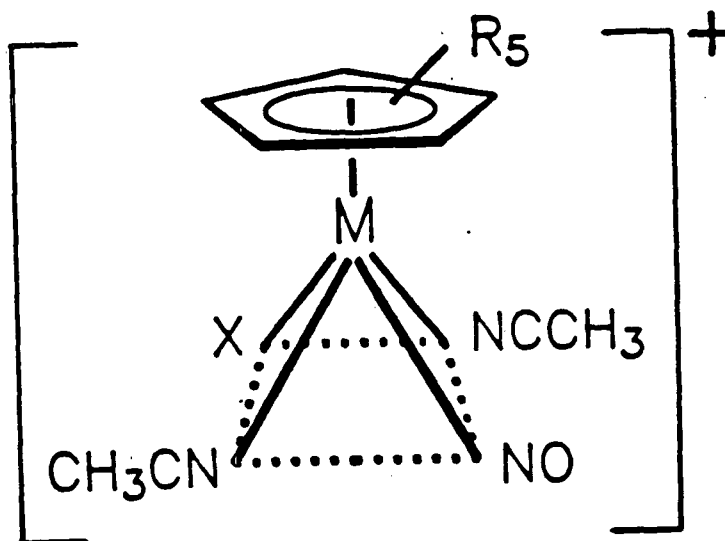


Figure 2.3 Proposed Structure of the  $[\text{Cp}'\text{M}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$  Complexes.

**(I-F) Synthetic Routes Used for the Preparation of the  
Complexes 1 - 8.**

Two principal synthetic routes to the cationic nitrosyl complexes 1 - 8 have been developed during this work. By the reaction of  $[\text{NO}]^+$  or  $[\text{Ag}]^+$  salts with the neutral precursors  $\text{Cp}'\text{M}(\text{NO})\text{X}_2$  in  $\text{CH}_3\text{CN}$ , I have been able to generate the cationic complexes 1 - 8 through an exchange of the halide group with the less coordinating  $\text{PF}_6^-$  or  $\text{BF}_4^-$  groups. Concomitant solvent incorporation ( $\text{CH}_3\text{CN}$ ) into the metal's coordination sphere also occurs. When  $[\text{NO}]^+$  salts are used, it is important that the  $[\text{NO}]^+$  reagent (dissolved in  $\text{CH}_3\text{CN}$ ) be added slowly in a dropwise manner to the organometallic reactant. Otherwise, the reactions do not proceed cleanly, and the cationic product complexes are subsequently difficult to isolate in a pure form. When  $[\text{Ag}]^+$  salts are added to solutions of the dihalo nitrosyl complexes, the transformations are rapid, straightforward and proceed with the immediate precipitation of the  $[\text{Ag}]\text{X}$  ( $\text{X} = \text{I}, \text{Br}$  or  $\text{Cl}$ ) salts. The precipitated  $[\text{Ag}]\text{X}$  salts can then be removed by filtration. Therefore,  $\text{Ag}(\text{I})$  salts are the reagents of choice for the synthesis of these cationic products.

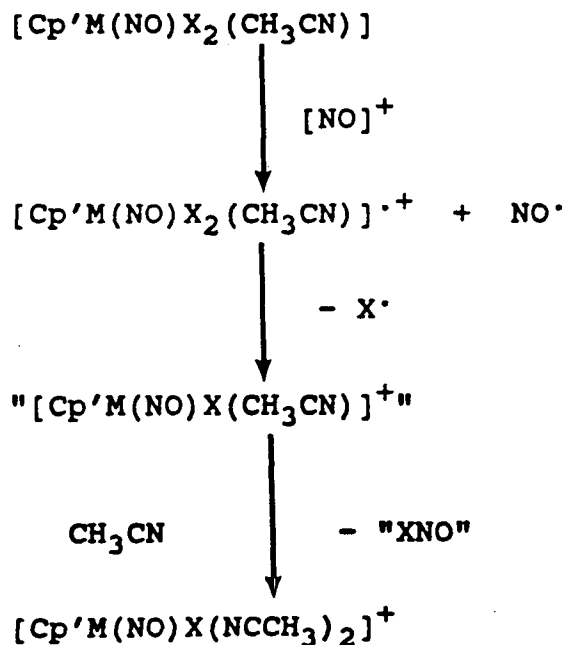
In all the above transformations, (as in Scheme 2.1), proceeding from the neutral dihalo nitrosyl  $\text{Cp}'\text{M}(\text{NO})\text{X}_2$  complexes to the cationic  $[\text{Cp}'\text{M}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$  complexes or



the dication  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3]^{2+}$ , no change in the formal oxidation state of the metal centre has taken place.

**(I-G) Proposed Mechanism for the Reaction of  $\text{Cp}'\text{M}(\text{NO})\text{X}_2$  with  $[\text{NO}]^+$ .**

The mechanism by which the monocationic  $[\text{Cp}'\text{Mo}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$  complexes originate in the reactions of  $[\text{NO}]^+$  with  $\text{Cp}'\text{Mo}(\text{NO})\text{X}_2$  complexes remains to be investigated. Nevertheless, a possible reaction pathway shown in Scheme 2.2 can be proposed.



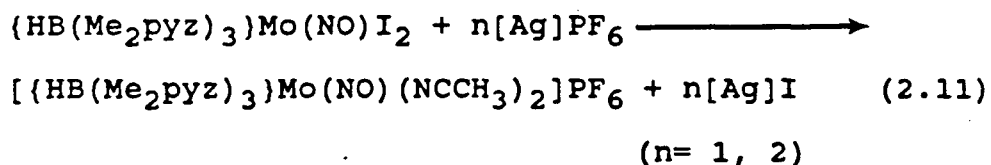
**Scheme 2.2**

In the reactions of  $[\text{NO}]^+$  with transition metals, there is evidence in the chemical literature that  $[\text{NO}]^+$  may sometimes behave as a nitrosylating agent<sup>21</sup> or as a one-electron oxidant.<sup>22</sup> The dihalo nitrosyl complexes  $\text{Cp}'\text{Mo}(\text{NO})\text{X}_2$  are assumed to be monomeric in  $\text{CH}_3\text{CN}$ , stabilized by the coordination of a  $\text{CH}_3\text{CN}$  molecule to the Mo centre. As summarized by Scheme 2.2, the initial step of the reaction may involve the oxidation of the 18-electron  $\text{Cp}'\text{Mo}(\text{NO})\text{X}_2(\text{NCCH}_3)$  complex to the 17-electron radical cation,  $[\text{Cp}'\text{M}(\text{NO})\text{X}_2(\text{CH}_3\text{CN})]^{+\cdot}$ , by  $[\text{NO}]^+$ , while  $[\text{NO}]^+$  is itself being reduced to NO. The postulated radical cation intermediate is consistent with the observations that the reactions of the perhydro complexes,  $\text{CpMo}(\text{NO})\text{X}_2$ , with  $[\text{NO}]^+$  require a longer reaction time to go to completion than the permethylated analogues, since the ease of oxidation of a transition metal complex generally increases with the increase in electron density on the metal centre. The formation of the 17-electron metal centre may labilize the halide ligand which could then result in the loss of "X" which may then be trapped by "NO" to form XNO (nitrosyl halides are well known inorganic compounds).<sup>23</sup> The resulting 16-electron intermediate  $[\text{Cp}'\text{Mo}(\text{NO})\text{X}(\text{NCCH}_3)]^+$  could then be further stabilized by

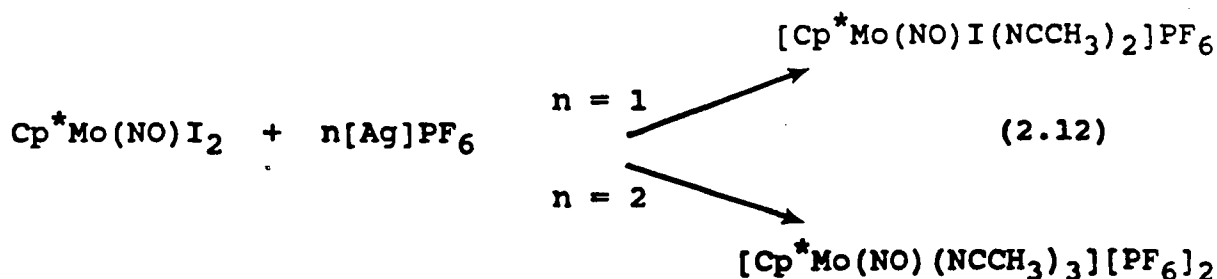
another molecule of  $\text{CH}_3\text{CN}$  to yield the 18-electron product,  $[\text{Cp}'\text{Mo}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$ .

**(I-G) Reactions of  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  and  $\{\text{HB}(\text{Me}_2\text{pyz})_3\}\text{Mo}(\text{NO})\text{I}_2$  with  $[\text{Ag}]\text{PF}_6$ .**

An interesting comparison can be made between  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  and the closely related  $\{\text{HB}(\text{Me}_2\text{pyz})_3\}\text{Mo}(\text{NO})\text{I}_2$  with respect to their reactivity with  $[\text{Ag}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$ . When  $\{\text{HB}(\text{Me}_2\text{pyz})_3\}\text{Mo}(\text{NO})\text{I}_2$  is treated with one equivalent of  $[\text{Ag}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$  (as in eq 2.11), a paramagnetic product  $[\{\text{HB}(\text{Me}_2\text{pyz})_3\}\text{Mo}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ , is obtained.<sup>13</sup> The same product is also obtained when two equivalents of  $[\text{Ag}]\text{PF}_6$  are used.



In contrast, when  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  is treated with one equivalent of  $[\text{Ag}]\text{PF}_6$  in  $\text{CH}_3\text{CN}$ , the diamagnetic complex 2 is obtained. However, when two equivalents of  $[\text{Ag}]\text{PF}_6$  are used, the dicationic complex 1 is formed, i.e.,



#### (I-H) Significance of Complexes 1 - 8.

Although cationic organometallic complexes containing the dinitrosyl fragment " $\text{Cp}'\text{M}(\text{NO})_2$ " are frequently encountered in Group 6 nitrosyl chemistry, cationic complexes containing the mononitrosyl fragment " $\text{Cp}'\text{M}(\text{NO})$ " are not as common. Complexes 1 - 8 can be viewed as "organometallic Lewis acids",  $[\text{Cp}'\text{M}(\text{NO})\text{X}]^+$  or  $[\text{Cp}^*\text{Mo}(\text{NO})]^{2+}$ , stabilized by the coordination of weakly basic  $\text{CH}_3\text{CN}$  ligands. These cationic complexes constitute a small class of isolable Group 6 electrophilic transition metal nitrosyl complexes containing the " $\text{Cp}'\text{M}(\text{NO})$ " fragment. The only other complexes belonging to this class reported in the chemical literature are the  $[\text{CpMo}(\text{NO})\text{I}(\text{L})_2]^+$  ( $\text{L}$  = phosphines) compounds.<sup>19,24</sup> Therefore, while the monocationic complexes 2 - 8 described in this work may have some precedence in the chemical literature, no dicationic compound containing the " $\text{Cp}^*\text{Mo}(\text{NO})$ " fragment has been reported to date. In other words, complex 1,  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ , is an unprecedented organometallic nitrosyl complex.

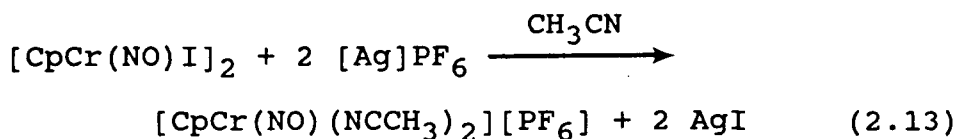
There have been several reports in the literature on the formation and synthetic applications of transition-metal acetonitrile complexes.<sup>25,26</sup> For example, Sen and co-workers<sup>25b</sup> have shown that the complexes  $[M(NO)_2(NCCH_3)_4]^{2+}$  ( $M = Mo, W$ ) and  $[Pd(NCCH_3)_4]^{2+}$  can induce the oligomerization of a wide range of olefins under mild conditions. This activity is attributed to the lability of the  $CH_3CN$  ligands in solution thus allowing easy solvent-substrate exchange in the metal's coordination sphere and further substrate activation which is induced by the presence of the cationic charge. In addition, the extensive chemistry exhibited by the cationic carbonyl complexes  $[(\eta^5-C_5R_5)Mo(CO)_2(NCCH_3)_2]^+$  and  $[(\eta^5-C_5R_5)M(CO)_{3-n}(NCCH_3)_n]^+$  ( $R = H, Me; M = Fe, Ru; n = 1, 2$ ) is well documented.<sup>26</sup> Also, the counterions  $PF_6^-$  or  $BF_4^-$  in the complexes 1 - 8 are non-coordinating (or at most weakly coordinating) which means that they can be replaced by other ligands under mild conditions. In view of the extensive chemistry exhibited by other cationic transition-metal acetonitrile complexes, this suggests that the cationic nitrosyl complexes 1 - 8 can, in principle, be utilized in organic synthesis and to serve as useful precursors to a variety of new nitrosyl complexes. The characteristic chemistry of these cationic complexes remains to be investigated.

(II) Synthesis, Characterization and Chemical Reactivity of  
 $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2][\text{PF}_6]$ , 9.

(II-A)  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ , 9

It has been previously observed<sup>19</sup> that under reducing conditions in the presence of Lewis bases  $[\text{CpCr}(\text{NO})\text{I}]_2$  and the  $[\text{CpM}(\text{NO})\text{X}_2]_2$  (M = Mo or W) compounds yield the neutral complexes having the general formula  $\text{CpM}(\text{NO})\text{L}_2$  (M = Cr, Mo and W; L = Lewis bases). As described in Part (I) earlier, treatment of the  $\text{Cp}'\text{M}(\text{NO})\text{X}_2$  (M = Mo or W) compounds with a silver(I) salt in  $\text{CH}_3\text{CN}$  yields the diamagnetic cations having the general formula  $[\text{Cp}'\text{M}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$ . In contrast, the product resulting from the treatment of  $[\text{CpCr}(\text{NO})\text{I}]_2$  with a silver(I) salt in  $\text{CH}_3\text{CN}$  does not resemble those produced by the Mo and W dihalo nitrosyl complexes.

More interestingly, treatment of the olive green acetonitrile solution of  $[\text{CpCr}(\text{NO})\text{I}]_2$  with two equivalents of  $[\text{Ag}]\text{PF}_6$  results in the formation of a bright green solution with the concomitant precipitation of  $\text{AgI}$ . This transformation is represented by eq 2.13.



Filtration of the mixture followed by addition of diethyl ether to the green filtrate results in the precipitation of the new complex **9**,  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ .

The new complex **9** is a paramagnetic green solid that can be handled in air for several hours without any noticeable decomposition. It is soluble in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NO}_2$ , and THF, and is sparingly soluble in  $\text{CH}_2\text{Cl}_2$  to yield bright green air- and moisture-sensitive solutions. The IR spectrum (Table 2.2) of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  in the solid state exhibits a strong absorption at  $1709\text{ cm}^{-1}$  attributable to the terminal NO ligand. In addition to the NO band, two weak bands at 2326 and  $2297\text{ cm}^{-1}$  in the  $\nu_{\text{CN}}$  region are also observed due to the coordinated acetonitrile ligands. This nitrosyl stretching frequency of **9** is shifted  $46\text{ cm}^{-1}$  higher than its neutral precursor,  $[\text{CpCr}(\text{NO})\text{I}]_2$ , which is consistent with the existence of decreased backbonding to the nitrosyl ligand in the cationic product. The  $\nu_{\text{NO}}$  of **9** may also be compared to the corresponding frequency in  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})^{27}$  ( $\nu_{\text{NO}}$   $1713\text{ cm}^{-1}$ ). The near coincidence of the nitrosyl stretching frequency between complex **9** and the dicarbonyl complex is presumably due to the higher formal oxidation state of the metal (Cr(I)) and poor  $\pi$  acceptor abilities of the  $\text{CH}_3\text{CN}$  ligands in **9** versus the lower formal oxidation state (Cr(0))

and good  $\pi$  acceptor abilities of the CO ligands in the neutral carbonyl complex.

The ESR spectrum of complex 9 as a DMF solution at room temperature shows a three line pattern ( $g = 1.984$ ) with approximately equal peak intensities (Figure 2.4). This pattern results from the hyperfine coupling of the unpaired electron with  $^{14}\text{N}$  ( $I=1$ ) of the NO ligand. The observed coupling constant to  $^{14}\text{N}$  is 5.21 G.

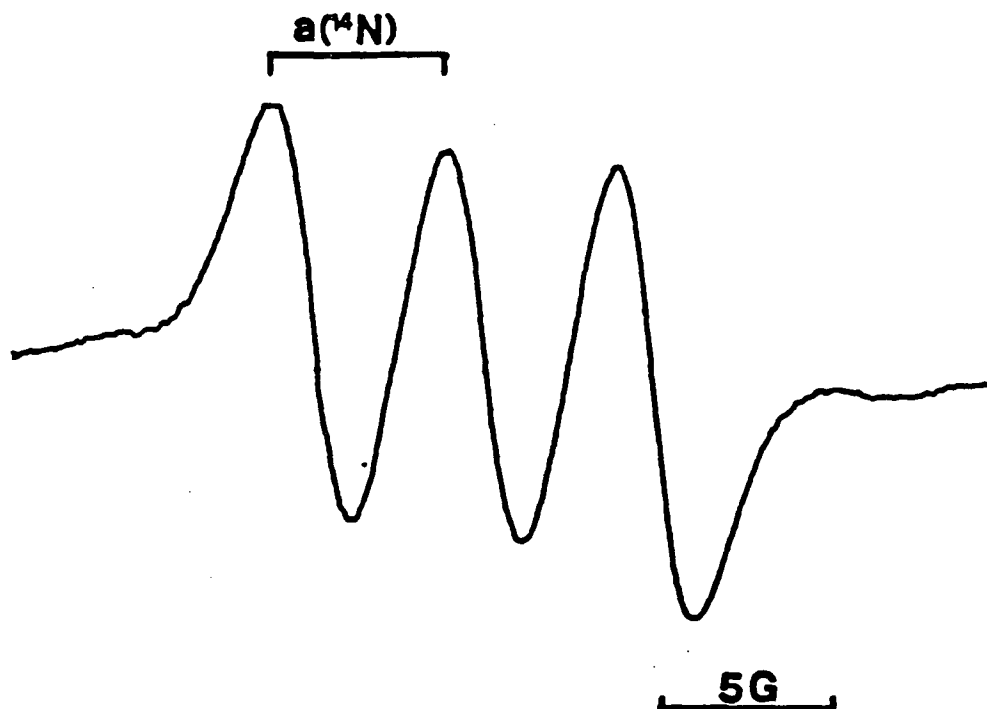
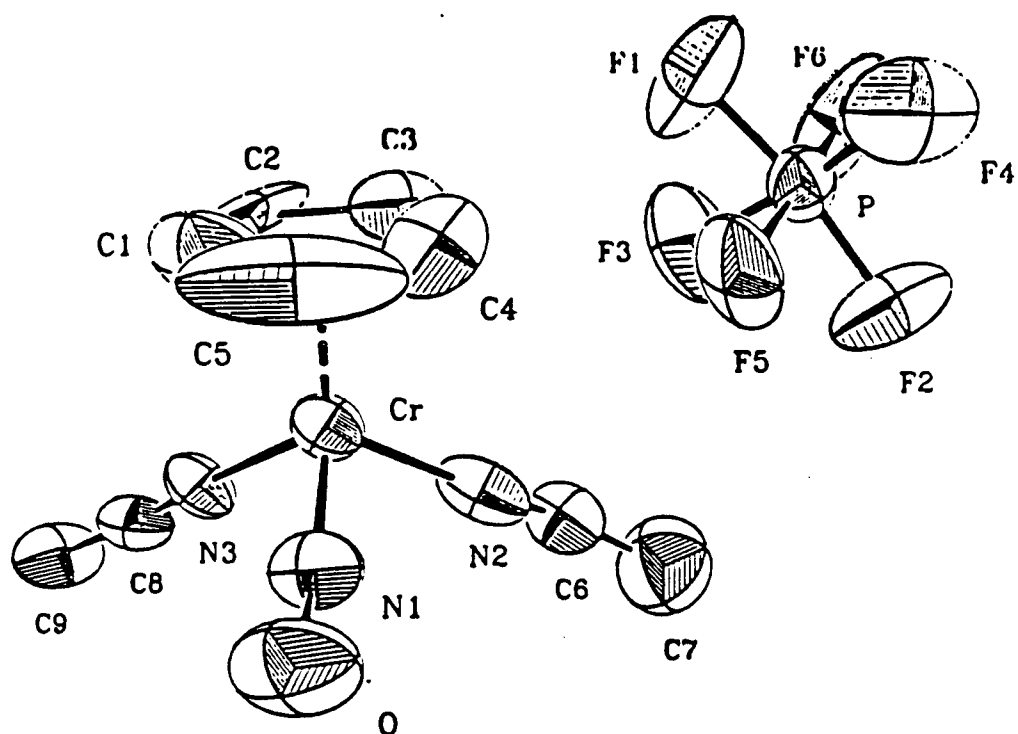


Figure 2.4. ESR spectrum of complex 9 in DMF.



There is a possibility that the 17-electron complex 9 may be dimeric, especially in the solid state. To examine this possibility, as well as to determine the mode of coordination of the acetonitrile ligands to the Cr centre an X-ray structure of complex 9 has been obtained.

The solid-state molecular structure of complex 9 is shown in Figure 2.5. Selected bond lengths and bond angles are given in Tables 2.8 and 2.9, respectively. As shown in Figure 2.5, complex 9 is a monomer with a three-legged piano stool molecular geometry. The distance of the Cr centre to the plane of the Cp ring in complex 9 is 1.857 Å. which is shorter than that of  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  at 1.884 Å. Within the CrNO moiety of complex 9, the Cr-N distance (1.686 Å) and the N-O distance (1.168 Å) are in very close agreement to the corresponding bond lengths observed for  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  (1.687 Å and 1.169 Å). The CrNO bond angle in complex 9 ( $170.4^\circ$ ) is essentially linear although it is more bent than in  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Cr}(\text{CO})_2(\text{NO})$  ( $178.9^\circ$ ). The two acetonitrile ligands are N-bonded (in a linear fashion) to the Cr centre in 9. The Cr-N bond lengths are in reasonable agreement with the previously determined structures of cationic Cr complexes with N-bonded acetonitrile ligands.<sup>28</sup>



**Figure 2.5.** Solid-state molecular structure of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2][\text{PF}_6]$ , complex 9.

**Table 2.8. Selected Bond Lengths (Å)**  
**for [CpCr(NO)(NCCH<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>], Complex 9.**

Bond	Length <sup>(a)</sup>
Cr - Cp	1.857(9)
Cr - N1	1.686(6)
Cr - N2	2.02(2)
Cr - N3	2.011(12)
O - N1	1.168(8)
N2 - C6	1.140(2)
N3 - C8	1.10(2)
C6 - C7	1.40(3)
C8 - C9	1.49(3)

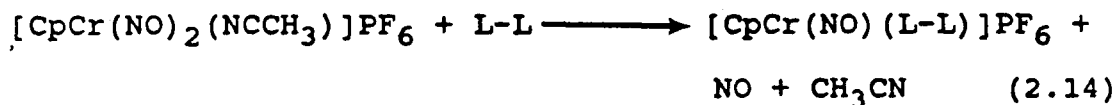
(a) E.s.d.'s are in parentheses.

**Table 2.9. Selected Bond Angles (deg) for  
[CpCr(NO)(NCCH<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>], Complex 9.**

Bond	Angle <sup>(a)</sup>
N1 - Cr - N2	97.1(6)
N1 - Cr - N3	98.6(7)
N1 - Cr - Cp	122.4(4)
N2 - Cr - N3	91.0(2)
N2 - Cr - Cp	118.3(6)
N3 - Cr - Cp	122.3(6)
Cr - N1 - O	170.4(11)
Cr - N2 - C6	175.7(15)
Cr - N3 - C8	176.7(15)
N2 - C6 - C7	173(2)
N3 - C8 - C9	176(2)

(a) E.s.d.'s are in parentheses.

There are very few examples of 17-electron neutral or cationic organometallic chromium nitrosyl complexes reported in the chemical literature to date. The only other known example of a 17-electron cation belonging to this class of compounds is  $[\text{CpCr}(\text{NO})(\text{L-L})]^+$  ((L-L) = phen or bpy).<sup>29</sup> This complex is prepared by the thermal substitution reaction presented in eq 2.14



This synthetic route (eq 2.14) to the radical cation is limited to strongly donating bidentate ligands since the reaction benefits thermodynamically from the "chelate effect". Also, the final products must be stable at high temperatures since the reaction only proceeds in refluxing  $\text{CH}_3\text{NO}_2$ . In comparison, reaction 2.13 proceeds at room temperature, and the reaction is driven by the precipitation of the silver halide salt. Also, the  $\text{CH}_3\text{CN}$  ligands in **9** are weaker N-donors than the bpy or phen ligands. This can be observed by comparing the IR spectrum of **9** with that of the  $[\text{CpCr}(\text{NO})(\text{L-L})]^+$  complexes. In  $\text{CH}_3\text{NO}_2$ , the IR spectrum of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  exhibits a strong nitrosyl absorption at  $1709 \text{ cm}^{-1}$ . The position of this band is at a higher frequency when compared to  $[\text{CpCr}(\text{NO})(\text{L-L})]\text{PF}_6$  ((L-L) = phen or bpy;  $\nu_{\text{NO}}$

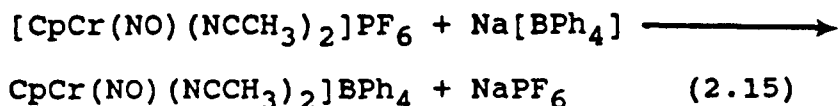
1690  $\text{cm}^{-1}$ ) suggesting that there is more electron density on the metal centre in the latter complexes to backdonate to the NO  $\pi^*$  ligand thus indicating the weaker donating ability of the  $\text{CH}_3\text{CN}$  ligands compared to the bidentate N-donor ligands.

(II-B) Reaction of  $[\text{CpCr}(\text{NO})\text{I}]_2$  with  $[\text{Ag}]\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$ .

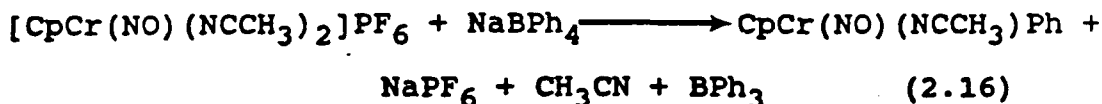
Since iodide abstraction from  $[\text{CpCr}(\text{NO})\text{I}]_2$  in a coordinating solvent ( $\text{CH}_3\text{CN}$ ) leads to the formation of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ , I next attempted reaction 2.13 in a non-coordinating solvent (ie.  $\text{CH}_2\text{Cl}_2$ ) to see if the corresponding  $[\text{CpCr}(\text{NO})(\text{CH}_2\text{Cl}_2)_2]^+$  complex can be generated since the loosely bound solvent molecules in this cation will render the cation more reactive. When the reaction between  $[\text{CpCr}(\text{NO})\text{I}]_2$  and  $[\text{Ag}]\text{PF}_6$  is carried out in  $\text{CH}_2\text{Cl}_2$ , the transformation that occurs is quite complex. Ultimately, a " $\text{CpCr}(\text{NO})_2^+$ " containing species is obtained as indicated by the IR spectrum of the reaction mixture ( $\nu_{\text{NO}}$  at 1842(s) and 1740(s)  $\text{cm}^{-1}$ ). However, attempts to isolate this complex only lead to extremely air-sensitive greenish-blue oils. Nevertheless, it can be derivatized to the known chloride complex,  $\text{CpCr}(\text{NO})_2\text{Cl}$ , by addition of  $[\text{PPN}]\text{Cl}$  (Bis(triphenylphosphineiminium chloride)) to the reaction mixture.

## (II-C) Some Chemical Reactivity of complex 9.

When  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  is treated with one equivalent of  $\text{NaBPh}_4$  in  $\text{CH}_2\text{Cl}_2$  solution, a metathesis of the  $\text{PF}_6^-$  anion for the  $\text{BPh}_4^-$  group occurs, i.e.,

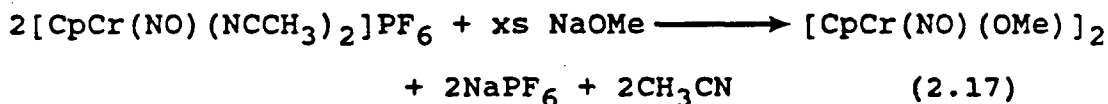


The cation, as its  $\text{BPh}_4^-$  salt, is isolated only in 20% yield. The low yield of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{BPh}_4$  isolated is somewhat surprising since the chemical transformation involved (eq. 2.15) is only a simple metathesis reaction. Probably another side reaction which may occur before or after the metathesis reaction is that in  $\text{CH}_2\text{Cl}_2$  one of the  $\text{CH}_3\text{CN}$  ligands is sufficiently labile to yield the electrophilic " $\text{CpCr}(\text{NO})(\text{NCCH}_3)^+$ " intermediate which can abstract a phenyl group from the  $\text{BPh}_4^-$  counterion to give an aryl complex  $\text{CpCr}(\text{NO})(\text{NCCH}_3)\text{Ph}$ , i.e.,



The neutral 17-electron aryl complex is probably thermally unstable at room temperature, a fact that would lead to its decomposition. The mode of reactivity for the organoboron complex cited in eq 2.16 is not without precedent since it has previously been observed that treatment of  $[\text{CpW}(\text{NO})_2]\text{BF}_4$  with  $\text{Na}[\text{BPh}_4]$  under similar conditions yields the aryl complex,  $\text{CpW}(\text{NO})_2\text{Ph}$ .<sup>30</sup>

When complex 9 is treated with excess  $\text{NaOMe}$  in  $\text{CH}_2\text{Cl}_2$ , the bimetallic complex  $[\text{CpCr}(\text{NO})(\text{OMe})]_2$  is obtained, i.e., eq 2.17. The product isolated from this



reaction is rather unexpected. One would anticipate the attack of the methoxide group to occur either at the  $\text{NO}$  or at the  $\text{CH}_3\text{CN}$  group since both ligands are known to engage in such reactions, especially when present in a cationic complex.<sup>31</sup> It can be proposed that the  $\text{OMe}^-$  group here first replaces the  $\text{PF}_6^-$  group to yield the 19-electron complex  $\text{CpCr}(\text{NO})(\text{OMe})(\text{NCCH}_3)_2$  which then loses its  $\text{CH}_3\text{CN}$  ligands and dimerizes to  $[\text{CpCr}(\text{NO})(\text{OMe})]_2$ . The propensity for the monomeric  $\text{Cr}$  complex to dimerize and form the bimetallic compound is not readily explicable. Similar tendencies are



also reflected in the unsuccessful attempts to make the 18-electron  $[\text{CpCr}(\text{NO})\text{I}_2]_2$  which readily converts to  $[\text{CpCr}(\text{NO})\text{I}]_2$  in  $\text{CH}_2\text{Cl}_2$ .<sup>6</sup> In contrast, the  $[\text{CpM}(\text{NO})\text{I}_2]_2$  ( $\text{M} = \text{Mo}, \text{W}$ ) compounds can be made in good yields and do not readily convert to the corresponding monohalo dimers,  $[\text{CpM}(\text{NO})\text{I}]_2$ .

Several attempts were made to synthesize the neutral analogue of the radical cation, i.e.  $\text{CpCr}(\text{NO})(\text{NCCH}_3)_2$ . Reduction of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$  with  $\text{Na}/\text{Hg}$  in THF only leads to a non-nitrosyl containing brown solution. A less potent reducing agent such as zinc dust leads to the formation of an extremely air-sensitive bright purple solid which is often contaminated with the radical cation. Attempts to purify the purple solid did not meet with success.

### Summary

This work has demonstrated that the treatment of the dihalo nitrosyl complexes of molybdenum and tungsten,  $\text{Cp}'\text{M}(\text{NO})\text{X}_2$ , with  $[\text{NO}]^+$  and  $[\text{Ag}]^+$  salts, in  $\text{CH}_3\text{CN}$  affords a series of new diamagnetic cationic nitrosyl complexes,  $[\text{Cp}'\text{M}(\text{NO})\text{X}(\text{NCCH}_3)_2]^+$  and  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3]^{2+}$ . The physical and spectroscopic properties of these cationic complexes are consistent with their possessing the conventional four-legged piano stool molecular geometry. In addition, treatment of  $[\text{CpCr}(\text{NO})\text{I}]_2$  with a  $[\text{Ag}]^+$  salt in  $\text{CH}_3\text{CN}$  leads to the successful isolation of the novel paramagnetic chromium cation,  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]^+$ . The complex is monomeric in the solid state possessing the familiar three-legged piano stool molecular geometry. A solution ESR measurement shows that the unpaired electron is delocalized on the nitrogen atom of the nitrosyl ligand.

Taking into account the lability of the  $\text{CH}_3\text{CN}$  ligands in solution and the "non-coordinating" characteristics of the counterion ( $\text{PF}_6$  or  $\text{BF}_4$ ) in the new organometallic complexes prepared in this work, this suggests that the organometallic cations may in principle serve as convenient precursors to novel nitrosyl complexes of Cr, Mo and W.

## References and Notes

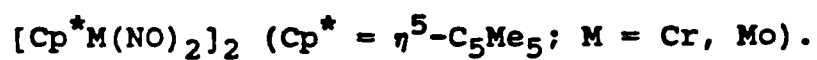
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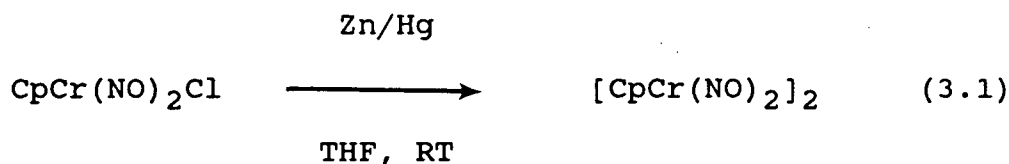
### Chapter 3

#### Synthesis and Characterization of the Dinitrosyl Dimers



### Introduction

The compound  $[\text{CpCr}(\text{NO})_2]_2$  was first reported by King and Bisnette in 1964.<sup>1</sup> It was first obtained in only 5% yield via the reduction of  $\text{CpCr}(\text{NO})_2\text{Cl}$  with  $\text{NaBH}_4$  in a two-phase water-benzene system. However, our research group subsequently discovered that it is best prepared in much higher yields by the reduction of  $\text{CpCr}(\text{NO})_2\text{Cl}$  with either  $\text{Zn/Hg}$  in  $\text{THF}$ <sup>2</sup> (i.e. eq 3.1) or  $\text{Na/Hg}$  in benzene<sup>3</sup>. The high yield synthesis of this dimer enabled an extensive



study of its physical and chemical properties to be undertaken.

In view of the extensive and varied chemistry of  $[\text{CpCr}(\text{NO})_2]_2$  that our research group has developed,<sup>4-7</sup> the preparation of the Mo and W analogues for comparative purposes is undoubtedly one of our prime objectives. Unfortunately, when the  $\text{CpM}(\text{NO})_2\text{Cl}$  ( $\text{M} = \text{Mo}, \text{W}$ ) complexes are subjected to the experimental conditions indicated in eq. 3.1, only intractable products are obtained. To date, the Mo and W dimers,

$[\text{CpM}(\text{NO})_2]_2$ , have yet to be isolated even though they have been the object of much synthetic effort.<sup>8</sup>

It has been shown that pentamethylcyclopentadienyl ( $\text{Cp}^*$ )-containing compounds often exhibit dramatically different chemistry from that shown by their unsubstituted cyclopentadienyl analogues.<sup>9</sup> It was thought that perhaps the reduction of the respective chloro complexes of Cr, Mo and W containing the  $\eta^5\text{-C}_5\text{Me}_5$  ligand (i.e.  $\text{Cp}^*\text{M}(\text{NO})_2\text{Cl}$ ) under the same conditions as those in eq. 3.1 should yield the respective dinitrosyl dimers  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$ . Indeed this expectation has been realized, and in this chapter the syntheses and characterization of the new dimers  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) are described. Furthermore, the physical and chemical properties of these dimers are compared and contrasted to their valence isoelectronic carbonyl analogues  $[\text{Cp}'\text{M}(\text{CO})_2]_2$  ( $\text{Cp}' = \text{Cp}$  or  $\text{Cp}^*$ ;  $\text{M} = \text{Fe}, \text{Ru}$ ), as well as their congeneric Cp analogue,  $[\text{CpCr}(\text{NO})_2]_2$ .



## Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions. General experimental procedures employed in this study were similar to those described in the preceding chapter.  $\text{Cp}^*\text{W}(\text{NO})_2\text{Cl}$ <sup>10</sup> and  $\text{Cp}^*\text{Cr}(\text{CO})_2(\text{NO})$ <sup>11</sup> were prepared by published procedures. The purity of all the complexes prepared was ascertained by elemental analyses and conventional spectroscopic techniques.

**Preparation of  $\text{Cp}^*\text{M}(\text{NO})_2\text{Cl}$  ( $\text{M} = \text{Cr}, \text{Mo}$ ).** Both of the  $\text{Cp}^*\text{M}(\text{NO})_2\text{Cl}$  complexes were prepared in a similar manner, but to achieve optimum yields the reactions were performed at  $-78^\circ\text{C}$ . The preparation of the Mo complex is described here as a representative example.

A stirred solution of  $\text{Cp}^*\text{Mo}(\text{CO})_2(\text{NO})$  (7.00 g, 22.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was treated dropwise with a  $\text{CH}_2\text{Cl}_2$  solution of nitrosyl chloride.<sup>12</sup> (The  $\text{ClNO}$  solution typically consisted of approximately 50 mmol of  $\text{ClNO}$  in 30 mL of  $\text{CH}_2\text{Cl}_2$ ). Gas evolution occurred, and the colour of the solution changed from orange to olive green. The progress of the reaction was monitored by IR spectroscopy, and the nitrosyl chloride solution was added until the carbonyl absorptions of the starting organometallic reactant ( $\nu_{\text{CO}}$  2004(s), 1923(vs)  $\text{cm}^{-1}$ ) had disappeared and new nitrosyl bands

had appeared at 1728(s) and 1641(vs)  $\text{cm}^{-1}$ . The final reaction mixture was concentrated in vacuo to approximately 20 mL and was filtered through a short (2 x 4 cm) Florisil column supported on a frit. The column was washed with  $\text{CH}_2\text{Cl}_2$  until the washings were colourless, and the filtrate was concentrated in vacuo to approximately 20 mL. Addition of hexanes (100 - 150 mL) resulted in the precipitation of an olive green microcrystalline solid. The olive green solid was collected by filtration, washed with 2x10 mL of cold ( $0^\circ\text{C}$ ) hexanes and dried in vacuo. This procedure afforded 5.75 g (17.6 mmol, 80% yield) of analytically pure  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$ .

Anal. Calcd. for  $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2\text{ClMo}$  : C, 36.81; H, 4.60; N, 8.59. Found : C, 36.63; H, 4.71; N, 8.50. IR (Nujol mull)  $\nu_{\text{NO}}$  1717(s), 1642(vs)  $\text{cm}^{-1}$ ; ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{NO}}$  1728(s), 1641(vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.89 ( $\text{C}_5(\text{CH}_3)_5$ ). Low resolution mass spectrum (probe temperature  $120^\circ\text{C}$ )  $m/z$  326  $[\text{P}]^+$ .

The chromium analogue was obtained similarly as a dark reddish-brown microcrystalline solid in 60% yield.

Anal. Calcd. for  $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2\text{ClCr}$  : C, 42.55; H, 5.32; N, 9.93. Found : C, 42.34; H, 5.40; N, 9.86. IR (Nujol mull)  $\nu_{\text{NO}}$  1763(s), 1681(vs)  $\text{cm}^{-1}$ ; ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{NO}}$  1782(s), 1682(vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.34 ( $\text{C}_5(\text{CH}_3)_5$ ). Low resolution mass spectrum (probe temperature  $120^\circ\text{C}$ )  $m/z$  282  $[\text{P}]^+$ .

**Preparation of  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$ .** A zinc amalgam was prepared by stirring zinc dust (0.46 g) with mercury (10 g) for 1 h. This amalgam was then stirred with a solution of  $\text{Cp}^*\text{Cr}(\text{NO})_2\text{Cl}$  (0.20 g, 0.71 mmol) in THF (30 mL) at room temperature. The progress of the reaction was monitored by IR spectroscopy. The reaction was allowed to proceed until the nitrosyl absorptions of the starting chloro complex ( $\nu_{\text{NO}}$  1777(s), 1677(s)  $\text{cm}^{-1}$ ) had completely disappeared and had been replaced by a band at 1638(s)  $\text{cm}^{-1}$  attributable to the  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  complex. During this time, the colour of the reaction mixture changed from reddish-brown to dark red-violet. The reaction mixture was filtered through a column of Celite (1 x 2 cm) supported on a frit, and the filtrate was taken to dryness in vacuo. The resulting residue was redissolved in benzene (10 mL) and chromatographed on an alumina column (Woelm, Basic, activity 3) with benzene as eluant. The single dark purple band that developed was collected and taken to dryness in vacuo to yield 0.080 g (45% yield) of dark purple, analytically pure  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$ .

Anal. Calcd. for  $\text{C}_{20}\text{H}_{30}\text{N}_4\text{O}_4\text{Cr}_2$  : C, 48.58; H, 6.07; N, 11.34. Found : C, 48.58; H, 5.96; N, 11.18. IR (KBr pellet)  $\nu_{\text{NO}}$  1630(s), 1487(w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.50 and 1.65 ( $\text{C}_5(\text{CH}_3)_5$ ).  $^{13}\text{C}(^1\text{H})$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  8.71 ( $\text{C}_5(\text{CH}_3)_5$ ), 109.32 ( $\text{C}_5(\text{CH}_3)_5$ ). Low resolution mass spectrum (probe temperature 120°C)  $m/z$  494  $[\text{P}]^+$ .

Preparation of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$ .  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$  (0.30 g, 0.92 mmol) was stirred with Zn amalgam (0.17 g of zinc dust in 10 g of mercury) in THF (60 mL). The progress of the reaction was again monitored by IR spectroscopy. After 15h, an IR spectrum of the supernatant solution revealed the consumption of the starting chloro complex ( $\nu_{\text{NO}}$  1723(s), 1638(s)  $\text{cm}^{-1}$ ) and the formation of a new nitrosyl-containing compound ( $\nu_{\text{NO}}$  1591(s)  $\text{cm}^{-1}$ ). The THF solution was filter cannulated away from the mercury-containing residues. The filtrate was taken to dryness in vacuo to yield a dark red-violet solid. This solid was extracted with hexanes (4 x 10 mL); the hexanes extracts were combined and taken to dryness. The dark purple residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL) and cooled to  $0^\circ\text{C}$  for 24h. The bright purple, microcrystalline solid that deposited was collected and dried in vacuo for 24h to yield elementally pure  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  (0.060 g, 23% yield).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{30}\text{N}_4\text{O}_4\text{Mo}_2$  : C, 41.20; H, 5.15; N, 9.62. Found : C, 41.50; H, 5.31; N, 9.54. IR (KBr pellet)  $\nu_{\text{NO}}$  1692(s), 1585(vs, br)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.47 ( $\text{C}_5(\text{CH}_3)_5$ ).  $^{13}\text{C}(^1\text{H})$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  9.39 ( $\text{C}_5(\text{CH}_3)_5$ ), 111.34 ( $\text{C}_5(\text{CH}_3)_5$ ). Low resolution mass spectrum (probe temperature  $120^\circ\text{C}$ )  $m/z$  582  $[\text{P}]^+$ .

### Attempted Syntheses of $[\text{Cp}^*\text{W}(\text{NO})_2]_2$ .

- (i) A THF solution (60 mL) of  $\text{Cp}^*\text{W}(\text{NO})_2\text{Cl}$  (0.20 g, 0.48 mmol) was stirred with zinc amalgam (0.20 g of Zn dust in 10 g of Hg) for 1 h. During this time the colour of the reaction mixture changed from green to greenish-brown. Monitoring the progress of the reaction by IR spectroscopy indicated the decrease in intensity of the NO bands of the chloro complex ( $\nu_{\text{NO}}$  1702(s), 1623(vs)  $\text{cm}^{-1}$ ) but no new nitrosyl absorptions were observed. Prolonged stirring of the reaction mixture eventually led to the consumption of the starting chloro complex.
- (ii) A THF solution (60 mL) of  $\text{Cp}^*\text{W}(\text{NO})_2\text{Cl}$  (0.20 g, 0.48 mmol) was stirred with a stoichiometric amount of Na/Hg at room temperature. After 15 min, the IR spectrum of the solution revealed the complete consumption of the starting organometallic reactant ( $\nu_{\text{NO}}$  1702(s), 1623(vs)  $\text{cm}^{-1}$ ) and the formation of a new nitrosyl-containing complex ( $\nu_{\text{NO}}$  1672(m), 1591(m)  $\text{cm}^{-1}$ ). During this time, the colour of the reaction mixture changed from green to light brown. The final mixture was filtered through a short column (2 x 2 cm) of Celite supported on a frit; the filtrate was taken to dryness to yield a small amount of a brown, oily solid. This oily residue was redissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL), layered with  $\text{Et}_2\text{O}$  (20 mL) and cooled at  $0^\circ\text{C}$  for 24 h. This procedure afforded a small amount of an air-sensitive yellow precipitate which was

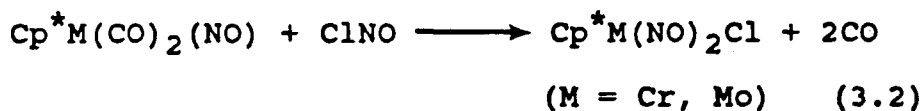
collected and dried in vacuo for several hours. Elemental analyses of this yellow solid prepared on two separate occasions showed it to be quite variable in C, H and N contents : C, 32.07; H, 4.22; N, 5.16 and C, 35.57; H, 4.83; N, 4.30.

**Reaction of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  with  $\text{SnCl}_2$ .** To a stirred THF solution (20 mL) of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  (0.050 g, 0.086 mmol) at room temperature was added  $\text{SnCl}_2$  (0.050 g, 0.26 mmol). The reaction mixture was stirred for 1 h during which time the colour of the solution changed from purple to green-brown. An IR spectrum of the solution exhibited two new nitrosyl bands at 1723 and 1638  $\text{cm}^{-1}$ . The solution was taken to dryness in vacuo, and the residue was redissolved in  $\text{CH}_2\text{Cl}_2$ . This  $\text{CH}_2\text{Cl}_2$  solution was then chromatographed on a Florisil column with  $\text{CH}_2\text{Cl}_2$  as the eluant. The green band that separated was collected, and the solvent was removed from the eluate in vacuo. The olive green residue was found to be  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$  by comparison of its spectroscopic properties to that of an authentic sample: IR (Nujol mull)  $\nu_{\text{NO}}$  1717(s), 1642(vs)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.89 (s,  $\text{C}_5(\text{CH}_3)_5$ ).

## Results and Discussion

### (I) Preparation of the $\text{Cp}^*\text{M}(\text{NO})_2\text{Cl}$ ( $\text{M} = \text{Cr}, \text{Mo}$ ) Complexes.

Treatment of the  $\text{Cp}^*\text{M}(\text{CO})_2(\text{NO})$  complexes with  $\text{ClNO}$  in  $\text{CH}_2\text{Cl}_2$ , according to eq. 3.2., results in the formation of the dinitrosyl chloride complexes,  $\text{Cp}^*\text{M}(\text{NO})_2\text{Cl}$ , in good yields. The transformation in eq. 3.2 is similar to that



observed for the corresponding Cp-containing complexes.<sup>13</sup>

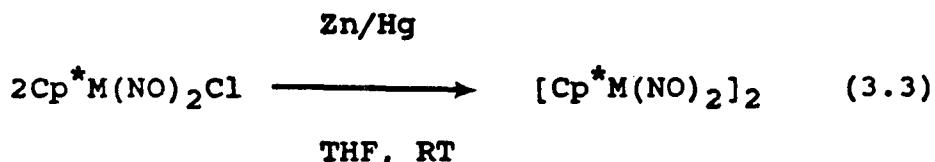
The  $\text{Cp}^*\text{Cr}(\text{NO})_2\text{Cl}$  complex is a dark reddish-brown crystalline solid that is sparingly soluble in hexanes and  $\text{Et}_2\text{O}$  but very soluble in  $\text{CH}_2\text{Cl}_2$ , THF and toluene. The Mo analogue is a green crystalline solid with similar solubility properties. In their pure form, both complexes can be stored under  $\text{N}_2$  at room temperature for extended periods of time and may be handled in air for short periods of time without noticeable decomposition.

### (II) The $[\text{Cp}^*\text{M}(\text{NO})_2]_2$ ( $\text{M} = \text{Cr}, \text{Mo}$ ) Complexes

#### (II-A) Preparation of the $[\text{Cp}^*\text{M}(\text{NO})_2]_2$ ( $\text{M} = \text{Cr}, \text{Mo}$ ) Complexes.

Treatment of the  $\text{Cp}^*\text{M}(\text{NO})_2\text{Cl}$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) complexes with zinc amalgam in THF according to the general equation 3.3

affords the corresponding dinitrosyl dimer complexes,  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$ , in moderate yields. The progress of the reaction can be conveniently monitored by IR spectroscopy.



$[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  is best purified by column chromatography of the crude complex as a benzene solution on an alumina column. Pure  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  is a dark purple solid which is thermally stable at room temperature under  $\text{N}_2$  for several months. As a solid, it is air sensitive but may be handled quickly in air without noticeable decomposition. The complex is very soluble in THF,  $\text{CH}_2\text{Cl}_2$  and benzene, but only sparingly soluble in  $\text{Et}_2\text{O}$  and hexanes to yield dark purple solutions which are air- and moisture-sensitive.

During the synthesis of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$ , once the starting material is consumed, it is important that the solution be separated from the amalgam. Prolonged stirring of the reaction mixture beyond this time results in much lower yields of the desired product. While  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  can be purified by column chromatography, a benzene solution of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  decomposes immediately on an alumina column. Attempts to chromatograph a solution of crude  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  on



a Florisil column or an alumina column (Woelm, Basic, activity 2, 3 or 4) employing benzene, toluene or  $\text{CH}_2\text{Cl}_2$  as eluant only lead to the decomposition of the Mo dimer. The crude Mo dimer can be purified by repetitive extraction of the crude product with hexanes, taking the combined extracts to dryness, and redissolving the residue in  $\text{CH}_2\text{Cl}_2$ . Pure  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  can be isolated by crystallization from the  $\text{CH}_2\text{Cl}_2$  solution at  $0^\circ\text{C}$ . Pure  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  is a bright purple solid and is much more air- and moisture-sensitive than its Cr analogue in the solid state. If obtained in an impure form, the Mo dimer undergoes decomposition both in solution and in the solid state to a brown intractable solid even when stored under  $\text{N}_2$ . The solubility properties of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  are similar to that of its Cr congener. Its solutions are extremely air- and moisture-sensitive and decomposition of the complex<sup>14</sup> occurs readily even under  $\text{N}_2$  if the solvent is not rigorously dry. Even when it is analytically pure, the Mo dimer does not persist in solution for more than 4-5 days at low temperatures. It should be noted that in certain solvents, a slow reaction between  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  and the solvent occurs. For example, in  $\text{CCl}_4$  there is a slow conversion of the Mo dimer to the chloro complex,  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$ , over a period of 8-10 days. This transformation is accelerated by ultraviolet irradiation of the reaction solution.<sup>15</sup>

Regrettably, when  $\text{Cp}^*\text{W}(\text{NO})_2\text{Cl}$  is treated with zinc amalgam under the same experimental conditions as in eq 3.3, the corresponding  $[\text{Cp}^*\text{W}(\text{NO})_2]_2$  is not obtained. Using a more potent reducing agent, Na/Hg, also does not afford the W dimer.

**(II-B) Spectroscopic Properties of the  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$   
(M = Cr, Mo) Complexes.**

The low resolution mass spectra of  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  and  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  both display peaks attributable to their corresponding parent ions and ions corresponding to the loss of the nitrosyl ligands and other groups (e.g. fragmentation of the  $\text{Cp}^*$  rings). Unfortunately, the overlapping of some medium and strong intensity peaks in the lower mass range makes any definite further assignments difficult.

Several possible molecular structures of  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  having different combinations of bridging and terminal nitrosyl ligands can be envisaged. By analogy to the structurally characterized  $[\text{CpCr}(\text{NO})_2]_2$ ,<sup>16</sup> the molecular structure of  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  can be proposed to be the trans nitrosyl-bridged structure in the solid state (Figure 3.1-B). This proposal is based on the similarity in the NMR and IR spectral properties between  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  and its well known perhydro analogue. The proton NMR spectrum of  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$

in  $\text{CDCl}_3$  exhibits two singlets at 1.50 and 1.65 ppm with an intensity ratio of 21:1. By analogy to the  $[\text{CpCr}(\text{NO})_2]_2$  system, the high and low field singlets in the NMR spectrum of  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  can be assigned to the cis and trans bridged isomers, respectively (Figure 3.1-A and -B). The IR spectrum of  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  in the solid state (KBr pellet) exhibits a strong nitrosyl band at  $1630\text{ cm}^{-1}$  suggesting a terminal NO ligand and a weak band at  $1487\text{ cm}^{-1}$  suggesting a bridging NO ligand. By comparison, the IR spectrum of the perhydro analogue  $[\text{CpCr}(\text{NO})_2]_2$  in the solid state also exhibits two nitrosyl bands at 1662 and  $1504\text{ cm}^{-1}$  attributable to the terminal and bridging NO groups respectively.<sup>17</sup> The nitrosyl stretching frequencies for the  $\text{Cp}^*$  compound are shifted to a lower wavenumber than the Cp analogue; similar effects have been previously observed and are attributed to the greater electron donating ability of the  $\text{Cp}^*$  ligand as compared to the Cp ligand.<sup>18</sup>

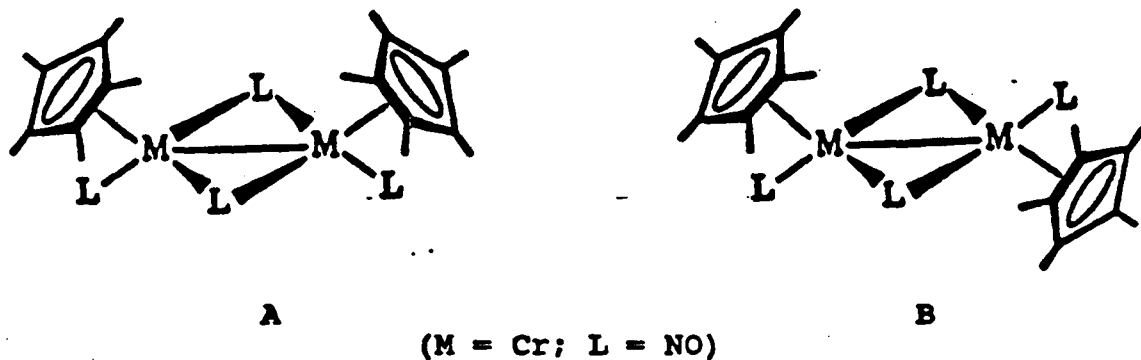


Figure 3.1. Probable Molecular Structures of  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$

Interestingly enough, the IR spectrum of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  in the solid state exhibits two nitrosyl bands in the terminal nitrosyl region ( $\nu_{\text{NO}}$  1692(s), 1585(vs, br)) but appears to lack any bands attributable to a bridging metal-nitrosyl linkage. In fact, it resembles the IR spectrum of its monomeric precursor  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$  ( $\nu_{\text{NO}}$  1721(s), 1644(vs, br). So, in the solid state, the Mo dimer can be simplistically viewed as two equivalent  $\text{Cp}^*\text{Mo}(\text{NO})_2$  moieties linked by a Mo-Mo bond with no bridging nitrosyl groups (Figure 3.2). In its proton NMR spectrum,  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  exhibits a singlet proton resonance at 1.47 ppm in  $\text{C}_6\text{D}_6$  which is attributable to the equivalent methyl protons on each of the  $\text{Cp}^*$  ligands.

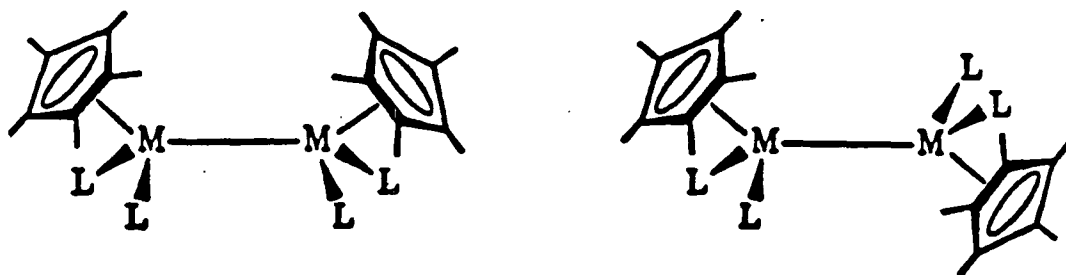
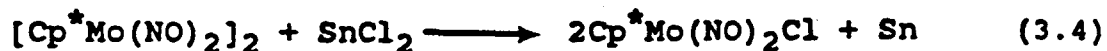


Figure 3.2. Probable Molecular Structures of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$

(II-C) Reaction of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  with  $\text{SnCl}_2$ .

Treatment of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  with excess  $\text{SnCl}_2$  in THF leads to the formation of  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$  (as in eq. 3.4).



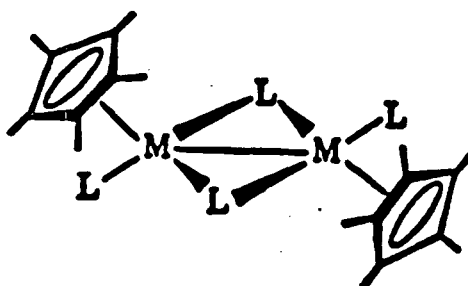
The progress of the reaction can be conveniently monitored by IR spectroscopy since the absorptions due to the nitrosyl groups of the reactant  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  occur at  $1591\text{ cm}^{-1}$  whereas those due to the product  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$  occur at  $1723$  and  $1638\text{ cm}^{-1}$ . The molybdenum chloro complex can be separated from the reaction mixture by column chromatography techniques. The propensity of the Mo dimer to abstract the chlorine ligands from  $\text{SnCl}_2$  is reminiscent of that observed for  $[\text{CpCr}(\text{NO})_2]_2$ .<sup>4</sup> In view of the fact that the  $[\text{CpCr}(\text{NO})_2]_2$  complex has been shown to selectively remove halogen from certain organic substrates,<sup>7</sup> this suggests that the new Mo dimer is also capable of this mode of reactivity towards organic substrates, perhaps with altered selectivities.

(II-D) A comparison of the  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) and the  $[\text{Cp}^*\text{M}(\text{CO})_2]_2$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) compounds.

Having now synthesized the  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) compounds, it is interesting to compare their properties to

those exhibited by their valence isoelectronic carbonyl analogues  $[\text{Cp}'\text{M}(\text{CO})_2]_2$  ( $\text{Cp}' = \text{Cp}$  or  $\text{Cp}^*$ ;  $\text{M} = \text{Fe}, \text{Ru}$ ) as well as the known  $[\text{CpCr}(\text{NO})_2]_2$ . Like the  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$  compounds,  $[\text{CpCr}(\text{NO})_2]_2$  also exists as a purple solid. It is, however, less soluble than the corresponding  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  compound. In its mass spectra,  $[\text{CpCr}(\text{NO})_2]_2$  also exhibits a highest peak attributable to the parent ion as well as peaks corresponding to the sequential loss of the nitrosyl ligands. As mentioned earlier,  $[\text{CpCr}(\text{NO})_2]_2$  has been shown to possess a trans NO bridged structure in the solid state, but it exists as a mixture of cis and trans bridged isomers in solution. The  $\text{Cp}^*$  analogue,  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$ , is apparently similar.

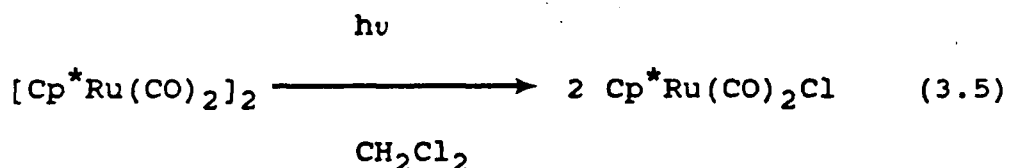
The carbonyl compound,  $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ , was first reported by King and co-workers some time ago.<sup>19</sup> It is a red-violet solid and is sparingly soluble in non-polar organic solvents but very soluble in polar organic solvents. Its molecular structure has been proposed to exist exclusively as the trans carbonyl bridged isomer (Figure 3.3) in solution (cyclohexane).



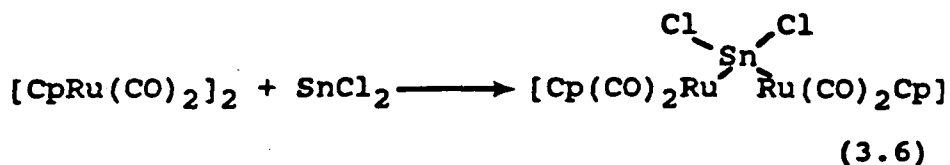
**Figure 3.3** Structure of the Group 8 Carbonyl Complexes

By comparison, the congeneric Ru carbonyl dimer,  $[\text{Cp}^*\text{Ru}(\text{CO})_2]_2$ , apparently also exists as the trans bridged carbonyl isomer. In relation to this, the structurally characterized carbonyl complex  $[(\text{C}_5\text{Me}_4\text{Et})\text{Ru}(\text{CO})_2]_2$  has been shown to possess the trans carbonyl bridged structure as well (Figure 3.3).<sup>20</sup>

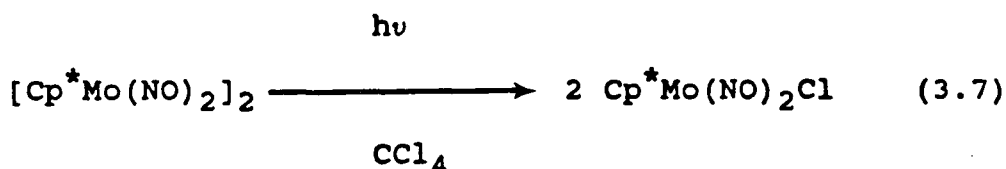
The UV irradiation of  $[\text{Cp}^*\text{Ru}(\text{CO})_2]_2$  in chlorinated solvents (e.g.  $\text{CH}_2\text{Cl}_2$ ) leads to the formation of the corresponding chloro complex  $\text{Cp}^*\text{Ru}(\text{CO})_2\text{Cl}$ <sup>21</sup>, i.e.,



Upon treatment with  $\text{SnCl}_2$ , the Ru carbonyl dimer,  $[\text{CpRu}(\text{CO})_2]_2$ , undergoes an oxidative addition reaction with  $\text{SnCl}_2$  to yield a product which contains a Ru-Sn bond<sup>22</sup> i.e. eq. 3.6.



By way of contrast,  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  apparently exists as a non-nitrosyl bridged dimer in the solid state. However, the behaviour of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  in chlorinated solvents is quite similar to the carbonyl complex,  $[\text{Cp}^*\text{Ru}(\text{CO})_2]_2$ . Thus, the UV irradiation of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  in chlorinated solvents (e.g.  $\text{CCl}_4$ ) also yields the corresponding molybdenum chloro complex, i.e.,



On the other hand, the chemical reactivity of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  with  $\text{SnCl}_2$  is quite different when compared to the Ru carbonyl complex. Instead of forming a Mo-Sn bond, the Mo dimer abstracts the chloro ligands from  $\text{SnCl}_2$  to yield  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$  (as shown in eq. 3.4). In view of the extensive chemistry that has been performed on  $[\text{Cp}^*\text{Ru}(\text{CO})_2]_2^{21}$ , this observation suggests that  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  should exhibit a varied and rich chemistry although its characteristic reactivity has not been explored in detail yet.



### Summary

This work describes the synthesis of  $[\text{Cp}^*\text{M}(\text{NO})_2]_2$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) by the treatment of  $\text{Cp}^*\text{M}(\text{NO})_2\text{Cl}$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) with zinc amalgam in THF. Both the complexes exist as relatively thermally stable, air- and moisture-sensitive diamagnetic purple solids. In the solid state, the Cr dimer is proposed to possess the trans NO bridged structure while the Mo dimer apparently possess the non NO bridged structure. The  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  dimer reacts with  $\text{SnCl}_2$  in THF to yield  $\text{Cp}^*\text{Mo}(\text{NO})_2\text{Cl}$ . The preparation of these dimers provides access to a relatively unexplored area of Group 6 organometallic nitrosyl complexes.

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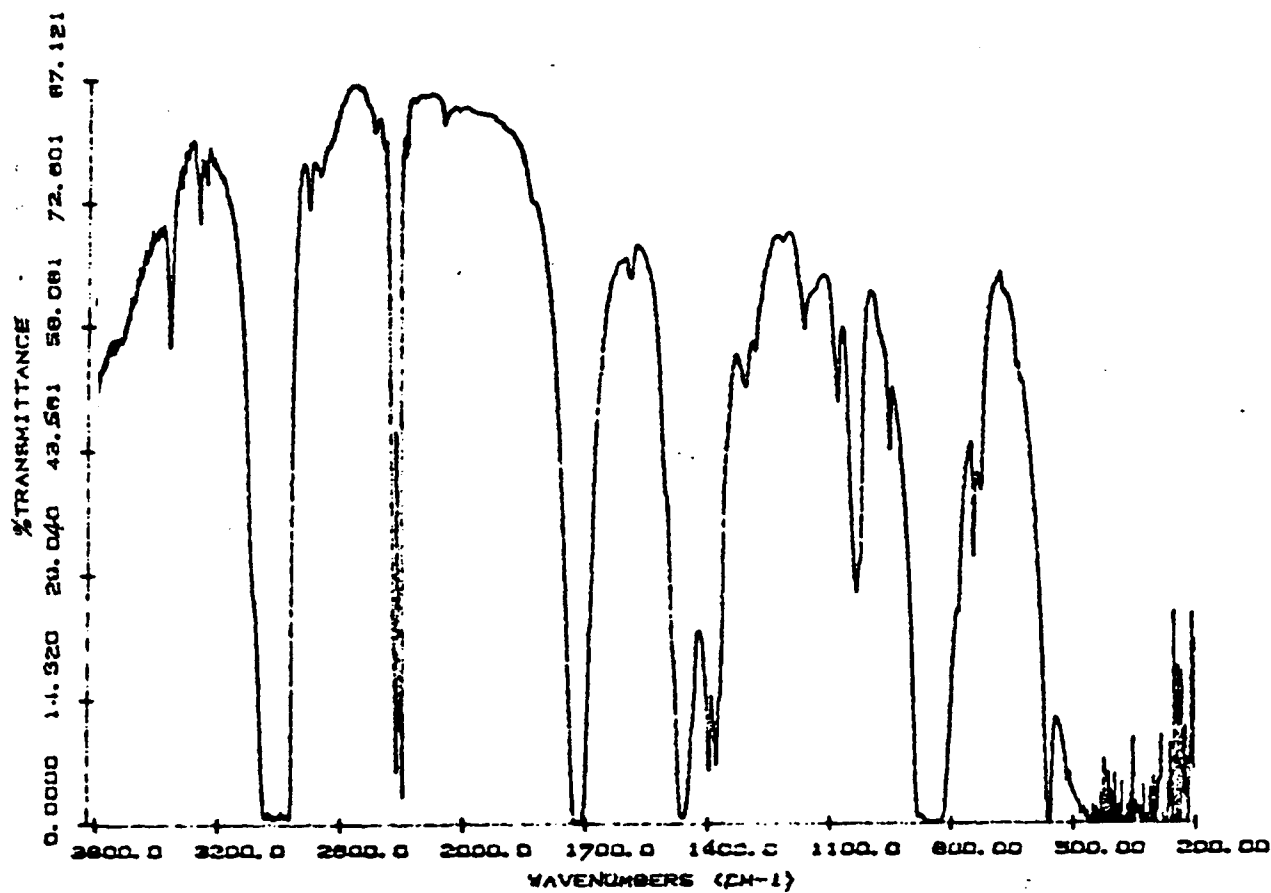
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14. In THF, Et<sub>2</sub>O and benzene, the Mo dimer decomposes to an orange complex whose identity remains to be ascertained. The IR spectra (Nujol mull) of the orange complex exhibits 2 nitrosyl bands at 1693(s) and 1612(s) cm<sup>-1</sup>. Its low resolution mass spectrum exhibits a highest peak at 526.

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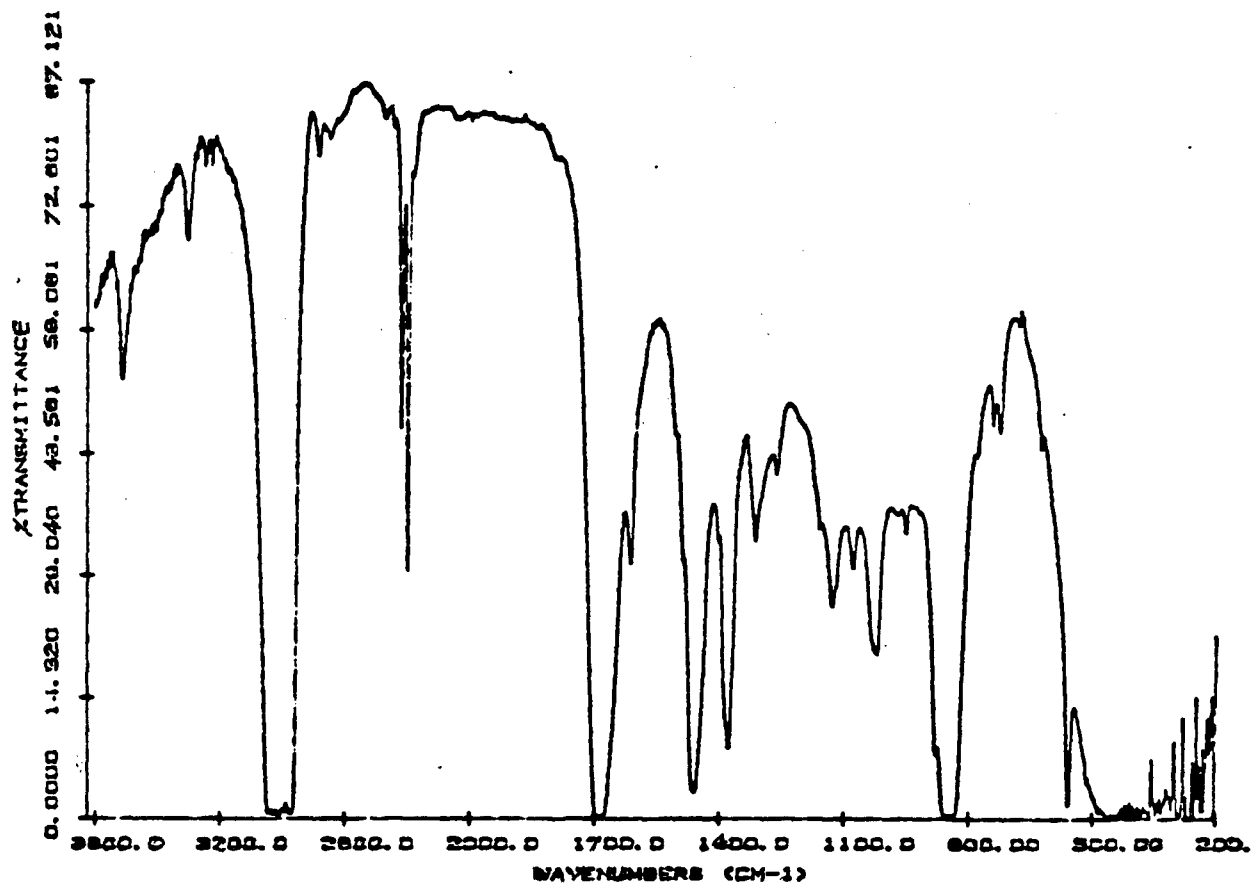
**Spectral Appendix**

**Selected Infrared and NMR Spectra of Compounds.**

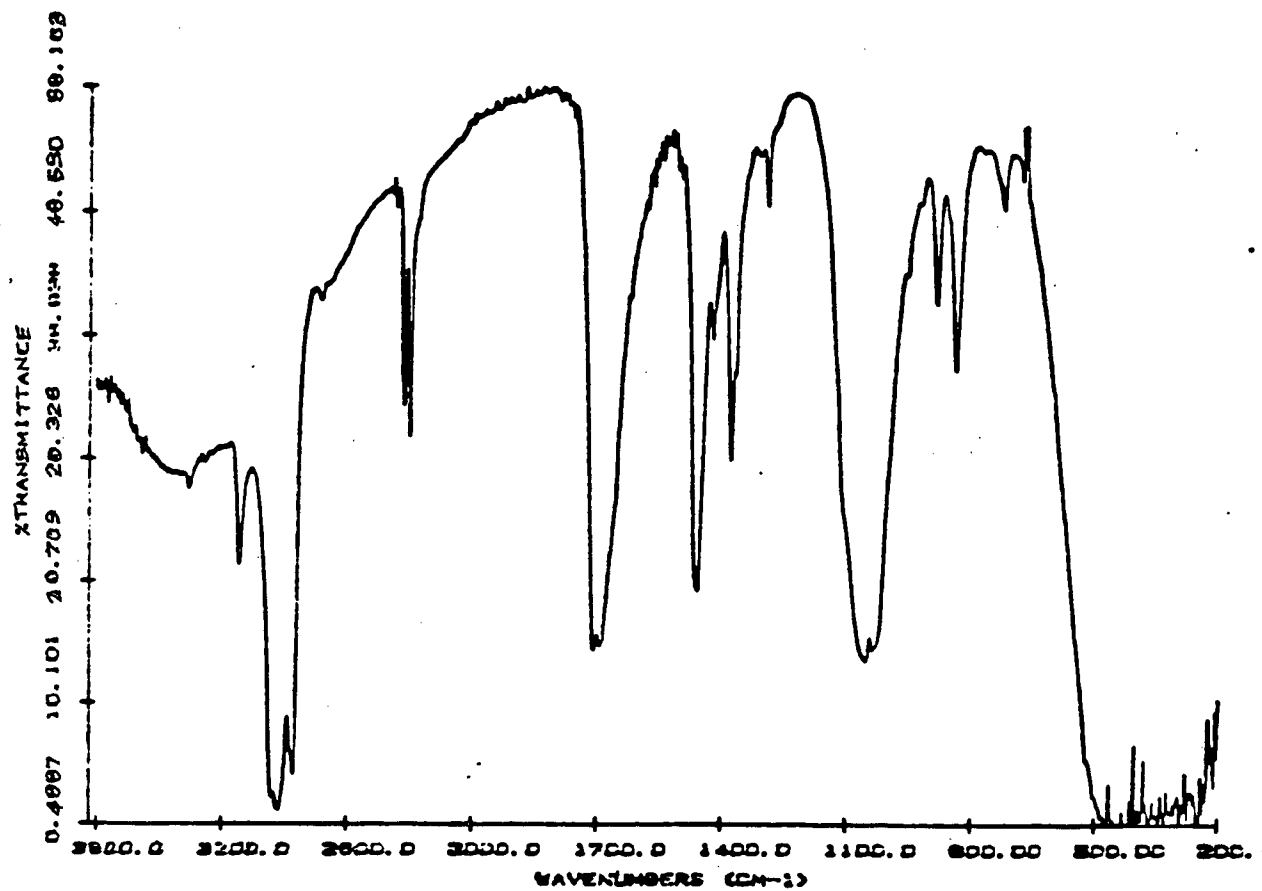
IR spectrum of  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{NCCH}_3)_3][\text{PF}_6]_2$ , 1 as a Nujol mull.



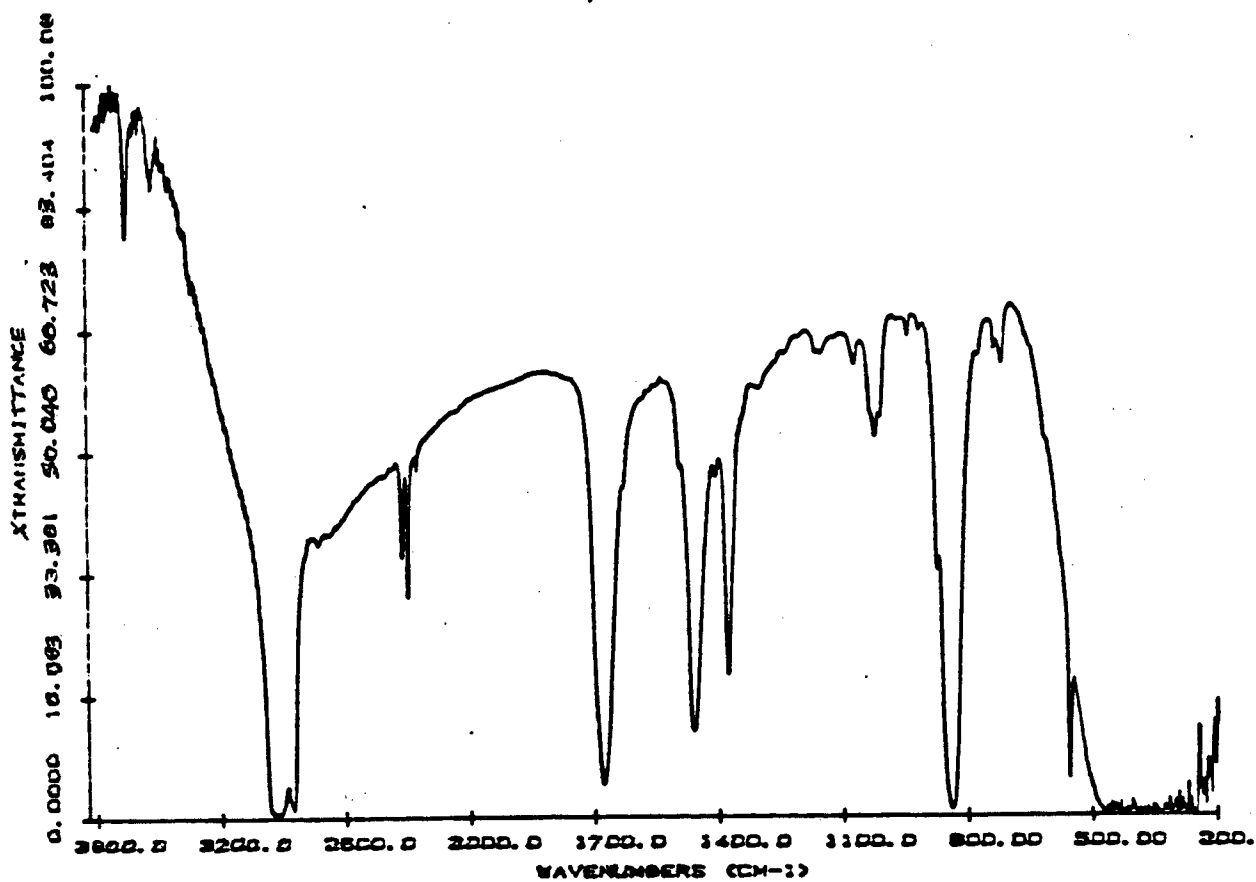
IR spectrum of  $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{PF}_6$ , 2 as a Nujol mull.



IR spectrum of  $[\text{CpMo}(\text{NO})\text{Br}(\text{NCCH}_3)_2]\text{BF}_4$ , 3 as a Nujol mull.

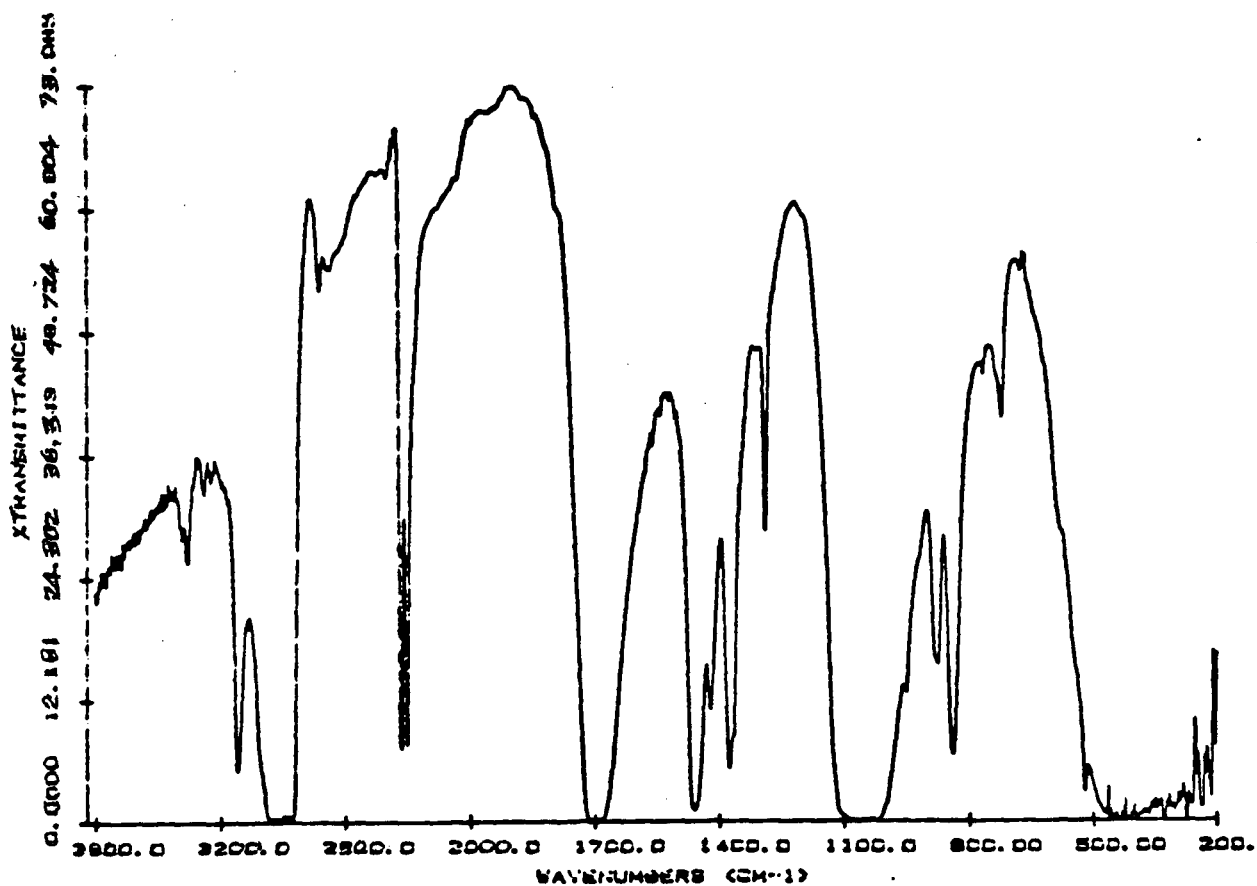


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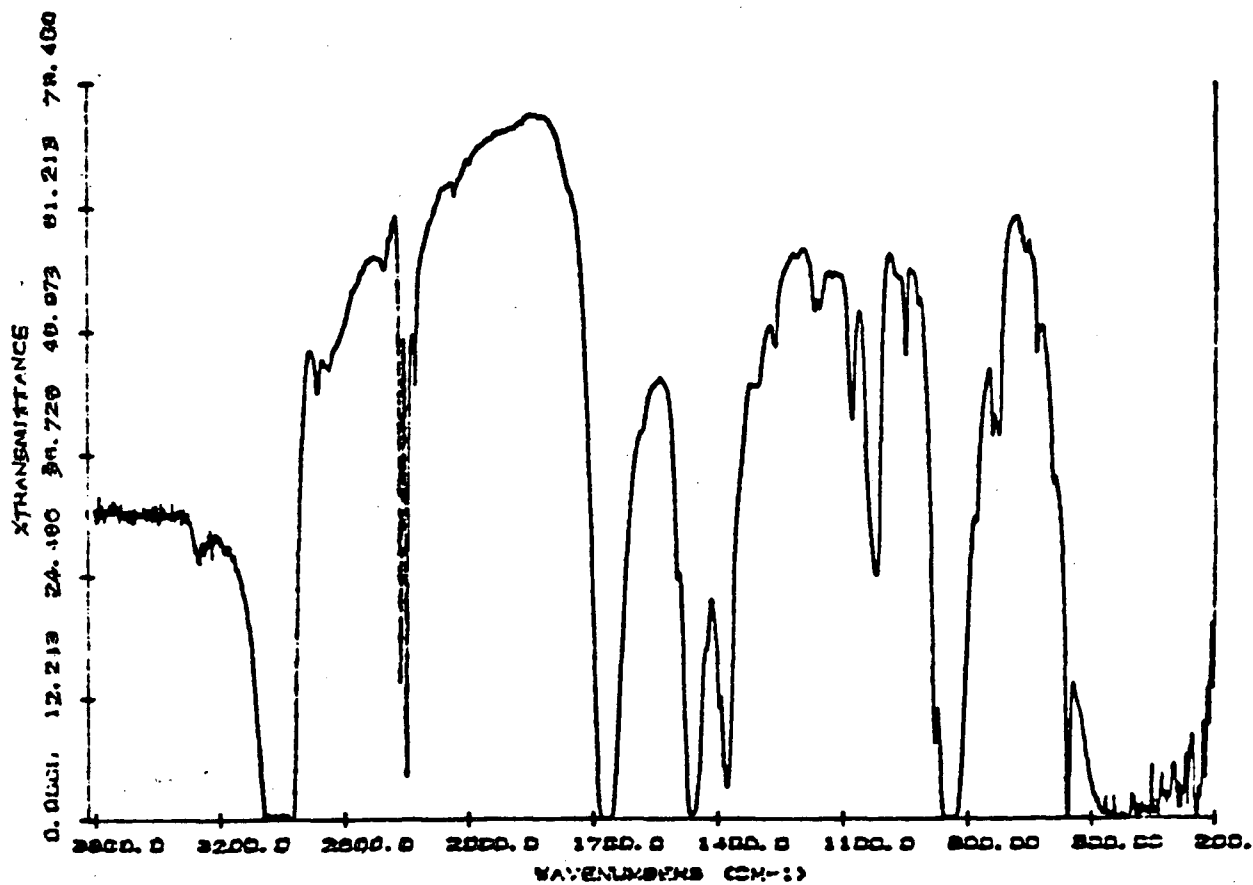




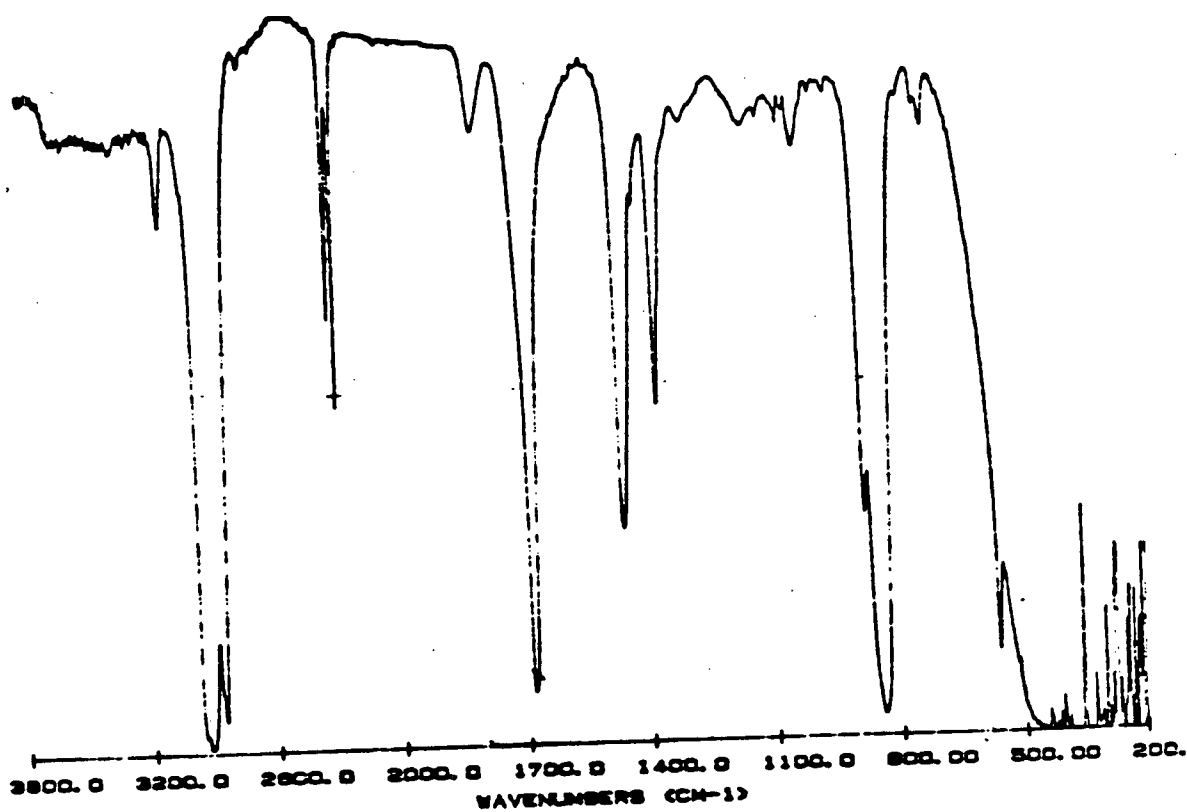
IR spectrum of  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2]\text{BF}_4$ , 5 as a Nujol mull.



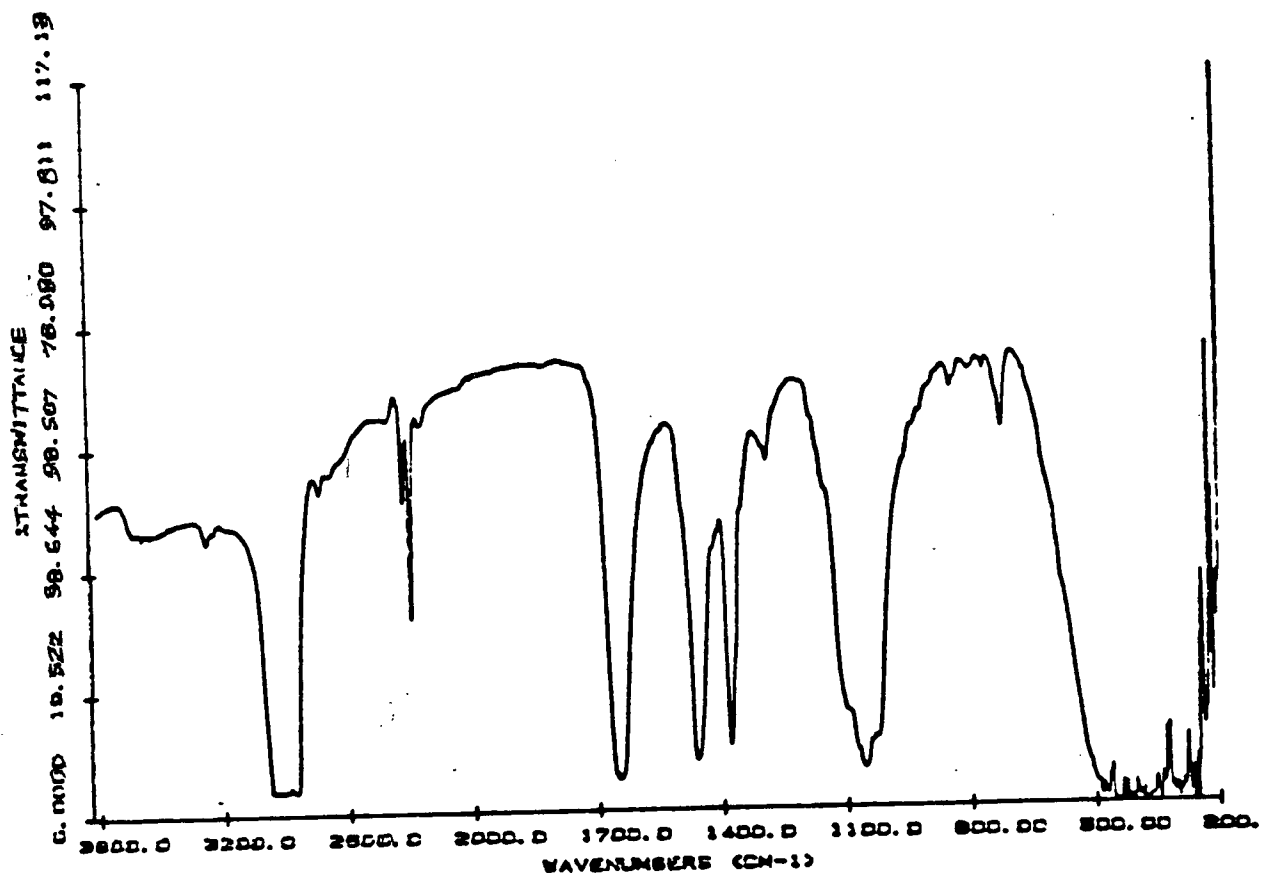
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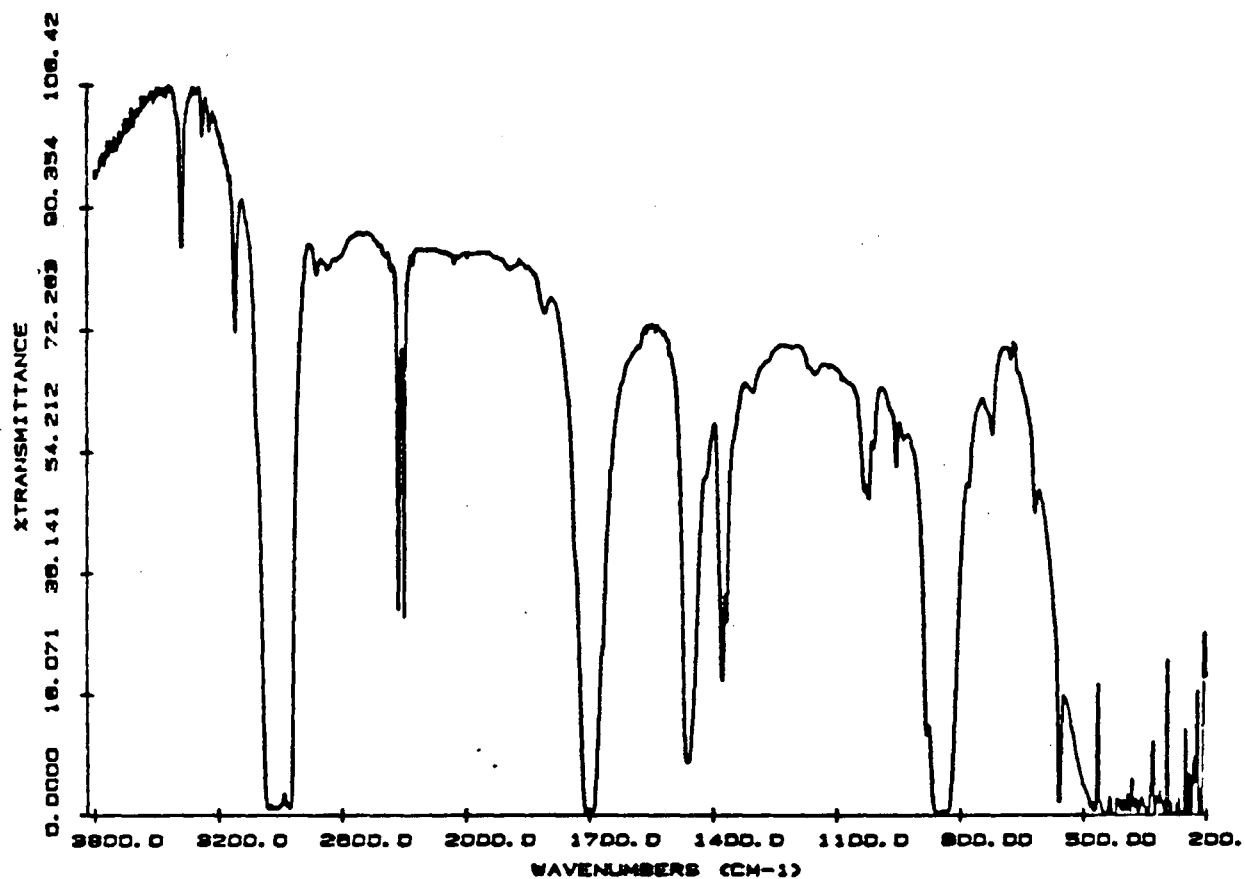
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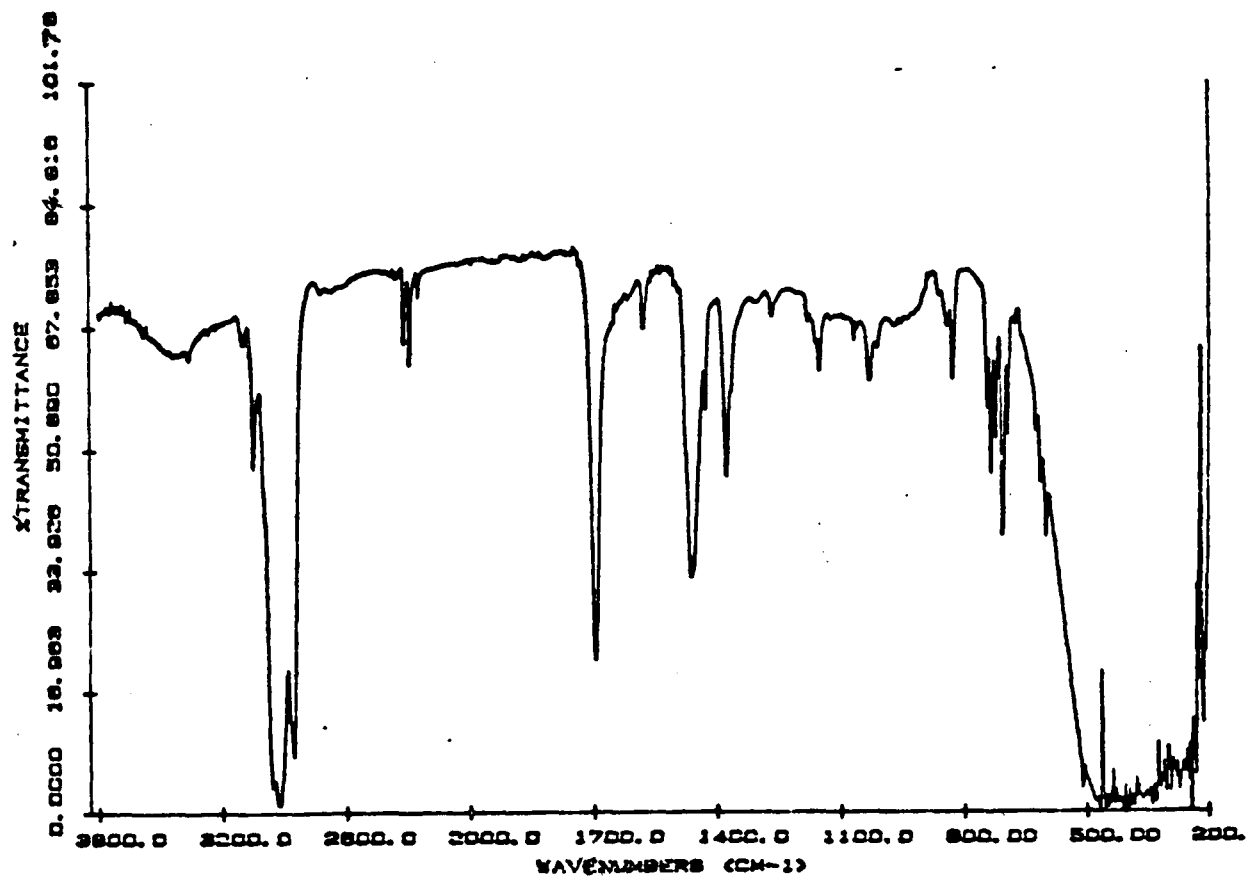
IR spectrum of  $[\text{Cp}^*\text{W}(\text{NO})\text{I}(\text{NCCH}_3)_2]\text{BF}_4$ , **8** as a Nujol mull.



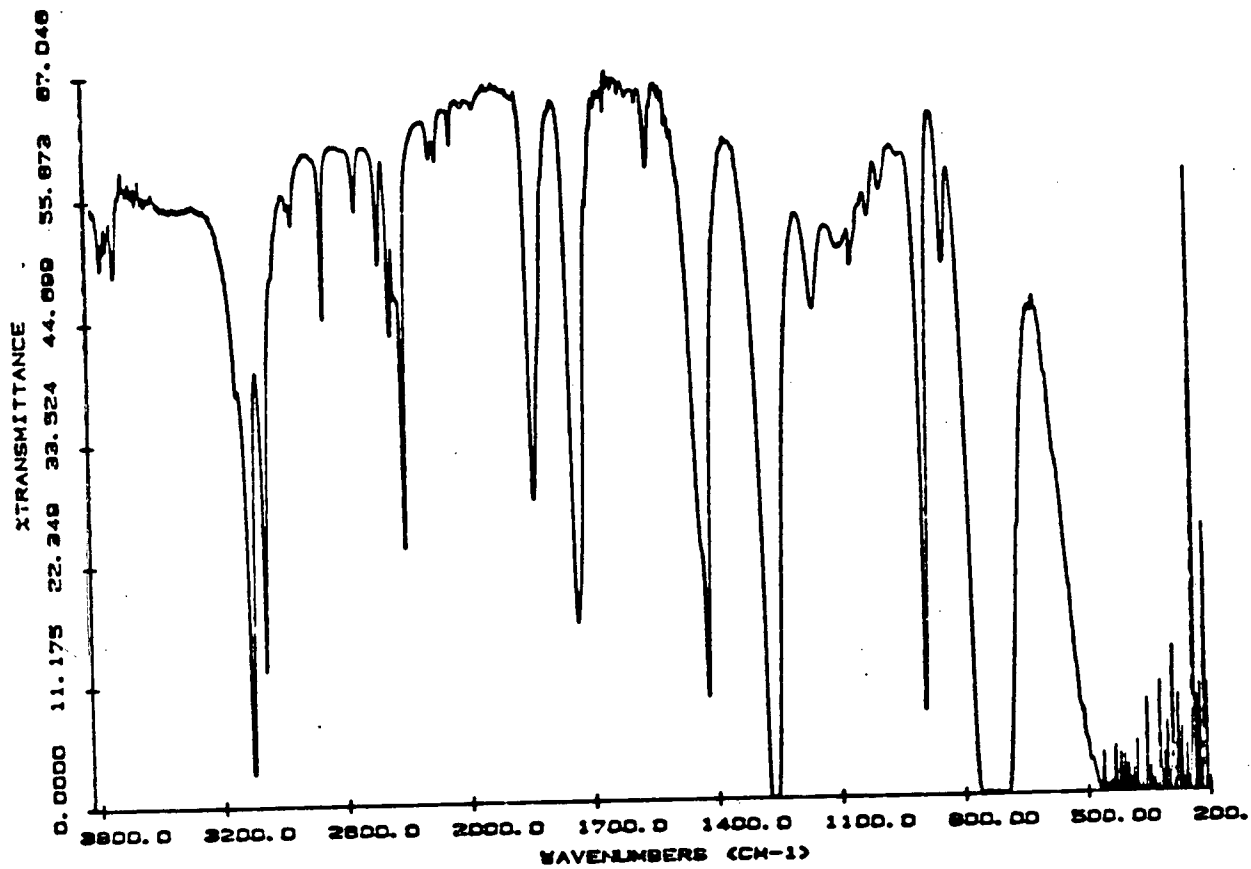
IR spectrum of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{PF}_6$ , 9 as a Nujol mull.



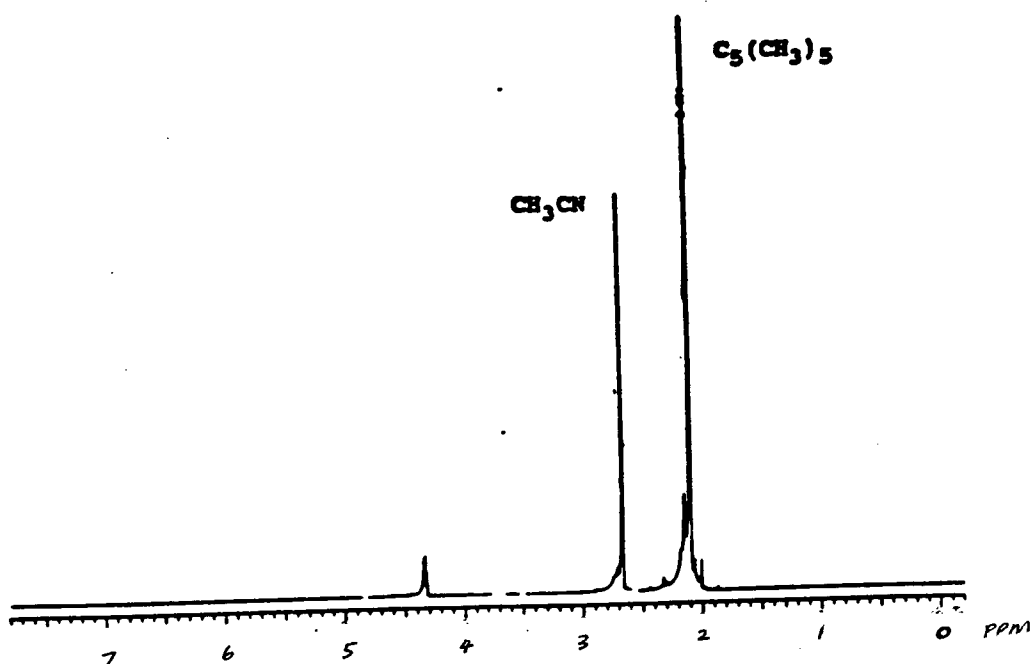
IR spectrum of  $[\text{CpCr}(\text{NO})(\text{NCCH}_3)_2]\text{BPh}_4 \cdot 1/2 \text{CH}_3\text{CN}$  as a Nujol mull.



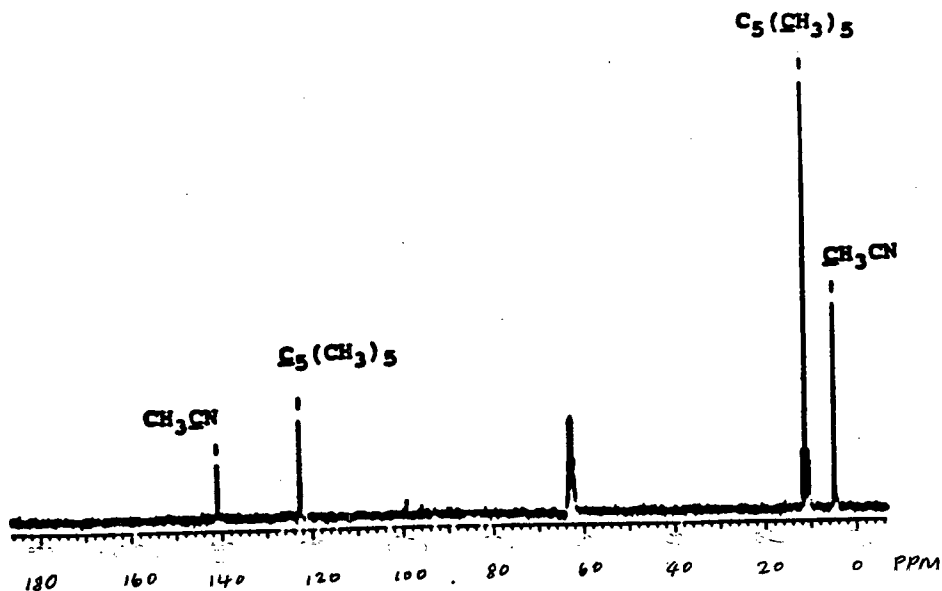
IR spectrum of  $[\text{CpCr}(\text{NO})_2]\text{BF}_4$  as a  $\text{CH}_2\text{Cl}_2$  solution.



$^1\text{H}$  NMR spectrum of  $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}(\text{NCCH}_3)_2][\text{PF}_6]$ , 2 in  $\text{CD}_3\text{NO}_2$ .

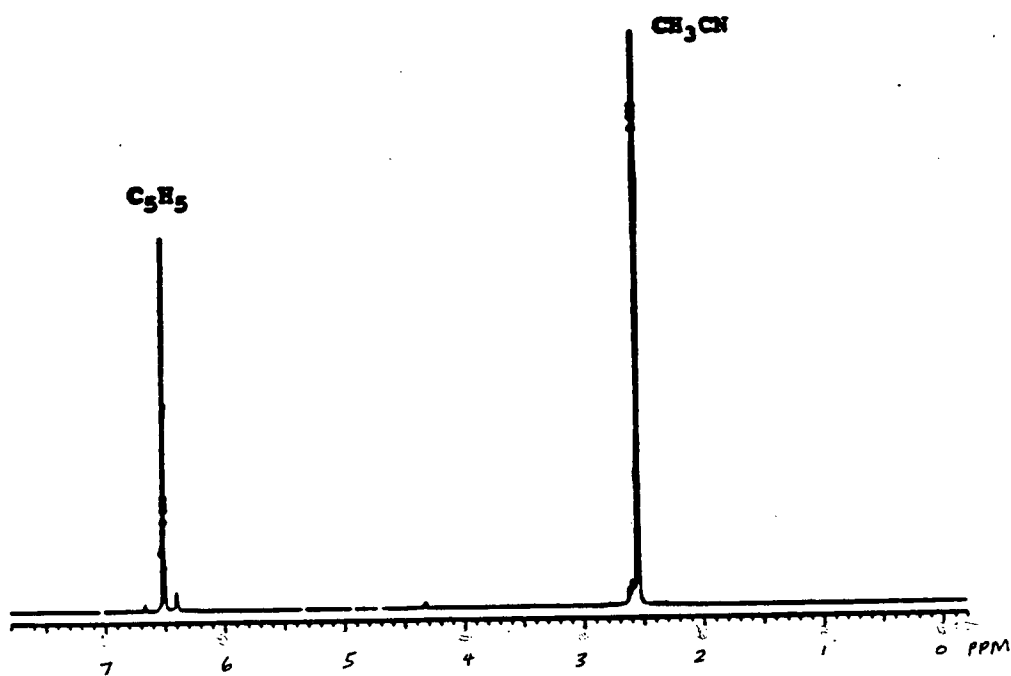


$^{13}\text{C}(^1\text{H})$  NMR spectrum of  $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}(\text{NCCH}_3)_2][\text{PF}_6]$ , 2 in  $\text{CD}_3\text{NO}_2$ .

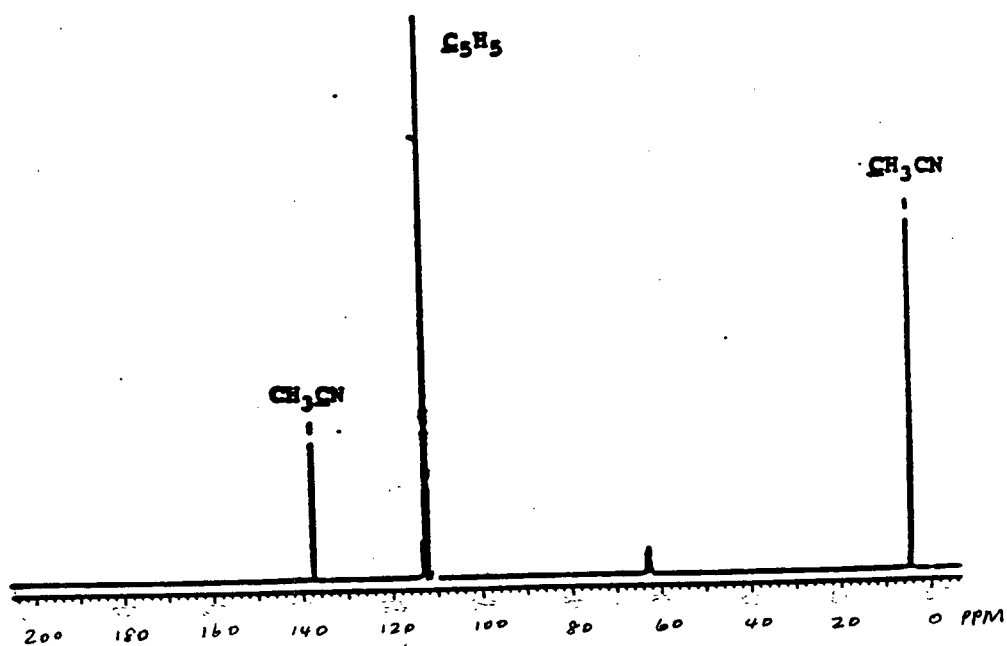




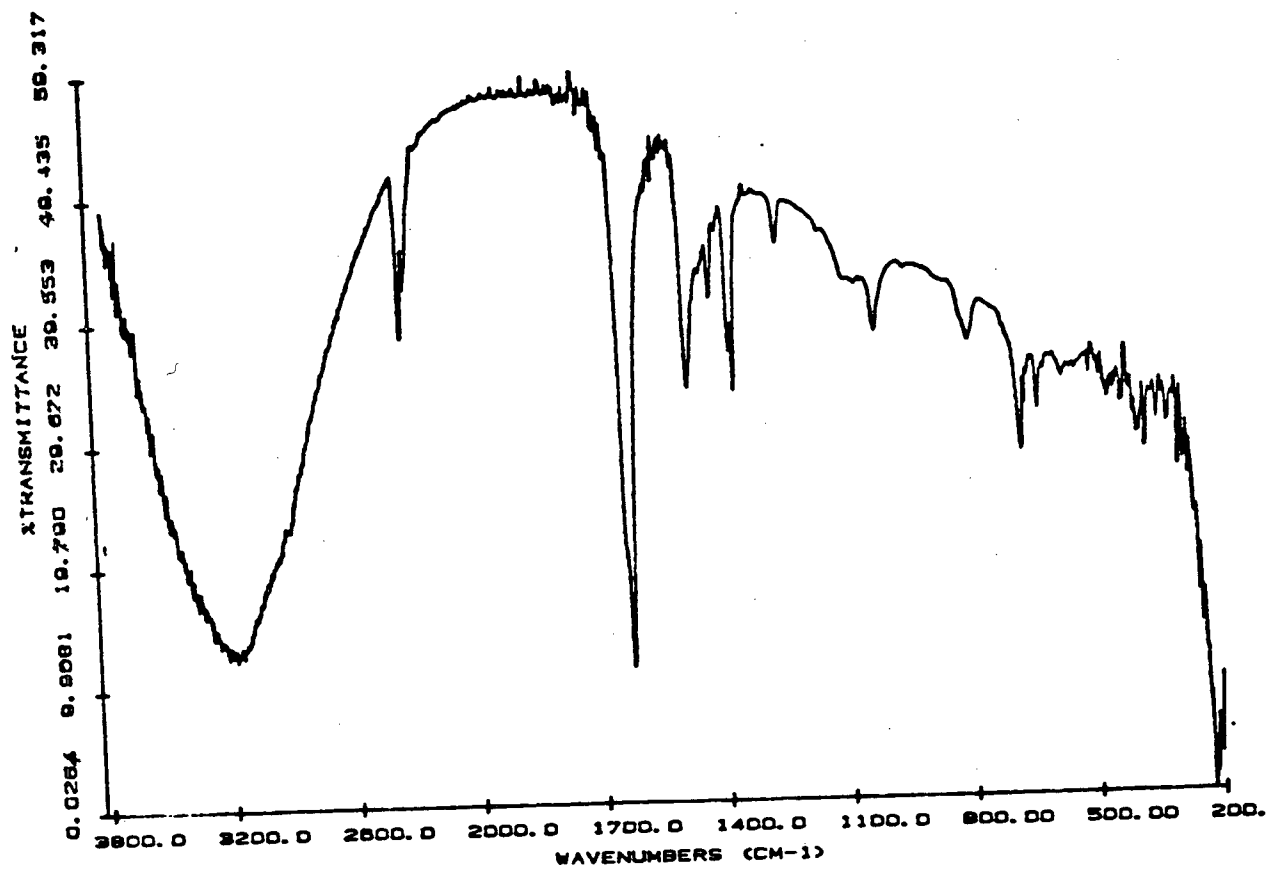
$^1\text{H}$  NMR spectrum of  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2][\text{BF}_4]$ , 5 in  $\text{CD}_3\text{NO}_2$ .



$^{13}\text{C}(^1\text{H})$  NMR spectrum of  $[\text{CpMo}(\text{NO})\text{Cl}(\text{NCCH}_3)_2][\text{BF}_4]$ , 5 in  $\text{CD}_3\text{NO}_2$ .



IR spectrum of  $[\text{Cp}^*\text{Cr}(\text{NO})_2]_2$  as a KBr pellet.



IR spectrum of  $[\text{Cp}^*\text{Mo}(\text{NO})_2]_2$  as a KBr pellet.

