

C. I.

NITROSYL HYDRIDES AND CATIONS
OF GROUP VI TRANSITION METALS

by

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ABSTRACT

The novel bimetallic hydrides $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}]_2$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ can be prepared sequentially by the metathesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$ with $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$. Analyses of the ^1H NMR spectra of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}]_2$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ show the former contains hydride ligands bound to tungsten in a terminal fashion, while the latter possesses two terminal and two bridging hydrides. Addition of a Lewis base to $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}]_2$ results in the formation of hydride species $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IHL}$ ($\text{L} = \text{P}(\text{OPh})_3, \text{P}(\text{OMe})_3, \text{PPh}_3$); in like manner, the dimer $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ is cleaved by triphenylphosphite to form the monomer cis or trans $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$. A comparison is made of the reactivity of the tungsten-hydrogen link in the nitrosyl hydrides $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}[\text{P}(\text{OPh})_3]$, $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$, and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$.

The $\text{Mo}(\text{NO})_2^{2+}$ unit is obtained as the tetrakis-solvate via chloride abstraction from $\text{Mo}(\text{NO})_2\text{Cl}_2$ by AgBF_4 or nitrosylation of $\text{Mo}(\text{CO})_6$ by NOPF_6 in coordinating solvents such as nitromethane, acetonitrile, or tetrahydrofuran. The unsolvated complex $[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$ is produced if the latter reaction is performed in dichloromethane; however, it readily converts to $[\text{Mo}(\text{NO})_2\text{S}_4](\text{PF}_6)_2$ upon exposure to coordinating solvents (S). Hard Lewis bases ($\text{L} = \text{CH}_3\text{CN}, \text{OPPh}_3$ or $\text{L}_2 = 2,2'$ -bipyridine) replace the solvent molecules in $[\text{Mo}(\text{NO})_2\text{S}_4]\text{X}_2$ ($\text{X} = \text{BF}_4^-, \text{PF}_6^-$) forming complexes $[\text{Mo}(\text{NO})_2\text{L}_4]^{2+}$ or $[\text{Mo}(\text{NO})_2\text{L}_2\text{S}_2]^{2+}$ depending upon the solvent employed. Reagents capable of being oxidized appear to reduce the dinitrosyl dication without permanent

coordination to the molybdenum centre. Reduction of $[\text{Mo}(\text{NO})_2\text{S}_4](\text{PF}_6)_2$ or $[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$ is effected by sodium amalgam (one equivalent); addition of a ligand L_2 ($\text{L}_2 = 2,2\text{-bipyridyl}$, $3,4,7,8\text{-tetramethyl-1,10-phenanthroline}$) to the reaction mixture permits the isolation of $[\text{Mo}(\text{NO})_2\text{L}_2](\text{PF}_6)_2$. Addition of excess ligand results in the formation of non-nitrosyl containing species $[\text{Mo}(\text{L}_2)_3]\text{PF}_6$ ($\text{L} = \text{OPPh}_3$ or $\text{L}_2 = 3,4,7,8\text{-tetramethyl-1,10-phenanthroline}$). Decomposition of the nitrosyl species results from attempts to reduce $[\text{Mo}(\text{NO})_2\text{S}_4]^{2+}$ by two electrons. New complexes are identified by the aid of IR and ^1H , ^{19}F , or ^{31}P NMR spectroscopy and conductance measurements.

Attempts to prepare thionitrosyl analogues of $[\text{Mo}(\text{NO})_2\text{L}_4]^{2+}$ have met with limited success; the only well-characterized thionitrosyls isolated in this study are the known $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2\text{NS}$ and the new $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{NS})\text{PPh}_3]\text{BF}_4$.

Also discussed is the interaction of NOPF_6 with solvents. NOPF_6 has been found to react slowly with acetonitrile, a common solvent for nitrosonium salts.

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ABBREVIATIONS AND COMMON NAMES

acac	acetylacetonate anion
Anal. Calcd	analysis calculated
asym	asymmetric
atm	atmospheres
bipy	2,2'-bipyridine
br	broad
Bu	butyl
°C	degrees Celsius
cm ⁻¹	wave numbers in reciprocal centimeters
Cp	pentahapto-cyclopentadienyl
d	doublet
dd	doublet of doublets
das	o-phenylenebis(dimethylarsine)
dec	decomposes
diglyme	bis(2-methoxyethyl) ether
diphos	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
e ⁻	electron(s)
en	1,2-diaminoethane
eq	equivalent
Et	ethyl
h	hour(s)
Hz	Hertz, cycles per second
hν	irradiation

IR	infrared
J	magnetic resonance indirect coupling constant
L	any unidentate ligand
m	medium intensity (IR) or multiplet (NMR)
M	molar
Me	methyl
min	minute(s)
mL	millilitre(s)
mm	millimeters of mercury
mmol	millimole(s)
mp	melting point
NMR	nuclear magnetic resonance
Ph	phenyl
phen	1,10-phenanthroline
phen'	3,4,7,8-tetramethyl-1,10-phenanthroline
ppm	parts per million
PPN ⁺	bis(triphenylphosphoranydiyl)nitrogen(1 ⁺)
Pr ⁱ	isopropyl
psi	pounds per square inch
R	alkyl or aryl
s	strong intensity (IR) or singlet (NMR)
sh	shoulder
sym	symmetric
t	triplet

$t_{1/2}$	half-life
td	triplet of doublets
THF	tetrahydrofuran
TMS	tetramethylsilane
δ	NMR chemical shift in ppm
η^5	pentahapto
ν	IR stretching frequency
\sim	approximately
%	percent

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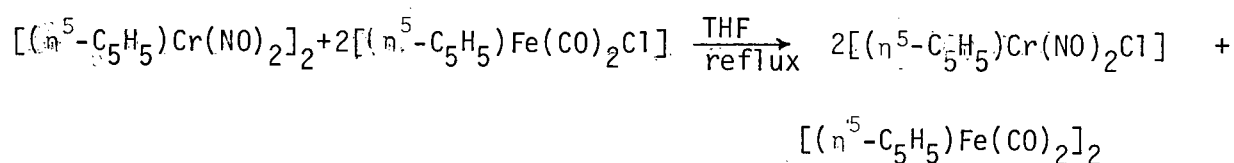
I wish to thank the faculty and technical staff of the University of British Columbia chemistry department for their assistance throughout this study, particularly Mr. P. Borda. I wish to extend special thanks to the members of my guidance committee Drs. L.S. Weiler, F. Aubke, and R.E. Pincock and to Dr. M.D. Fryzuk and P.A. MacNeil for their helpful suggestions. I would like to thank B. Wassink and A.D. Hunter who proofread this manuscript. Finally I wish to express my gratitude to Peter Legzdins for his support and guidance throughout this work and to the University of British Columbia for financial support through a University Graduate Fellowship.

Introduction

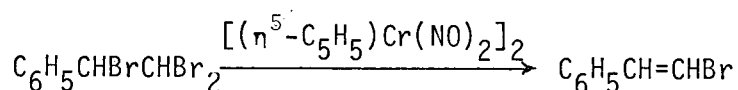
Since the preparation of the first transition-metal carbonyl $\text{Pt}(\text{CO})_2(\text{Cl})_2$ ¹ in 1868 and the formulation of the bonding in carbonyl transition metals (1950's),² volumes have been published on their preparation, reactivity, and use in organic synthesis and catalysis.³ In comparison transition-metal nitrosyl complexes are much less well studied. Nitrogen monoxide, though possessing one electron more than carbon monoxide, is similar to that molecule in both structure and bonding. When bonded to a metal centre in a linear fashion, analogous to a carbonyl ligand, the nitrosyl ligand is formally considered to be a three-electron donor; and the hybridization of orbitals around nitrogen is sp . However, unlike the carbonyl ligand the nitrosyl has another mode of bonding available to it. When the orbitals around the nitrogen atom are sp^2 hybridized, the M-N-O angle is bent ($\sim 120^\circ$). A nitrosyl group bonded in this manner is considered to be a formal one-electron donor. An example of a complex containing both these modes of bonding is $[\text{Ru}(\text{PPh}_3)_2(\text{NO})_2\text{Cl}]^+$.⁴

The fact that the same ligand can act as a three- or a one-electron donor offers the possibility that an additional coordination site could be made available on a metal centre without the necessity of ligand dissociation but rather through the tautomerization of a linear nitrosyl to a bent one. Thus, it is anticipated that nitrosyl complexes might have different chemical and catalytic properties from their carbonyl analogues. One nitrosyl complex which has demonstrated unique chemistry is $\text{Fe}(\text{CO})_2(\text{NO})_2$.⁵ When butadiene is treated with a catalytic amount (1% by weight) of this

iron nitrosyl, the anticipated dimer, 4-vinylcyclohex-1-ene, is formed as the only product despite the introduction of other possible reactants such as ethylene or propene. Nor do the additives triethylaluminum, triphenylphosphine, or pyridine have any influence on the yield or specificity of the reaction. Evidently the presence of the nitrosyl ligand is essential since a variety of carbonyl derivatives of iron exhibit no catalytic activity. Further, it has been reported that $\text{Fe}(\text{NO})_2\text{S}_2$ (S = a donor solvent), a possible intermediate in the dimerization, performs the reaction with equal specificity.⁶ More recently this group has studied the behaviour of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$ and that of the isoelectronic carbonyl $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$.⁷ The two compounds exhibit some chemical similarities, e.g., reacting with halogens to form the monomeric halides; but in other aspects their chemistry is quite different, e.g., reduction of the iron dimer by sodium amalgam leads to $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ while under identical conditions the chromium dimer decomposes. The dominant feature of the nitrosyl dimer's reactivity is its propensity to abstract halogen atoms from inorganic or organometallic halides. It has been employed



to specifically abstract vicinal halides from organic reagents.⁸



The general objectives at the outset of this work were to prepare new transition-metal nitrosyl species and to study their reactivity. Accordingly, Part I deals with the preparation, characterization, and reactivity of some nitrosyl hydrides of the Group VIB and VIIB metals; and Part II describes the synthesis of Group VIB nitrosyl and thionitrosyl cations.

Part I

Nitrosyl Hydride Complexes of Tungsten and Manganese

Hieber⁹ in 1931 reported the discovery of the first discrete complexes containing transition metals covalently bonded to hydrogen; these were the unstable species $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{HCo}(\text{CO})_4$. For some years these compounds were incorrectly formulated as $\text{Fe}(\text{COH})_2(\text{CO})_2$ and $\text{Co}(\text{COH})(\text{CO})_3$ because they were acidic in character. These complexes remained a curiosity until 1955 when this field was opened up by the discovery of bis(η^5 -cyclopentadienyl)hydridorhenium by Wilkinson.¹⁰ This was followed by the discovery of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$ ($\text{M} = \text{Cr}$ or Mo) by Fisher¹¹ in the same year and two years later by the preparation of $\text{trans-HPtCl}(\text{PEt}_3)_2$ by Chatt, Duncanson, and Shaw.¹² These latter discoveries came at a time when NMR spectrometers were becoming available as commercial instruments. This was important in the characterization of these compounds for their hydride resonances were discovered to have enormous upfield chemical shifts compared to those of hydrogens attached to main group elements. This aided in their detection and identification.

In the twenty year period 1939-1959 transition-metal hydride complexes were studied using IR, NMR, broad-line NMR, and electron diffraction techniques. The conclusion of these investigations was that the hydrogen atom exerted no stereochemical influence; it was buried in the electron core of the metal atom. (This idea was used to explain the large high field chemical shift of the hydride resonance observed by NMR). But this

was not the case. With the first X-ray diffraction studies performed on transition-metal hydrides in 1960 and later with neutron diffraction studies it was determined that the hydride ligand occupies a normal coordination position in these compounds, which in terminal hydride ligands is an essentially covalent, two-electron bond and in doubly bridging hydrides is considered as a three-centre, electron-deficient bent bond.¹³

The two techniques used most frequently for establishing the presence of a metal-hydrogen bond are infrared and nuclear magnetic resonance spectroscopy.¹⁴ The infrared spectra of most transition-metal hydride complexes show absorptions in the region $1700\text{--}2300\text{ cm}^{-1}$ which can be assigned to the metal-hydrogen stretching mode. Since other absorptions can occur in this range (e.g. νCO , CN , N_2), for the purposes of unambiguous assignment the metal-deuteride analogue is prepared and its infrared spectrum compared with that of the hydride; a shift in the stretching frequency to lower wavenumbers by a factor of 1.4 is expected. Hydrogens bridging two metal atoms exhibit stretching frequencies in the range $900\text{--}1400\text{ cm}^{-1}$. The metal-hydrogen deformation absorption ($700\text{--}950\text{ cm}^{-1}$) is difficult to assign due to its low intensity and to the presence of other absorptions in this region. Even the intensity of the metal-hydrogen stretching absorption is sometimes too weak to be observed.

Nuclear magnetic resonance spectroscopy has proved to be the most valuable diagnostic tool for detecting transition metal hydrides. Hydrogens attached to transition-metals usually have nuclear magnetic resonance absorptions in a region of the proton spectrum completely separated from the resonance of hydrogen in other chemical environments. The proton resonances

of most organic molecules and of the main group hydrides lie downfield of TMS ($\delta > 0$). Transition-metal hydrides, with the exception of some containing the early transition-metals¹⁵ exhibit a proton resonance upfield of TMS in the range $\delta = 0 \rightarrow -50$; most are in the region $\delta = -5 \rightarrow -20$. Thus nuclear magnetic resonance studies are regarded as a reliable method for hydride detection. Further, NMR experiments can be used to determine the number of hydride ligands present and the nature of their chemical and magnetic environments. Observation of metal-hydrogen coupling, possible with the spin 1/2 nuclei such as ^{103}Rh , ^{183}W , ^{187}Os , and ^{195}Pt , provides strong evidence for direct metal-hydrogen bonding. Nuclear magnetic resonance studies of other nuclei to which the hydride is coupled yield additional information about the molecular conformation. ^{31}P NMR studies are widely employed in this regard.¹⁶

Prior to the development of spectroscopic techniques, chemical reactions were used to determine the presence and number of hydride ligands, though none were completely quantitatively or qualitatively reliable. Among transition-metal hydride chemistry four patterns of reactivity were frequently observed.

I. Thermal decomposition to produce H_2

For the simple carbonyl hydrides or cyclopentadienyl hydrides hydrogen is evolved quantitatively upon thermolysis, but thermal behaviour varies greatly according to the metal and the other ligands attached to it. Ligands which stabilize a low-oxidation state of the metal centre usually increase thermal stability, e.g., $\text{HCo}(\text{CO})_3\text{PPh}_3$ ¹⁷ decomposes to H_2 and

and $[\text{Co}(\text{CO})_3\text{PPh}_3]_2$ at $\sim 20^\circ\text{C}$, while $\text{HCo}(\text{CO})_2(\text{PPh}_3)_2$ ¹⁸ is stable to $\sim 140^\circ\text{C}$. Likewise, thermal stability generally increases with increasing atomic number for a series of congeneric hydride complexes, e.g., for the series $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$ the decomposition point increases $57^\circ < 110^\circ < 180^\circ$ as $\text{M} = \text{Cr} < \text{Mo} < \text{W}$.¹¹

II. Acidic character

The acidic strength of transition-metal hydride complexes varies greatly depending on the nature of the other ligands. Most hydrido-carbonyls appear to act as Lowry-Brønsted acids, but substitution of phosphine for carbonyl greatly reduces the acid strength of the metal-hydrogen bond, e.g., the K_a determined for $\text{HCo}(\text{CO})_4$ ¹⁹ is < 2 while for $\text{HCo}(\text{CO})_3\text{PPh}_3$ ¹⁷ it is $\sim 10^{-7}$.

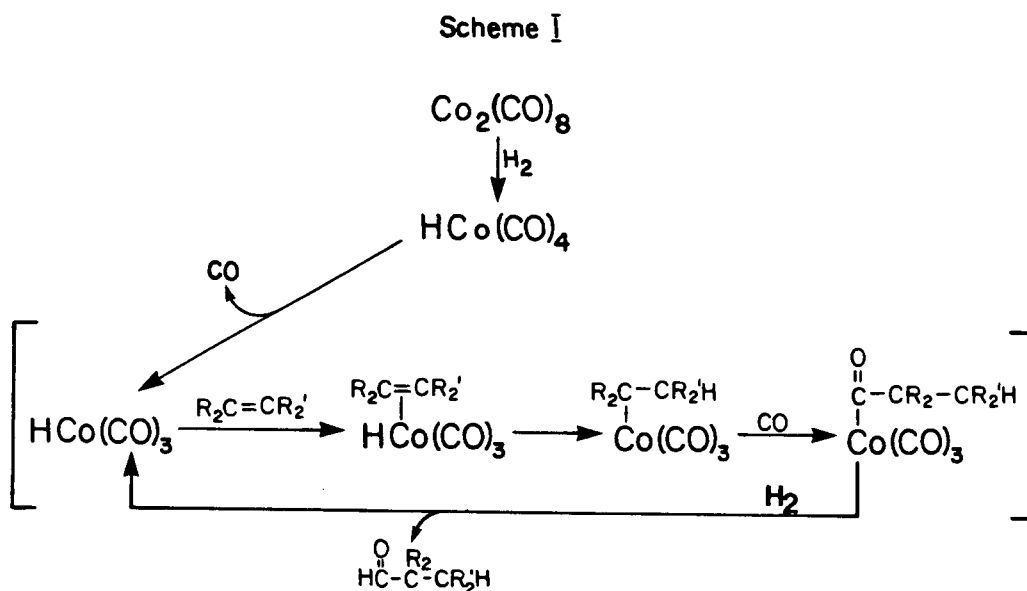
III. Reaction with halogens and halogenated hydrocarbons

Treatment of hydride complexes with halogens generally results in the replacement of the hydride ligand by a halide along with the formation of H_2 or HX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Halogenated hydrocarbons can react with the metal-hydrogen bond to produce metal halides; the hydride is transferred to the halogenated hydrocarbon. The reactivity of the halogenated hydrocarbon toward the metal hydride increases with increasing halide substitution; thus, the reaction of metal hydrides with CCl_4 is often used to establish the presence of a metal-hydrogen link.

IV. Treatment with acid to produce H_2

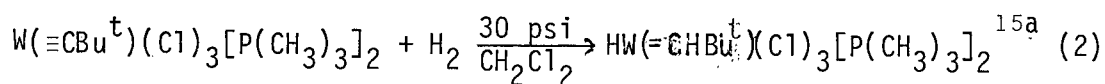
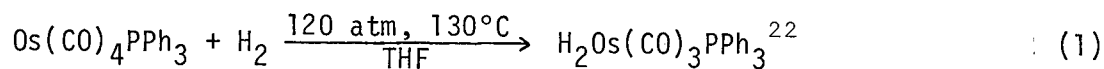
The reaction of hydridometal complexes with aqueous or alcoholic acids often gives complete replacement of the hydrides. This reaction has sometimes been employed to determine the number of hydride ligands by measurement of evolved hydrogen; however, it is not completely reliable, e.g., $IrH_5(PEt_2Ph)$ was originally formulated as a trihydride on the basis of its degradation by HCl .²⁰

Transition-metal hydride complexes are either postulated or observed to participate in a number of important homogeneous catalyses. One of the most important roles of the metal-hydrogen bond is to add to an unsaturated substrate. When the substrate is an olefin, the overall result can be isomerization, hydrosilation, hydrogen exchange, hydrogenation, or hydroformylation. The "oxo" reaction, a hydroformylation reaction employed commercially to convert olefins to saturated aldehydes, illustrates the type of mechanism postulated for these reactions (Scheme I).²¹

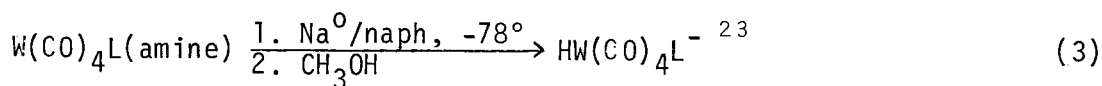


There are a number of routes used in the synthesis of transition-metal hydrides:

I. Direct hydrogenation



II. Protonation of organometallic anions

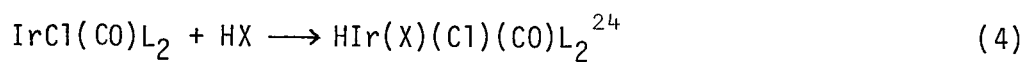


Na^0/naph = sodium naphthalenide

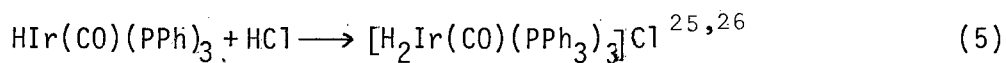
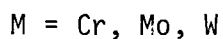
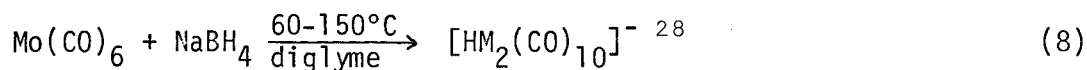
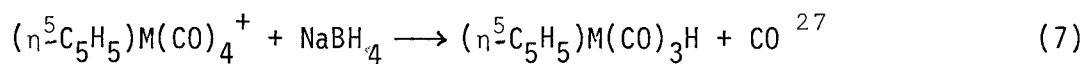
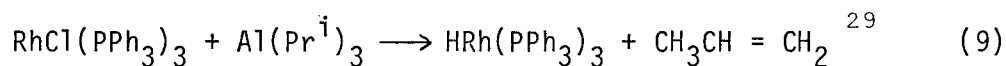
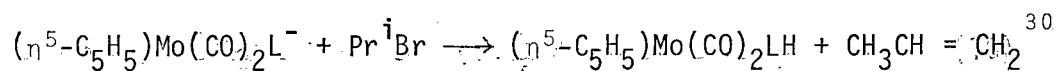
$\text{L} = \text{P}(\text{OCH}_3)_3, \text{P}(\text{CH}_3)_3, \text{PPh}_3$

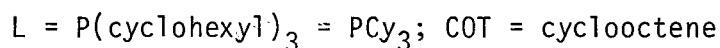
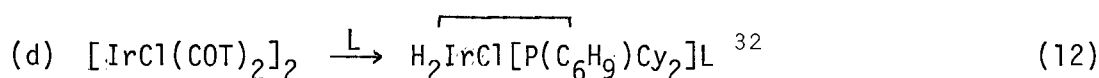
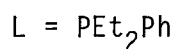
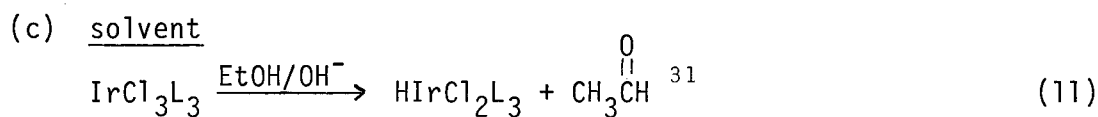
III. Reactions with HX, X = halides, CN^- , SiR_3 , or SnR_3

(a) oxidative addition

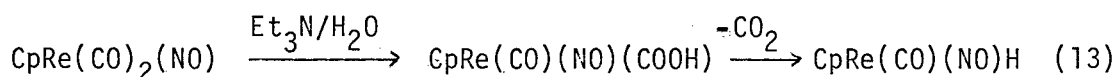


$\text{L} = \text{PEt}_2\text{Ph}; \text{X} = \text{Cl} \text{ or } \text{Br}$

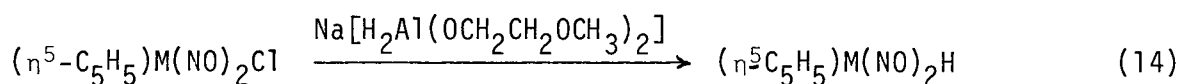
(b) protonationIV. Reactions with complex hydridesV. Elimination reactions from alkyls(a) Grignard(b) alkyl halide



Hydridocarbonyls are known for the majority of the transition metals. For the group VIB metals alone there are at least twenty such species. Yet only a handful of nitrosyl hydride complexes have been reported; of these only a few are organometallic hydrides, three monomers^{33,34,35} and a few ruthenium and osmium clusters.³⁶ The first organometallic nitrosyl hydride was prepared in 1972 by Graham³³ via the route shown in reaction 13.



Subsequently, the phosphine analogue has been synthesized by Gladysz and co-workers.³⁴ In 1978 in our group $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2\text{H}$ ($\text{M} = \text{Mo}$ or W) were prepared by the route shown in reaction 14, but only the tungsten species was of sufficient thermal stability to be isolated.³⁵



Spectroscopic measurements show that $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ exhibits a relatively low field hydride resonance (NMR δ 2.77 C_6D_6) and a $\nu\text{M-H}$ (IR) at 1900 cm^{-1} (CH_2Cl_2). Its characteristic chemistry is to function as a source of H^- ; hence, it is inert to CHCl_3 , CCl_4 , and Et_3N but reacts readily with *p*-toluenesulfonic acid and trityl tetrafluoroborate (in CH_3CN) to yield $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2(\text{CH}_3\text{CN})]\text{BF}_4$, respectively. In view of the surprising hydridic character of this species it is of interest to prepare other organometallic nitrosyl hydride species of the same metal. The choice in the manner used to generate nitrosyl hydrides is based upon the abundance of possible precursors. Since a large number of nitrosyl halide complexes are available, two methods are employed to synthesis nitrosyl hydrides: (1) the reaction of a nitrosyl cation (generated from a nitrosyl halide) with BH_4^- ; (2) the metathesis of a nitrosyl halide with $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$.³⁷

Experimental Section

All manipulations were performed so as to maintain all chemicals under an atmosphere of prepurified nitrogen either on the bench using conventional techniques for the manipulation of air-sensitive compounds³⁸ or in a Vacuum Atmospheres Corporation Dri-Lab model HE-43-2 dry box. All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Melting points were taken in capillaries using a Gallenkamp Melting Point apparatus and are uncorrected. All solvents were dried by standard procedures³⁹ and distilled just prior to use. Unless specified otherwise, the chemical reactions described below were effected at ambient temperatures.

Infrared spectra were recorded on Perkin-Elmer 457 or 598 spectrophotometers and were calibrated with the 1601 cm^{-1} band of polystyrene film. Proton magnetic resonance spectra were obtained on a Varian Associates T-60 spectrometer with tetramethylsilane employed as an internal standard or on Bruker WP-80, WH-400, Varian Associates XL-100, or Nicolet-Oxford H-270 spectrometer with reference to the solvent used. All ^1H chemical shifts are reported relative to Me_4Si at 0.0 ppm. Mrs. M.M. Tracey, Ms. M.A. Heldman, Ms. L.K. Darge, and Mrs. M.T. Austria assisted in obtaining these data. Solution ^{31}P NMR spectra were recorded at 40.5 MHz on a Varian Associates XL-100 spectrometer using ^2D as the internal lock. Resonances were referenced to external $\text{P}(\text{OCH}_3)_3$ which is considered to be

+141 parts per million downfield from H_3PO_4 .⁴⁰ All samples were prepared in the dry box, using dry, deoxygenated C_6D_6 in five-millimeter tubes. Solution ^{19}F NMR spectra were recorded on a Varian Associates EM-360 L spectrometer at 56.45 MHz. CFCl_3 was used as the external reference. Fluorine-19 chemical shifts are reported in parts per million from CFCl_3 ; positive chemical shifts are upfield of the external fluorine standard.

Mass spectra were recorded at 70eV on an Atlas CH4B or a Kratos MS-50 spectrometer using the direct-insertion method with the assistance of Dr. G.K. Eigendorf, Mr. J.W. Nip, and Mr. M.A. Lapawa. Elemental analyses were performed by Mr. P. Borda.

Computer simulations of NMR spectra were performed on a Bruker Aspect 2000 using the program: Parameter Adjustment in NMR by Iteration Calculation.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2(\text{PPh}_3)$ with AgBF_4 and PPh_3 . To an acetonitrile (10 mL) solution of AgBF_4 (0.14 g, 0.69 mmol) was added an orange, dichloromethane (30 mL) solution of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2\text{PPh}_3$ (0.55 g, 0.69 mmol). Immediately a white precipitate formed, but the mixture was allowed to stir 2 h to insure completion of the reaction. Monitoring of the infrared absorption during this time indicated the loss of the νNO band at $\sim 1645\text{ cm}^{-1}$, characteristic of the starting material, and the appearance of a new νNO band at $\sim 1665\text{ cm}^{-1}$. Filtration of the final reaction mixture through a 3 x 2 cm column of Celite supported on a medium porosity frit and dropwise addition of diethyl ether (15 mL) led to the precipitation of an orange solid, presumably $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{PPh}_3)]\text{-}$

$(\text{CH}_3\text{CN})\text{BF}_4$ (vide infra). If prior to the addition of diethyl ether solid PPh_3 (0.18 g, 0.69 mmol) was added to the dichloromethane filtrate, the IR band of the νNO shifted from 1665 to 1645 cm^{-1} . Subsequent addition of diethyl ether led to the isolation of orange crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{-IPPh}_3]_2\text{BF}_4$, (0.40 g, 57% yield), mp $\cdot 213^\circ\text{C}$ dec.

Anal. Calcd for $\text{C}_{41}\text{H}_{35}\text{WNOIP}_2\text{BF}_4$: C, 48.38; H, 3.44; N, 1.38. Found: C, 47.98; H, 3.39; N, 1.41. IR (CH_2Cl_2): $\nu(\text{NO})$ 1646 (s); also 1092 (s), 1057 (s), 1036 (s) cm^{-1} . IR (Nujol): $\nu(\text{NO})$ 1657 (s); $\nu(\text{BF})$ 1084 (s) cm^{-1} ; also 1045 (s), 1031 (s), 845 (w), 749 (m), 693 (m) cm^{-1} . ^1H NMR (CD_3NO_2): δ 7.64 (m, 30H, $\text{P}(\text{C}_6\text{H}_5)_3$), 5.97 (t, 5H, C_5H_5) [$^3J_{\text{H}-31\text{P}} = 2\text{Hz}$]. ^{31}P NMR (CD_3NO_2): δ 1.9 [$^1J_{183\text{W}-31\text{P}} = 220\text{ Hz}$] (broad-band proton decoupled). ^{19}F NMR (CD_3NO_2): δ 151 (s).

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2[\text{P}(\text{OPh})_3]$ with AgBF_4 and NaCl . When an orange, dichloromethane (40 mL) solution, containing 0.50 g (0.59 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2\text{P}(\text{OPh})_3$, was added to a 10 mL acetonitrile solution of AgBF_4 (0.12 g, 0.62 mmol), a white precipitate formed immediately. The IR band of the nitrosyl functionality was observed to shift from 1660 cm^{-1} to 1680 cm^{-1} . After it was stirred for 1h the reaction mixture was filtered through a 3 x 2 cm Celite column supported on a medium porosity frit. The solvent was removed from the filtrate in vacuo; the resulting orange oil presumably contained the cation $\{(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}[\text{P}(\text{OPh})_3](\text{CH}_3\text{CN})\}\text{BF}_4$. The orange oil was dissolved in nitromethane (10 mL); 0.04 g of NaCl were added; the mixture was stirred 14 h; and then the solvent was removed under reduced pressure. The red-orange oil which resulted was extracted with dichloromethane (4 x 5 mL). These combined aliquots were filtered, and the filtrate

was concentrated to ~10 mL. Dropwise addition of diethyl ether (35 mL) precipitated a rust-orange solid, $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{Cl})[\text{P}(\text{OPh})_3]$ (0.30 g, 68% yield), mp 144°C dec.

Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{WNO}_4\text{IClP}$: C, 36.73; H, 2.66; N, 1.86; O, 8.52; I, 16.90. Found: C, 37.70; H, 2.86; N, 2.08; O, 8.86; I, 16.09.

IR (CH_2Cl_2): $\nu(\text{NO})$ 1657 (s); also 1588 (m), 1487 (s), 1210 (m), 1182 (s), 1160 (s), 1074 (w), 1026 (w), 1010 (w), 930 (s, br), 836 (w) cm^{-1} .

IR (Nujol): $\nu(\text{NO})$ 1651 (s); also 1587 (m), 1208 (s), 1180 (s), 1156 (s), 1071 (w), 1024 (w), 1009 (w), 957 (s), 936 (s), 912 (s), 897 (s), 857 (m), 782 (s), 766 (s), 688 (m) cm^{-1} . ^1H NMR (C_6D_6): δ 7.11 (m, 15H, $\text{P}(\text{OC}_6\text{H}_5)_3$), 5.45 (d, 5H, C_5H_5) ($^3J_{\text{H-P}} = 2.93$ Hz). ^1H NMR (CDCl_3): δ 7.29 (m, 15H, $\text{P}(\text{OC}_6\text{H}_5)_3$), 6.01 (d, C_5H_5 , ~2.5H) ($^3J_{\text{H-P}} = 2.93$ Hz), 5.99 (d, C_5H_5 , ~2.5H) ($^3J_{\text{H-P}} = 2.93$ Hz).

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2[\text{P}(\text{OPh})_3]$ with AgBF_4 and $(\text{CH}_3\text{CH}_2)_4\text{NBH}_4$.

In order to generate a solution of $\{(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}[\text{P}(\text{OPh})_3](\text{CH}_3\text{CN})\}\text{BF}_4$, an acetonitrile solution (10 mL) of AgBF_4 (0.23 g, 1.2 mmol) and a dichloromethane solution (60 mL) of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2[\text{P}(\text{OPh})_3]$ (1.0 g, 1.2 mmol) were stirred together 3h and then were filtered through a Celite column (2 x 3 cm) which was supported on a frit. The orange filtrate was cooled to -78°C and a solution of $(\text{CH}_3\text{CH}_2)_4\text{NBH}_4$ (0.17 g, 1.2 mmol) dissolved in dichloromethane (10 mL) was added dropwise. No color change was observed,

but the infrared spectrum showed that the νNO absorption of the cation at 1660 cm^{-1} had disappeared and a band of much smaller intensity had appeared at 1640 cm^{-1} . The solvent was removed in vacuo, the product was suspended in benzene (10 mL), and the slurry was transferred to the top of a 2 x 4 cm Florisil column. Elution of the column with benzene resulted in the development of a single yellow-orange band which was collected and taken to dryness under reduced pressure. Recrystallization from dichloromethane/hexanes afforded orange crystals of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{-I}(\text{H})[\text{P}(\text{OPh})_3]$ (0.11 g, 13% yield).

Anal. Calcd. for $\text{C}_{23}\text{H}_{21}\text{WNO}_4\text{PI}$: C, 38.52; H, 2.95; N, 1.95.
 Found: C, 38.46; H, 2.93; N, 1.94. IR (CH_2Cl_2): $\nu(\text{NO})$ 1642 (s); also 1589 (s), 1482 (s), 1217 (m), 1186 (s), 1158 (s), 1070 (w), 1023 (m), 1006 (w), 926 (s), 862 (w), 827 (w) cm^{-1} . IR (Nujol): $\nu(\text{W-H})$ 1865 (w); $\nu(\text{NO})$ 1627 (s); also 1586 (s), 1420 (w), 1290 (w), 1218 (m), 1195 (s), 1173 (s), 1153 (s), 1073 (m), 1021 (m), 1009 (w), 1002 (w), 936 (s), 914 (s), 905 (s), 887 (s), 843 (w), 826 (m), 786 (m), 766 (s), 693 (s) cm^{-1} . ^1H NMR (C_6D_6): δ 7.45 (m, 6H, $\text{P}(\text{OC}_6\text{H}_5)_3$ ortho), 7.00 (m, 9H, $\text{P}(\text{OC}_6\text{H}_5)_3$ para/meta), 4.82 (s, 5H, C_5H_5), -2.07 (1H, W-H), [$^2J_{^1\text{H}-^{31}\text{P}} = 112\text{ Hz}$, $^1J_{^1\text{H}-^{183}\text{W}} = 55\text{ Hz}$]. ^1H NMR (CDCl_3): δ 7.33 (m, 15H, $\text{P}(\text{OC}_6\text{H}_5)_3$), 5.32 (s, 5H, C_5H_5), -1.98 (1H, W-H), [$^2J_{^1\text{H}-^{31}\text{P}} = 111\text{ Hz}$, $^1J_{^1\text{H}-^{183}\text{W}} = 54\text{ Hz}$]. ^{31}P NMR (C_6D_6): δ 115 [$^2J_{^{31}\text{P}-^1\text{H}} = 112\text{ Hz}$]. Mp. 112°C dec. Mass spectrum (probe temperature 150°C): $[(\text{C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{P}(\text{OPh})_3]^+$, $[(\text{C}_5\text{H}_5)\text{W}(\text{NO})\text{HP}(\text{OPh})_3]^+$, $[(\text{C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]^+$, $[(\text{C}_5\text{H}_5)\text{WI}_2]^+$, $[\text{WI}_2]^+$, $[(\text{C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}_2]^+$, and $[(\text{C}_5\text{H}_5)\text{WI}]^+$.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2[\text{P}(\text{OPh})_3]$ with $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$.

While a benzene suspension (50 mL) of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2[\text{P}(\text{OPh})_3]$ (1.0 g, 1.2 mmol) was stirred at room temperature, a benzene solution (3.5M) containing 1.2 mmol (0.34 mL) of $\text{NaH}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2^{37}$ was added dropwise. The original orange-red solution became brown, a brown solid precipitated, and the νNO infrared absorption shifted from 1660 cm^{-1} to 1640 cm^{-1} ; its intensity decreased. The final reaction mixture was treated with distilled water (0.04 mL) and filtered through a column of anhydrous MgSO_4 ; the filtrate was taken to dryness in vacuo. The resulting brown product in a benzene (10 mL) slurry was transferred to the top of a 2 x 4 cm Florisil column. Elution of the column with benzene resulted in the development of a single yellow-orange band which was collected. Recrystallization from a dichloromethane/hexanes mixture resulted in orange crystals of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{I})(\text{H})[\text{P}(\text{OPh})_3]$ (0.20 g, 34% yield) (vide supra).

Reaction of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{NO})(\text{PPh}_3)\text{I}$ with $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$.

To a stirred benzene solution (40 mL) containing 2.0 g (3.6 mmol) of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{NO})(\text{PPh}_3)\text{I}^{41}$ at ambient temperature was added a benzene solution (1.0 mL) containing an equimolar amount of $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$. As the addition proceeded, the colour of the former solution changed immediately from brown to red-brown; some gas evolution occurred; and a brown solid precipitated. Water (15 mL) was added to the final reaction mixture, and it was stirred for an additional 5 min. The benzene layer was then removed by syringe, and the remaining contents of the reaction flask were washed with benzene (6 x 20 mL). The benzene solutions were combined and were filtered through a 3.5 x 4 cm column of alumina (acti-

vity grade 1). The solvent was removed from the filtrate under reduced pressure to obtain a red oil.

Subsequent manipulations were performed in an argon atmosphere. The red oil was suspended in hexanes (60 mL), and the suspension was transferred onto a 2 x 8 cm column of alumina (activity grade 4). Elution of the column with hexanes first developed a green band which was collected. Removal of solvent from the eluate afforded a small amount of a green solid which has yet to be identified and a large amount of triphenylphosphine. Continued elution with hexanes developed next a broad, orange band which required a 50/50 mixture of hexanes/benzene for complete removal from the column. The orange eluate was taken to dryness in vacuo to obtain 0.30 g (20% yield) of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{NO})(\text{PPh}_3)\text{H}$ as an orange, air-sensitive solid.

Anal. Calcd for $\text{C}_{24}\text{H}_{23}\text{MnNOP}$: C, 67.45; H, 5.42; N, 3.28. Found: C, 67.68; H, 5.57; N, 3.05. IR (C_6H_6): ν_{NO} 1683 cm^{-1} . ^1H NMR (C_6D_6): δ 7.66-6.98 (m, 15H, $\text{P}(\text{C}_6\text{H}_5)_3$), 4.60 (s, 1H), 4.46 (s, 1H), 3.92 (s, 2H), 1.86 (s, 3H, $-\text{CH}_3$), -6.48 (d, 1H, $\text{Mn}-\text{H}$) [$^2J_{^1\text{H}-^{31}\text{P}}$ 88.8 Hz]. Mp (under N_2) 42.5°C dec.

Further elution of the column with benzene as eluant resulted in the development of a dark green band which was collected and taken to dryness under reduced pressure. The residue was recrystallized from CH_2Cl_2 /hexanes to obtain air-stable, green microcrystals (0.016 g, 1% yield) of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_3\text{Mn}_3(\text{NO})_4^{7,42}$ which was characterized by its mass spectrum (probe temperature 190°C): $[\text{Mn}_3(\text{C}_6\text{H}_7)_3(\text{NO})_x]^+$ (for $x = 4, 2$,

or 1 and $[\text{Mn}_2(\text{C}_6\text{H}_7)_2(\text{NO})_y]^+$ for $y = 2$ or 1); and spectral properties (IR in CH_2Cl_2 : $\nu(\text{NO})$ 1538, 1483, and 1333 cm^{-1} ; ^1H NMR in CDCl_3 : δ 4.78 (s, 12H, C_5H_4), 1.83 (s, 9H, $-\text{CH}_3$)).

Reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$ with $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$.

To a green-brown solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2^{43}$ (3.0 g, 2.8 mmol) in dichloromethane (40 mL)/benzene (160 mL) at ambient temperature was added dropwise a benzene solution (3.5M, ~ 0.8 mL) containing 2.8 mmol of $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$. The solution became deep green in colour and a green solid precipitated; infrared monitoring showed the disappearance of the nitrosyl absorption at $\sim 1660\text{ cm}^{-1}$ of the starting material and the appearance of a new nitrosyl absorption at $\sim 1640\text{ cm}^{-1}$. The final reaction mixture was treated with distilled water (0.1 mL) and filtered through a short (3 x 4 cm) column of anhydrous MgSO_4 supported on a medium porosity frit. As the filtrate was concentrated in vacuo to a total volume of ~ 8 mL, deep green microcrystals formed. These were collected on a frit and rinsed with benzene (3 x 8 mL). This preparation led to analytically pure $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{I})(\text{H})]_2$ (1.4 g, 61% yield), mp (under N_2) 174°C dec.

Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{W}_2\text{N}_2\text{O}_2\text{I}_2$: C, 14.74; H, 1.47; N, 3.44; I, 31.20; Found: C, 14.91; H, 1.51; N, 3.40; I, 30.95. IR (CH_2Cl_2): $\nu(\text{NO})$ 1640 cm^{-1} . IR (Nujol): $\nu(\text{NO})$ 1634 (s), 1616 (s); also 846 (m) cm^{-1} . ^1H NMR (C_6D_6): δ 5.25 (s, 5H, C_5H_5), -1.24 (s, 1H, W-H). ^1H NMR (CDCl_3): δ 6.13 (s, 5H, C_5H_5), -1.24 (1H, W-H), ($^4J_{\text{H-}^{183}\text{W}} = 3.7\text{ Hz}$, $^1J_{\text{H-}^{183}\text{W}} = 88.3\text{ Hz}$, and $^3J_{\text{H-}^{183}\text{W}} = 70.8\text{ Hz}$) (see Figure 1 and discussion). Mass spectrum (probe temperature 130°C : $[(\text{C}_5\text{H}_5)_2\text{W}_2(\text{NO})_2\text{IH}_2]^+$, $[(\text{C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2\text{H}]^+$, $[(\text{C}_5\text{H}_5)\text{WI}_2]^+$, $[\text{WI}_2]^+$, $[(\text{C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}_2]^+$, and $[(\text{C}_5\text{H}_5)\text{WI}]^+$.

Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}]_2$ with Lewis Bases (L) These experiments were performed similarly, and the reaction with $\text{L} = \text{P}(\text{OPh})_3$ is described as a representative example. To a green benzene solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}]_2$, generated from $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$ (1.5, 1.4 mmol) and Red-al (vide supra), was added by syringe neat triphenylphosphite (0.70 mL, 2.7 mmol). After a few minutes the solution colour darkened to orange. The reaction mixture was concentrated under reduced pressure to 10 mL and transferred to the top of a 2 x 5 cm Florisil column. Elution of the column with benzene resulted in the development of a single yellow-orange band, which was collected. The benzene was removed in vacuo; the orange oil was dissolved in dichloromethane (25 mL); hexanes (15 mL) was added; and the solution was concentrated to yield orange crystals of analytically pure $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{I})(\text{H})[\text{P}(\text{OPh}_3)]$ (0.86 g, 70% yield) (vide supra).

For $\text{L} = \text{P}(\text{OCH}_3)_3$ the yield of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{I})(\text{H})[\text{P}(\text{OCH}_3)_3]$ was 69%. mp 102-103°C. Anal. Calcd for $\text{C}_8\text{H}_{15}\text{WNO}_4\text{IP}$: C, 18.08; H, 2.82; N, 2.64; I, 23.92; O, 12.05. Found: C, 18.19; H, 2.88; N, 2.58; I, 23.71; O, 12.17. IR (CH_2Cl_2): $\nu(\text{NO})$ 1627 (s); also 1060 (m), 1023 (s) cm^{-1} . IR (Nujol): $\nu(\text{W-H})$ 1918 (w); $\nu(\text{NO})$ 1616 (s); also 1174 (m), 1071 (m), 1012 (s, br), 845 (w), 840 (w), 824 (m), 797 (s), 750 (s) cm^{-1} . ^1H NMR (C_6D_6): δ 5.12 (s, 5H, C_5H_5), 3.36 (d, 9H, $\text{P}(\text{OCH}_3)_3$), [$^1\text{J}_{\text{H-31P}} = 12$ Hz], -1.41 (1H, W-H), [$^2\text{J}_{\text{H-31P}} = 101$ Hz, $^1\text{J}_{\text{H-183W}} = 57$ Hz]. ^1H NMR (CDCl_3): δ 5.77 (s, 5H, C_5H_5), 3.67 (d, 9H, $\text{P}(\text{OCH}_3)_3$), [$^1\text{J}_{\text{H-31P}} = 12$ Hz], -1.42 (1H, W-H), [$^2\text{J}_{\text{H-31P}} = 101$ Hz, $^1\text{J}_{\text{H-183W}} = 57$ Hz]. ^{31}P NMR (C_6D_6): δ 131 [$^2\text{J}_{\text{P-H}} = 101$ Hz].

For $L = PPh_3$, the product was $(\eta^5-C_5H_5)W(NO)(I)(H)(PPh_3)$ isolated in 66% yield. Mp $142^\circ C$ dec. Anal. Calcd for $C_{23}H_{21}WNOIP$: C, 41.26; H, 3.14; N, 2.09. Found: C, 41.20; H, 3.18; N, 2.15. IR (CH_2Cl_2): $\nu(NO)$ 1615 (s); also 1482 (w), 1094 (m), 823 (m) cm^{-1} . IR (Nujol): $\nu(W-H)$ 1936 (w); $\nu(NO)$ 1617 (s); also 1095 (m), 1087 (m), 821 (w), 693 (m) cm^{-1} . 1H NMR (C_6D_6): δ 7.70 (m, 6H, $P(C_6H_5)_3$ ortho), 7.05 (m, 9H, $P(C_6H_5)_3$ para/meta), 5.10 (s, 5H, C_5H_5), 0.10 (1H, W-H), [$^2J_{^1H-^31P} = 85$ Hz, $^1J_{^1H-^{183}W} = 58$ Hz]. 1H NMR ($CDCl_3$): δ 7.44 (m, 15H, $P(C_6H_5)_3$), 5.63 (s, 5H, C_5H_5), 0.31 (1H, W-H), [$^2J_{^1H-^31P} = 85$ Hz, $^1J_{^1H-^{183}W} = 58$ Hz]. ^{31}P NMR (C_6D_6): δ 14.1 [$^2J_{^31P-^1H} = 85$ Hz].

Reaction of $[(\eta^5-C_5H_5)W(NO)(I)(H)]_2$ with $Na[H_2Al(OCH_2CH_2OCH_3)_2]$.

To a suspension of green crystalline $[(\eta^5-C_5H_5)W(NO)(I)(H)]_2$ (0.65 g, 0.80 mmol) in toluene (100 mL) was added 0.3 mL (1.05 mmol) Red-al by syringe. Both the colour of the solution and that of the particulate matter changed from green to brown; infrared monitoring indicated the loss of the νNO absorption at ~ 1640 cm^{-1} , characteristic of the starting material, and the appearance of a new νNO absorption at ~ 1600 cm^{-1} . Distilled water (0.04 mL) was added, and the reaction mixture was filtered through a 3 x 4 cm column of anhydrous $MgSO_4$ supported on a medium porosity frit. The filtrate was concentrated in vacuo to approximately 15 mL at which point a fine orange powder had precipitated. The solid was collected on a frit and washed with 8 mL portions of toluene until the washings had no green tint but were slightly orange in color (about six aliquots). Analytically pure $[(\eta^5-C_5H_5)W(NO)H_2]_2$ was thus obtained in 16% yield (0.07 g), mp $130^\circ C$ dec.

Anal. Calcd for $C_{10}H_{14}W_2N_2O_2$: C, 21.35; H, 2.49; N, 4.98; O, 5.69. Found: C, 21.69; H, 2.63; N 4.95; O, 6.00. IR (CH_2Cl_2): $\nu(NO)$ 1596 (s) cm^{-1} . IR (Nujol): 3108 (w), 3088 (w); $\nu(W-H)$ 1934 (m); $\nu(NO)$ 1563 (s, br); also 1430 (m), 1421 (m), 1365 (w), 1317 (w), 1064 (w), 1016 (m), 927 (w), 845 (s), 749 (m) cm^{-1} . 1H NMR (C_6D_6): δ 7.01 (m, 2.6H, $W-H$), 6.64 (dd, 2H, $W-H$), 5.26 (s, 10H, C_5H_5), 5.23 (s, 13H, C_5H_5), 1.66 (m, 1H, $W-H$), -1.90 (m, 2.6H, $W-H$), -5.99 (td, 1H, $W-H$). 1H NMR ($CDCl_3$): δ 6.98 (m, 2.6H, H_5 and H_6), [$\frac{1}{2}(^1J_{H_5-183W} + ^1J_{H_6-183W}) = 94$ Hz], 6.54 (dd; 2H, H_1 and H_2). [$^2J_{13} = ^2J_{23} = 2.9$ Hz; $^2J_{14} = ^2J_{24} = 8.6$ Hz; $\frac{1}{2}(^1J_{H_1-183W} + ^1J_{H_2-183W}) = 97$ Hz], 5.94 (s, 13H, C_5H_5), 5.93 (s, 10H, C_5H_5), 1.39 (m, 1H, H_3) [$^2J_{31} = ^2J_{32} = 2.9$ Hz; $^2J_{34} = 2.3$ Hz; $^1J_{H_3-183W} = 91$ Hz], -2.02 (m, 2.6H, H_7 and H_8) [$\frac{1}{2}(^1J_{H_7-183W} + ^1J_{H_8-183W}) = 92$ Hz], -5.93 (td, 1H, H_4) [$^2J_{41} = ^2J_{42} = 8.6$ Hz; $^2J_{43} = 2.3$ Hz; $^1J_{H_4-183W} = 95$ Hz] (see Figure 5 and discussion). Mass Spectrum (probe temperature 120°C): $[(C_5H_5)_2W_2(NO)_2H_3]^+$.

Reactions of $[(\eta^5-C_5H_5)W(NO)H_2]_2$ with $P(OPh)_3$. Neat triphenylphosphite (0.30 mL, 1.6 mmol) was added by syringe to a benzene (50 mL) suspension of $[(\eta^5-C_5H_5)W(NO)H_2]_2$ (0.30 g, 0.50 mmol). The reaction mixture was stirred until most of the solid had dissolved and a burgundy-coloured solution had formed (about 3h). The solution was filtered, concentrated to ~15 mL, and diluted with 10 mL hexanes. A brown solid precipitated which was removed by filtration and discarded. Further addition of hexanes (~30 mL) to the purple solution resulted in the formation of a deep purple powder $(\eta^5-C_5H_5)W(NO)H_2[P(OPh)_3]$ (0.20 g, 32% yield).

Anal. Calcd for $C_{23}H_{22}WNO_4P$: C, 46.70; H, 3.72; N, 2.37. Found: C, 47.10; H, 3.75; N, 2.65. IR (CH_2Cl_2): $\nu(NO)$ 1591 (s); also 1487 (s), 1194 (s), 1186 (s), 1160 (m) cm^{-1} . IR (Nujol): 1589 (s); $\nu(NO)$ 1574 (s); also 1217 (m), 1196 (s), 1185 (s), 1159 (s), 1069 (w), 1023 (w), 1005 (w), 913 (s), 895 (s), 881 (s), 822 (w), 780 (s), 770 (s), 708 (w), 694 (s) cm^{-1} . 1H NMR (C_6D_6): δ 7.58 (d, 6H, $P(C_6H_5)_3$ ortho), 7.20 (t, 6H, $P(C_6H_5)_3$ meta), 6.94 (t, 3H, $P(C_6H_5)_3$ para), 5.17 (s, 5H, C_5H_5), 1.32 (m, 2H, W-H). 1H NMR ($CDCl_3$): δ 7.35 (m, 15H, $P(C_6H_5)_3$), 4.97 (s, 5H, C_5H_5), 1.10 (m, 2H, W-H). ^{31}P NMR (C_6D_6): 151 (t) [$\frac{1}{2}(^2J_{31P-1H_1} + ^2J_{31P-1H_2}) = 24$ Hz; $^1J_{31P-183W} = 595$ Hz]. Mp 85°C dec. Mass spectrum (probe temperature 120°C): $[(C_5H_5)W(NO)HP(OPh)_3]^+$, $[(C_5H_5)WP(OPh)_3]^+$, and $[WH_2P(OPh)_3]^+$.

When recrystallization of purple $(\eta^5-C_5H_5)W(NO)H_2[P(OPh)_3]$ was attempted employing dichloromethane/hexanes instead of benzene/hexanes, the colour of the purple solution slowly lightened until in approximately 3 hours the solution was orange. The light orange powder isolated from this solution still had the empirical formula $(C_5H_5)W(NO)H_2[P(OPh)_3]$.

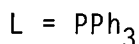
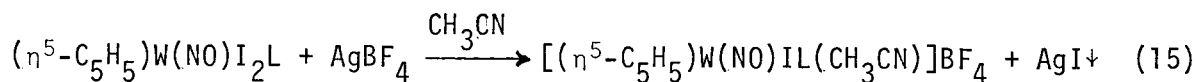
Anal. Calcd for $C_{23}H_{22}WNO_4P$: C, 46.70; H, 3.72; N, 2.37. Found: C, 46.55; H, 3.84; N, 2.50. IR (CH_2Cl_2): $\nu(NO)$ 1606 (s); also 1591 (s), 1487 (s), 1220 (m), 1194 (s), 1164 (m), 1073 (w), 1025 (m), 1009 (w), 965 (w), 916 (s), 865 (m), 827 (m) cm^{-1} . IR (Nujol): $\nu(W-H)$ 1856 (w), 1831 (w); $\nu(NO)$ 1601 (s); also 1586 (s), 1190 (s), 1151 (s), 1069 (w), 1028 (w), 1004 (w), 928 (m), 913 (m), 903 (s), 887 (s), 824 (w), 820 (w), 776 (s), 770 (m), 691 (m) cm^{-1} . 1H NMR (C_6D_6): 7.42-6.92 (m, 15H, $P(C_6H_5)_3$), 4.69 (s, 5H, C_5H_5), -1.58 (2H, W-H) [$^2J_{1H-31P} = 87$ Hz;

$^1J_{1H-183W} = 87 \text{ Hz}$]. 1H NMR ($CDCl_3$): δ 7.28 (m, 15H, $P(C_6H_5)_3$), 5.10 (s, 5H, C_5H_5), -1.82 (2H, W-H) [$^2J_{1H-31P} = 86 \text{ Hz}$; $^1J_{1H-183W} = 88 \text{ Hz}$].
 ^{31}P NMR (C_6D_6): δ 137 (t) ($^2J_{31P-1H} = 87 \text{ Hz}$). Mp $91^\circ C$ dec.

Results and Discussion

Preparation and Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{solvent})]\text{BF}_4$ (I).

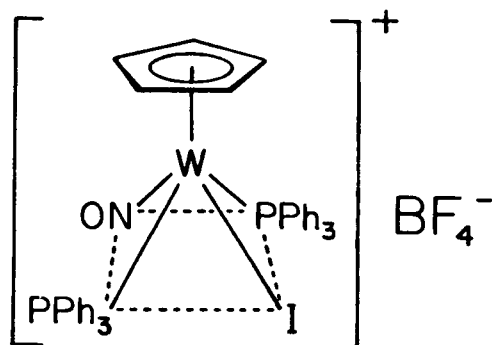
When the iodine bridges in $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$ are cleaved by a Lewis base, L, $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2\text{L}$ is formed in good yield. A "four-legged piano stool" geometry is assumed for the molecular structures of the $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2\text{L}$ complexes; and although this allows for the possibility of cis-trans geometric isomers, ^1H and ^{13}C NMR spectra indicate the presence of only one isomer in solution.⁴³ When $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2\text{L}$ is treated with one equivalent of AgBF_4 in a dichloromethane/acetonitrile mixture, silver iodide rapidly forms. Monitoring the reaction by infrared spectroscopy shows a shift in the νNO absorptions from that of the starting material to that of the product (I) $[1645 \text{ to } 1665 \text{ cm}^{-1}$ for $\text{L} = \text{PPh}_3$ and $1660 \text{ to } 1680 \text{ cm}^{-1}$ for $\text{L} = \text{P}(\text{OPh})_3]$. For $\text{L} = \text{PPh}_3$ attempts to isolate the product lead to an orange solid $[\nu(\text{NO}) = 1657 \text{ (s) cm}^{-1} (\text{CH}_2\text{Cl}_2), \nu(\text{NO}) = 1656 \text{ cm}^{-1} \text{ (s) (Nujol), } \nu(\text{CN}) = 2310 \text{ (w), } 2275 \text{ (w) cm}^{-1} \text{ (Nujol), and } \nu(\text{BF}) = 1054 \text{ (s, br) (Nujol)}]$. The ^1H NMR spectrum (CD_3NO_2) consists of three multiplets: phenyl ($\delta 8.1 \rightarrow 7.4$), cyclopentadienyl ($\delta 6.23 \text{ (t), } ^2J_{\text{H-31P}} = 2.2 \text{ Hz}$) and acetonitrile ($\delta 2.8 \rightarrow 2.2$) of relative intensities 15 to 5 to 3. These observations are consistent with the abstraction of one iodo ligand to yield a cationic product which in time loses some of its coordinated acetonitrile:



(a) Reaction of I with PPh₃. Addition of PPh₃ to the solvated cation $[\text{CpW}(\text{NO})\text{I}(\text{PPh}_3)(\text{CH}_3\text{CN})]\text{BF}_4$ shifts the νNO in the IR spectrum of the reaction solution from 1665 cm^{-1} to 1645 cm^{-1} as is expected when the more electron-donating ligand PPh₃ replaces CH₃CN. The resulting cation $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{PPh}_3)_2]\text{BF}_4$ is a yellow-orange, diamagnetic solid which is soluble in acetonitrile and nitromethane and slightly soluble in dichloromethane. Its IR spectrum (Nujol) exhibits a strong nitrosyl absorption at 1657 cm^{-1} and a tetrafluoroborate absorption at 1084 cm^{-1} , which are characteristic of a terminal nitrosyl ligand^{4a, 44} and an uncoordinated anion,⁴⁵ respectively.

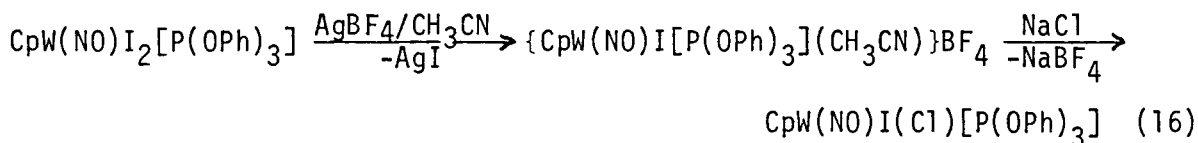
The ¹H NMR spectrum of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{PPh}_3)_2]\text{BF}_4$ consists of a multiplet at δ 7.64 (30H) due to the phenyl protons and a triplet at δ 5.97 (5H) [³J_{1H-31P} = 2.0 Hz] corresponding to the cyclopentadienyl protons. The triplet pattern exhibited by the cyclopentadienyl protons must be the result of coupling to two equivalent phosphorus atoms; a more complex pattern would be expected in the case of inequivalent phosphine ligands. The order of magnitude of the coupling is the same as that found in $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2\text{L}$ (³J_{1H-31P} = 3.0 Hz for L = P(OPh)₃; ³J_{1H-31P} = 1.2 Hz for L = PPh₃).⁴³ The equivalence of the phosphines is confirmed by the broadband proton decoupled ³¹P NMR spectrum which is a three line pattern—a

large singlet centred in a small doublet which is of the proper intensity ratio to the larger resonance (1 to 11.4 to 1) to be attributed to the NMR pattern of the isotopomer $[(\eta^5\text{-C}_5\text{H}_5)^{183}\text{W}(\text{NO})\text{I}(\text{PPh}_3)_2]\text{BF}_4$ (the natural abundance of $^{183}\text{W} = 14\%^{46}$). The observed tungsten-phosphorus coupling ($^1J_{^{31}\text{P}-^{183}\text{W}} = 220 \text{ Hz}$) is of the same order of magnitude as that reported for tungsten phosphinocarbonyl complexes.⁴⁷ The presence of a tetrafluoroborate anion with tetrahedral symmetry is confirmed by the singlet at $\delta 151$ observed in the ^{19}F NMR spectrum.⁴⁸ It seems likely that the $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IL}_2]^+$ cation ($\text{L} = \text{PPh}_3$) is isostructural with $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2\text{L}$ and possesses the same "four-legged piano stool" conformation. For this structure both cis and trans geometries are possible; but as the nuclear magnetic resonance experiments indicate two equivalent phosphine ligands, only the trans isomer appears to exist in solution:

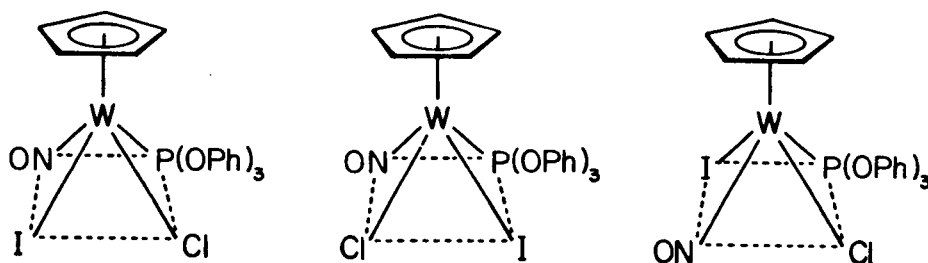


(b) Reaction of I with NaCl. The mixed halide complex $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{Cl})[\text{P}(\text{OPh})_3]$ is formed when sodium chloride and $\{(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}[\text{P}(\text{OPh})_3](\text{CH}_3\text{CN})\}\text{BF}_4$ are stirred together in nitromethane for 14 h. The net

reaction is simply the substitution of chloride for iodide:

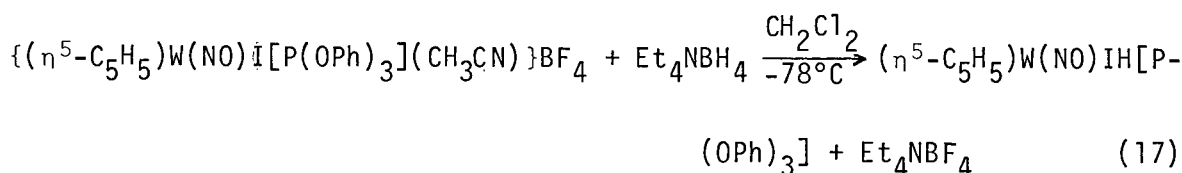


$(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)I(Cl)}[\text{P(OPh)}_3]$ has spectral properties similar to the parent halide $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)I}_2[\text{P(OPh)}_3]$.⁴³ Both exhibit a nitrosyl absorption at 1651 cm^{-1} in their IR spectrum (Nujol). The ^1H NMR spectrum of the diiodo precursor displays a multiplet at δ 7.19 (CDCl_3) due to the triphenylphosphite protons and a doublet at δ 5.90 due to the cyclopentadienyl protons with $^3J_{\text{H-31P}} = 3.0\text{ Hz}$; thus, though both cis and trans diiodo ligands are possible, only one isomer is observed. Only one isomer of $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)I(Cl)}[\text{P(OPh)}_3]$ appears to exist in d^6 -benzene: δ 7.17 (m, 15H, $\text{P(OC}_6\text{H}_5)_3$) and 5.45 (d, 5H, C_5H_5) with $^3J_{\text{H-31P}} = 2.9\text{ Hz}$. However, a proton NMR spectrum of the mixed halide species obtained in d-chloroform on a 270 MHz spectrometer manifests two sets of C_5H_5 resonances; both are doublets, $^3J_{\text{H-31P}} = 2.9\text{ Hz}$, of approximately equal intensity centred at δ 6.01 and 5.99. Thus, of the three potential geometric configurations two are in evidence in chloroform solutions.



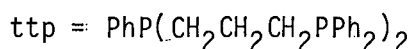
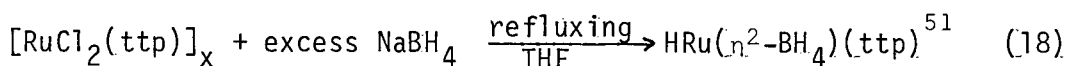
(c) Reaction of I with $(\text{CH}_3\text{CH}_2)_4\text{NBH}_4$. Previous efforts in these laboratories have succeeded in synthesizing $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{H}$ in good yields

(~60%) both by metathesis of the corresponding chloride complex (reaction 14)³⁵ and by addition of a hydride source to " $\text{CpW}(\text{NO})_2^+$ " generated in situ.⁴⁹ It, thus, seemed likely that $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}[\text{P}(\text{OPh})_3]$ could be obtained in good yield from the reaction of the cation and an H^- source. Indeed, the organometallic hydride is formed in the reaction of tetraethylammonium borohydride with a cold (-78°C) dichloromethane solution of $\{(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}[\text{P}(\text{OPh})_3](\text{CH}_3\text{CN})\}\text{BF}_4$ and can be identified by its IR spectrum (Nujol): $\nu(\text{W-H})$ 1865 (w); $\nu(\text{NO})$ 1627 (s) and ^1H NMR spectra (CDCl_3): δ 7.33 (m, 15H, $\text{P}(\text{OC}_6\text{H}_5)_3$), 5.32 (s, 5H, C_5H_5), -1.98 (1H, W-H), ($^2\text{J}_{\text{H-31P}} = 111 \text{ Hz}$, $^1\text{J}_{\text{H-183W}} = 54 \text{ Hz}$). (A detailed discussion of the properties of this hydride will follow in a later section.) Unfortunately, the yield of reaction 17 is poor (13%). IR monitoring reveals that as

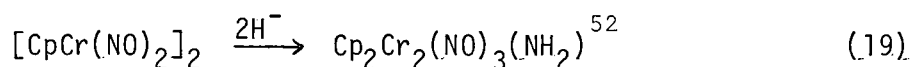


$(\text{CH}_3\text{CH}_2)_4\text{NBH}_4$ is dripped into the cation solution the νNO band of the cation (1660 cm^{-1}) disappears and the only nitrosyl absorption which appears is small in intensity and is that associated with the product (1640 cm^{-1}).

Borohydride is chosen as the hydride source because it is a relatively mild reducing agent, but under some circumstance it can contribute more than one hydride.⁵⁰ Further difficulties may arise from coordination of the BH_4 group to the metal centre as has been found for



Another complication may arise from the nitrosyl ligand, which itself is susceptible to hydride attack, e.g.

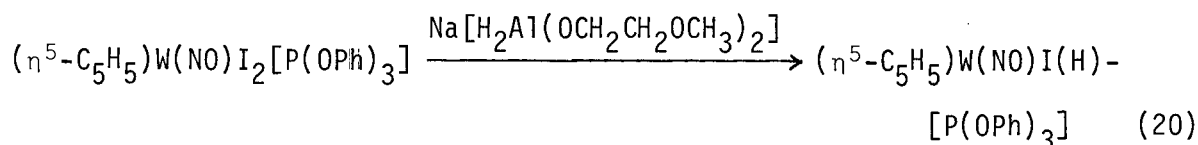


Evidently another reaction occurs besides simple addition of H^- to the metal centre which results in the loss of the nitrosyl moiety. That the iodide abstraction is not the low yield step can be assumed from the good yields of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{PPh}_3)_2]\text{BF}_4$ and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{Cl})[\text{P}(\text{OPh})_3]$ produced via the same abstraction step (vide supra).

Metathetical Reactions of $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ with Some Monomeric Halonitrosyl Complexes.

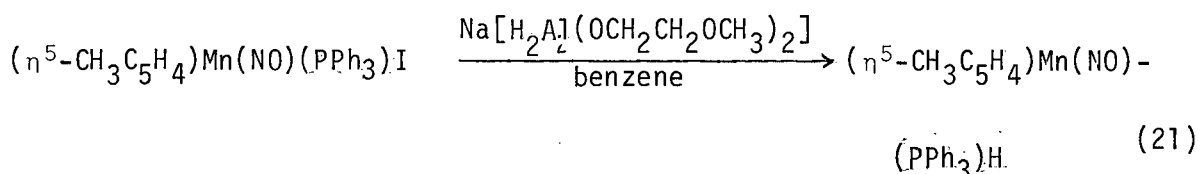
(a) $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2[\text{P}(\text{OPh})_3]$. Formation of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{-}[\text{P}(\text{OPh})_3]$, produced by the reaction of $(\text{CH}_3\text{CH}_2)_4\text{NBH}_4$ with $\{(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I-}[\text{P}(\text{OPh})_3](\text{CH}_3\text{CN})\}\text{BF}_4$, is also successfully effected by the reaction of one equivalent of sodium dihydridobis(2-methoxyethoxy)aluminate on $(\eta^5\text{-C}_5\text{H}_5)\text{W-}(\text{NO})\text{I}_2[\text{P}(\text{OPh})_3]$ in a benzene solution at room temperature. As the Red-al³⁷ is added, the originally orange suspension darkens and a brown solid forms. The nitrosyl infrared absorption shifts from 1660 cm^{-1} to 1640 cm^{-1} ,

decreasing markedly in intensity. Then a slight stoichiometric excess of water is added to quench the aluminum reagent. The yellow-orange species isolated from chromatography on a benzene/Florisil column is identified by IR and by ^1H NMR spectroscopy (vide infra) to be the hydride $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$. The yield of reaction 20



(34%) represents a slight improvement over the quantity of hydride obtained via the cation (reaction 17).

(b) $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{NO})[\text{PPh}_3]\text{I}$. Just as with $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2[\text{P}(\text{OPh})_3]$, sodium dihydridobis(2-methoxyethoxy)aluminate also undergoes a simple metathetical reaction with $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{NO})(\text{PPh}_3)\text{I}^{41}$ to produce the hydridonitrosyl species.

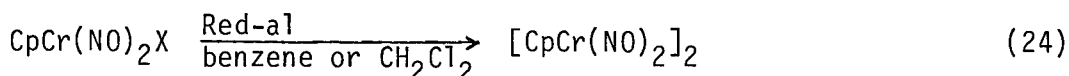
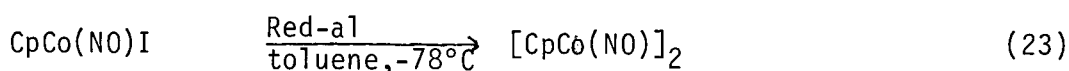
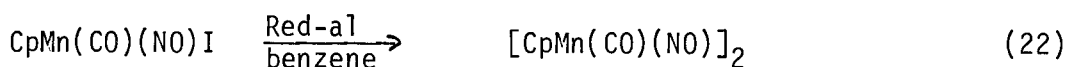


Again, the optimum stoichiometry of the reactants is 1:1, and the transformation proceeds to give the hydride in low yield.

$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{NO})(\text{PPh}_3)\text{H}$ is an orange, air-sensitive solid (mp 42.5°C dec.) which is freely soluble in benzene, is sparingly soluble in hexanes, and reacts with CH_2Cl_2 . The ^1H NMR spectrum of the compound in

C_6D_6 exhibits resonances assignable to the PPh_3 [δ 7.66-6.98 (m, 15H)], $\eta^5-C_5H_5$ [δ 4.60 (s, 1H), 4.46 (s, 1H), 3.92 (s, 2H), 1.86 (s, 3H)], and W-H [δ -6.48 (d, 1H); $^2J_{1H-31P} = 88.8$ Hz] ligands. Its IR spectrum in benzene displays a strong absorption at 1683 cm^{-1} attributable to a terminal nitrosyl group. However, the complex decomposes slowly both in solution and in the solid state when maintained in an atmosphere of pre-purified argon. For instance, a red benzene solution of $(\eta^5-C_5H_5)Mn(NO)(PPh_3)H$ at room temperature slowly becomes dark green and deposits a brown solid. Monitoring of this transformation by 1H NMR spectroscopy reveals a gradual diminution of the resonances due to the hydrido complex and a concomitant increase in intensity of two sharp signals at δ 1.64 and 4.60 of relative intensity 3:4 due to the well-known, green trimetallic complex $(\eta^5-C_5H_5)_3Mn_3(NO)_4$.^{7,42} The transformation is complete after 48 h. Consequently, purification of the hydrido product of reaction 21 by column chromatography also affords trace amounts of the trimetallic species. The fact that $(\eta^5-C_5H_5)Mn(NO)(PPh_3)H$ decomposes thermally in this manner rather than to $[(\eta^5-C_5H_5)Mn(NO)(PPh_3)]_2$ is presumably a reflection of the considerable lability of the PPh_3 group.

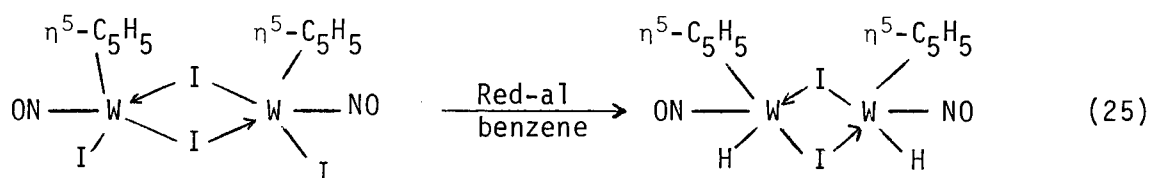
When a similar reaction is performed with Red-al and $(\eta^5-C_5H_5)Mn(CO)(NO)I$ ⁴¹ the hydridonitrosyl species is not the product. Instead, the product is the dimer $[(\eta^5-C_5H_5)Mn(CO)(NO)]_2$. Dimers are also produced by the reaction of Red-al with either $(\eta^5-C_5H_5)Co(NO)I$ or $(\eta^5-C_5H_5)Cr(NO)_2X$ ($X = NO_3, NO_2, I, n^1-C_5H_5$, or BF_4) as summarized in eqs. 22, 23, and 24.⁵²



These dimeric products probably arise from the thermal decomposition of the corresponding monomeric hydridonitrosyl complexes (such a decomposition pathway has been reported for $(\eta^5\text{-C}_5\text{H}_5)\text{Cr(CO)}_3\text{H}^{53}$), but no direct physical evidence for the existence of these species has been obtained. Support for the involvement of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr(NO)}_2\text{H}$ as an intermediate is provided by the observation that $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr(NO)}_2]_2$ is formed in comparable yields during the reaction of Red-al with a variety of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr(NO)}_2\text{X}$ precursors ($\text{X} = \text{NO}_3, \text{NO}_2, \text{I}, \eta^1\text{-C}_5\text{H}_5$ or BF_4^{52} or Cl^{35}), while the reactions of Red-al with $(\eta^5\text{-C}_5\text{H}_5)\text{M(NO)}_2\text{Cl}$ ($\text{M} = \text{Mo}$ or W)³⁵ produce the hydride species $(\eta^5\text{-C}_5\text{H}_5)\text{M(NO)}_2\text{H}$. Consistent with the view that $(\eta^5\text{-C}_5\text{H}_5)\text{Mn(CO)(NO)H}$ is the labile intermediate in reaction 22 is the fact that $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(NO)}(\text{PPh}_3)\text{H}$ can be isolated from reaction 21. Evidently, introduction of the better electron-donating $\text{CH}_3\text{C}_5\text{H}_4$ and PPh_3 groups into the coordination sphere of the manganese atom stabilizes the latter hydride, whereas the analogous hydridocarbonyl complex in reaction 22 is so unstable that it cannot be detected by conventional spectroscopic techniques.

Reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$ with $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$.

In view of the reactivity patterns of $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ described above, it was of interest to investigate its reactions with complexes containing both bridging and terminal halide ligands. It seemed reasonable that selective substitution of the terminal halides could be achieved while leaving the halide bridges intact. Indeed, just such a transformation does occur when $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$ the precursor of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{-I}_2[\text{P}(\text{OPh})_3]$ is treated with one equivalent of Red-al at room temperature, i.e.



The unprecedented product of reaction 25 is a bright green, air-sensitive solid which is soluble in most common organic solvents except paraffin hydrocarbons. However, the compound is thermally unstable in solution (benzene > CH_2Cl_2 > THF in order of decreasing stability), decomposing to a brown, intractable solid. Nevertheless, analytically pure samples of this compound can be obtained. Its physical properties are consistent with it having the molecular structure shown in eq. 25.

The solid state infrared spectrum (Nujol) reveals two strong nitrosyl absorptions (1634 and 1616 cm^{-1}), but no tungsten-hydride stretching absorpt-

tion is evident. The two nitrosyl absorptions may result from packing disorder in the crystal lattice. Its IR spectrum in dichloromethane displays a strong nitrosyl absorption at 1640 cm^{-1} .

Only one isomer of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})]_2$ is observed in its ^1H NMR in d^6 -benzene or d -chloroform. The ^1H NMR spectrum of a dilute sample consists of two singlets at δ 5.25 and -1.25 in d^6 -benzene or at δ 6.13 and -1.24 in d -chloroform of relative intensity 5:1 assignable to the cyclopentadienyl protons and hydrides, respectively. The two hydride ligands are isochronous but not magnetically equivalent; with a more concentrated sample the signal to noise ratio increases such that ^1H - ^{183}W coupling becomes observable, and the NMR pattern of the hydride region becomes more complex (see Figure 1a). An AA'X pattern emerges around the central resonance which is the expected 86% of the total intensity. Coupling constants were tentatively assigned using algebraic equations derived for the interpretation of second order spectra;⁵⁴ these assignments were confirmed by computer simulation of the ^{183}W satellite region of the spectrum (Figure 1b). It is assumed that there is small probability of both tungsten atoms in the same molecule being the spin $\frac{1}{2}$ isotope. Where H is the hydride directly attached to ^{183}W , the coupling constant assignments are $^4J_{\text{HH}'} = 3.7\text{ Hz}$, $^1J_{\text{H-}^{183}\text{W}} = 88.3\text{ Hz}$, and $^3J_{\text{H-}^{183}\text{W}} = 70.8\text{ Hz}$.

The dimeric nature of the complex is further confirmed by its mass spectrum (at a probe temperature of 130°C) which exhibits peaks attributable to the parent ion and ions corresponding to the sequential loss of ligands. Unfortunately, overlapping of some medium to strong intensity peaks in the

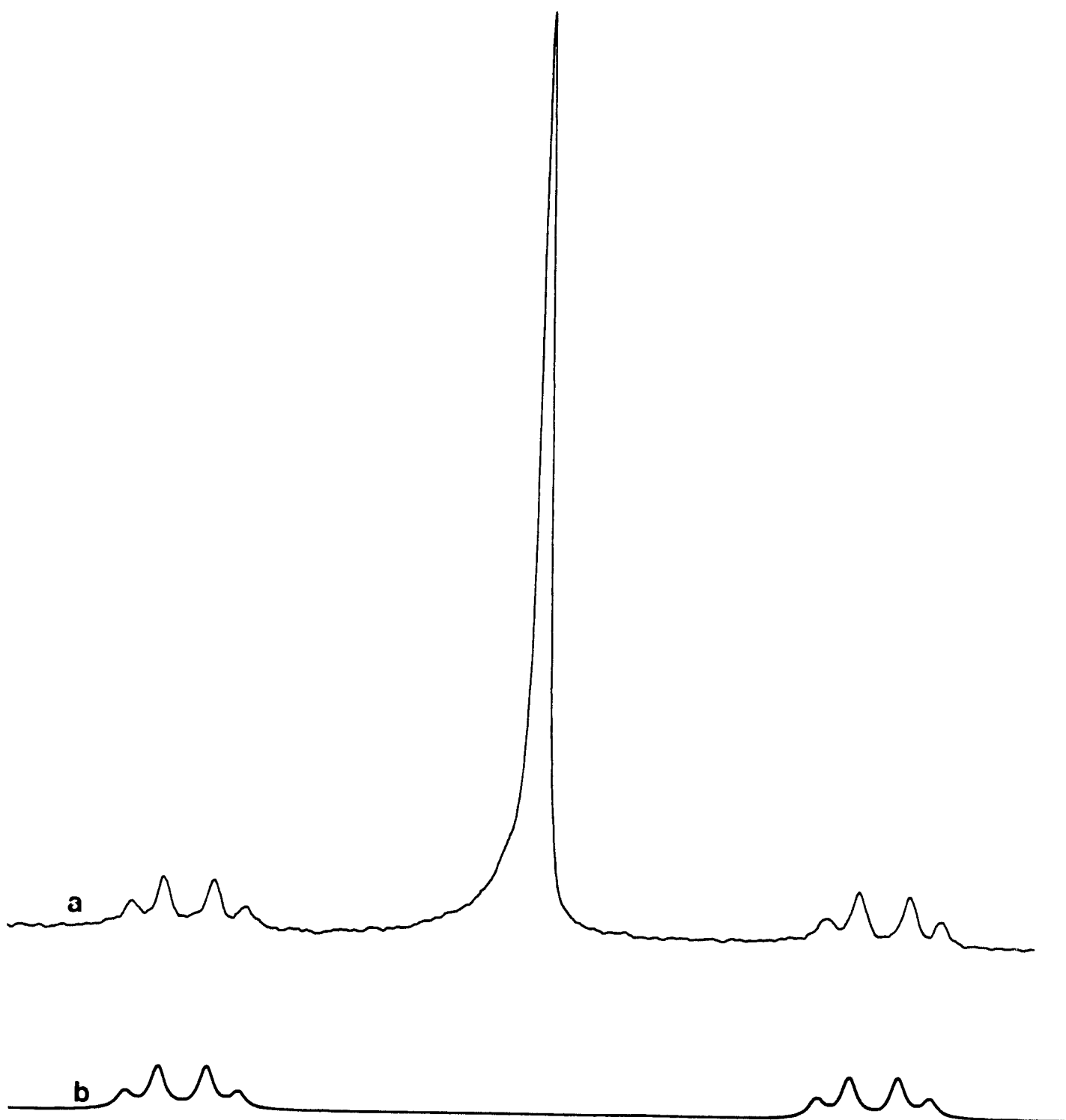
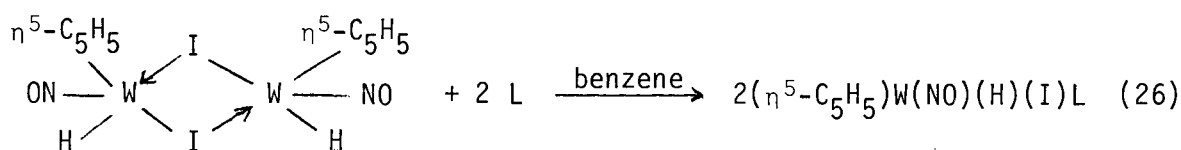
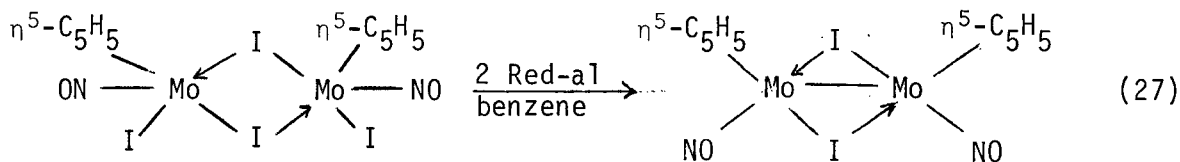


Figure 1. a. ^1H NMR Spectrum of the Hydride Region of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})]_2$ in CDCl_3 (400 MHz)
b. Computer Simulation of the Tungsten-Hydride Couplings

lower mass range makes unambiguous assignments difficult, especially in the light of the polyisotopic nature of tungsten. The dimeric product of reaction 25 can also be characterized chemically since it readily reacts with a variety of Lewis bases L to produce new tungsten hydrido-nitrosyl complexes, i.e.



When $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}_2]_2$ is treated with one equivalent of Red-al at room temperature, the well-known dimer $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}]_2^{55}$ is formed in 6% yield. The yield can be improved to 18% when two equivalents of Red-al are employed, i.e.⁵²



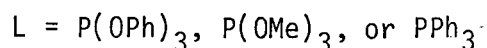
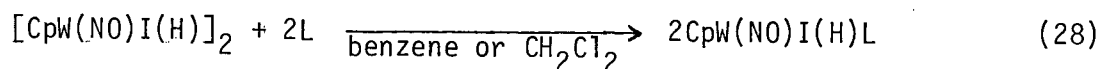
By analogy with the tungsten congener (cf. reaction 25), it seems likely that reaction 27 probably proceeds via the unstable dihydrido intermediate $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{H})\text{I}]_2$. During the reaction, a green colour perhaps due to the intermediate, appears after the addition of each aliquot of $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$; but this colour persists only for several seconds

before being replaced by the characteristic orange colour of the final product. The species responsible for the green color cannot be detected by IR spectroscopy. Curiously, thermal decomposition of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})]_2$ in solution does not result in the formation of the analogous $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}]_2$; a complex which has yet to be prepared.

Mention needs to be made of the stoichiometry of reactions 20, 21 and 25. In each of these transformations one equivalent of the aluminum reagent per equivalent of reactant is necessary to ensure completion of the reaction. For the monomeric reactants $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2[\text{P}(\text{OPh})_3]$ and $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{NO})(\text{PPh}_3)\text{I}$ this means $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ is acting as the source of only one hydride. For bis $[(\eta^5\text{-cyclopentadienyl})\text{diiodo-nitrosyltungsten}]$ the aluminum reagent must be acting as a source of two hydrides. Unlike the case in reaction 27 an extra equivalent of Red-al does not increase the yield of the product, the hydridonitrosyl dimer; rather, it initiates a further reaction (vide infra). Since in all cases the transfer of one hydride from the aluminum reagent would be expected to result in the same aluminum byproduct, it must be the relative inertness of the monomers that prevents acceptance of a hydride from this source.

Reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})]_2$ with Lewis Bases.

The iodine bridges in $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})]_2$ are easily cleaved by a variety of Lewis bases, L, to form the monomeric complexes $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{L}$ (eq. 28):

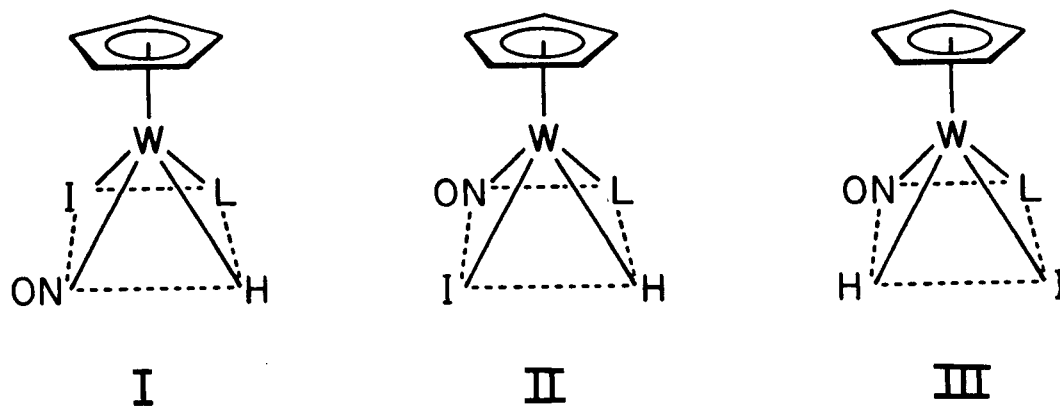


The products of reaction 28 are orange, diamagnetic solids which can be handled in air for short periods of time without the occurrence of noticeable decomposition. They are quite soluble in polar organic solvents, but only sparingly soluble in nonpolar ones, to give air-sensitive orange solutions. Their spectral properties confirm the monomeric nature of the complexes and the presence of the W-H bond. Their IR spectra (Table I) display single nitrosyl stretching absorptions in the range $1615 - 1642 \text{ cm}^{-1}$ (CH_2Cl_2) and a weak hydride stretching absorption in the range $1865 - 1936 \text{ cm}^{-1}$ (Nujol). The decrease in ν_{NO} as L varies in the order $\text{P}(\text{OPh})_3 > \text{P}(\text{OMe})_3 > \text{PPh}_3$ is consistent with the documented electron-donating and -accepting properties of these ligands.^{56,57} The tungsten-hydride stretching absorptions are broad, weak bands in the range expected for organometallic hydrides, $1900 \pm 300 \text{ cm}^{-1}$.¹⁴ The mass spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$ (at a probe temperature of 150°C) displays peaks corresponding to the parent ion $[\text{CpW}(\text{NO})\text{I}(\text{H})\text{P}(\text{OPh})_3]^+$, $[\text{CpW}(\text{NO})\text{HP}(\text{OPh})_3]^+$, $[\text{CpW}(\text{NO})\text{I}_2]^+$, $[\text{CpWI}_2]^+$, $[\text{WI}_2]^+$, $[\text{CpW}(\text{NO})\text{I}(\text{H})_2]^+$, and $[\text{CpWI}]^+$.

If the molecular structure of these complexes is assumed to be a 4-legged piano stool geometry,⁵⁸ then there exists the possibility of three geometric isomers (configurations I, II and III) as well as their corresponding enantiomers.

Table I. Spectral Properties of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{L}$ [$\text{L} = \text{P}(\text{OPh})_3$, $\text{P}(\text{OMe})_3$, or PPh_3] Complexes

L				^1H NMR						
	IR cm^{-1}	IR cm^{-1}	IR cm^{-1}	L, δ	C_5H_5 , δ	H, δ	$^2\text{J}_{\text{H}-^{31}\text{P}}$	$^1\text{J}_{\text{H}-^{183}\text{W}}$	^{31}P NMR	
	CH_2Cl_2	Nujol	Nujol	(CDCl_3)	(CDCl_3)	(CDCl_3)	Hz	Hz	$\delta, \text{C}_6\text{D}_6$	$^2\text{J}_{^{31}\text{P}-^1\text{H}}$
	$\nu(\text{NO})$	$\nu(\text{NO})$	$\nu(\text{W-H})$	(C_6D_6)	(C_6D_6)	(C_6D_6)			relative to H_3PO_4	Hz
$\text{P}(\text{OPh})_3$	1642	1627	1865	7.33(15H,m)	5.32(5H,s)	-1.98(1H)	111	54	115	112
				7.45 and 7.00(15H,m)	4.82(5H,s)	-2.07(1H)	112	55		
$\text{P}(\text{OMe})_3$	1627	1616	1918	3.67(9H,d)($^2\text{J}_{\text{H}-^{31}\text{P}}=12\text{Hz}$)	5.77(5H,s)	-1.42(1H)	101	57	131	101
				3.36(9H,d)($^2\text{J}_{\text{H}-^{31}\text{P}}=12\text{Hz}$)	5.12(5H,s)	-1.41(1H)	101	57		
PPh_3	1615	1617	1936	7.44(15H,m)	5.63(5H,s)	0.31(1H)	85	58	14.1	85
				7.70 and 7.05(15H,m)	5.10(5H,s)	0.10(1H)	85	58		



However, their spectral properties (Table I) suggest that only one isomer exists in solution. Thus, the ^1H NMR spectra consist of a single sharp resonance in the range δ 4.82 - 5.12 (C_6D_6) assignable to the cyclopentadienyl protons and a high field resonance pattern, a doublet each half of which is surrounded by a smaller doublet, assignable to the hydrides which reflects couplings to both the ^{183}W and ^{31}P atoms (see Figure 2). When $\text{L} = \text{P}(\text{OPh})_3$ or PPh_3 there is a broad phenyl resonance around δ 7.4 (CDCl_3) which is split into ortho and meta/para proton regions when the solvent is changed to d^6 -benzene. When $\text{L} = \text{P}(\text{OCH}_3)_3$ there is a sharp doublet $\sim \delta$ 3.4 (C_6D_6), coupling between the methyl protons and the phosphorus atom being 12 Hz.

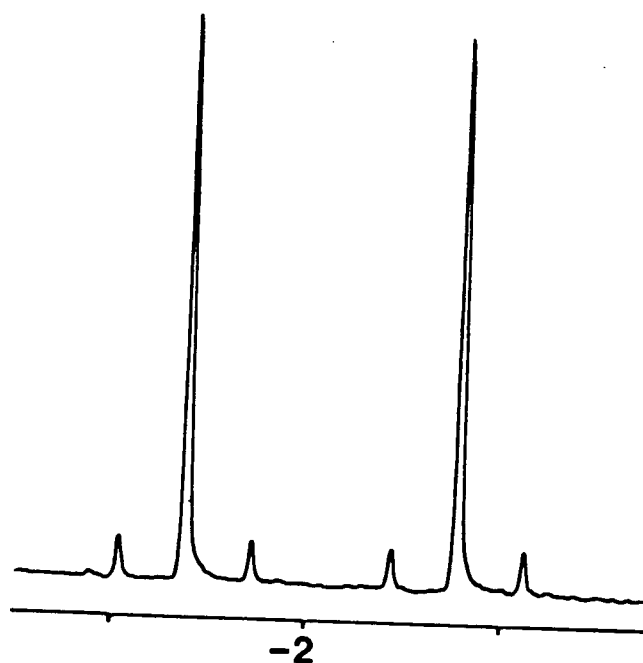


Figure 2. ^1H NMR Spectrum (80 MHz) of Hydride Region of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$ in C_6D_6

The NMR pattern of the hydride region of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$ illustrated in Figure 2 is representative of all three hydride species. The centre of the hydride pattern ranges from δ +0.10 to -2.07 (C_6D_6), somewhat upfield from the hydride resonance in $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ ³⁵ [δ 2.77 (C_6D_6)]. Nevertheless, these hydride resonances are at relatively low field; these resonances are usually observed at high fields, typically in the range δ -5 to -20.¹⁴ For example, $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{NO})\text{H}$ ³³ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{PPh}_3)(\text{NO})\text{H}$ ³⁴ display signals due to the hydride ligand at δ -8.2 (C_6D_6) and δ -9.15 (C_6D_6), respectively. A low field resonance is not unknown for transition-metal hydrides, but to date it has been characteristic only of early transition-metal complexes.¹⁵ The shift of the hydride resonance of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IHL}$ to lower field as L varies in the order $\text{P}(\text{OPh})_3 > \text{P}(\text{OCH}_3)_3 > \text{PPh}_3$, follows the same trend as previously noted for the decrease in νNO in the infrared spectrum. However, the tendency toward higher field hydride resonance with a variation in L toward better electron donating ligands (judging donor/acceptor character of L by νCO frequencies) has been reported by Tolman⁵⁷ for the coordination hydrides HfNiL_3CN . While Darensbourg²³ claims to find no correlation between the hydride chemical shift and a variation in L ligands in the $[\text{HW}(\text{CO})_4\text{L}]^-$ system, the hydride resonance when $\text{L} = \text{PPh}_3$ is at lower field than when $\text{L} = \text{P}(\text{OCH}_3)_3$.

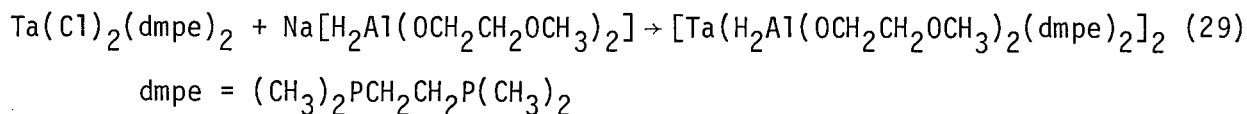
The spin-spin coupling of the hydrogen with tungsten provides additional evidence for a direct W-H bond. The major factors in determining the magnitude of the coupling constant are the magnetogyric ratio of the nuclei concerned and the Fermi contact interaction. For tungsten-hydride,

coupling constants in the range 20-70 Hz have been observed.¹⁶ For $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{L}$ $^1\text{J}_{\text{H-183W}}$ are in a narrow range 54-58 Hz. The slight increase in $^1\text{J}_{\text{H-183W}}$ observed as L varies from $\text{P}(\text{OPh})_3 < \text{P}(\text{OCH}_3)_3 < \text{PPh}_3$ may reflect the donor ability of the Lewis base, but the variation is probably too small to be of any real significance.

The phosphorus-hydrogen coupling constants are observed to increase ($^2\text{J}_{\text{H-31P}} = 85, 100, \text{ and } 111 \text{ Hz}$ for $\text{L} = \text{PPh}_3, \text{P}(\text{OCH}_3)_3, \text{ and } \text{P}(\text{OPh})_3$) in the same order as the hydride chemical shifts move upfield. This trend has been observed in $\text{CpMo}(\text{CO})_2\text{HL}$ ⁵⁸ and $[\text{HW}(\text{CO})_4\text{L}]^{-23}$ and been attributed to shortening of the M-P bond due to the steric or electronic properties of L. Observation and analysis of hydrogen-phosphorus couplings have been instrumental in the establishing of the stereochemistry of hydride species. In most octahedral and square-planar complexes $^2\text{J}_{\text{H-31P}}$ cis ($\sim 5\text{-}30 \text{ Hz}$) is much smaller than $^2\text{J}_{\text{H-31P}}$ trans ($\sim 60\text{-}150 \text{ Hz}$).¹⁶ However, for other systems this correlation does not hold; for $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{HL}$ where $\text{M} = \text{Mo or W}$ $^2\text{J}_{\text{H-31P}}$ cis ≈ 60 while $^2\text{J}_{\text{H-31P}}$ trans ≈ 20 .^{58,59} If this trend can be applied to $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{L}$, then the observed $^2\text{J}_{\text{H-31P}}$ ranging from 85-112 Hz are indicative of a cis geometry (configuration I or II). The cis geometry of the hydrogen and phosphorus is not surprising in view of the trend for strong trans effect ligands (which H^- , PR_3 , and $\text{P}(\text{OR})_3$ are) to avoid occupying a position trans to one another. What is surprising is the fact that no cis/trans tautomerism is indicated in the solution spectra of these tungsten hydridonitrosyl compounds while $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2\text{LH}$ for $\text{M} = \text{Mo and W}$ undergo rapid isomerization at room temperature.^{58,59}

The ^{31}P NMR spectra of the $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{L}$ complexes have been obtained with off-resonance decoupling of only the protons of the phosphorus ligands and cyclopentadienyl ligands. In all three cases only a sharp doublet is observed which confirms the presence of only one conformer in solution. When a phosphine is coordinated to a metal atom its ^{31}P NMR resonance is shifted, usually downfield, relative to the position of the free ligand;⁶⁰ no correlation has been made with phosphites.⁴⁷ In the ^{31}P NMR spectra of these hydridonitrosyls a downfield shift was observed for $\text{L} = \text{triphenylphosphine}$, while for $\text{L} = \text{triphenylphosphite}$ or $\text{trimethylphosphite}$ a slight upfield shift was detected (see Figure 3).

The yields of reaction 28 with any of the chosen ligands are close to 70%. For $\text{L} = \text{P}(\text{OPh})_3$ a 70% yield represents a considerable improvement over the yields of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$ obtained from reaction 17 (13%) or reaction 20 (34%). If the overall yield from their common starting material $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$ is considered (Figure 4), it becomes apparent that the low yield step is consistently the addition of H^- . As in the case when borohydride is the hydride source, several reaction modes of $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ can be envisioned which would not lead to the desired tungsten nitrosyl hydride. The nitrosyl ligand can be lost through reduction (see reaction 19). Alternatively, coordination of the alkoxyaluminum reagent to the metal atom may occur as has been reported⁶¹ for



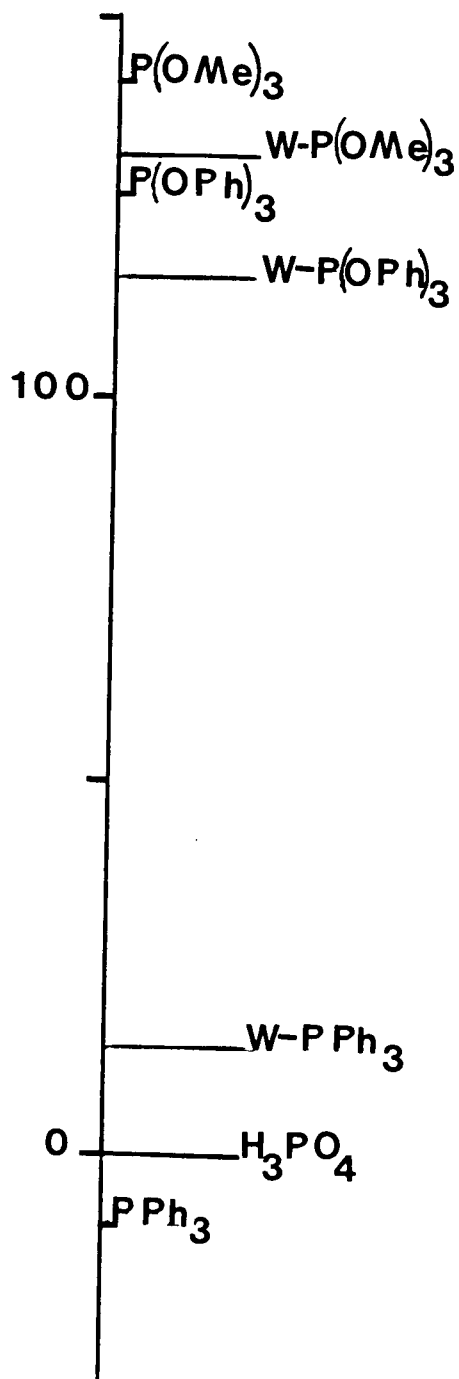


Figure 3. ^{31}P NMR Chemical Shifts in δ .
 $\text{W} = (\eta^5\text{-C}_5\text{H}_5)\text{W(NO)I(H)}$.

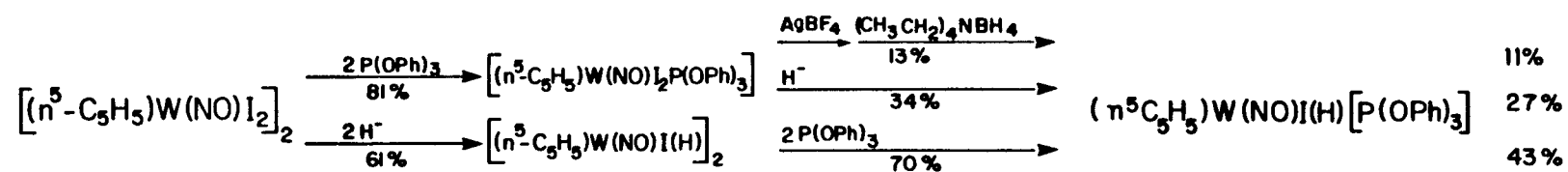


Figure 4. Formation of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\left[\text{P(OPh)}_3\right]$ from $\left[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2\right]_2$ via Three Routes.

Nevertheless, it appears that reaction 28 represents the best method as well as a generally applicable one for the synthesis of a series of complexes of the type $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{L}$ where L is any ligand capable of donating two electrons to the metal centre.

Reactivity of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$.

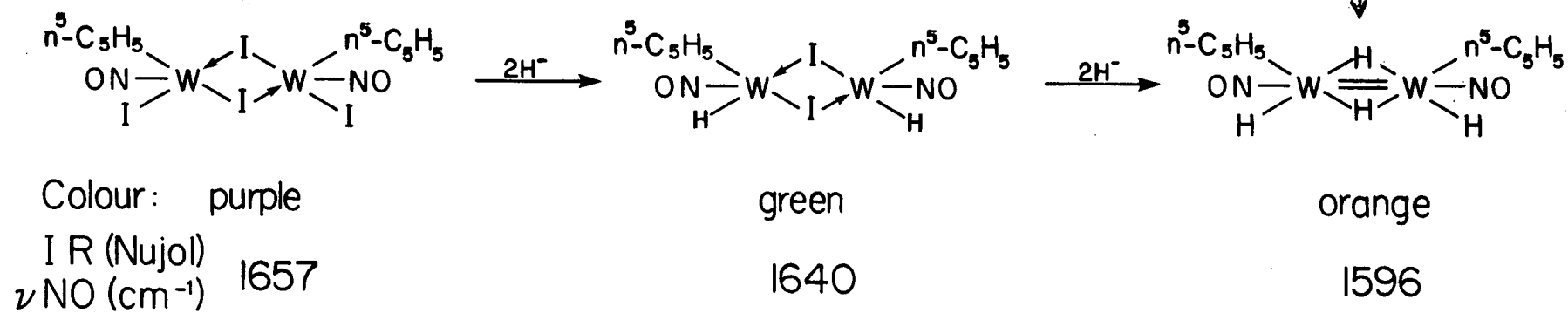
In light of the anomalous hydridic character of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$, it was anticipated that other hydridonitrosyl complexes of tungsten might show similar reactivity. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$, however, is surprisingly inert. Whereas many hydridocarbonyls are Lowry-Brønsted acids in polar solvents¹⁴ reacting with $(\text{CH}_3\text{CH}_2)_3\text{N}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ acts as a H^- source reacting with p-toluenesulfonic acid, $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$ is largely unchanged by exposure to either of these reagents. Although some decomposition occurs, after 24h no shift is observed in the nitrosyl absorption of the infrared spectrum of the reaction solution; and the hydride resonance remains visible in the ^1H NMR spectrum, exhibiting its characteristic hydrogen-phosphorus and hydrogen-tungsten couplings. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ stirred in an acetonitrile solution with the well-known hydride abstractor triphenylcarbenium tetrafluoroborate is converted to the cation $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2(\text{CH}_3\text{CN})]\text{BF}_4$.³⁵ But although $\{(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}[\text{P}(\text{OPh})_3](\text{CH}_3\text{CN})\}\text{BF}_4$ has been shown to be a viable species (vide supra) an acetonitrile solution of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$ and $(\text{C}_6\text{H}_5)_3\text{CBF}_4$ after 24h of stirring shows no shift in its νNO ; and though some precipitate forms, ^1H NMR retains the characteristic hydride pattern.

Reactions with chloroform or carbon tetrachloride are often employed to establish the presence of a metal-hydrogen bond;¹⁴ however, $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ does not react with either halocarbon. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$ is stable for days in chloroform but does react with CCl_4 forming $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{Cl})[\text{P}(\text{OPh})_3]$. But even with excess CCl_4 , after two weeks ^1H NMR monitoring of the reaction reveal that the reaction is incomplete ($t_{1/2} \approx 280$ h). A stoichiometric amount of hydrochloric acid added to a dichloromethane solution of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$ also induces the formation of the chloride as well as an intractable blue precipitate. Again, both the resonance patterns of the hydride and the chloride species are visible in the ^1H NMR spectrum.

Reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})]_2$ with $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$.

The solution colour darkens to brown, a brown precipitate forms, and the nitrosyl absorption in the IR spectrum shifts from $\sim 1640\text{ cm}^{-1}$ to $\sim 1600\text{ cm}^{-1}$ when one equivalent of sodium dihydridobis(2-methoxyethoxy)-aluminate is added to a green toluene or benzene suspension of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})]_2$. Filtration followed by concentration of the filtrate under reduced pressure leads to the precipitation of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ as an orange powder in 16% yield. The reaction sequence shown in Scheme II is the net conversion of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$ into $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ in approximately 10% yield. Direct synthesis of the orange hydride dimer from the iododimer can be effected; however, for optimum yield the aluminum byproduct should be removed after the first equivalent of Red-al has

Scheme II

 $4H^-$ 

produced the green solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})]_2$. Then less than one equivalent (~ 0.6 eq. based on the initial amount of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$) of the alkoxyaluminum hydride yields $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$.

This novel product is a bright orange, diamagnetic solid which is freely soluble in dichloromethane, less soluble in chloroform and benzene, and completely insoluble in hexanes. Its solutions are air sensitive, but the solid itself can be handled in air for short periods of time without noticeable decomposition. An infrared spectrum of a dichloromethane solution of the species exhibits a strong absorption at 1596 cm^{-1} which can probably be assigned to terminal nitrosyl ligands.^{4a,44} Also visible in the infrared spectrum of the Nujol mull of the complex is a band of moderate intensity at 1934 cm^{-1} . This can be attributed to terminally bonded hydrides.

The compound is best formulated as a dimer $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ with a tungsten tungsten double bond since a monomeric formulation would leave the tungsten atom with two electrons less than the favored 18-electron configuration. Its dimeric nature is confirmed by its mass spectrum (at a probe temperature of 120°C) which exhibits peaks attributable to the parent ion and ions corresponding to the sequential loss of ligands. Unfortunately, overlapping of some medium to strong intensity peaks makes unambiguous assignment difficult, especially in light of the polyisotopic nature of tungsten.

The proton NMR spectra recorded both in d^6 -benzene and d -chloroform on 80 and 400 MHz instruments as well as selective decoupling experiments provide further insight as to the structural nature of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$.

Figure 5 shows its proton NMR spectrum in deuteriochloroform. Evident are two large singlets at δ 5.94 (13H) and 5.93 (10H) assignable to cyclopentadienyl protons. In addition there are five other complex resonances at δ 6.98 (2.6H), 6.54 (2H), 1.39 (1H), -2.02 (2.6H) ... and -5.93 (1H) which are attributed to hydride resonances due to the visible tungsten-hydride couplings, which are approximately 94 Hz. Selective decoupling experiments in d-chloroform reveal the manner in which these resonances are related (see Figure 6). Irradiation at the frequency corresponding to δ 6.98 alters only the multiplet at δ -2.02; it becomes a sharp singlet. Likewise, with irradiation at δ -2.02 the multiplet at δ 6.98 becomes a singlet. When decoupling is centered at δ 6.54 the multiplet at δ 1.39 becomes a doublet, while the triplet of doublets (δ -5.93) becomes a simple doublet. Decoupling at δ +1.39 changes the doublet of doublets centered at δ 6.54 into a doublet, and the triplet of doublets (δ -5.93) becomes a triplet. Finally, irradiation at δ -5.93 transforms the pattern at δ 6.54 into a doublet and that at δ 1.39 into a triplet. This study not only facilitates the assigning of coupling constants but also demonstrates that two distinct species, two isomers, exist in the solution.

Careful integration of the peak areas allows pairing of the cyclopentadienyl proton resonances with the hydride groupings. The C_5H_5 resonance at δ 5.94 is grouped with the hydrides resonating at δ 6.98 and -2.02 with the internal ratio 10:2:2 (isomer 1). The C_5H_5 resonance at δ 5.93 is grouped with the hydride resonances at δ 6.54, 1.39, and -5.93

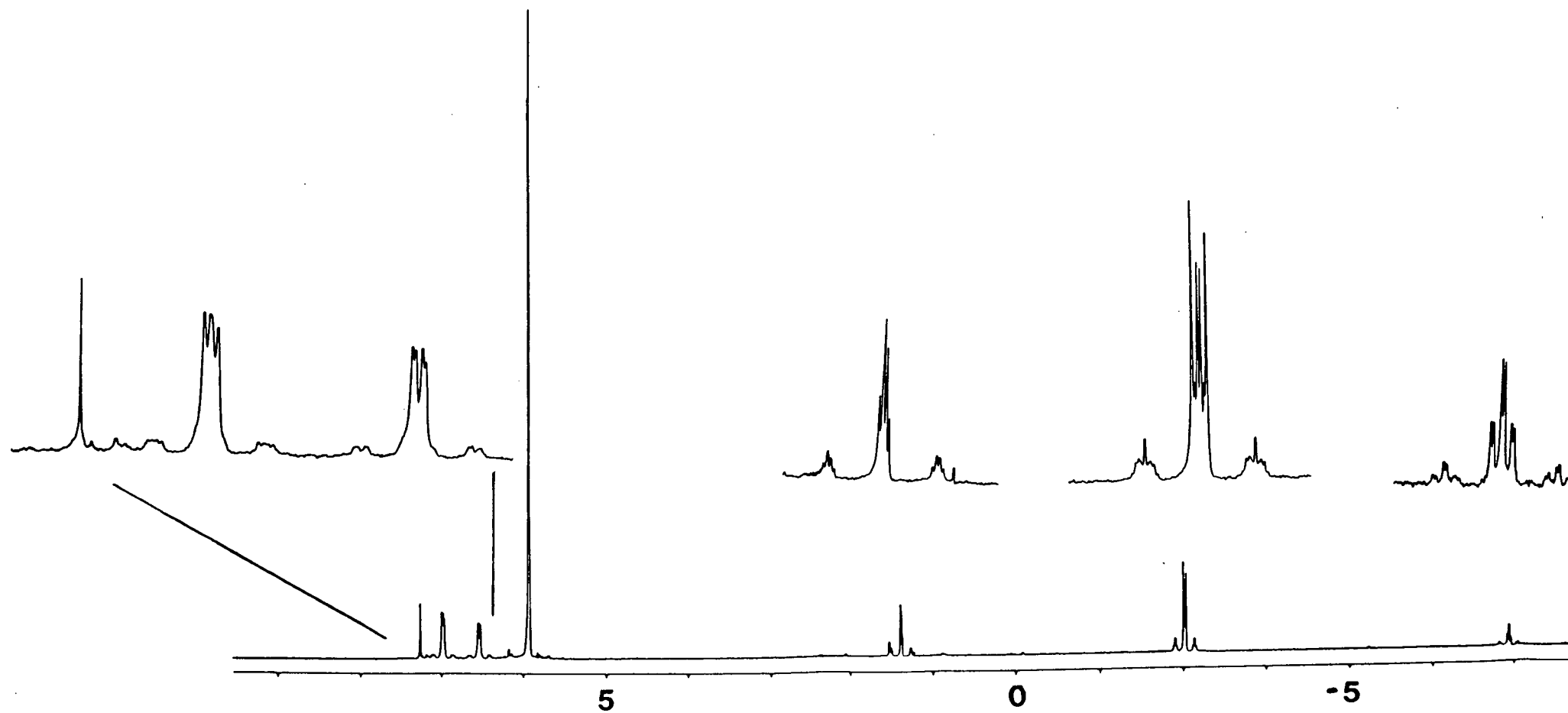


Figure 5. ^1H NMR Spectrum of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ in CDCl_3 (400 MHz).

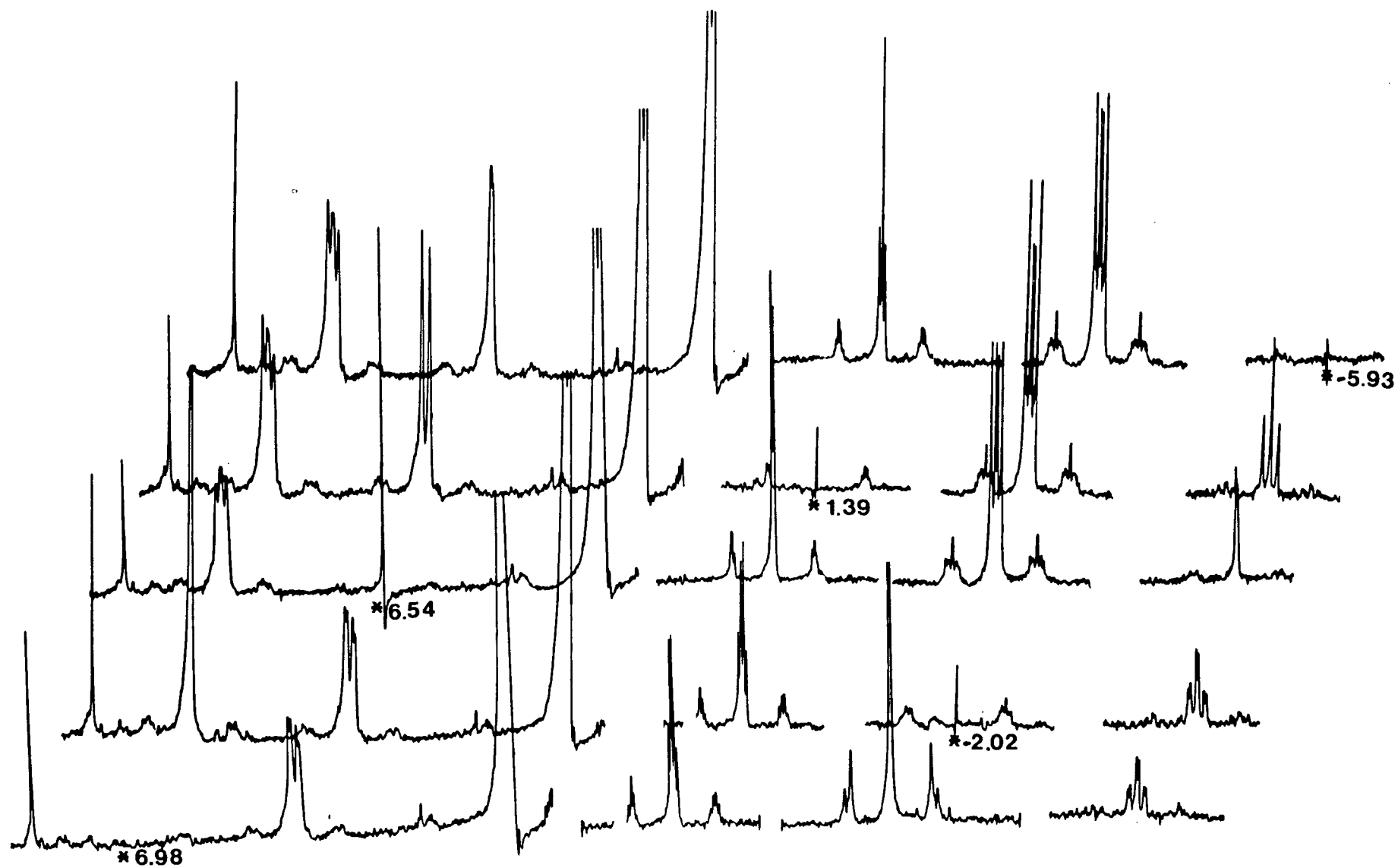


Figure 6. ^1H NMR Spectra of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ at 400 MHz, Decoupling Centred at *

with the internal ratio of this grouping being 10:2:1:1 (isomer 2).

The ratio of isomer 1 to isomer 2 is approximately 1.3 to 1, a ratio which is invariant in d^6 -benzene or d -chloroform.

Detailed analysis of the hydrogen patterns allows speculation as to the conformation of these isomers. The hydride pattern in isomer 1 is an AA'XX pattern. Unfortunately, the pattern is not sufficiently resolved to permit unambiguous assignment of the hydrogen-hydrogen couplings. Isomer 2 displays an A_2MX hydride pattern for which coupling assignments have been made with the aid of computer simulation (see Table II and Figure 7). An important feature of the 1H NMR spectra of both these isomers is the abnormally low field values for the tungsten-hydrogen protons at δ 6.98 (2H) (isomer 1) and δ 6.54 (2H) (isomer 2). The only tungsten complex with a comparably low-field hydride shift is Schrock's recently reported $W(CHCMe_3)HCl_3(PMe_3)_2$ (δ WH = 9.88).^{15a} It has been noted^{14d} that, for derivatives of the same metal, the resonance of the bridging hydrogen in a hydridometal cluster is often evidenced at higher field than that of terminally bonded hydrogen. Darensborg,²³ for example, has observed the hydrogen resonance in $PPN[HW_2(CO)_9P(OMe)_3]$ at δ -12.2 (CD_3CN), a compound assumed on the basis of the similarity of its ν_{CO} in the IR spectrum to that of the well-characterized $\mu H[Mo(CO)_4(PMePh_2)]_2^-$ to have a bridging hydrogen ligand; under similar conditions the terminal hydride of $PPN[HW(CO)_4P(OMe)_3]$ has a chemical shift of δ -4.5. Following this line of reasoning, the lowest field resonance of each isomer, each of which represents two protons, is assigned to terminally bonded hydrogens.

57 Table II. ^1H NMR Spectral Data of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$

	C_5H_5 (δ)	H (δ)	H (δ)	H (δ)
<hr/>				
Isomer 1				
CDCl_3	5.94 (s, 10H)	6.98 (m, 2H)	-2.02 (m, 2H)	
C_6D_6	5.23 (s, 10H)	7.01 (m, 2H)	-1.90 (m, 2H)	
Isomer 2				
		$\text{H}_{1,2}$	H_3	H_4
CDCl_3	5.93 (s, 10H)	6.54 (dd, 2H)	1.39 (m, 1H)	-5.93 (td, 1H)
		($J_{13} = J_{23} = 2.9 \text{ Hz}$)	($J_{34} = 2.3 \text{ Hz}$)	
		($J_{14} = J_{24} = 8.6 \text{ Hz}$)		
C_6D_6	5.26 (s, 10H)	6.64 (dd, 2H)	1.66 (m, 1H)	-5.99 (td, 1H)

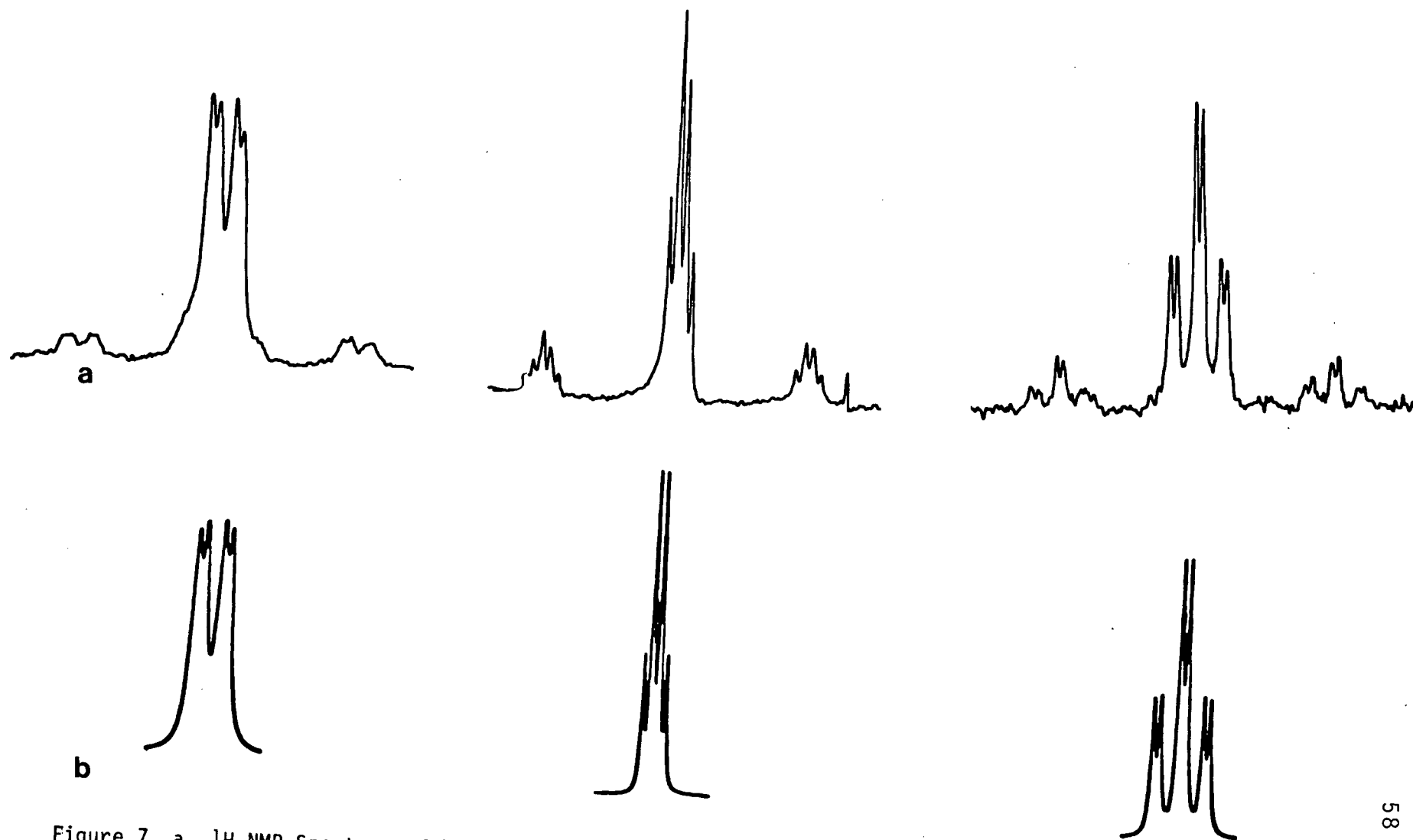
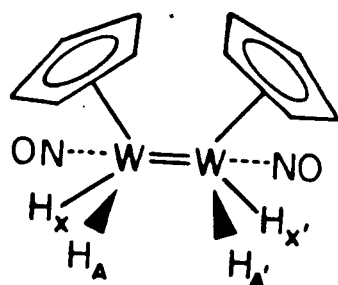


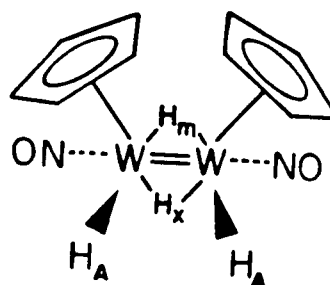
Figure 7. a. ^1H NMR Spectrum of Hydride Resonances of Isomer 2 of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ in CDCl_3 (δ 6.54, 1.39, -5.93, left to right) at 400 MHz.
 b. Computer Simulation of the Hydride Resonances of Isomer 2.

The proton NMR data makes it possible to preclude from consideration totally symmetrical molecular conformations for $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ such as all four hydride or both nitrosyl ligands bridging the two metals or four terminal and mutually trans hydride ligands. In such arrangements all the hydrides would be chemically and magnetically equivalent, and only one hydride resonance would be observed in the proton NMR spectrum; such is not the case. There remains a number of possible structural configurations (see Figure 8): an arrangement in which all the ligands are terminally bonded and the hydride ligands are mutually cis (A); a structure possessing two terminally bound and two bridging hydrogens either perpendicular (B or D) or parallel to the plane of the cyclopentadienyl rings (C or E).

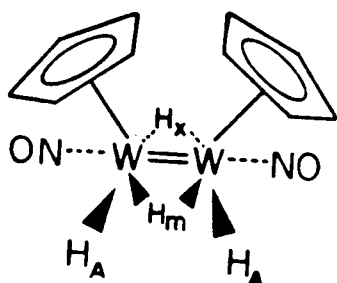
The dominant species in solution, isomer 1, in which the hydride ligands exhibit an AA'XX' pattern in the proton NMR spectrum, may adopt one of the configurations illustrated in Figure 8 by A, D, or E. Although structure A cannot be dismissed totally, one would not expect two terminal hydrides in such an environment to have chemical shifts differing by almost 9 ppm. For example, the hydride resonances of $\text{ReH}_2(\text{NO})(\text{PPh}_3)_3$ overlap to form a multiplet at -1.5; the individual hydrogens are considered to have chemical shifts -0.9 and -2.1.⁶² Therefore, it seems more feasible that isomer 1 assumes the conformation shown in example D or E; the resonance at δ 6.98 would then be assigned to the two terminal hydrides and the one at δ -2.02 to the two bridging ones. The requirement that isomer 2 have a hydride pattern A_2MX can be satisfied by structures B or C. It then follows that the resonance at δ 6.54 can be assigned to the two terminal hydride ligands and the resonances at δ 1.39 and δ -5.93 can each be attributed to



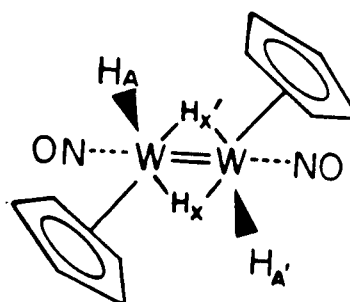
A. For cis or trans Cp rings
AA'XX'



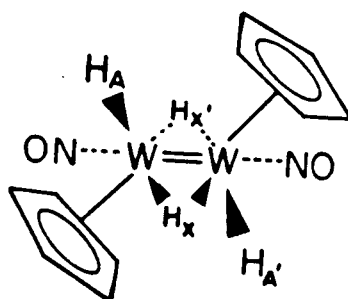
B. For cis Cp rings and cis terminal H
For cis Cp rings and trans terminal H
A₂MX



C. For cis Cp rings and cis terminal H
For trans Cp rings and cis terminal H
A₂MX



D. For trans Cp rings and trans terminal H
For trans Cp rings and cis terminal H
AA'XX'

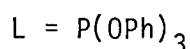
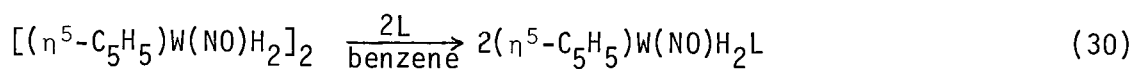


E. For cis Cp rings and trans terminal H
For cis Cp rings and trans terminal H
AA'XX'

one of the inequivalent bridging hydrogens. The infrared spectrum consisting of a single nitrosyl absorption at 1596 cm^{-1} in dichloromethane provides no further clues as to structural nature of these species.

Reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ with $\text{P}(\text{OPh})_3$.

Bis $[(\eta^5\text{-cyclopentadienyl)dihydridonitrosyltungsten}]$ reacts with the Lewis base triphenylphosphite in benzene to form the purple complex $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$ in 32% yield (reaction 30).

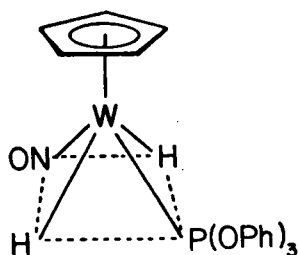


When the product of reaction 30 is isolated by fractional crystallization from a benzene/hexanes mixture, the major component is this purple product. However, when recrystallizations are performed from dichloromethane/hexanes the major product is an orange solid which also has the empirical formulation $(\text{C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$.

Purple $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$ is an air-sensitive, diamagnetic solid which is freely soluble in common organic solvents but only sparingly soluble in paraffin hydrocarbons to give highly air-sensitive intensely purple solutions which turn yellow in minutes upon exposure to air. An infrared spectrum of the solid in a Nujol mull displays a single nitrosyl absorption at 1574 cm^{-1} , but the tungsten-hydride stretching absorptions are not observable. Its mass spectrum shows a peak corresponding to

$[(C_5H_5)W(NO)HP(OPh)_3]^+$ (m/z 590) as well as peaks due to $[(C_5H_5)WP(OPh)_3]^+$ and $[WH_2P(OPh)_3]^+$ clearly identifiable by the correct tungsten isotope pattern.

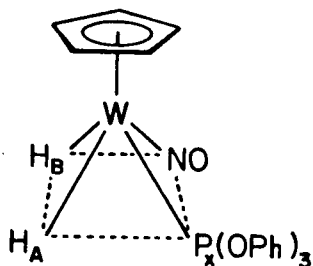
Orange $(\eta^5-C_5H_5)W(NO)H_2[P(OPh)_3]$ is an air-sensitive solid which can be formed from the purple complex with attendant decomposition. Its IR spectrum displays a ν_{NO} absorption at 1601 cm^{-1} (Nujol), slightly higher than its purple analogue. Furthermore, there are weak bands at 1856 and 1831 cm^{-1} which can be assigned as terminally bonded W-H stretching absorptions. However, it is best characterized by its 1H NMR spectrum. The phenyl and cyclopentadienyl protons resonate at a similar frequency to the purple species, δ 7.32 (15H) and 5.10 (5H) (C_6D_6); but the hydride resonances are centered at δ -1.82 (2H) and display the familiar six-line pattern (1:5.9:1, 1:5.9:1) (cf. Figure 2) reflecting coupling to both the tungsten and phosphorus atoms. The $^1J_{H-183W}$ coupling (88 Hz) affirms the tungsten-hydride link while the $^2J_{H-31P}$ coupling (86 Hz) allows the dihydride species to be easily distinguished from its monohydrido-moniodo analogue. Lack of any observable hydride-hydride coupling and the simplicity of the resonance pattern indicate that the two ligands are magnetically as well as chemically equivalent and, therefore, must be trans to each other. The ^{31}P NMR spectrum confirms



the equivalence of the hydride ligands displaying a single resonance, a triplet, only slightly shifted from that of the cis isomer (δ 137 (t), $^2J_{31P-1H} = 87$ Hz).

The designation of the purple form of $[(\eta^5-C_5H_5)W(NO)H_2P(OPh)_3]$ as the cis isomer is based on its 1H NMR spectrum. There are three distinctive patterns in the phenyl region δ 7.54 \rightarrow 7.20 (15H) attributable to the ortho, para, and meta protons of the phenyl rings of triphenylphosphite. In addition there is a sharp singlet at δ 5.10 (5H) assignable to the cyclopentadienyl protons and a complex hydride pattern centred at δ 1.32 (2H) (shown in Figure 9). The spectrum in deuterochloroform is similar, though with less detail in the phenyl region; but in this solvent the cis-dihydride is observed by 1H NMR to rearrange to the trans isomer; with time the multiplet centred at δ 1.10 is lost and the familiar six-line pattern of the trans-dihydride appears at δ -1.82. The same rearrangement occurs to some degree in benzene, but in this case it takes a matter of days instead of hours. The proton coupled ^{31}P NMR spectrum is a triplet centred at δ 151 (relative to H_3PO_4); average $^2J_{31P-1H} = 24$ Hz. This phosphorus chemical shift has the expected downfield⁶⁰ shift from the free triphenylphosphite (δ 126).⁴⁰

The complex hydride resonance pattern is invariant on an 80 or 400 MHz NMR instrument. For the cis structure an ABX pattern would be expected. In an ABX spectrum the AB portion may be divided into two



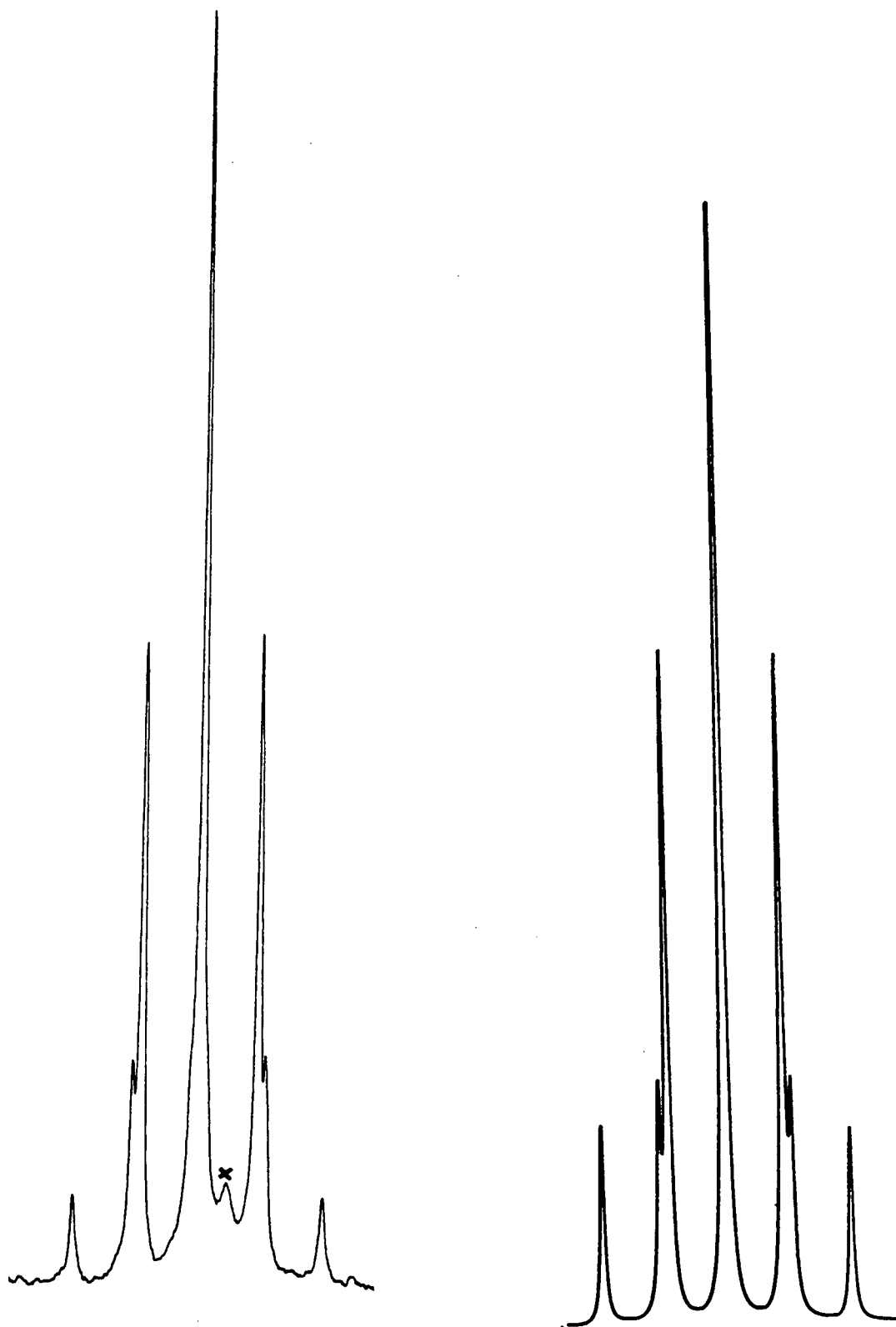


Figure 9. (left) ^1H NMR Spectrum (400 MHz) of Hydride Region of $\text{cis}-(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$ in C_6D_6
(right) Computer Simulation of Hydride Region

AB-type quartets.⁵⁴ In this case there is an overlap of the two quartets which produces the observed seven-line pattern. From the analysis of the spacing of these quartets and computer simulation (Figure 9), the best fit designates the chemical shifts of H_A and H_B as coincidental (δ 1.32 C_6D_6) and assigns the couplings $^2J_{H_A-H_B} = 27.7$ Hz, $^2J_{H_AP_X} = 67.5$, and $^2J_{H_BP_X} = -19.5$. Thus, the $^2J_{1H-31P}$ observed in the coupled ^{31}P NMR spectrum is an average $\frac{1}{2}(^2J_{P_XH_A} + ^2J_{P_XH_B}) = 24$ Hz. (Note that the signs of the phosphorus-hydrogen couplings are only relative to each other and do not represent an absolute assignment.) The hydride ligand trans to the phosphite is assigned the smaller coupling constant (-19.5 Hz) based on the analogy to the $(\eta^5-C_5H_5)M(CO)_2HL$ system^{16,58,59} (vide supra). The large hydrogen-hydrogen coupling is an anomaly, but this assignment appears to be the only reasonable one.

When reaction 30 is performed using $L = P(OCH_3)_3$, the orange solution of $[(\eta^5-C_5H_5)W(NO)H_2]_2$ darkens to a red-violet colour upon addition of the phosphite. However, if the solvent is not removed in vacuo within 90 min., the solution colour begins to lighten until it is yellow-orange. The 1H NMR spectrum of the reaction mixture indicates that trans- $(\eta^5-C_5H_5)W(NO)H_2P(OCH_3)_3$ is formed: (C_6D_6) δ 5.63 (s, 5H, C_5H_5), δ 3.63 ($P(OCH_3)_3$), -1.90 (2H, W-H) [$^2J_{1H-31P} = 81$ Hz, $^1J_{1H-183W} = 81$ Hz]. Again, as in the case with $(\eta^5-C_5H_5)W(NO)IHL$, a decrease in $^2J_{1H-31P}$ is seen with a change in L from $P(OPh)_3$ to $P(OCH_3)_3$. The same correlation is also observed in the infrared spectrum — ν_{NO} moving down from 1601 cm^{-1} (Nujol) in

trans-($\eta^5\text{-C}_5\text{H}_5$)W(NO)H₂P(OPh)₃ to 1564 cm⁻¹ in trans-($\eta^5\text{-C}_5\text{H}_5$)W(NO)H₂-P(OCH₃)₃. The mass spectrum of the latter confirms its formulation; at probe temperature 120°C two groupings of peaks are seen with the characteristic tungsten isotope pattern: one at 403 corresponding to [(C_5H_5)W(NO)P(OCH₃)₃]⁺, (P)⁺, and one at 372 corresponding to (P-NO)⁺. Attempts to isolate this dihydride as a pure solid have so far been frustrated by the large amount of attendant decomposition in this reaction. Yields of product are estimated to be less than 10% of that isolated when L = P(OPh)₃. It appears that when L is trimethylphosphite the purple isomer is much shorter lived and converts readily to the orange isomer trans-($\eta^5\text{-C}_5\text{H}_5$)W(NO)H₂L.

The Nature of the cis-trans Isomerism

Detailed ¹H NMR studies of the cis-trans conversions of complexes of the general form ($\eta^5\text{-C}_5\text{H}_5$)Mo(CO)₂LR (where L is a phosphine or phosphite and R is hydrogen, halogen, benzyl, or methyl) have been discussed by Faller⁵⁸ and by Poilblanc.⁵⁹ Both conclude that the isomerization is an intramolecular exchange phenomenon occurring via angle bending, not by ligand dissociation. The purple-orange conversion differs markedly from the reported systems. Kinetic Consideration: Faller observes that the rates of isomerization vary less than 25% from solvent to solvent. In the ($\eta^5\text{-C}_5\text{H}_5$)W(NO)H₂[P(OPh)₃] case a dramatic difference in rate is observed—the purple→orange conversion taking place in days in benzene and in hours in dichloromethane. However, decomposition is detected in both these sol-

vents occurring more slowly in benzene than in dichloromethane. Free phosphite is observed in aged solutions. It is possible that ligand dissociation is one pathway to this isomerization. Triethylamine promotes the formation of the orange isomer within an hour, albeit with some decomposition (*vide infra*). Thermodynamic Considerations: Poilblanc observes that the *cis* carbonyl compounds are thermodynamically more stable than the *trans*. This means in the case of $\text{CpM}(\text{CO})_2\text{HL}$ that *cis* hydride/phosphorus geometry is favored. The ^1H NMR spectra of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{-H}_2[\text{P}(\text{OPh})_3]$ make evident that the isomer with *trans* hydride ligands is the one favored thermodynamically, for the transformation from the purple (*cis*) to the orange (*trans*) isomer occurs in a matter of hours in any polar solvent and in a matter of days in benzene. This *trans* arrangement of the hydrides allows both to remain *cis* to the phosphorus atom, a requirement which is evidently more important for the hydride ligands than for the carbonyl ligands in $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{LR}$.^{58,59} This *cis* arrangement of the hydrogen and phosphorus atoms is the only one observed in the monohydrido compounds $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{L}$ (*vide supra*). It appears that a primary structural constraint is that the hydride ligand is not *trans* to another strong *trans* effect ligand such as phosphine or phosphite.

Reactivity of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$.

The principal mode of reaction of *cis*- $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$ is rearrangement, forming a mixture of the *cis* and *trans* isomers in a matter of hours in chloroform, dichloromethane,

or tetrahydrofuran solutions. Due to the intense purple colour of the cis isomer, no change in solution colour can be noted until most of the species is trans. The cis/trans mixture can be totally converted to the trans isomer by exposure to $(\text{CH}_3\text{CH}_2)_3\text{N}$ for 1 hour as evidenced by a colour change in the dichloromethane solution from purple to orange, a loss of the cis hydride pattern in the ^1H NMR spectrum and the appearance of the trans hydride resonance pattern. No further reaction with triethylamine is evident.

Addition of p-toluenesulfonic acid to a THF solution of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{-H}_2[\text{P}(\text{OPh})_3]$ results in an immediate colour change in the solution from purple to green-brown. Most of the nitrosyl-containing species precipitates out of solution as an intractable green solid (determined by an IR spectrum of a Nujol mull of this solid). No hydride resonance can be observed in the ^1H NMR of the supernatant.

A purple acetonitrile solution of cis and trans $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$ immediately takes on an orange-brown colour when the hydride abstractor triphenylcarbenium tetrafluoroborate is added to it. The principal features of the ^1H NMR spectrum of the reaction solution are a hydride pattern centred around δ -1.99 (1H) with $^3J_{\text{H-31P}} = 112$ Hz and cyclopentadienyl resonances at δ 5.29 (5H) and 5.56 (12H). This suggests the presence of two species — a new hydride-containing species possibly a monohydride such as $\{(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}[\text{P}(\text{OPh})_3](\text{CH}_3\text{CN})\}\text{BF}_4$ (cf. $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}[\text{P}(\text{OPh})_3]$ with hydride resonance at δ -1.98 and $^2J_{\text{H-31P}} = 112$ Hz) and a non-hydride-containing species.

Prolonged exposure of $\text{trans}-(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$ to carbon tetrachloride results in the formation of a new hydrido-containing species. Although the doublet of the original $(\eta^5\text{-C}_5\text{H}_5)^{184}\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$ is still visible in the ^1H NMR spectrum at δ -1.28 and -2.35 [$^2J_{\text{H-}^{31}\text{P}} = 86$ Hz], a new doublet which overlaps with the original one grows in at δ -1.28 and -2.70 ($^2J_{\text{H-}^{31}\text{P}} = 113$ Hz). It is possible this is evidence of the formation of $(\eta^5\text{-C}_5\text{H}_5)^{184}\text{W}(\text{NO})\text{Cl}(\text{H})[\text{P}(\text{OPh})_3]$ (cf. hydride pattern of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$ — δ -1.98, $^2J_{\text{H-}^{31}\text{P}} = 112$ Hz). The appearance of new cyclopentadienyl proton resonances in the ^1H NMR spectrum indicate new non-hydride-containing complexes are also formed.

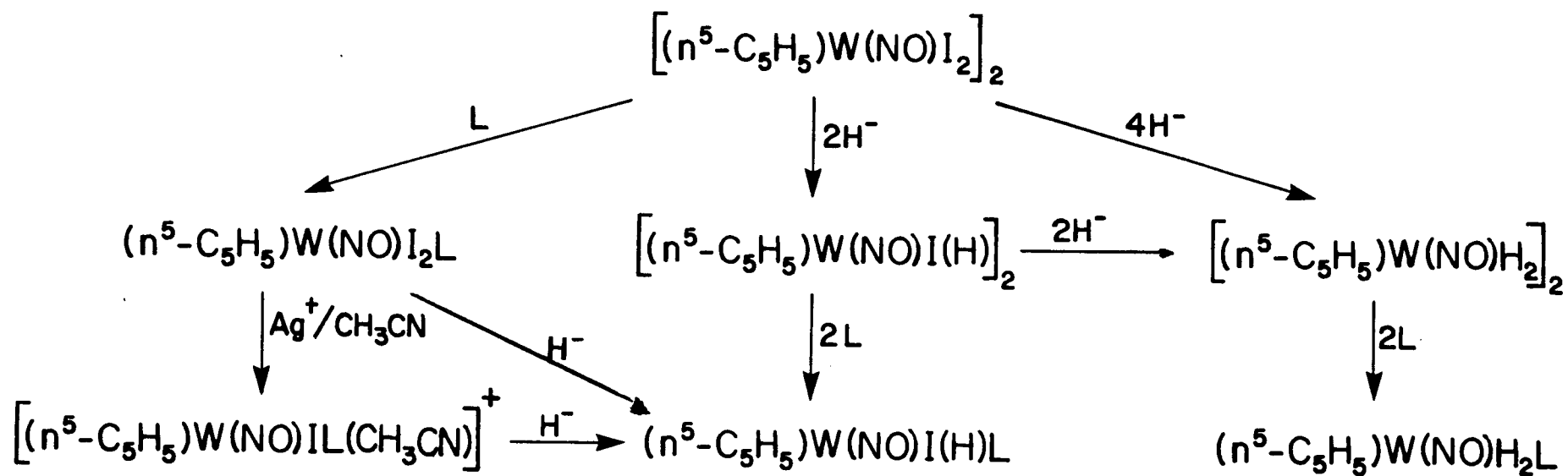
Thus $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2[\text{P}(\text{OPh})_3]$ undergoes the most common of typical hydride reactions — reaction with halocarbons and hydride abstraction by triphenylcarbenium. But like $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ it acts as a H^- source interacting with the acidic reactant, *p*-toluenesulfonic acid, rather than the basic one triethylamine. Overall, it is much more reactive than $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})[\text{P}(\text{OPh})_3]$. To facilitate further study of this unique nitrosyl dihydride it would be desirable to improve the yield from the basic starting material $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}_2]_2$ which is unoptimized at 3.2%. Nevertheless, it appears reaction 30 represents a general route for the series of complexes of the type $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2\text{L}$ where L is a two-electron donor.

In comparing the reactivity of the three hydrido nitrosyl species $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{L}$, $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{NO})\text{H}$, and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{HHL}$ (where L = $\text{P}(\text{OPh})_3$), the inertness of the iodohydride is striking. It may be that the

halogen ligand provides a certain stability to the tungsten-hydrogen link due to its ability both to donate electrons, as a π donor, and to withdraw electrons by its inductive effect. The influence of the halogen deserves further study. The reactivities of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2\text{L}$ are similar — both appear to act as a source of H^- . However, one would hesitate to draw a conclusion about the general effects of the nitrosyl ligand until other metal centres have been employed.

Successful syntheses of organometallic nitrosyl hydrides by metathesis of the corresponding halides with a hydridoaluminate reagent opens the door to a great number of nitrosyl hydride complexes. The preparation in this manner of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ in 61% yield, of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}]_2$ in 61% yield, and of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{I}(\text{H})\text{L}$ ($\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3, \text{P}(\text{OPh})_3$) in ~43% yield is promising. The low yield obtained in the preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{IH}[\text{P}(\text{OPh})_3]$ (34%) by metathesis of the diiodo monomer and in the preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})\text{H}_2]_2$ (16%) notwithstanding, metathesis by $\text{Na}[\text{H}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ appears to be the method of choice. In short, the hydrido complexes, the syntheses of which are summarized in Scheme III, embody the first such group of organometallic nitrosyl hydrides available for systematic studies.

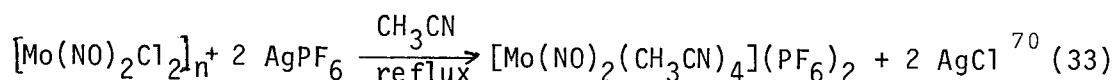
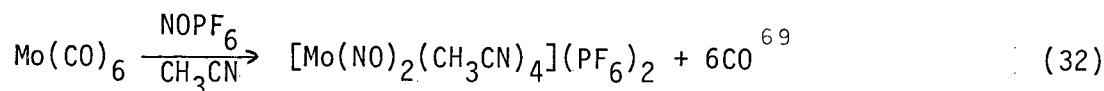
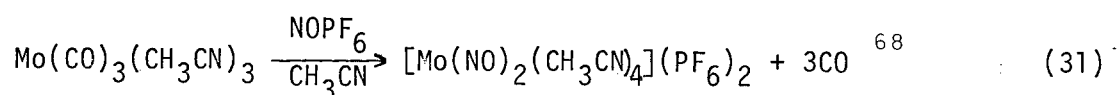
Scheme III



Part II

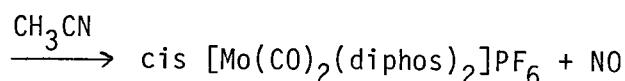
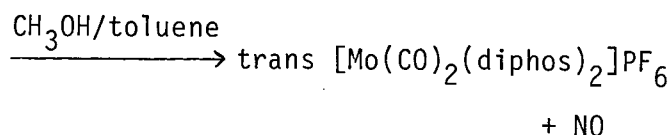
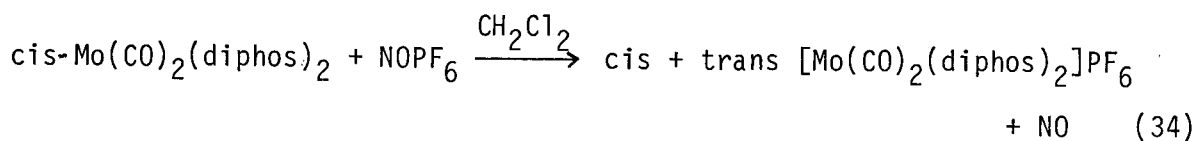
A. Cationic Nitrosyl Complexes of Molybdenum

The nitrosyl ligand is generally acknowledged to be a better π acceptor than CO.⁶³ Yet, though a great many anionic carbonyl species exist,³ attempts by this group to prepare anionic nitrosyl complexes have been repeatedly frustrated. This dilemma suggested the desirability of investigating the redox properties of a simple metal nitrosyl. However, binary nitrosyls $M_x(NO)_y$, unlike simple carbonyls, $M_x(CO)_y$, are unstable compounds. Of the few reported, i.e., $Co(NO)_3$,⁶⁴ $Cr(NO)_4$,⁶⁵ $Fe(NO)_4$,⁶⁶ $Ru(NO)_4$,⁶⁷ only the former two have been well-characterized. Although simple neutral nitrosyl complexes are a rarity, it has been known for some time that solvated derivatives of the $[M(NO)_2]^{2+}$ cations where $M = Cr, Mo, \text{ or } W$ may be synthesized by reactions such as

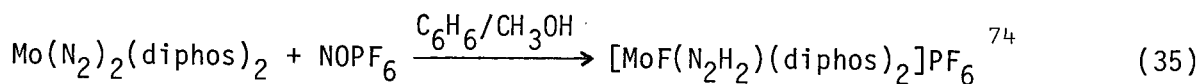


Thus, binary nitrosyl cations being more readily attainable, a study was initiated to investigate the fundamental moiety " $Mo(NO)_2^{2+}$ ".

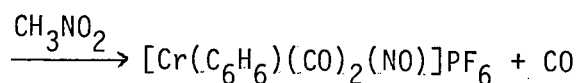
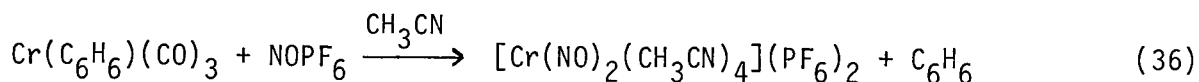
Choice of solvent can have a profound effect on the outcome of reactions involving NOPF_6 . The stereochemistry of the product may vary from solvent to solvent:⁷¹



Protonation sometimes occurs when the solvent system is toluene/methanol due to the equilibrium:^{72, 73} $\text{CH}_3\text{OH} + \text{NO}^+ \rightleftharpoons \text{CH}_3\text{ONO} + \text{H}^+$, for example



As has already been demonstrated a solvent which is a good donor may become attached to the metal centre.⁷⁵



Consequently, it was expected that transformations of types 32' and 33 when effected in solvents of poor coordinating and good solvating abilities⁷⁶ would afford the desired binary nitrosyl cations.

Herein is reported the successful synthesis of the $[\text{Mo}(\text{NO})_2]^{2+}$ cation and described in detail is its characteristic chemistry which provides some insight concerning:

- (a) the Lewis acid properties of the binary nitrosyl cations and how they are modified by the presence of ancillary ligands, and
- (b) the feasibility of forming neutral nitrosyl complexes by reduction of $\text{M}(\text{NO})_2^{2+}$ -containing compounds.

Experimental

All experimental procedures described here were performed under the same general conditions outlined in Part I with the exception that ^{31}P NMR spectra were recorded at 32.3 MHz on a Bruker WP-80 spectrometer using ^{2}D as the internal lock. Chemical shifts were referenced to external NaPF_6 (δ -144. (CD $_3$ CN)) upfield of H_3PO_4) but are reported in ppm upfield from H_3PO_4 . All samples were prepared in a dry box using dry deoxygenated deuteroacetonitrile and sealed in 10 mL tubes. Low-temperature ^1H NMR spectra were obtained on a Bruker WP-80 spectrometer equipped with a Bruker B-VT-1000 probe. The conductivities of solutions of various complexes were measured at ambient temperature with a YSI Model 31 conductivity bridge and a micro solution cell with platinized electrodes. The cell was calibrated with a $9.49 \times 10^{-4} \text{ M}$ nitromethane solution of Et_4NBr ; it had a cell constant of 1.08 cm^{-1} . The specific conductance of the nitromethane employed was $4.3 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$. EPR spectra of $\sim 10^{-3} \text{ M}$ nitromethane solutions were recorded on a Varian E-3 spectrometer at ambient temperature.

Reactions of $\text{Mo}(\text{CO})_6$ with NOPF_6 . (a) In CH_2Cl_2 (Procedure A).

To a rapidly stirred, colourless solution of $\text{Mo}(\text{CO})_6$ (3.02 g, 11.4 mmol) in CH_2Cl_2 (140 mL) was added solid NOPF_6 (2.00 g, 11.4 mmol), whereupon gas evolution occurred, and the mixture developed a yellow-brown colouration. After 40 h, the final reaction mixture consisted of a green solid and a green solution whose IR spectrum displayed two weak

nitrosyl absorptions at ~ 1815 and ~ 1685 (br) cm^{-1} in addition to the strong $\nu(\text{CO})$ at ~ 1980 cm^{-1} characteristic of $\text{Mo}(\text{CO})_6$. The solid was collected by filtration, washed with CH_2Cl_2 (3×20 mL), and dried in vacuo (5×10^{-3} mm) for 1 h to obtain 1.23 g (48.4% yield based on NO) of $\text{Mo}(\text{NO})_2(\text{PF}_6)_2$. [Unreacted $\text{Mo}(\text{CO})_6$ (1.60 g) could be recovered by sublimation (60°C , 5×10^{-3} mm) of the residue remaining after the filtrate had been taken to dryness under reduced pressure.]

Anal. Calcd for $\text{MoN}_2\text{O}_2\text{P}_2\text{F}_{12}$: C, 0.00; H, 0.00; N, 6.28; Mo, 21.52. Found: C, 0.76; H, 0.54; N, 6.32; Mo, 23.0. IR (Nujol mull): $\nu(\text{NO})$ 1811 (s), 1683 (s, br) cm^{-1} ; also 1265 (m, br), 1154 (m), 948 (m, br), 885 (m, br), 843 (m, br) 565 (s) cm^{-1} . ^{19}F NMR (CD_3CN): δ 72.0 (d, $^1\text{J}_{19\text{F}-31\text{P}} = 707$ Hz). ^{31}P NMR (CD_3CN): δ -144 (sept., $^1\text{J}_{31\text{P}-19\text{F}} = 707$ Hz). Mp: 110°C dec.

The analytical data presented above are representative. Some preparations of this complex, however, afforded materials having slightly higher carbon and hydrogen contents. Nevertheless, the following modifications of the given experimental procedure did not alter the basic nature of the isolated product: (a) sealing the reaction vessel under N_2 , (b) bubbling NO continuously through the reaction mixture, or (c) refluxing the initial reaction mixture for 2 - 6 h either under an N_2 or NO atmosphere.

If rigorously anhydrous conditions were not maintained the isolated green solid had the following properties.

Anal. Calcd for $\text{MoN}_2\text{O}_6\text{P}_2\text{F}_4$: C, 0.00; H, 0.00; N, 7.82. Found C, 0.64; H, 0.36; N, 8.02. IR (Nujol mull): $\nu(\text{NO})$ 1821 (s), 1693 (s, br) cm^{-1} ; also 1265 (m, br), 1163 (m), 955 (m), 901 (m), and 569 (m) cm^{-1} .

^{19}F NMR (CD_3CN): δ 81.7 (d, $J_{^{19}\text{F}-^{31}\text{P}} = 957$ Hz). ^{31}P NMR (CD_3CN): δ -17.9 (t, $J_{^{31}\text{P}-^{19}\text{F}} = 957$ Hz). Mp: $>220^\circ$.

(b) In CH_3NO_2 (Procedure B). To a stirred suspension of $\text{Mo}(\text{CO})_6$ (1.50 g, 5.68 mmol) in CH_3NO_2 (10 mL) was added dropwise a solution of NOPF_6 (2.00 g, 11.4 mmol) in CH_3NO_2 (10 mL) over a period of 0.5 h. Gas evolution occurred throughout. When one-half of the NOPF_6 solution had been added, the supernatant solution was red-brown in colour and its IR spectrum displayed a number of absorptions in the carbonyl (~ 2185 (w), ~ 2100 (s), ~ 1980 (s) cm^{-1}) and nitrosyl (~ 1830 (m), ~ 1815 (m), ~ 1780 (m), ~ 1710 (s, br), ~ 1690 (s) cm^{-1}) regions. When the addition of NOPF_6 was complete, the carbonyl reactant had dissolved and the reaction mixture consisted of a green solution. The IR spectrum of this solution verified that all the $\text{Mo}(\text{CO})_6$ had been consumed (i.e. the absorbance at 1980 cm^{-1} was absent) and revealed three new bands at ~ 1880 (w), ~ 1850 (s, br), and ~ 1745 (s) cm^{-1} in addition to the other absorptions noted above. The green solution was stirred for an additional 2.5 h, whereupon its final IR spectrum exhibited only two strong νNO at ~ 1860 and ~ 1750 cm^{-1} . The solution was then concentrated to one-half of its original volume in vacuo before being treated dropwise with CH_2Cl_2 (40 mL) to induce the precipitation of a green solid. The solid was collected by filtration, washed with CH_2Cl_2 (3 x 20 mL) and dried in a stream of dinitrogen for 0.5 h to obtain 2.41 g (61% yield) of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$.

Anal. Calcd for $\text{MoN}_6\text{O}_{10}\text{C}_4\text{H}_{12}\text{P}_2\text{F}_{12}$: C, 6.96; H, 1.74; N, 12.17. Found: C, 7.43; H, 1.77; N, 11.70. IR (Nujol mull): $\nu(\text{NO})$ 1853 (s), 1743 (s, br) cm^{-1} ; also 1570 (s), 1316 (s), 1162 (w), 1103 (m), 843 (s, br), 741 (m), 673 (m) cm^{-1} , ^1H NMR (CD_3CN): δ 4.34 (s). ^{19}F NMR (CD_3CN): δ 72.0

(d, $J_{19F-31P} = 706$ Hz). ^{31}P NMR (CD_3CN): δ -144 (sept $J_{31P-19F} = 706$ Hz). Λ_m (CH_3NO_2): $202 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Mp: 88°C dec.

As with Procedure A, the analytical data presented above are representative. Different preparations of this complex afforded materials having slightly different C, H and N contents, a feature which reflected the varying amounts of CH_3NO_2 present. For instance, attempts to dry the isolated solids in vacuo (5×10^{-3} mm) produced complexes containing less CH_3NO_2 than indicated above.

Materials similar to those described above precipitated when the original reaction was performed in a mixed solvent system using $NOPF_6$ in CH_3NO_2 (10 mL) and $Mo(CO)_6$ suspended in CH_2Cl_2 (50 mL).

Reactions of $[Mo(NO)_2Cl_2]_n$ with $AgBF_4$. (a) In CH_3NO_2 (Procedure C).

To a stirred green suspension of partially dissolved $[Mo(NO)_2Cl_2]_n^{7.7}$ (0.50 g, 2.2 mmol) in CH_3NO_2 (20 mL) was added solid $AgBF_4$ (0.86 g, 4.4 mmol). Gradually, the solution intensified in colour and a flocculent white precipitate formed. Monitoring of the progress of the conversion by IR spectroscopy of the supernatant solution revealed the disappearance of the ν_{NO} 's characteristic of the nitrosyl reactant at ~ 1805 and $\sim 1695 \text{ cm}^{-1}$ and the concomitant growth of new absorptions at ~ 1860 and $\sim 1750 \text{ cm}^{-1}$. After 2h, the precipitated $AgCl$ was removed by filtration, and the green solution of $[Mo(NO)_2(CH_3NO_2)_4](BF_4)_2$ thus generated was used directly in subsequent reactions.

(b) In THF (Procedure D). A bright green THF solution of $[\text{Mo}(\text{NO})_2(\text{THF})_4](\text{BF}_4)_2$ was generated in a manner analogous to that described in the preceding paragraph. During this transformation in THF, however, the nitrosyl absorptions displayed by the supernatant solution remained invariant at ~ 1795 and $\sim 1675 \text{ cm}^{-1}$.

Preparation of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$. A sample of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ (0.45 g, $\sim 0.65 \text{ mmol}$) prepared by Procedure B was dissolved in CH_3CN (20 mL), and the resulting green solution was stirred at ambient temperature for 40 h. At the end of this time, the volume of the solution was reduced to 10 mL under reduced pressure, and CH_2Cl_2 (50 mL) was added. Cooling of the resulting solution to -78°C for 2 h induced the crystallization of 0.28 g ($\sim 70\%$ yield) of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2^{68}$ as bright green crystals which were collected by filtration.

Anal. Calcd for $\text{MoN}_6\text{O}_2\text{C}_8\text{H}_{12}\text{P}_2\text{F}_{12}$: C, 15.75; H, 1.98; N, 13.77; Mo, 15.73. Found: C, 15.83; H, 1.93; N, 13.59; Mo, 15.41. IR (Nujol mull): $\nu(\text{NO})$ 1863 (s), 1754 (s, br) cm^{-1} ; also 2333 (m), 2305 (m), 844 (s, br) cm^{-1} . Mp: 95°C dec..

$\text{Mo}(\text{NO})_2(\text{PF}_6)_2$ (prepared by Procedure A) afforded the same product in comparable yield when subjected to the identical experimental procedure.

Preparation of $[\text{Mo}(\text{NO})_2(\text{bipy})_2](\text{PF}_6)_2$. To a bright green solution of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ (1.00 g, $\sim 2.24 \text{ mmol}$, prepared by Procedure B) in CH_3NO_2 (15 mL) was added a quantity (0.70 g, 4.5 mmol) of solid 2,2'-bipy-

ridine (bipy, $C_{10}H_8N_2$). The resulting solution was stirred for 18 h whereupon it became darker green in colour. IR monitoring of the reaction in the nitrosyl region of the spectrum revealed the gradual replacement of the absorptions due to the reactant by four strong, lower energy bands at ~ 1825 , ~ 1800 (br), ~ 1725 and ~ 1685 (br) cm^{-1} . Volatiles were removed from the final solution in vacuo, and the remaining green oil was dissolved in CH_3CN (4 mL). Dropwise addition of CH_2Cl_2 (40 mL) to the CH_3CN solution caused the precipitation of $[Mo(NO)_2(bipy)_2](PF_6)_2$ as a green solid (0.47 g, $\sim 28\%$ yield) which was collected by filtration, washed with CH_2Cl_2 (2 x 8 mL), and dried at 5×10^{-3} mm.

Anal. Calcd for $MoN_6O_2C_{20}H_{16}P_2F_{12}$: C, 31.66; H, 2.11; N, 11.08. Found: C, 31.59; H, 2.00; N, 11.08. IR (Nujol mull): $\nu(NO)$ 1816 (s), 1716 (s, br) cm^{-1} ; also 1603 (m), 1497 (w), 1321 (m), 881 (m), 840 (s, br), 765 (s), 730 (m) cm^{-1} . IR (CH_3NO_2): $\nu(NO)$ 1825 (s), 1726 (s) cm^{-1} ; also 878 (w), 849 (s) cm^{-1} . IR (CH_3CN): $\nu(NO)$ 1824 (s), 1724 (s) cm^{-1} ; also 1605 (m), 1500 (w), 1323 (m), 880 (m), 847 (s), 752 (m), 733 (w) cm^{-1} . 1H NMR (CD_3CN): δ 7.5 - 9.2 (m). ^{19}F NMR (CD_3CN): δ 71.3 (d, $J_{19F-31P} = 707$ Hz). ^{31}P NMR (CD_3CN): δ -144 (sept., $J_{31P-19F} = 707$ Hz). Mp: $182^\circ C$: dec.

Preparation of $[Mo(NO)_2(bipy)_2](BF_4)_2 \cdot 0.75 CH_2Cl_2$. To a stirred, bright green THF solution (20 mL) of $[Mo(NO)_2(THF)_4](BF_4)_2$ (~ 2.2 mmol, generated by Procedure D) was added dropwise a colourless THF solution (10 mL) of bipyridine (bipy, $C_{10}H_8N_2$; 0.69 g, 4.4 mmol). As the addition proceeded, the solution darkened to a green-black colour, and a black precipitate

formed. Solvent was removed from the final reaction mixture under reduced pressure, and the remaining green-black tar was extracted with CH_3NO_2 (20 mL) to obtain a deep green solution whose IR spectrum exhibited absorptions at ~ 1830 (s), ~ 1795 (s), ~ 1725 (s), and ~ 1690 (m) cm^{-1} attributable to nitrosyl groups. The extracts were taken to dryness in vacuo, and the resulting green oil was crystallized by dissolution in CH_3CN (3 mL) and the dropwise addition of CH_2Cl_2 (25 mL). In this manner, 0.54 g (38% yield) of analytically pure $[\text{Mo}(\text{NO})_2(\text{bipy})_2](\text{BF}_4)_2 \cdot \sim 0.75 \text{ CH}_2\text{Cl}_2$ were obtained as a green solid.

Anal. Calcd for $\text{MoN}_6\text{O}_{20}\text{C}_{20.75}\text{H}_{17.5}\text{B}_2\text{F}_8\text{Cl}_{1.5}$: C, 35.28; H, 2.48; N, 11.90. Found: C, 35.39; H, 2.67; N, 11.92. IR (Nujol mull): $\nu(\text{NO})$ 1816 (s), 1707 (s, br) cm^{-1} ; also 1603 (m), 1503 (w), 1329 (w), 1057 (s, br), 775 (m), 737 (m) cm^{-1} . IR (CH_3NO_2): $\nu(\text{NO})$ 1828 (s), 1727 (s) cm^{-1} ; also 771 (m), 733 (m) cm^{-1} . IR (CH_3CN): $\nu(\text{NO})$ 1828 (s), 1727 (s) cm^{-1} ; also 1606 (m), 1059 (s), 750 (m), 731 (w) cm^{-1} . ^1H NMR (CD_3CN) δ 7.5 - 9.2 (m, 16H), 5.44 (s, 1.6 H). Mp: 194°C dec. $\Lambda_m(\text{CH}_3\text{NO}_2)$: $191 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

The analogous reaction between $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{BF}_4)_2$ (generated by Procedure C) and bipyridine in CH_3NO_2 afforded the same product in comparable yield.

Preparation of $[\text{Mo}(\text{NO})_2(\text{diphos})_2](\text{PF}_6)_2$. A stirred, green suspension of $\text{Mo}(\text{NO})_2(\text{PF}_6)_2$ (0.60 g, 1.35 mmol; prepared by Procedure A) in CH_2Cl_2 (20 mL) was treated with solid $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ⁷⁸ (diphos, 1.07 g, 2.69 mmol), whereupon the supernatant solution became slightly darker green in colour.

The reaction mixture was refluxed for 18 h and then stirred at ambient temperature for 14 days until all visible traces of the nitrosyl reactant had disappeared. The final red-brown solution (displaying ν_{NO} 's at ~ 1800 and $\sim 1675 \text{ cm}^{-1}$ in its IR spectrum) was taken to dryness in vacuo, and the remaining brown oil was washed with benzene (3 x 20 mL). The oil was then dissolved in CH_2Cl_2 (10 mL) and transferred by syringe to the top of a silica gel column (2.5 x 6 cm) made up in CH_2Cl_2 . Elution of the column with CH_2Cl_2 produced a brown band which was removed and collected. The volume of the eluate was reduced in vacuo to ~ 10 mL, and benzene (45 mL) was added dropwise to induce the precipitation of a brown powder. This powder was collected and dried in the customary manner (vide supra) to obtain 0.8 g (48% yield based on Mo) of $[\text{Mo}(\text{NO})_2(\text{diphos})_2](\text{PF}_6)_2$.

Anal. Calcd for $\text{MoN}_2\text{O}_2\text{C}_{52}\text{H}_{48}\text{P}_6\text{F}_{12}$: C, 50.24; H, 3.86; N, 2.25. Found: C, 50.00; H, 4.00; N, 2.24. IR (CH_2Cl_2): $\nu(\text{NO})$ 1800 (m), 1676 (s) cm^{-1} ; also 1593 (m), 1481 (w), 1437 (s), 1310 (m), 1127 (s, br), 1029 (m), 1000 (m), 845 (s, br) cm^{-1} . ^1H NMR (CD_3CN): δ 7.37 – 7.59 (m, 40H), 2.78 (br, 8H). ^{19}F NMR (CD_3CN): δ 71.0 (d, $J_{19\text{F}-31\text{P}} = 707 \text{ Hz}$). ^{31}P NMR (CD_3CN , 5mm tube): δ -144 (m, $J_{31\text{P}-19\text{F}} = 707 \text{ Hz}$), 38.5 (s). Mp: 150 – 151°C.

Preparation of $[\text{Mo}(\text{NO})_2(\text{OPPh}_3)_4](\text{PF}_6)_2$. A stirred green suspension of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ (0.5 g, $\sim 1.1 \text{ mmol}$, prepared by Procedure B) in CH_2Cl_2 (20 mL) was treated with Ph_3PO (0.62 g, 2.2 mmol). After being stirred for 18 h, the reaction mixture consisted of a green solution and a light green solid. The solid was collected by filtration, redissolved

in a minimum of CH_3CN (5 mL), and reprecipitated by the addition of CH_2Cl_2 (~300 mL). The final precipitate was isolated by filtration, washed with cold (0°C) CH_2Cl_2 (4 x 2 mL), and dried in vacuo (5×10^{-3} mm) to obtain 0.40 g (46% yield based on Ph_3PO) of $[\text{Mo}(\text{NO})_2(\text{OPPh}_3)_4](\text{PF}_6)_2$ as a lime green solid.

Anal. Calcd for $\text{MoN}_2\text{O}_6\text{C}_{72}\text{H}_{60}\text{P}_6\text{F}_{12}$: C, 55.46; H, 3.85; N, 1.80. Found: C, 55.09; H, 4.15; N, 1.63. IR (CH_3CN): $\nu(\text{NO})$ 1800 (s), 1680 (s) cm^{-1} ; also 1594 (w), 1125 (s), 1000 (m), 847 (s), 731 (s), 697 (m) cm^{-1} . ^1H NMR (CD_3CN): δ 7.0 - 7.8 (m). Mp (in air): $>220^\circ\text{C}$.

Preparation of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_2(\text{OPPh}_3)_2](\text{BF}_4)_2$. To a stirred, green solution of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ ⁷⁹ (3.06 g, 6.20 mmol) in CH_3CN (20 mL) was added solid OPPh_3 (3.00 g, 10.8 mmol). No colour change in the green solution was apparent, but its IR spectrum showed a general shift of the original nitrosyl absorptions to lower wave numbers (i.e. from ~1860 (s), ~1830 (m), ~1760 (s) and ~1730 (m) cm^{-1} to ~1832 (s), ~1810 (m), ~1720 (s) and ~1695 (m) cm^{-1}). After 15 min, the solvent was removed in vacuo, and the green oil remaining was dissolved in CH_2Cl_2 (100 mL). Addition of toluene (40 mL) to this latter solution induced the formation of bright green crystals (3.10 g, 59% yield based on OPPh_3) of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_2(\text{OPPh}_3)_2](\text{BF}_4)_2$ which were collected by filtration.

Anal. Calcd for $\text{MoN}_4\text{O}_4\text{C}_{40}\text{H}_{36}\text{P}_2\text{B}_2\text{F}_8$: C, 49.59; H, 3.72; N, 5.79. Found: C, 49.33; H, 3.69; N, 5.77. IR (Nujol mull): $\nu(\text{NO})$ 1827 (s), 1713

(s) cm^{-1} ; also 2320 (w), 2300 (w), 1143 (m), 1126 (m), 1056 (s, br), 1036 (m), 766 (w), 726 (m) cm^{-1} . IR (CH_3CN): $\nu(\text{NO})$ 1832 (s), 1721 (s) cm^{-1} ; also 1140 (w), 1124 (m), 1059 (s), 733 (m) cm^{-1} . IR (CH_2Cl_2): $\nu(\text{NO})$ 1831 (s), 1720 (s) cm^{-1} ; also 1446 (m), 1125 (s), 1067 (s, br), 1049 (m), 1001 (w) cm^{-1} . ^1H NMR (CDCl_3): δ 7.5 - 7.7 (m, 30H), 2.22 (s, 6H). ^{19}F NMR (CDCl_3): δ 147 (s). ^{31}P NMR (CD_3CN): δ 50.6 (s, 1P), 28.8 (s, 1P). Mp: 134°C dec. $\Lambda_m(\text{CH}_3\text{NO}_2)$: 179 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

Preparation of $[\text{Mo}(\text{NO})_2(\text{bipy})]_2(\text{PF}_6)_2$. A sample of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4]-(\text{PF}_6)_2$ (1.0 g, ~1.5 mmole) prepared by Procedure B) was dissolved in acetonitrile (20 mL) and stirred for 6 h. The solution was then cooled to 0°C, and a sodium amalgam (1.5 mmole Na in 7 mL of mercury) was added dropwise over a period of 15 min. The solution darkened from bright green to olive green, and a shift in ν_{NO} was observed by IR, i.e. 1828 and 1716 cm^{-1} to 1800 and 1682 cm^{-1} . After being stirred for 1 h the supernatant solution was filtered and solid 2,2' bipyridine (0.46 g, 3.0 mmoles) was added, whereupon the colour of the solution darkened to brown green. The acetonitrile was removed in vacuo and the product was recrystallized twice: first by adding THF (60 mL) dropwise to a CH_3NO_2 (5 mL) solution; second by dropping CH_2Cl_2 (40 mL) into an CH_3CN (2 mL) solution. By this method was obtained 0.35 g (51% yield) of green-brown microcrystals of $[\text{Mo}(\text{NO})_2(\text{bipy})]_2-(\text{PF}_6)_2$.

Anal. Calcd for $\text{MoN}_4\text{O}_2\text{C}_{10}\text{H}_8\text{PF}_6$: C, 26.26; H, 1.75; N, 12.25. Found: C, 26.15; H, 2.00; N, 12.40. IR (Nujol Mull): $\nu(\text{NO})$ 1775 (s), 1639 (s, br) cm^{-1} ;

also 1602 (s), 1492 (w), 1318 (m), 1244 (w), 1163 (w) 1109 (w), 1075 (w), 1060 (w), 1047 (w), 1032 (w), 1020 (w), 845 (s), 768 (m), 733 (m) cm^{-1} . IR (CH_3CN): $\nu(\text{NO})$ 1774 (s), 1650 (s, br) cm^{-1} ; also 1602 (s), 873 (w), 850 (s) cm^{-1} . ^1H NMR (CD_3CN) δ 10.2 - 7.0 (m, vbr). ^{19}F NMR (CD_3CN): δ 71.2 (d, $J_{^{19}\text{F}-^{31}\text{P}} = 707$ Hz). ^{31}P NMR (CD_3CN): δ -144 (sept., $J_{^{31}\text{P}-^{19}\text{F}} = 707$ Hz). Mp: 208°C dec.

Preparation of $[\text{Mo}(\text{NO})_2(\text{phen}')]_2(\text{PF}_6)_2$. To a green THF (40 mL) suspension of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ (1.0 g, ~ 1.5 mmol, prepared by Procedure B) was added successively, solid $\sim 2\%$ sodium amalgam (1.55 g, 1.5 mmol of Na) and mercury (~ 5 mL), and the mixture was stirred until all the nitrosyl reactant had dissolved (~ 120 min). IR monitoring of the progress of the reaction revealed a shift in the initial nitrosyl absorptions to lower wave numbers, i.e. from 1790 and 1680 cm^{-1} to 1780 and 1673 cm^{-1} . The olive green supernatant solution was removed from the final reaction mixture by syringe and was filtered through a Celite column (4 x 5 cm) supported on a medium porosity frit. The filtrate was treated dropwise with a THF/ CH_2Cl_2 solution (20/10 mL) of 3,4,7,8-tetramethyl-1,10-phenanthroline (phen', 0.64g, 2.7 mmol) whereupon a fine pale yellow precipitate formed. The precipitate was removed by filtration. The solvent was evaporated from the filtrate in vacuo, and the resultant green tar extracted with CH_3CN (3 x 5 mL). The CH_3CN was removed in vacuo and the green oil dissolved in CH_2Cl_2 (30 mL). The dichloromethane solution was filtered and to it toluene (5 mL) was added dropwise; the solution was

concentrated to ~8 mL. The precipitated green brown solid was collected on a medium porosity frit and rinsed with toluene (3 x 8 mL) then hexanes (3 x 8 mL) to obtain 0.4 g (47% yield) of golden-green $[\text{Mo}(\text{NO})_2(\text{phen})]_2(\text{PF}_6)_2$.

Anal. Calcd for $\text{MoN}_4\text{O}_2\text{C}_{16}\text{H}_{16}\text{PF}_6$: C, 35.75; H, 2.98; N, 10.43. Found: C, 35.80; H, 3.20; N, 10.12. IR (Nujol mull): $\nu(\text{NO})$ 1786 (s), 1660 (s, br) cm^{-1} ; also 1530 (m), 1304 (w), 1007 (w), 845 (s), 740 (w), 723 (m) cm^{-1} . IR (CH_2Cl_2): $\nu(\text{NO})$ 1782 (s), 1661 (s, br) cm^{-1} ; also 1530 (w), 849 (s) cm^{-1} . ^1H NMR (CD_2Cl_2): δ 9.5 - 7.2 (m, 2H), 3.1 - 0.8 (m, 12H). ^{19}F NMR (CD_2Cl_2): δ 71.5 (d, $J_{19\text{F}-31\text{P}} = 707$ Hz). ^{31}P NMR (CD_3NO_2 , 5 mm tube): δ -147 (m, $J_{31\text{P}-19\text{F}} = 707$ Hz). Mp: 187°C dec.

Preparation of $\text{Mo}(\text{NO})_2(\text{acac})_2$. A quantity of solid $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ (1.40 g, ~2.02 mmol, prepared by Procedure B) was added to a suspension of Na_2CO_3 (0.34 g, 3.3 mmol) in acetylacetone (acacH, 10 mL), and the mixture was stirred for 3 days. During this time, the original green supernatant solution gradually became brown, but white solid matter remained suspended throughout. Solvent was removed from the final mixture under reduced pressure, and the remaining brown oil was extracted with hot hexanes (2 x 80 mL). The hexanes extracts were concentrated in vacuo to ~5 mL in volume and were then transferred to the top of a Florisil column (1 x 12 cm) made up in hexanes. Development of the column with hexanes afforded a green band which was eluted with benzene. Removal of volatiles from the eluate under reduced pressure produced 0.50 g (70% yield based on Mo) of a green solid. This solid was identified by its IR [(CH_2Cl_2) : ν_{NO} 1773 (s), 1658 (s)]

cm^{-1} ; also 1570 (s), 1524 (s), 1373 (s), 1024 (m), 934 (m) cm^{-1}] and ^1H NMR [(CDCl_3) : δ 5.60 (s, 2H), 2.20 (s, 6H), 1.98 (s, 6H)] spectra as $\text{Mo}(\text{NO})_2(\text{acac})_2$.^{68,70,80}

Subsequent elution of the column with THF removed an orange-brown band which was collected and taken to dryness in vacuo. The residue was recrystallized from CH_2Cl_2 /hexanes to obtain 0.23 g (25% yield based on Mo) of $\text{Mo}(\text{NO})(\text{acac})_2(\text{CH}_3\text{C}(\text{O})\text{C}(\text{NO})\text{C}(\text{O})\text{CH}_3)$ ⁸¹ as an orange-brown solid.

Anal. Calcd for $\text{MoC}_{15}\text{H}_{20}\text{N}_2\text{O}_8$: C, 39.82; H, 4.42; N, 6.19. Found: C, 39.73; H, 4.64; N, 6.18. IR (CH_2Cl_2): 1718 (m), 1680 (s), 1637 (m), 1580 (s), 1522 (s), 1377 (s), 1177 (m), 1023 (m), 934 (w). ^1H NMR (CDCl_3): δ 5.62 (s, 2H), 2.23 (m, 18H).

Reaction of $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$ with $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]$. To a green solution of $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$ ⁷⁷ (0.50 g, 2.2 mmol) in THF (10 mL) at -78°C was added $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]$ ^{53,82a} (1.59, 4.47 mmol) partially dissolved in THF (30 mL) at -78°C , and the mixture was stirred at this temperature for 1 h before being permitted to warm to room temperature. The final reaction mixture consisted of a brown precipitate and a dark red solution whose IR spectrum displayed absorptions at ~ 2300 (w), ~ 2075 (w), ~ 2020 (m), ~ 1980 (m), ~ 1950 (s), ~ 1915 (s, br), ~ 1785 (m), ~ 1745 (w), and ~ 1640 (m, br) cm^{-1} . The mixture was filtered through a medium-porosity frit, and solvent was removed from the filtrate in vacuo to obtain a red residue. A slurry of this residue in benzene (5 mL) was transferred to the top of a Florisil column (1 x 17 cm) made up in benzene. Elution of the column with benzene

developed first an orange band and then a red band. The orange band was eluted with benzene and collected. Removal of solvent from the eluate and sublimation of the residue (60°C, 0.005 mm) onto a water-cooled probe afforded 0.06 g (4% yield) of an orange solid which was identified as $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NO})$ ^{82a} by its IR $[(\text{CH}_2\text{Cl}_2): \nu_{\text{CO}} 2010 (\text{s}), 1925 (\text{s}); \nu_{\text{NO}} 1655 (\text{s})]$ and its ^1H NMR $[(\text{CDCl}_3): \delta 5.60 (\text{s}, \text{C}_5\text{H}_5)]$ ^{82b} and its mass spectra. Further elution of the column with CH_2Cl_2 removed the red band which was collected and taken to dryness under reduced pressure to obtain $[(\eta^5\text{-C}_5\text{H}_5)\text{-W}(\text{CO})_3]_2$ (0.43 g, 29% yield) as a red solid identifiable by its characteristic spectral properties [IR $(\text{CH}_2\text{Cl}_2): \nu_{\text{CO}} 1958 (\text{s}), 1910 (\text{s}); ^1\text{H}$ NMR $(\text{CDCl}_3): \delta 5.33 (\text{s}, \text{C}_5\text{H}_5).$]⁸³ Finally, elution of the column with THF produced a yellow solution (ν_{CO} at $\sim 2070 (\text{m}), \sim 1970 (\text{m}), \sim 1940 (\text{s})$ and $\sim 1880 (\text{m}) \text{ cm}^{-1}$), which when taken to dryness in vacuo provided only trace amounts of a yellow solid.

In a similar manner, IR spectral monitoring of the reaction between $[\text{Mo}(\text{NO})_2\text{Cl}_2]_{\eta^5}$ (0.23 g, 1.0 mmol) and $\text{K}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ ⁸⁴ (0.43 g, 2.0 mmol) in THF (35 mL) at -78°C revealed the disappearance of the nitrosyl absorptions at ~ 1795 and $\sim 1675 \text{ cm}^{-1}$ due to $[\text{Mo}(\text{NO})_2\text{Cl}_2]_{\eta^5}$ and only the appearance of carbonyl absorptions at ~ 1985 , ~ 1945 and $\sim 1780 \text{ cm}^{-1}$ characteristic of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (compared to an authentic sample).

Analogous reactions between $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ and $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]$ or $\text{K}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ in THF resulted in products identical to those described in the preceding paragraphs. In no case were any molybdenum-containing products isolable.

Reaction of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ with $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$.

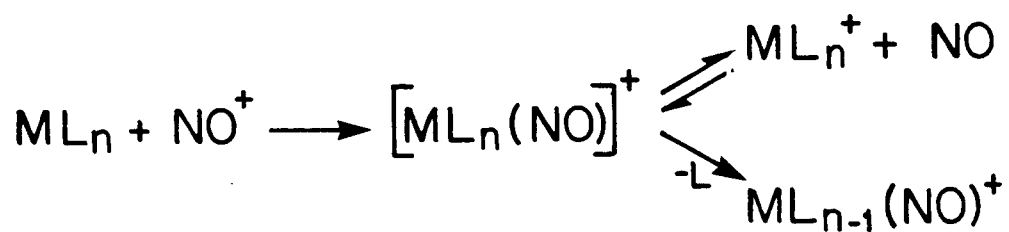
Solid $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ (0.31 g, 0.50 mmol) was added to a violet dichloromethane (20 mL) solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$ ⁸⁵ (0.18 g, 0.50 mmol). After three days the reaction mixture was brown in colour and a green-brown precipitate had formed. An IR spectrum revealed the complete loss of the nitrosyl absorption at $\sim 1510\text{ cm}^{-1}$ of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$ (its IR spectrum in CH_2Cl_2 consisting of two nitrosyl absorptions 1667 (s) and 1512 (m) cm^{-1}); new nitrosyl absorptions were visible at ~ 1845 (s), ~ 1775 (w), and ~ 1745 (s) cm^{-1} ; and the initial ν_{NO} band at 1665 cm^{-1} ($[(\eta^5\text{-C}_5\text{H}_5)\text{-Cr}(\text{NO})_2]_2$) had diminished in intensity. The brown reaction mixture was filtered; THF (15 mL) and hexanes (10 mL) were added to the filtrate; and the filtrate was concentrated in vacuo to give a green gold solid (0.15 g, 83% yield) which was identified by its spectral properties to be $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2(\text{CH}_3\text{CN})]\text{PF}_6$.⁸⁶ IR (Nujol): $\nu(\text{NO})$ 1862 (s), 1757 (s); $\nu(\text{CN})$ 2312 (m); $\nu(\text{PF})$ 840 (s, br) cm^{-1} . $^1\text{H NMR}$ (CD_3NO_2): δ 5.97 (s, 5H, C_5H_5), 2.40 (s, 3H, CH_3).

Result and Discussion

Generation of "Mo(NO)₂²⁺" from Mo(CO)₆ and NOPF₆

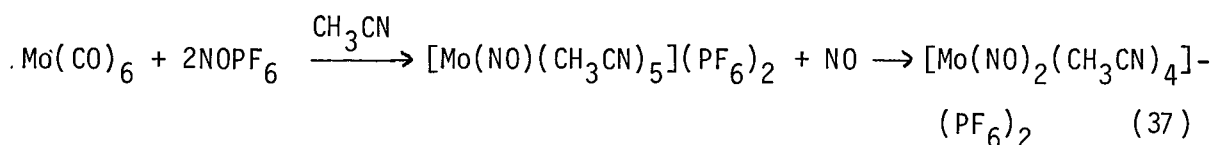
A. Dichloromethane Solvent. Due to the electrophilic nature of the nitrosonium salts, they can function as oxidizing as well as nitrosylation agents. Connolly⁸⁷ has proposed a general mechanism that accounts for this dual mode of reactivity as is seen in Scheme IV.

Scheme IV



Specific reaction conditions determine whether oxidation or substitution occurs; accordingly, these are examined minutely.

The mixing of NOPF_6 with a dichloromethane solution of molybdenum hexacarbonyl always results in the precipitation of an amorphous, dull-green solid which exhibits two nitrosyl stretching bands in the infrared spectrum of its Nujol mull. The ratio of the two reactants, (i.e. Mo(CO)_6 to NOPF_6 being 1:1, 1:2, or 1:3) does not appear to influence the outcome of the reaction. Nitrosonium hexafluorophosphate, being extremely hygroscopic, is weighed in an inert atmosphere glove box and on the bench is transferred into the reaction flask under a strong stream of N_2 . The inert gas is introduced into the flasks via gas inlets connected by latex hosing to a silica gel drying tower. The reaction flask is kept under dry dinitrogen atmosphere either by passing N_2 over the mouth of the flask or by maintaining a constant positive nitrogen pressure. Since minor CO bands are visible in the IR spectrum of some of the collected samples, the reaction flask is flushed with N_2 to facilitate removal of the CO gas displaced. However, the solution is not sparged with N_2 as Connolly has claimed⁶⁹ that in acetonitrile the dinitrosyl cation results from the reaction of generated NO and that efficient removal of the NO gas results in a mononitrosyl containing product:

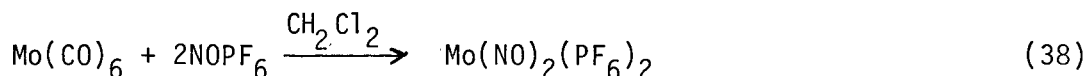


Nevertheless, with these precautions a reproducible product cannot be obtained and etching of the reaction vessel and discolouration of the latex hosing is sometimes observed. When further effort is expended to ensure rigorous exclusion of water from the reaction vessel by use of Schlenk-type glassware attached to the nitrogen manifold of a double manifold high vacuum line via all glass connections, glassware remains unetched and a product which from its elemental analysis is formulated as $\text{Mo}(\text{NO})_2(\text{PF}_6)_2$ is obtained reproducibly.

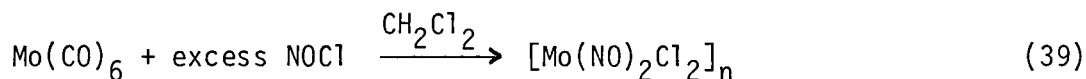
$\text{Mo}(\text{NO})_2(\text{PF}_6)_2$ is a highly air-sensitive, hygroscopic green solid which decomposes upon heating to 110°C . The infrared spectrum of its Nujol mull contains two strong nitrosyl stretching absorptions, 1811 and 1683 cm^{-1} and several bands of medium intensity 1265 (br), 1154, 948, 885, 843, and 565 cm^{-1} , which are not indicative of a hexafluorophosphate anion with octahedral symmetry (a strong $\nu_{\text{P-F}_{\text{sym}}} \approx 830\text{ cm}^{-1}$).⁸⁸ The fact that the species $\text{Mo}(\text{NO})_2^{2+}$ would be extremely electron deficient suggests that $\text{Mo}(\text{NO})_2(\text{PF}_6)_2$ might possess coordinated PF_6^- . A coordinated PF_5 has been claimed in the case of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{PF}_6$ ⁸⁹ and in that of $(\eta^5\text{-C}_5\text{H}_5)\text{-Cr}(\text{NO})_2\text{PF}_6$.⁸⁶ However, little significant alterations are observed in the IR spectrum of a coordinated PF_6^- anion.^{89,90} The strong absorption at $\sim 840\text{ cm}^{-1}$ may split into bands at ~ 880 and 810 cm^{-1} , but this splitting may be obscured by the broadness of the bands. The absorptions seen in the IR spectrum of $\text{Mo}(\text{NO})_2(\text{PF}_6)_2$ at 1265, 1154, and 948 certainly do not originate from a PF_6^- anion coordinated or uncoordinated. The origin of these bands will be discussed in the next section.

Beck reports that the metal-fluorine link in $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3\text{PF}_6$ is so weak that even a weakly donating solvent such as dichloromethane can displace it.^{8,9} Indeed, when $\text{Mo(NO)}_2(\text{PF}_6)_2$ is placed in any solvent in which it dissolves an octahedrally symmetric PF_6^- is detectable by infrared and ^{31}P or ^{19}F NMR spectroscopy (a septet δ -144, $^1J_{^{31}\text{P}-^{19}\text{F}} = 707$ Hz (CD_3CN), in the ^{31}P NMR spectrum and a doublet δ 72, $^1J_{^{19}\text{F}-^{31}\text{P}} = 707$ Hz (CD_3CN)₃ in the ^{19}F NMR spectrum are characteristic of an octahedral hexa-fluorophosphate anion^{40,48}). Proton NMR spectroscopy performed in deuterio-acetonitrile verifies that no dichloromethane is incorporated into the green solid, but in acetonitrile $\text{Mo(NO)}_2(\text{PF}_6)_2$ is converted to $[\text{Mo(NO)}_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ and can be isolated as such.

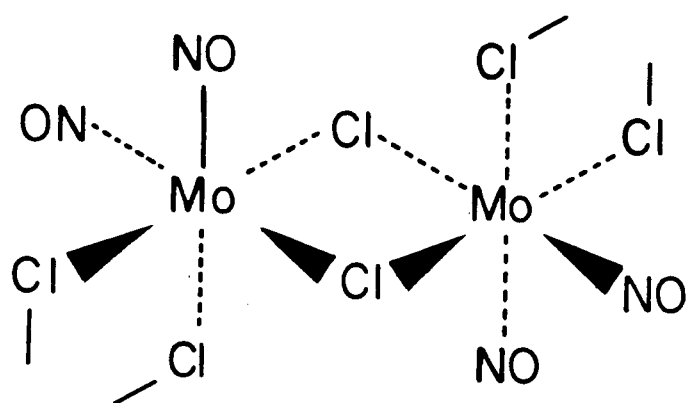
$\text{Mo(NO)}_2(\text{PF}_6)_2$ formed by reaction 38 can be compared to $[\text{Mo(NO)}_2\text{Cl}_2]_n$,



the product of a similar reaction 39. $[\text{Mo(NO)}_2\text{Cl}_2]_n$ is also a hygroscopic green



solid with nitrosyl stretching absorptions in the Nujol mull infrared spectrum 1805 and 1690 cm^{-1} . It is apparently a polymer which readily dissociates into monomeric species in coordinating solvents. Its polymeric structure is suggested as



It is possible that $\text{Mo}(\text{NO})_2(\text{PF}_6)_2$ is a like polymer with cis nitrosyls accounting for the two NO absorptions in the IR spectrum.

The alternate result of reaction 38, seemingly produced when conditions are not rigorously anhydrous, is also a green solid the infrared spectrum (Nujol) of which displays two strong nitrosyl absorptions 1821 and 1693 cm^{-1} and bands of medium intensity at 1265, 1163, 955, 901, and 569 cm^{-1} . It is highly air sensitive, fumes when exposed to the atmosphere, but does not

show noticeable decomposition when heated under a dinitrogen atmosphere to 220°C. Its ^{31}P and ^{19}F NMR spectra differ markedly from that of $[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$. The ^{31}P NMR spectrum consists of a triplet δ -17.9, $^1J_{^{31}\text{P}-^{19}\text{F}} = 957$ Hz, while the ^{19}F spectrum is a doublet centred at δ 81.7 ($J_{^{19}\text{F}-^{31}\text{P}} = 957$ Hz). This data is not in accord with the presence of a PF_6^- anion but, rather, with that of O_2PF_2^- (see Table III). For this formulation the fingerprint region of the infrared spectrum can be assigned 1265 (asym PO_2), 1163 (sym PO_2), 955 (asym PF_2), and 901 (sym PF_2) cm^{-1} . Since all these vibrational bands closely match those reported in the system $\text{R}_2\text{Sn}(\text{O}_2\text{PF}_2)_2$ ^{94,95} in which the O_2PF_2^- moiety is bidentate, it seems likely this is also the mode of its coordination in this molybdenum nitrosyl cation. Cole-Hamilton⁹² has suggested that the symmetric PO stretching frequency can be correlated to the bonding mode of O_2PF_2^- , i.e., monodentate 1130 - 1140 cm^{-1} , chelating 1165 - 1200 cm^{-1} ; bridging, bidentate 1157 - 1175 cm^{-1} . Ionic O_2PF_2^- has been observed to possess $\nu_{\text{asym}} \text{PO}$ 1270 - 1310 and $\nu_{\text{sym}} \text{PO}$ 1137 - 1164 cm^{-1} .⁹⁶ Guided by these classifications the difluorophosphate under consideration would also be said to coordinate in a bidentate fashion though whether to one or two molybdenum centres is not certain. Further evidence is needed in order to make a more specific assignment; conductance data which will be presented later along with the elemental analysis suggest the correct formulation to be $[\text{Mo}(\text{NO})_2(\text{O}_2\text{PF}_2)]\text{O}_2\text{PF}_2$ with one coordinated and one ionic difluorophosphate.

Table III. ^{19}F and ^{31}P NMR Spectral Data for Complexes Containing PF_6^- or O_2PF_2^-

	^{19}F NMR ^a (δ)	$^1\text{J}_{^{19}\text{F}-^{31}\text{P}}$ (Hz)	^{31}P NMR ^b (δ)	Reference
$\text{Re}(\text{CO})_5(\text{O}_2\text{PF}_2)$		969	-12.7(t) ^c	91
$\text{Re}(\text{CO})_3(\text{bipy})(\text{O}_2\text{PF}_2)$		969	-12.7(t) ^c	91
$\text{trans}-[\text{Ru}(\text{CO})(\text{dppm})_2(\text{O}_2\text{PF}_2)]\text{PF}_6$	76.8(d, O_2PF_2) 74 (d, PF_6)	955 708	-16.8(t, O_2PF_2) ^d -145 (septet, PF_6)	92
$\text{trans}-\{[\text{Ru}(\text{CO})(\text{dppm})_2(\text{O}_2\text{PF}_2)](\text{PF}_6)_3$	89 (d, O_2PF_2) 74 (d, PF_6)	951 708	-15.3(t, O_2PF_2) ^d -145(septet, PF_6)	92
$\{[(\eta^5-\text{C}_5\text{H}_5)\text{Rh}]_2(\text{O}_2\text{PF}_2)_3\}\text{PF}_6$	65.3(d) 74.4(d)	952 708	-33.1(t, 3P, O_2PF_2) ^e -166.2(septet, 1P, PF_6)	93
$(\eta^5-\text{C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{FPF}_5$	75.5 ^d	750		86
$[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$	72.0(d) ^{d, f}	707	-144(septet) ^f	this work
$\text{Mo}(\text{NO})_2(\text{O}_2\text{PF}_2)_2$	81.7(d)	957	-17.9(t) ^f	this work
$[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$	72.0(d)	706	-144(septet) ^f	this work

(a) values standardized to CFC_3 (b) values standardized to H_3PO_4 (c) CD_2Cl_2

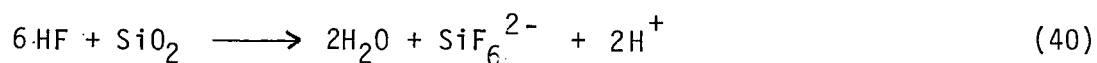
(d) nitromethane

(e) solvent unspecified

(f) CD_3CN

The hexafluorophosphate ion undergoes slow hydrolysis in acidic media to form the phosphate salt; certain metal centres have been reported to facilitate this hydrolysis.⁹⁷ The transformation of hexafluorophosphate into difluorophosphate in organometallic complexes is unusual but not unprecedented. For example, when $[W(o\text{-phenylenebis(dimethylarsine))](CO)_3(NO)]PF_6$ is refluxed in "dry" acetone the O_2PF_2 salt forms.⁹⁸

^{19}F NMR samples of $[Mo(NO)_2(PF_6)_2]_n$ in d^3 -acetonitrile when allowed to age in unsealed NMR tubes show a decrease in the intensity of the doublet at δ 72 ($^1J_{31P-19F} = 707$ Hz) characteristic of PF_6^- and the growth of a new doublet at δ 82 ($^1J_{31P-19F} = 957$) characteristic of $O_2PF_2^-$ and a broad resonance at δ +160. Thus, the source of variability in reaction 38 is evident; $[Mo(NO)_2(PF_6)_2]_n$ is the initial product in any case, but in the presence of trace amounts of water it is converted to the difluorophosphate salt and HF. HF can in turn initiate the production of more water and cause the observed etching of glassware via reaction 40.



Indeed, aqueous solutions of $[Mo(NO)_2(PF_6)_2]_n$ and $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$ have $pH = 3.35$. The previously cited IR spectrum of $[Mo(NO)_2(PF_6)]_n$ as a Nujol mull appears to display some incipient decomposition to $O_2PF_2^-$ (e.g. the bands at 1265, 1154, 948 cm^{-1}). This reflects the difficulty in obtaining a mull IR spectrum under anhydrous conditions. In this case the ^{19}F and ^{31}P NMR spectra prove the more useful diagnostic tools since NMR samples can be

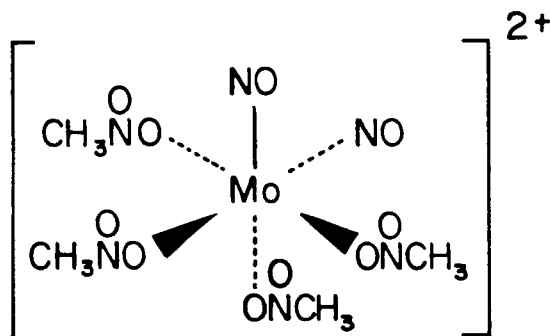
sealed from the environment more effectively than the infrared samples.

B. Nitromethane Solvent. In performing reaction 38 it was initially of concern that since nitrosyl hexafluorophosphate is insoluble in dichloromethane, it might be occluded in the equally insoluble product. Accordingly, the analogous reaction was attempted in nitromethane with the thought that as a good solvator it is capable of dissolving NOPF_6 but as a poor donor it is not likely to become involved in the reaction.⁷⁶ Unfortunately, the latter did not prove to be the case. Instead the product formed is $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$.

The addition of a nitromethane solution of NOPF_6 to a nitromethane slurry of $\text{Mo}(\text{CO})_6$ results in violent bubbling. IR monitoring of the reaction solution shows a decrease in the ν_{CO} band of $\text{Mo}(\text{CO})_6$ at 1980 cm^{-1} and an appearance of two new bands at 2185 and 2100 cm^{-1} . This suggests a reaction path leading through a CO containing intermediate such as $[\text{Mo}(\text{NO})_2(\text{CO})(\text{solvent})_3](\text{PF}_6)_2$ which has been reported for $\text{M} = \text{W}$.^{68,80} After two hours two IR bands are visible, 1860 and 1750 cm^{-1} , indicating the presence of cis nitrosyl functionalities as well as a strong absorption at 843 cm^{-1} indicating an octahedrally symmetric PF_6 anion.⁸⁸ The reaction solution fumes and is extremely hygroscopic. Indeed, infrared monitoring is difficult for the ν_{NO} bands of both the reaction solution and the isolated product shift to lower wave numbers if the solution is allowed to sit in the IR cell as long as 4 minutes. Since this shift is not affected by the utilization of KRS-5 (TlBr/TlCl) instead of NaCl IR windows it is not

due to reaction with the NaCl plates as is observed with some organometallic cations.⁹⁹ It is probably due to hydrolysis since the aged solution also exhibits ν_{OH} at 3400 cm^{-1} . A similar shift in ν_{NO} absorptions has been reported for $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ but was speculated to be due to an equilibrium between the tetrakisacetonitrile and the bisacetonitrile species.⁸⁰ The solvate ligands are labile; ^1H NMR studies have demonstrated this.⁷⁰ [Nuclear magnetic resonance experiments performed in d^3 -acetonitrile on $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ confirm the presence of the CH_3NO_2 (^1H : δ 4.34 (m)) and the PF_6 [^{31}P : δ -144 (septet) (CD_3CN or CD_3NO_2): ^{19}F : δ +72, $^1J_{^{19}\text{F}-^{31}\text{P}} = 706\text{ Hz}$]. However, in acetonitrile the nitromethane ligand is displaced; $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ can be isolated from this solution. Monitoring of the ^{19}F NMR spectrum reveals the ease with which the compound is hydrolyzed from the PF_6 salt (δ +72, $J_{^{19}\text{F}-^{31}\text{P}} = 706\text{ Hz}$) to the O_2PF_2 salt (δ +82, $J_{^{19}\text{F}-^{31}\text{P}} = 957\text{ Hz}$) (vide supra).

$[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ is an amorphous green solid which loses nitromethane when subjected to high vacuum and decomposes upon heating to 88°C . It is highly hygroscopic and must be handled only in a dry atmosphere. It deliquesces upon exposure to atmospheric conditions. Coordination of nitromethane to the metal centre in an organometallic compound is unusual, but the presence of the nitromethane is established by the IR (1570 (s) (Nujol)) and the ^1H NMR (δ 4.34(CD_3CN)) spectra and by the elemental analysis of the complex. Donation would likely be through one oxygen in a monodentate fashion so an octahedron such as

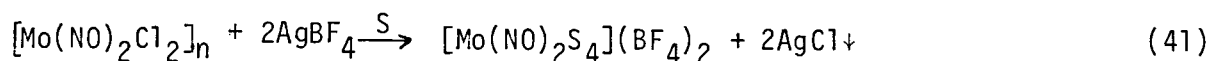


can be envisioned, fulfilling the requirement of cis nitrosyl ligands.

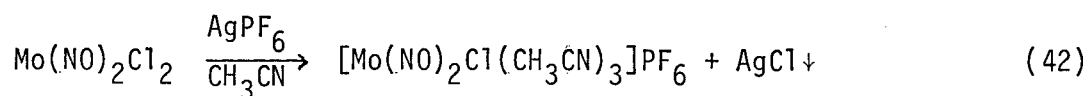
Generation of "Mo(NO)₂²⁺" from [Mo(NO)₂Cl₂]_n and AgBF₄:

C. Nitromethane Solvent. Like [Mo(NO)₂(CH₃CN)₄](BF₄)₂,⁷⁹

[Mo(NO)₂(CH₃NO₂)₄](BF₄)₂ can be prepared by abstraction of chloride from [Mo(NO)₂Cl₂]_n⁷⁷ by AgBF₄ in the appropriate solvent.

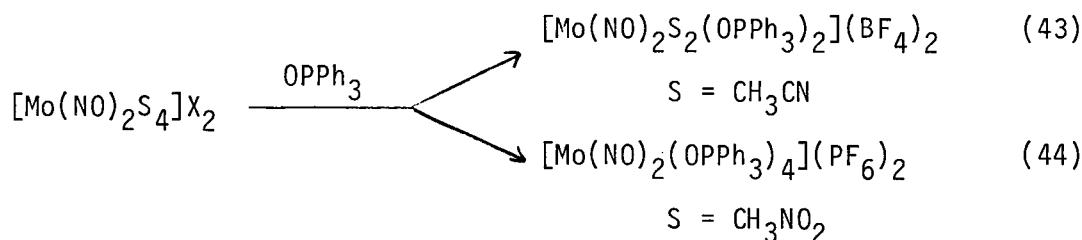


Unfortunately at room temperature when S = CH₃CN, reaction 41 does not go to completion as is apparent from the continual precipitation of AgCl over a period of days. The analogous reaction employing AgPF₆ is reported to go to completion under reflux conditions⁷⁰ but stops at an intermediate [Mo(NO)₂Cl(CH₃CN)₃](PF₆) if only stirred at room temperature.



However, in nitromethane reaction 41 is complete upon stirring 2 hours at ambient temperature, possibly due to decreased solubility of AgCl in this solvent.

The product $[\text{Mo}(\text{NO})_2\text{S}_4]^{2+}$ with coordinated nitromethane has certain advantages over the complex with $\text{S} = \text{acetonitrile}$. In addition to the ease of producing the product via the chloride abstraction, the nitromethane is less likely to be retained in subsequent reactions, i.e.



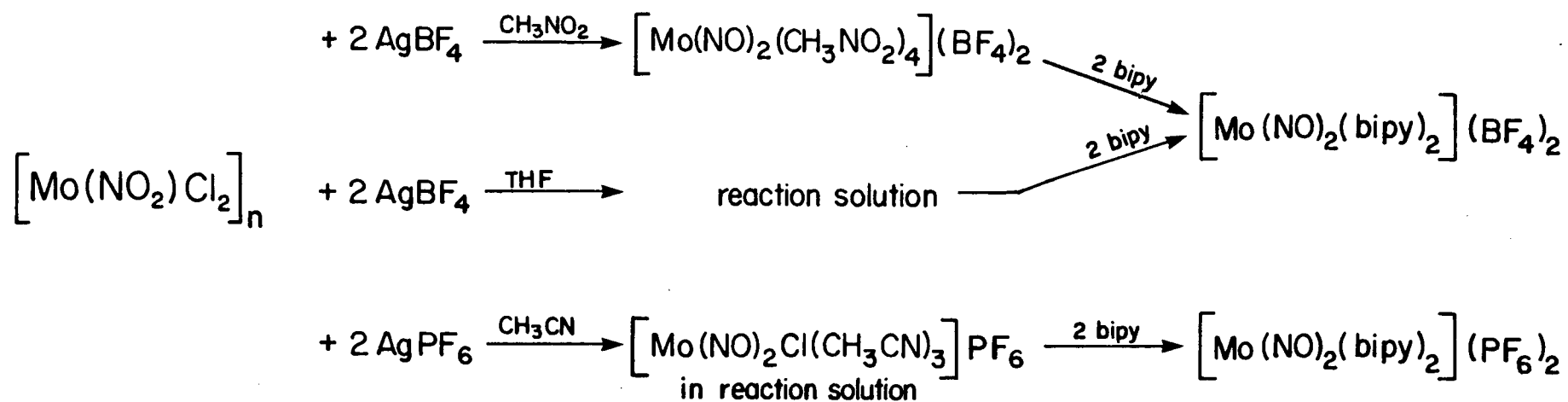
These products will be discussed in detail later.

D. Tetrahydrofuran Solvent. Interestingly no shift in the nitrosyl stretching frequencies is observed when chloride abstraction (reaction 41) is performed in tetrahydrofuran. Even if only one chloride is removed, as is the case when the solvent is CH_3CN (reaction 42), some ν_{NO} change would be expected. The fact that the same product $[\text{Mo}(\text{NO})_2(\text{bipy})_2](\text{X})_2$ $\text{X} = \text{PF}_6^-$ or BF_4^- (reaction 45, vide infra) is formed when 2,2'-bipyridine is added to the

nitrosyl cation whether it is generated in CH_3NO_2 or THF cannot be taken as proof that reaction 41 goes to completion in THF, for the same product is obtained from the reaction solution of reaction 42⁷⁰ (see Scheme V). (Although no mention is made of the fact in the original paper,⁷⁰ further chloride abstraction must be evidenced in the presence of 2,2'-bipyridine.) However, the fact that no further precipitation of AgCl is evident does seem to argue that the chloride abstraction does go to completion in THF media.

Tetrahydrofuran solutions of the dications cannot be easily differentiated on the basis of their infrared spectra; $[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$, $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$, and $[\text{Mo}(\text{NO})_2(\text{O}_2\text{PF}_2)](\text{O}_2\text{PF}_2)$ all have virtually the same ν_{NO} absorptions. This may be due in part to the fact that they all become THF solvates. But when a THF solution of either of the hexafluorophosphate dications is exposed to a sodium amalgam, product formation is accompanied by very small shifts in the ν_{NO} bands as compared to those seen when the comparable reaction is performed in acetonitrile (vide infra). No attempt has been made to isolate $[\text{Mo}(\text{NO})_2(\text{THF})_4](\text{BF}_4)_2$ from the reaction solution (41); rather the species is used in situ. Four coordinated THF are assumed on the basis of the analogous dications formed in CH_3CN or CH_3NO_2 .

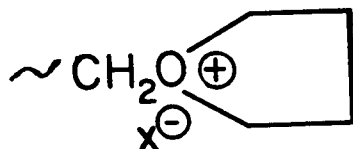
In practice, an undesirable complication makes tetrahydrofuran a less attractive solvent for reaction 41 than nitromethane. When this reaction is effected in THF or when either $[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$ or $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ are stirred in tetrahydrofuran for any length of time (longer than two hours), the green solutions became viscous. After 12 hours the solutions are extremely syrupy and in some instances form gels.

Scheme V

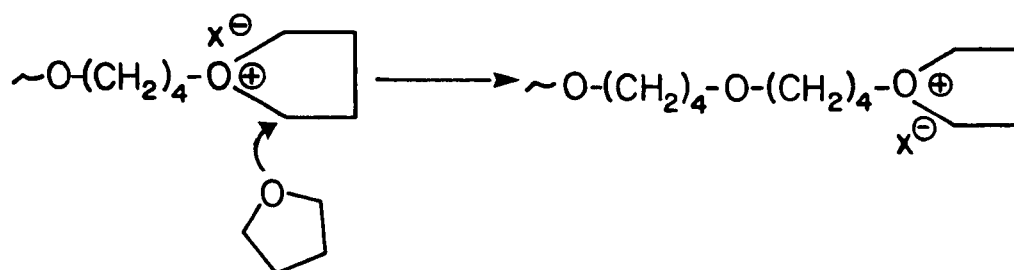
If the gelling has occurred to only a slight extent the desired molybdenum species can be salvaged by removal of the solvent under vacuum and extraction of the resultant green tar with nitromethane or acetonitrile to produce a green solution and leave a gummy white residue.

In the progress of these experiments it was observed and it has since been reported¹⁰⁰ that NOPF_6 reacts violently with THF, evolving gas, and in hours polymerizing the THF. In fact, it has been claimed that NOPF_6 is one of the most promising catalysts for the polymerization of tetrahydrofuran.¹⁰¹ In light of this it is surprising that THF is occasionally employed as a solvent for reactions involving NOPF_6 .^{102,103} It is possible that polymerization occurs at a rate appreciably slower than that of the desired reaction.

Polymerization of THF is believed to occur only by an ionic mechanism — a cationic ring-opening.¹⁰¹ The propagating species in the polymerization is a tertiary oxonium ion:



Propagation occurs by an $\text{S}_{\text{N}}2$ mechanism: a tetrahydrofuran monomer adds to the tertiary-oxonium ion chain end:



The required tertiary oxonium ion can be formed by several methods:

- (1) direct acylation or alkylation of the oxygen of THF;
- (2) in situ generation by a variety of reagents such as a halide and a Lewis acid or a halide and a metal salt or sometimes a Lewis acid alone;
- (3) strong protonic acid addition to the oxygen of THF to form an intermediate secondary oxonium ion which is subsequently converted to a tertiary oxonium ion.

Depending upon the presence or absence of a reactive halide, nitrosyl hexafluorophosphate can initiate polymerization of tetrahydrofuran by either method 2 or 3.

Originally it appeared the dications might be losing NO^+ and thus promoting THF polymerization. But $\text{CpMo}(\text{CO})_2(\text{NO})$ and $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ which are both readily nitrosylated by NOPF_6 ,^{104,105} fail to form any

nitrosyl products when stirred in an acetonitrile solution of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ even under reflux conditions. A paper has recently been published¹⁰⁶ claiming it is a general phenomenon that electrophilic transition metal complexes react with olefins to generate incipient carbonium ions which can then oligomerize. It reports that $[\text{M}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$, where $\text{M} = \text{Mo}, \text{W}$, initiates the polymerization of a number of substituted olefins. Thus, it appears to be an intrinsic property of the dications $[\text{Mo}(\text{NO})_2\text{S}_4](\text{PF}_6)_2$ to react with monomeric THF probably via method 3 to generate the tertiary oxonium ion which in turn initiates THF polymerization.

Conductivity Studies

Conductance studies are used to determine the electrolytic character of a complex and by comparison with conductivities of related compounds can provide insight into its solution structure. Molar conductance (in units $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$) is calculated:

$$\Lambda_m = \frac{\text{cell constant}}{R \cdot C_m}$$

where R is the resistance of the solution (ohms) and C_m is the molar concentration (moles/cm^3). The cell constant (cm^{-1}) is determined by measuring the resistance (R) across a Wheatstone bridge of a known concentration (C_m) of a salt for which the molar conductivity (Λ_m) is known:

$$\text{cell constant} = \Lambda_m \cdot R \cdot C_m$$

The purity of the solvent employed is judged by its specific conductivity κ , determined by measuring its intrinsic resistance R in a cell of known cell constant:

$$\kappa = \frac{\text{cell constant}}{R}$$

Table IV contains conductivity values determined for various compounds containing PF_6^- and O_2PF_2^- moieties. Geary¹⁰⁷ has compiled conductance data in nonaqueous media to produce expected ranges for molar conductivities ($\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) for the different electrolytic types in various solvents. In nitromethane the range is 60 - 115 for 1:1, 115 - 250 for 2:1, and 220 - 260 for 3:1 electrolytes. In acetone 1:1 electrolytes range from 100 to 140, 2:1 from 160 to 200, and 3:1 starts about 270 $\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$. For dilute nitromethane solutions ($\sim 10^{-3} \text{ M}$) of NaPF_6 and of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ the molar conductivities were found to be 116 and 202 $\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, respectively. These values place NaPF_6 in Geary's range for 1:1 electrolytes and $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ in that of the 2:1 electrolytes (see Table IV). The difficulty with this method is that it requires the assumption of a molecular weight which may be erroneous.

In a case in which the degree of molecular complexity of a compound is unknown ($[\text{ML}_n]X_m$ vs $[\text{ML}_n]_a[X_m]_a$) equivalent conductance Λ_e ($\text{ohm}^{-1} \text{ cm}^2 \text{ equivalents}^{-1}$) is determined

Table IV. Molar Conductivities

	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)	Electrolyte Type	Solvent	Reference
$[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{NO})\text{PPh}_3]\text{PF}_6$	147	1:1	acetone	73
$[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{NO})\text{PPh}_3]\text{PF}_6$	132	1:1	acetone	73
$[\text{Mn}(\text{CO})_5(\text{CH}_3\text{CN})]\text{PF}_6$	143	1:1	acetone	73
$[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$	315	2:1	acetone	73
$\text{trans}[\text{Ru}(\text{CO})(\text{dppm})_2(\text{O}_2\text{PF}_2)]\text{PF}_6$	82	1:1	unspecified	92
$\text{cis}[\text{Ru}(\text{CO})_2(\text{dppm})_2](\text{PF}_6)_2$	197	2:1	unspecified	92
NaPF_6	116	1:1	nitromethane	this work
$[\text{Mo}(\text{OPPh}_3)_6]\text{PF}_6$	77.9	1:1	nitromethane	this work
$[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$	202	2:1	nitromethane	this work
$[\text{Mo}(\text{NO})_2(\text{bipy})_2](\text{BF}_4)_2 \cdot 3/4 \text{CH}_2\text{Cl}_2$	191	2:1	nitromethane	this work
$[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_2(\text{OPPh}_3)_2](\text{BF}_4)_2$	179	2:1	nitromethane	this work

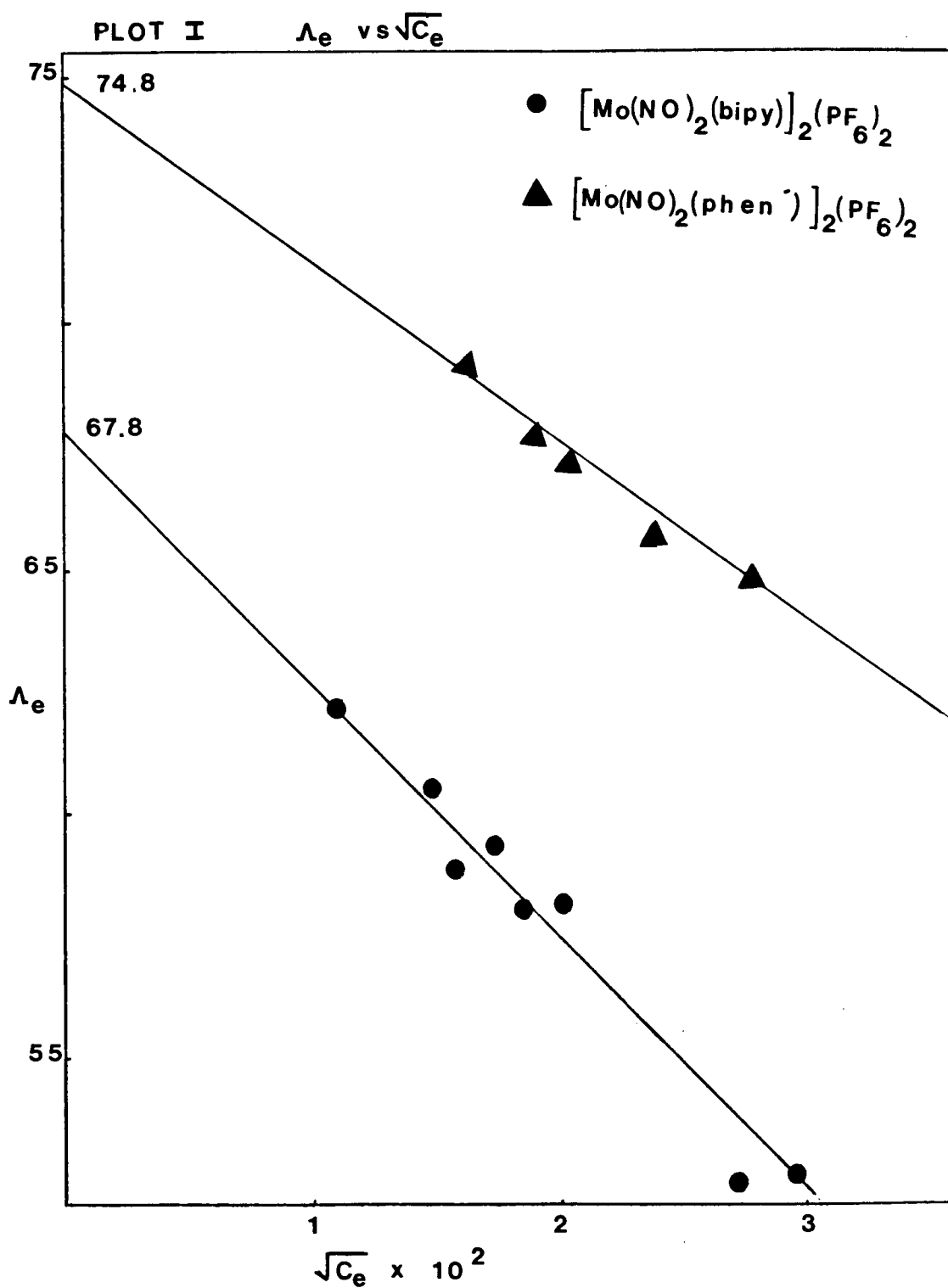
$$\Lambda_e = \frac{\text{cell constant}}{R \cdot C_e}$$

(where C_e = equivalent concentration in equivalents/cm³) over a range of concentrations, and a simplification of Onsager's law is applied:

$$\Lambda_0 - \Lambda_e = K(C_e)^{1/2}$$

where K is a combination of terms dependent on such factors as the charges on the ions concerned, their mobilities, and Λ_0 , molar conductivity at infinite dilution. The plotting of Λ_e vs $(C_e)^{1/2}$ gives an intercept Λ_0 . A sample of such a plot is seen in Plot 1. A second plot of $\Lambda_0 - \Lambda_e$ vs $(C_e)^{1/2}$ has slope K which reflects the electrolyte type (e.g. see Plot 2). Feltham and Hayter¹⁰⁸ have elaborated this technique. From published slope values (see Table V)^{108,109} it appears that K ranges from 150 to 220 for 1:1 electrolytes and from 390 to 570 for 2:1 electrolytes. If it is ambiguous whether or not the anion is in the coordination sphere of the metal, K values must be determined for each possible case, i.e. for $[ML_n]X_2$ and for $[ML_nX]X$. Hopefully, only one of these K values will fall in its proper range.

Conductivity data for $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$ confirm that it is a simple 2:1 electrolyte in nitromethane solution. For the hydrolyzed species $Mo(NO)_2(O_2PF_2)_2$ Table V shows the two possibilities for which Λ_e vs \sqrt{C} and $(\Lambda_0 - \Lambda_e)$ vs \sqrt{C} plots were drawn. Comparing the K values for each to the acceptable range of values for K , it can be seen that only $[Mo(NO)_2(O_2PF_2)](O_2PF_2)$ with a slope of 179 falls close to the proper range



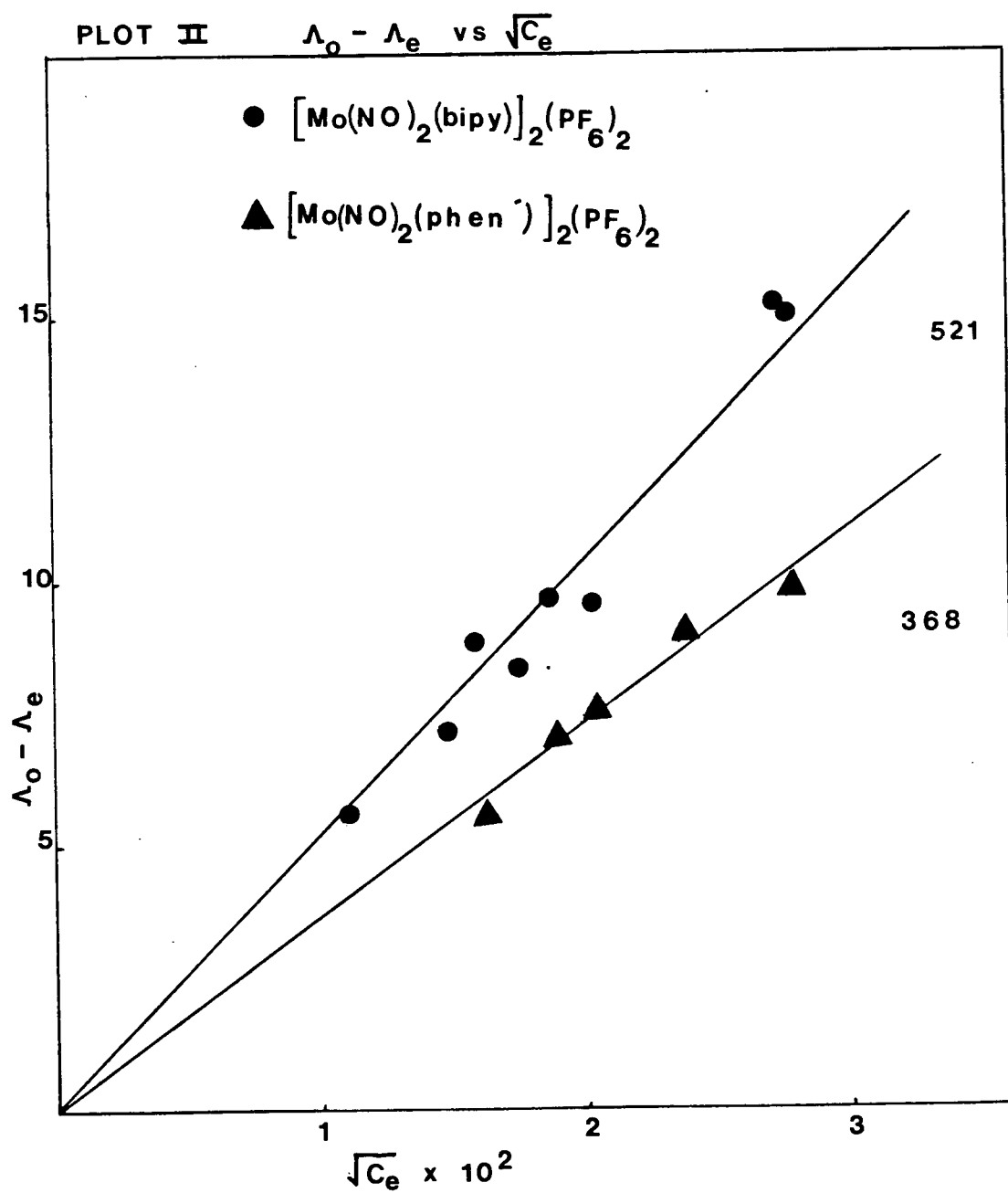


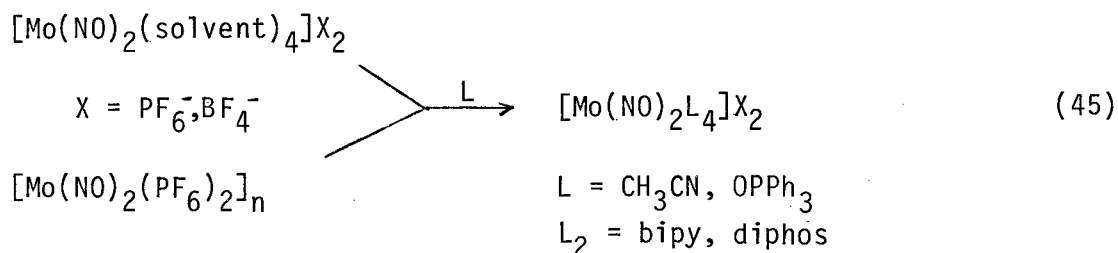
Table V. Conductivity Measurements in Nitromethane

	Λ_0	Slope	Electrolyte Type	Reference
$[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$	85.5	151	1:1	108
$[\text{CoBr}(\text{NO})(\text{das})_2]\text{Br}$	93.8	150	1:1	109
$[\text{CoI}(\text{NO})(\text{das})_2]\text{I}$	96.5	213	1:1	109
$[\text{CoCl}(\text{NO})(\text{en})_2]\text{ClO}_4$	101.3	172	1:1	109
$[\text{Pd}_2(\text{PEt}_2)_2(\text{phen})_2](\text{BPh}_4)_2$	88.0	392	2:1	108
$[\text{Pd}_2(\text{PEt}_2)_2(\text{diphos})_2](\text{BPh}_4)_2$	76.0	410	2:1	108
$[\text{Pd}_2(\text{PPh}_2)_2(\text{en})_2](\text{BPh}_4)_2$	86.4	430	2:1	108
$[\text{Co}(\text{NO})(\text{das})_2](\text{ClO}_4)_2$	126.5	571	2:1	109
$[\text{Mo}(\text{NO})_2(\text{O}_2\text{PF}_2)](\text{O}_2\text{PF}_2)$	33.2	178	1:1	this work
or				
$[\text{Mo}(\text{NO})_2](\text{O}_2\text{PF}_2)_2$	16.5	68.4		this work
$[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$	874	4320	?	this work
$[\text{Mo}(\text{NO})_2(\text{bipy})]_2(\text{PF}_6)_2$	67.8	521	2:1	this work
$[\text{Mo}(\text{NO})_2(\text{phen}')]_2(\text{PF}_6)_2$	74.8	368	2:1	this work
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{NS})\text{PPh}_3]\text{BF}_4$	77.0	186	1:1	this work

for its type, i.e. 150 - 220 for 1:1 electrolytes. However, the Λ_0 value seems abnormally low, possibly due to incomplete dissociation. The data obtained for $[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$ does not lend itself readily to interpretation. Clearly in nitromethane solution it does not convert immediately to $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$

Reactivity of " $\text{Mo}(\text{NO})_2$ "²⁺

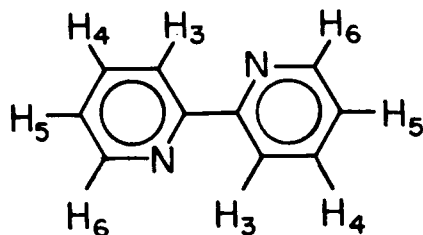
With Neutral Ligands: The molybdenum dications react readily with neutral ligands:



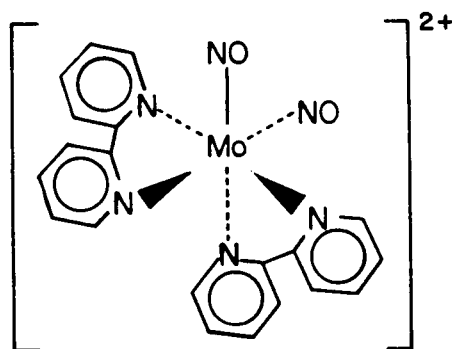
The acetonitrile adduct is well known,^{68,70,79,80} and does not merit further delineation. For $X = \text{PF}_6^-$, the bipyridyl complex has been reported, but only its ν_{NO} IR absorptions have been published^{70,80} so its properties will be detailed here. $[\text{Mo}(\text{NO})_2(\text{bipy})_2](\text{PF}_6)_2$ is formed in good yield from the addition of 2,2'-bipyridine to a solution of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$. Addition of dichloromethane to the solution precipitates deep green micro-crystals which decompose upon heating to 182°C. The IR spectrum (Nujol) consists of two ν_{NO} absorptions 1816 and 1716 cm^{-1} which indicate cis

nitrosyl ligands and a band at 840 cm^{-1} due to an octahedrally symmetric PF stretching absorption. It is only soluble in strongly solvating solvents, i.e., acetonitrile and nitromethane. ^{31}P NMR shows a septet $\delta -144$ ($J_{^{31}\text{P}-^{19}\text{F}} = 707\text{ Hz}$), while the ^{19}F NMR pattern is a doublet $\delta +71.3$. The BF_4^- salt $[\text{Mo}(\text{NO})_2(\text{bipy})_2](\text{BF}_4)_2$ can be formed in nitromethane although here the reaction is reported in THF. It is qualitatively the same as the PF_6^- salt. Upon heating it decomposes at a slightly higher temperature (194°C) than the PF_6^- salt. The infrared spectrum of the solid (Nujol mull) or of the solution (CH_3CN or CH_3NO_2) is virtually the same as that of the PF_6^- salt except for the absence of the PF stretching band at 840 cm^{-1} and the presence of the BF_4^- band at 1057 cm^{-1} .

The ^1H NMR spectra of both $[\text{Mo}(\text{NO})_2(\text{bipy})_2]\text{X}_2$ ($\text{X} = \text{BF}_4^-$ or PF_6^-) in CD_3CN are a complex series of resonances extending from $\delta 9.22$ to 7.53 . Free 2,2'-bipyridine adopts a trans configuration in solution;¹¹⁰ its proton chemical shifts are somewhat solvent dependent, but the basic pattern is a doublet $\delta 8.68$ (H_6), a doublet 8.49 (H_3), a triplet 7.80 (H_4) and a triplet 7.28 (H_5) (CDCl_3).^{111,112}



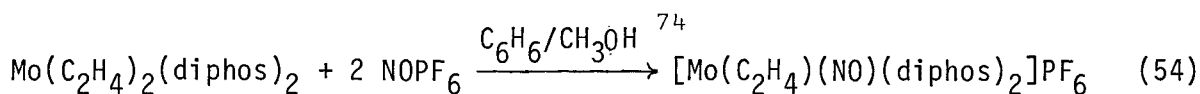
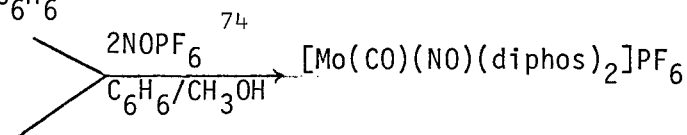
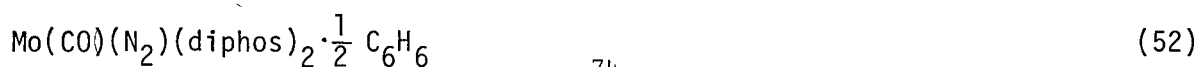
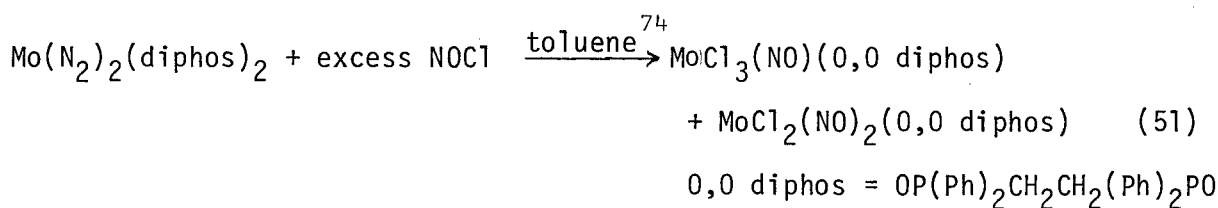
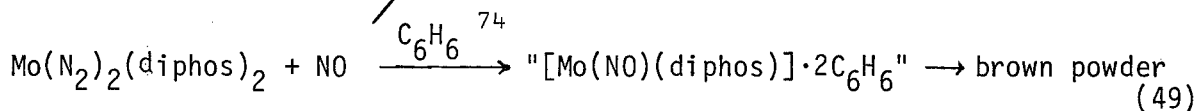
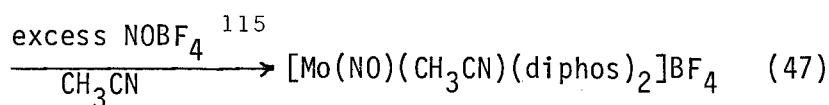
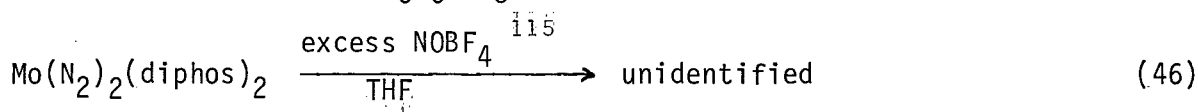
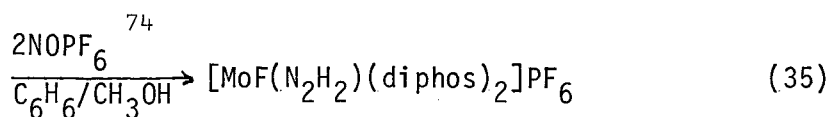
When dipyridyl is coordinated symmetrically to a metal centre the basic pattern is maintained, two doublets and two triplets; although H_6 may experience an upfield shift, there is a general downfield shift of the proton resonances due to less charge density on the ligand, e.g. $\text{Mo(CO)}_4\text{-(bipy)}^{112}$ ^1H NMR (CD_2Cl_2): δ 9.12 (H_6), 8.16 (H_3), 7.95 (H_4), 7.39 (H_5). This would be the expected pattern if the nitrosyl ligands in $[\text{Mo(NO)}_2\text{-(bipy)}_2]^{2+}$ assume a trans configuration. However, in the case of cis- $[\text{Mo(NO)}_2\text{(bipy)}_2]^{2+}$ the pyridyl rings of each ligands are not magnetically



equivalent. An eight line pattern is possible, but resonances may overlap. The protons of the pyridyl without a dipyridyl neighbour would be shifted furthest downfield due to the absence of shielding by the aromatic ring.¹¹¹ For cis- $[\text{Mo(NO)}_2\text{(bipy)}_2]^{2+}$ a basic pattern of four resonances is distinguishable: a doublet 9.22 ($J_{H_6-H_5} = 5.4$ Hz) (1H), a multiplet 8.61 (3H), a multiplet 8.13 (2H), and a multiplet 7.53 (2H). From its coupling constant,¹¹¹ the first resonance can be assigned as H_6 on a pyridyl ring not influenced by an adjacent ring; the other coupling constants cannot be determined.

When the green solid $[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$ is stirred in a dichloromethane diphenylphosphinoethane (diphos) solution for a number of days, the green solid slowly disappears, the solution becomes red brown in colour, and the IR spectrum evidences nitrosyl stretching bands at 1800 and 1676 cm^{-1} . The brown solid $[\text{Mo}(\text{NO})_2(\text{diphos})_2](\text{PF}_6)_2$ isolated from this solution has a sharp melting point $150 - 151^\circ\text{C}$. Its ^1H NMR spectrum consists of a multiplet δ 7.56 (40 H) produced by the phenyl protons and a broad signal 2.78 (8 H) due to the methylene protons. It is not unusual for the methylene protons of $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ to be broadened.¹¹³ The ^{19}F NMR is a doublet typical of PF_6^- salts δ +71.0 ($^1\text{J}_{^{19}\text{F}-^{31}\text{P}} = 707\text{ Hz}$). ^{31}P NMR experiments show the usual septet δ -144 for PF_6 salts and a broad signal δ 38.6 due to the phosphorous atoms of the diphos ligands. For the cis nitrosyl formation demanded by IR evidence, the four phosphorus nuclei of the two diphenylphosphinoethane ligands cannot be chemically equivalent, for two phosphorus must be trans to NO ligands. Broad resonances have been reported as evidence of inequivalent diphenylphosphinoethane ligands,^{74,114} but in this case some broadening may be due to P-H coupling. Unfortunately, this reaction proves difficult to repeat. The brown solid obtained from subsequent attempts does not melt sharply at 150°C but decomposes around 170°C . Elemental analysis are slightly low in carbon and slightly high in nitrogen content.

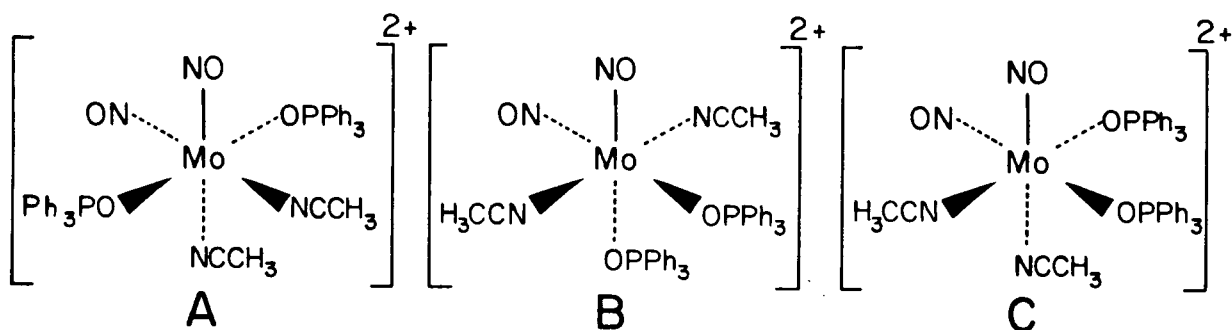
Of interest is the fact that reactions which potentially could generate $[\text{Mo}(\text{NO})_2(\text{diphos})_2](\text{PF}_6)_2$ fail to do so:



In order to circumvent the difficulties encountered when the coordinating ligand is a phosphorus donor, the less basic ligand tri-phenylphosphine oxide is employed. When OPPh_3 is added to a dichloromethane slurry of $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ and the mixture is stirred for days, the solution acquires a green colour; and the colour of the undissolved solid changes from medium green to light green. The light green precipitate is slightly soluble in CH_2Cl_2 and totally soluble in CH_3CN and CH_3NO_2 and THF. It is recrystallized by dropwise addition of dichloromethane to an acetonitrile solution of it. In CH_3CN the IR spectrum indicates cis dinitrosyls $1800(\text{s})$ and $1680(\text{s}) \text{ cm}^{-1}$. The ^1H NMR spectrum in CD_3CN or CD_3NO_2 consists of a wide resonance about δ 7.5, typical for phenylphosphine protons. The green solid does not decompose upon heating to 220°C . Elemental analysis gives results which are in good agreement with the formula $[\text{Mo}(\text{NO})_2(\text{OPPh}_3)_4](\text{PF}_6)_2$.

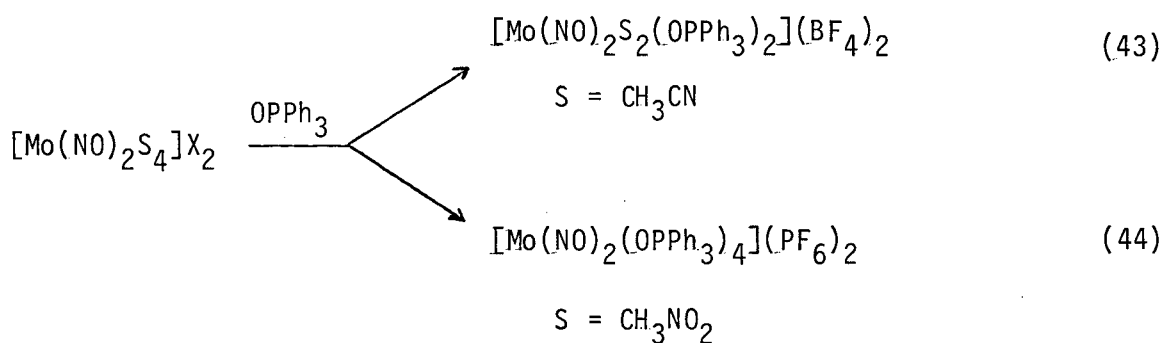
Interestingly, when the comparable reaction is performed using $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$, generated in situ, the same product is not obtained. The bright green microcrystals formed in this reaction are soluble in CH_2Cl_2 and chloroform, and they decompose upon heating to 134°C . The IR spectrum (CH_3CN) shows the ν_{NO} bands are at higher frequency than $[\text{Mo}(\text{NO})_2(\text{OPPh}_3)_4](\text{PF}_6)_2$, i.e., 1832 and 1721 cm^{-1} , indicating less electron density on the nitrosyl ligands. The proton NMR (CDCl_3) spectrum consists of two multiplets δ 7.65 (30H, $\text{P-C}_6\text{H}_5$) and 2.2 (6H, CH_3CN). ^{19}F NMR shows a singlet at δ +147 normal for BF_4^- salts.⁴⁸ The spectral data and the elemental analysis are consistent with the formulation $[\text{Mo}(\text{NO})_2(\text{OPPh}_3)_2(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$; only two

CH_3CN are replaced by OPPh_3 . IR evidence requires that this dication have cis nitrosyl moieties so there are three possible configurations: trans OPPh_3 ligands (A); trans CH_3CN ligands (B); all ligands cis (C).



However, the ^{31}P NMR spectrum consists of two single peaks +50.6 and +28.8; therefore, the phosphorus atoms must be inequivalent. Only the all cis structure C satisfies this requirement.

This reactivity with triphenylphosphine oxide serves to emphasize the possible advantages of employing $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ rather than $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ in reactions requiring a labile ligand.



With Sodium Amalgam: The reduction of $[\text{Mo}(\text{NO})_2(\text{PF}_6)_2]_n$ or $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ is effected by one equivalent of sodium amalgam in either a THF or CH_3CN solution. As previously mentioned the degree of

shift in NO absorption bands in the IR spectra during the reductions in THF are not nearly as marked as in acetonitrile (1790 and 1680 shift to 1780 and 1673 cm^{-1} in THF; 1828 and 1716 shift to 1800 and 1682 cm^{-1} in CH_3CN). To facilitate the isolation of the reduction product a Lewis base is added to the reaction solution. Choice of the ligand is prescribed by two considerations. First, phosphorus donating bases are avoided due to problems encountered with the dication (*vide supra*). Second, solubility of the resulting product has to be such that it can be separated from the side product of the reduction — NaPF_6 (soluble in THF, CH_3CN , and CH_3NO_2). For example 1,10-phenanthroline does not prove to be a satisfactory ligand. When it is added to a warm THF solution of the reduction product, immediately, a grey green precipitate forms, which has little solubility in any solvent. If this solid is refluxed in CH_3CN , the solution becomes light green in colour. Filtration, which leaves most of the original solid behind, and cooling of the filtrate result in the formation of a small amount of green powder that is virtually insoluble in even the most polar solvents. It has been formulated as impure $[\text{Mo}(\text{NO})_2(\text{phen})_2](\text{PF}_6)$ on the basis of its solid state properties. Anal. Calcd for $\text{MoN}_6\text{O}_2\text{C}_{24}\text{H}_{16}\text{PF}_6$: C, 43.57; H, 2.42; N, 12.71. Found: C, 43.72; H, 2.80; N, 13.46. IR (Nujol mull): $\nu(\text{NO})$ 1767 (s), 1645 (s) cm^{-1} ; also 1627 (s), 1605 (m), 1586 (m), 1500 (s), 1320 (s, br), 1220 (m), 1145 (m), 1055 (m, br), 850 (s, br), 730 (s) cm^{-1} . Mp. 165°C dec.

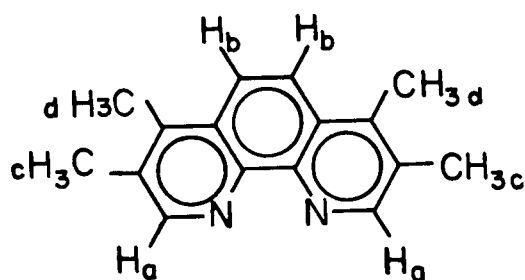
The ligands which best meet the criteria are nitrogen donor ligands 2,2'-bipyridine (bipy) and 3,4,7,8-tetramethyl-1,10-phenanthroline (phen'). Judged from the elemental analysis and the IR data each reacts with the

reduction product to give a complex with the formula $[\text{Mo}(\text{NO})_2\text{L}_2]\text{PF}_6$ where L_2 is the bidentate ligand 2,2'-bipyridine or 3,4,7,8-tetramethyl-1,10-phenanthroline. Both species are obtained in approximately 50% yield, and many of their physical properties are similar. For $\text{L}_2 = \text{bipy}$ the compound is green brown in colour, decomposes upon heating to 208°C , and has strong IR absorptions at $1775(\text{NO})$, $1639(\text{br})(\text{NO})$, and $845(\text{PF}) \text{ cm}^{-1}$ (Nujol mull). Its ^{19}F and ^{31}P NMR spectra in CD_3CN are typical for PF_6^- salts,^{48,40} being $\delta +71.2(\text{d})$ ($^1J_{^{19}\text{F}-^{31}\text{P}} = 707 \text{ Hz}$) and $\delta -144(\text{septet})$, respectively. For $\text{L}_2 = 3,4,7,8\text{-tetramethyl-1,10-phenanthroline}$, the solid is golden brown, decomposes at 187°C , and has strong IR bands in Nujol at $1786(\text{NO})$, $1660(\text{br})(\text{NO})$, and $845(\text{PF}) \text{ cm}^{-1}$. As expected for a PF_6 salt the ^{19}F NMR (CD_2Cl_2) consists of a doublet at $\delta +71.5$ ($^1J_{^{19}\text{F}-^{31}\text{P}} = 707 \text{ Hz}$) and the ^{31}P NMR shows a septet pattern centered at $\delta -147$. The solubility of each complex is dependent on L_2 . For $\text{L}_2 = 2,2'\text{-bipyridine}$ $[\text{Mo}(\text{NO})_2\text{L}_2]\text{PF}_6$ is soluble in CH_3CN , CH_3NO_2 , and very slightly soluble in THF. This lack of solubility in THF permits the NaPF_6 byproduct to be separated from the product. When phen' is the ligand used, it imparts a greater solubility to $[\text{Mo}(\text{NO})_2\text{L}_2]\text{PF}_6$ so that it is soluble in dichloromethane, and thus this nitrosyl species can be separated from the NaPF_6 .

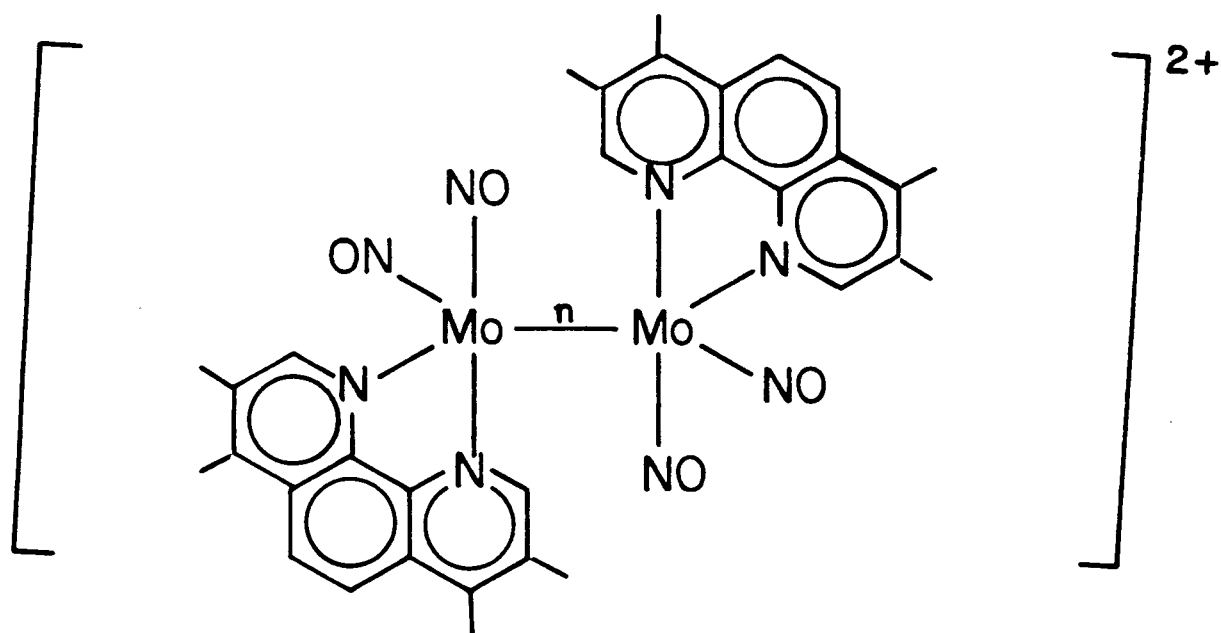
Dinitrosyl compounds of the type $[\text{M}(\text{NO})_2\text{L}_2]^+$ are known for cobalt¹¹⁸ with $\text{L} = \text{PPh}_3, \text{CH}_3\text{CN}, (\text{CH}_3)_2\text{CO}$ or $\text{L}_2 = \text{diphos}, \text{phenanthroline}, 1,5\text{-cyclo-octadiene}$. These are reported to be monomeric, obeying the eighteen electron rule. But a monomeric formulation for the case $\text{M} = \text{molybdenum}$ would leave the metal centre with formally only fifteen electrons. In such a case an

E.P.R. signal might be expected to be detected, but none is detected with a nitromethane ($\sim 10^{-3}M$) solution of the cation. Conductance data (Table V) give slopes for the plots $\Lambda_0 - \Lambda_e$ vs \sqrt{c} in the range of 2:1 electrolytes (vide supra). Taken together, these data suggest that the molybdenum dinitrosyl monocationic species are dimers, $[\text{Mo}(\text{NO})_2\text{L}_2]_2(\text{PF}_6)_2$. It is possible that under more forcing conditions, with the proper coordinating ligand, the metal-metal bond can be broken and another ligand introduced into the coordination sphere of the molybdenum. Such may be the explanation for the formation of $[\text{Mo}(\text{NO})_2(\text{phen})_2]\text{PF}_6$.

The ^1H NMR spectra which might be expected to elucidate the structure of these compounds are very complex. For $\text{L}_2 = \text{bipy}$ a very broad resonance is observed from 7.0 to 8.5 ppm with small doublets at 9.2 and 10.2 ppm in CD_3CN . Cooling the sample to -40°C , the solvent limit, did not improve the resolution. The ^1H NMR of $[\text{Mo}(\text{NO})_2\text{phen}']_2(\text{PF}_6)_2$ is also difficult to interpret. Free 3,4,7,8-tetramethyl-1,10-phenanthroline has a simple four line pattern in CDCl_3 : δ 8.91 (s, 2H_a): 8.01 (s, 2H_b); 2.66 (s, 6H_c); 2.31 (s, 6H_d).



Upon complexing to the molybdenum cation a myriad of resonances is seen in the regions δ 9.45 - 7.2 (1H, ring protons) and 3.2 - 0.8 (3H, -CH₃). The multitude of resonances in the methyl region of the phen' species seems to indicate the presence of several isomers. If one envisions a five coordinate molybdenum species with a Mo-Mo bond, a number of isomers is possible.



The phenanthroline ligands may be cis or trans to each other; the metal-metal bond order may be one (a 16 electron species) or three (an 18 electron

species); the arrangement of ligands around the molybdenum centres may be trigonal bipyramidal or square pyramidal.

Slow addition of one equivalent of LiBEt_3H ¹¹⁹ to a cold, -78°C , THF solution of the $[\text{Mo}(\text{NO})_2(\text{solvent})_4]^{2+}$ species also produces the same molybdenum dinitrosyl complex formed with one equivalent of sodium amalgam or sodium benzophenone. No evidence for a hydride species is detected by ^1H NMR.

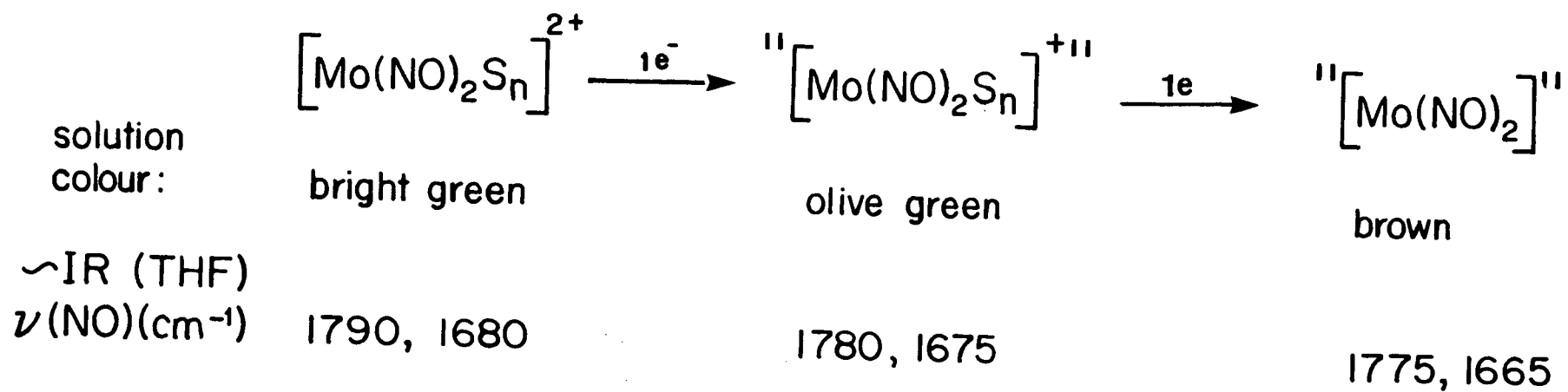
In some instances, when a large excess of a Lewis base L_2 is added to the reaction solution containing the monoreduced molybdenum dinitrosyl species, a white solid precipitates. This phenomenon has been observed when $\text{L}_2 = 1,10\text{-phenanthroline}$, $3,4,7,8\text{-tetramethyl-1,10-phenanthroline}$, or two triphenylphosphine oxides. Spot tests¹²⁰ reveal the presence of molybdenum, and IR data indicate the presence of L_2 and of PF_6^- . For example, when $\text{L}_2 = 2(\text{OPPh}_3)$ strong IR (Nujol) absorptions are visible at 1440, 1200, 1122, 843 (br) cm^{-1} , and when $\text{L}_2 = (\text{phen}')$ absorptions are observed at 1514 (m), 1016 (m), and 842 (s, br). ^1H NMR spectra merely confirm the presence of a coordinated L_2 in a symmetric environment (^1H NMR for $\text{L}_2 = 2(\text{OPPh}_3)(\text{CD}_3\text{NO}_2)$: δ 7.61 (m); for $\text{L}_2 = \text{phen}'(\text{CD}_3\text{NO}_2)_2$: δ 8.76 (s, 2H), 8.21 (s, 2H), 2.75 (s, 6H), 2.53 (s, 6H)). ^{19}F NMR spectra confirm the presence of the anion (^{19}F NMR for $\text{L}_2 = 2(\text{OPPh}_3)(\text{CD}_3\text{NO}_2)$: δ 72.7 (d, $^1\text{J}_{19\text{F}-31\text{P}} = 707$ Hz) and for $\text{L}_2 = \text{phen}'(\text{CD}_3\text{NO}_2)_2$: δ 73.0 (d, $^1\text{J}_{19\text{F}-31\text{P}} = 707$ Hz)). The ^{31}P NMR spectrum of the product $\text{L}_2 = 2(\text{OPPh}_3)$ not only affirms the presence of the PF_6^- anion (δ -144 (m, $^1\text{J}_{31\text{P}-19\text{F}} = 707$ Hz, CD_3CN)) but also that of equivalent phosphine oxide ligands (δ 29.8 (s; CD_3CN)).

On the basis of the elemental analyses and the data already cited these white solids have been tentatively formulated as $[\text{Mo}(\text{L}_2)_3]\text{PF}_6$ ($\text{L}_2 = 2(\text{OPPh}_3), \text{phen}', \text{ or phen}$). [Elemental analyses: (a) $\text{L}_2 = 2(\text{OPPh}_3)$, anal. calcd for $\text{MoO}_6\text{C}_{108}\text{H}_{90}\text{P}_7\text{F}_6$: C, 67.89; H, 4.71; N, 0.00; found: C, 68.13; H, 4.56; N, 0.00; (b) $\text{L}_2 = \text{phen}'$, anal. calcd. for $\text{MoN}_6\text{C}_{48}\text{H}_{48}\text{PF}_6$: C, 60.70; H, 5.06; N, 8.85; found: C, 61.99; H, 5.54; N, 9.01; and (c) $\text{L}_2 = \text{phen}$, anal. calcd for $\text{MoN}_6\text{C}_{36}\text{H}_{24}\text{PF}_6$: C, 55.31; H, 3.07; N, 10.76; found C, 56.30; H, 3.33; N, 10.82.] These species appear to be extremely hygroscopic. A nitromethane solution of $\text{Mo}(\text{OPPh}_3)_6\text{PF}_6$ ($\sim 10^{-4}\text{M}$) has a molar conductivity of $77.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ and is therefore in Geary's¹⁰⁷ range for a 1:1 electrolyte. $\text{Cr}(\text{phen})_3^+$ has been claimed¹²¹ as the product of disproportionation between $\text{Cr}(\text{phen})_3$ and $\text{Cr}(\text{phen})_3^{2+}$, but the molybdenum analogue has not previously been reported.

All attempts to isolate a neutral molybdenum nitrosyl compound by addition of two equivalents of reducing agent have failed. IR monitoring reveals a shift in the two ν_{NO} absorptions to even lower wave numbers than the monoreduced species. The solutions darken from the bright green colour of the dication to the dark green of the monocation to brown of the supposed neutral species, the transformation outlined in Scheme VI.

Providing " $\text{Mo}(\text{NO})_2^{2+}$ " with two electrons either through the agency of sodium amalgam or that of an anionic reagent (vide infra) in all cases produced the gradual decomposition of the resulting product. Formation of the non-nitrosyl containing species when a Lewis base is added to the monocationic nitrosyl suggests one pathway of decomposition is through loss of the nitrosyl ligand.

Scheme VI

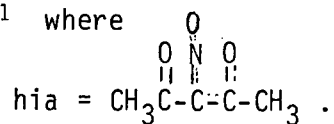


With Anionic Reagents: A. Sodium Acetylacetonate: Treatment of

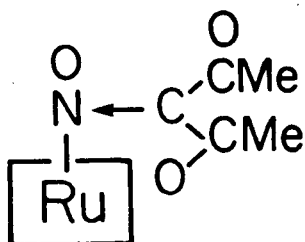
$[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ or $[\text{Mo}(\text{NO})_2\text{Cl}]_2$ with acetylacetone in the presence of sodium carbonate leads to the formation of $\text{cis-Mo}(\text{NO})_2(\text{acac})_2$.^{68,70,80}

The analogous reaction with $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ leads to the formation of green $\text{cis-Mo}(\text{NO})_2(\text{acac})_2$ as the major product and a minor amount of

$\text{Mo}(\text{NO})(\text{hia})(\text{acac})_2$ ⁸¹ where



The former compound was identified by its characteristic IR and ^1H NMR spectra. The latter was identified by its IR, ^1H NMR, and mass spectra, and elemental analysis. It has been identified previously⁸¹ as a product of the reaction of acac with dinitrosylmolybdenum derivatives in aqueous aerobic conditions. A similar transformation of acetylacetonate has been observed in the reaction of RuCl_3NO with that reagent in an acidic aqueous solution and has been ascribed as the result of nucleophilic attack on the nitrogen of the coordinated nitrosyl ligand by the γ carbon atom of an acetylacetonato ligand.¹²²



The following reactions fail to give isolable molybdenum nitrosyl products.

B. Sodium Cyclopentadienides: Like $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n^{123}$ $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4]-(\text{PF}_6)_2$ fails to give a tractable species when a THF or toluene solution of it is stirred with one or with two equivalents of sodium cyclopentadienide at room temperature or at -78°C . When NaCp is added, the green solution turns red brown in colour and a brown solid precipitates. A similar transformation is observed when the base is sodium methylcyclopentadienide. There is no observable change in colour or IR spectrum when cyclopentadiene is added to a THF solution of the dication. Neither of the hoped for products $[\text{CpMo}(\text{NO})_2\text{S}]^+$ nor $\text{Cp}(\eta^1\text{-Cp})\text{Mo}(\text{NO})_2$ is isolated.

C. Potassium Cyclooctatetraene: When either $[\text{Mo}(\text{NO})_2\text{Cl}_2]$ or $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4](\text{PF}_6)_2$ are treated with one equivalent of K_2COT at -78°C , the solution changes from green to red brown in colour; and on warming to room temperature a red brown, intractable solid precipitates. In the case of the reaction with the PF_6^- salt ν_{NO} bands are still visible in the IR spectrum of the supernatant, but no tractable species can be isolated. No reaction is observed when 1,3,5,7-cyclooctatetraene is added to a THF solution of the molybdenum hexafluorophosphate dication. No COT nitrosyl complex can be isolated.

D. $\text{Na}[\text{CpW}(\text{CO})_3]$ and $\text{K}[\text{CpFe}(\text{CO})_2]$: Adding $\text{Na}[\text{CpW}(\text{CO})_3]$ or $\text{K}[\text{CpFe}(\text{CO})_2]$ to a cold (-78°C) THF solution of either $\text{Mo}(\text{NO})_2\text{Cl}_2$ or $\text{Mo}(\text{NO})_2(\text{CH}_3\text{NO}_2)_4(\text{PF}_6)_2$ results in a reaction from which no molybdenum containing product can be isolated. In the case of the tungsten reagent two products are identified by means of their mass and infrared spectra: the major, $[\text{CpW}(\text{CO})_3]_2$ and the minor, $\text{CpW}(\text{CO})_2(\text{NO})$. With the iron reagent only the formation of $[\text{CpFe}(\text{CO})_2]_2$ is observed by infrared monitoring. The lack of any iron nitrosyl species is not surprising as it has been previously observed to be a strong nucleophile with NOCl , preferring to be oxidized rather than nitrosylated.¹²⁴ However, it had been hoped that either the Lewis base¹²⁵ $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]^-$ or $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ might combine with the Lewis acid $[\text{Mo}(\text{NO})_2\text{S}_4]^{2+}$ to form a multimetallic species with the molybdenum centre attached to the Lewis base either via a metal-metal bond or through a carbonyl oxygen. A tungsten-molybdenum bimetallic species is a possible intermediate in nitrosyl ligand transfer from molybdenum to tungsten. But electron transfer from $[\text{CpFe}(\text{CO})_2]^-$ to $\text{Mo}(\text{NO})_2^{2+}$ may occur by an inner or outer sphere mechanism.

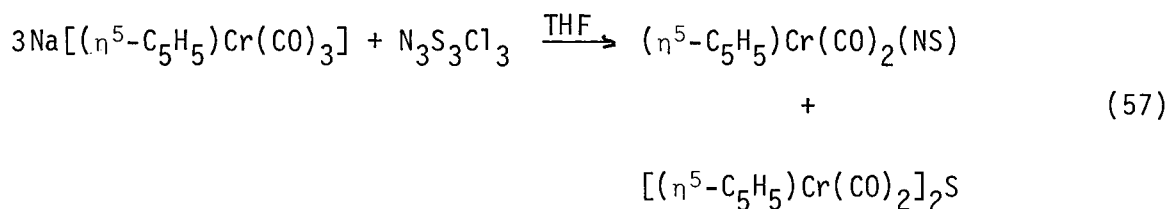
With $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2]_2$: Although the molybdenum dication fails to react with $\text{CpMo}(\text{CO})_2(\text{NO})$ or $(\text{CH}_3\text{C}_5\text{M}_4)\text{Mn}(\text{CO})_3$ (vide supra), $[\text{Mo}(\text{NO})_2(\text{CH}_3\text{CN})_4]-(\text{PF}_6)_2$ has been observed to act as an oxidizing agent with another neutral organometallic species. When $[\text{CpCr}(\text{NO})_2]_2$ ⁸⁵ is stirred with the molybdenum nitrosyl in CH_2Cl_2 in a 1:1 ratio, after three days the chromium dimer is consumed (inferred from loss of its bridging nitrosyl absorption (1510 cm^{-1}) in the IR spectrum). The chromium complex isolated is $[\text{CpCr}(\text{NO})_2(\text{CH}_3\text{CN})]-(\text{PF}_6)$, identified by its characteristic IR and ^1H NMR spectra.⁸⁶ Although

ν_{NO} bands are visible in the reaction solution that are not those of the identified chromium product, no molybdenum containing species can be isolated. Since this reaction and all subsequent work-up do not employ acetonitrile, that coordinated to the chromium must have originated from the molybdenum dication. Once again an acid/base adduct is presumably an intermediate.

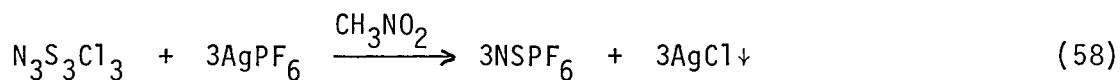
The molybdenum dinitrosyl dications appears to be Lewis acids which prefer to coordinate hard Lewis bases such as OPPh_3 , 2,2'-bipyridine, CH_3CN . However, any reagent capable of being oxidized readily gives up an electron to the molybdenum nitrosyl without resulting coordination, forming the molybdenum dinitrosyl monocation which can be isolated with bases such as 2,2-bipyridine and 3,4,7,8-tetramethyl-1,10-phenanthroline. " $\text{Mo}(\text{NO})_2^{2+}$ " readily accepts one or two electrons, but the neutral species is unstable and cannot be isolated. Just as hydride attack⁵² (vide supra) sometimes occurs at the coordinated nitrosyl resulting in the loss of that moiety, so it is possible electron transfer may disrupt the integrity of the nitrosyl ligand. This may account for the paucity of anionic nitrosyl complexes.¹²⁶

B. Cationic Thionitrosyl Complexes of Molybdenum and Other Group VIB Metals

Few thionitrosyl complexes exist¹²⁷ because no convenient source of NS^+ has been available. In this group $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2\text{NS}$ ¹²⁸ has been prepared by the reaction of $\text{N}_3\text{S}_3\text{Cl}_3$ ¹²⁹ in THF on $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]$ (reaction 57)



Unfortunately, this has not proved to be a general synthetic route to new thionitrosyl compounds. Recently, Herberhold¹³⁰ has reported that three equivalents of AgPF_6 added to a nitromethane solution of $\text{N}_3\text{S}_3\text{Cl}_3$ produce an in situ source of NSPF_6 presumably via reaction 58.



The filtrate when added to an acetonitrile solution of $\text{Cr}(\text{CO})_6$ produced $[\text{Cr}(\text{NS})(\text{CH}_3\text{CN})_5](\text{PF}_6)_2$ in 23% yield. Here are reported attempts to use this in situ NS^+ to prepare the thionitrosyl analogues of several known nitrosyl species which can be formed with nitrosonium salts, including some of those reported in Part IIA.

Experimental

All experimental procedures described here were performed under the same general conditions outlined in Part I and IIA. $\text{N}_3\text{S}_3\text{Cl}_3$ was prepared by the method of Jolly.¹²⁹ A nitromethane solution of "NSBF₄" was prepared following the outline reported by Herberhold.¹³⁰ Both $(\text{NSCl})_3$ and AgBF_4 were weighed and transferred into a three-necked flask in an inert atmosphere glove box. Once outside the glove box and attached to the dinitrogen manifold of a high vacuum line, the reaction flask was charged with nitromethane (15 mL). The orange reaction mixture was stirred for three or four minutes and then was filtered through a medium porosity frit, to remove the precipitated AgCl , through all glass connections directly into the flask containing a solution or slurry of the organometallic reactant.

Reaction of "NSBF₄" with $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]$ ($\text{M} = \text{Cr or Mo}$). When a freshly prepared nitromethane solution (10 mL) of "NSBF₄" (~2.0 mmol) was added to a cold (0°C) nitromethane solution (20 mL) of $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]$ ^{53,82} (0.45 g, 2.0 mmol), the solution turned green in colour and gas evolved. The solvent was removed in vacuo, and the residue extracted with hexanes (10 x 25 mL) and filtered. The filtrate was taken to dryness in vacuo, and sublimation of the green brown residue onto a dry-ice-cooled probe (30°C, 5×10^{-3} mm) afforded red crystals of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NS})$ (0.05 g, 11% yield), identified by its spectroscopic properties;¹²⁸ IR (hexanes): ν_{CO} 2033, 1962 cm^{-1} ; ν_{NS} 1180 cm^{-1} ; ^1H NMR (CDCl_3): δ 5.08 (s).

The green hexanes residue which did not sublime was recombined with the original reaction residue. These combined solids were suspended in toluene and transferred to the top of a 3 x 10 cm Florisil column. Elution of the column with toluene afforded a broad green band which was collected and taken to dryness under reduced pressure. The green residue which resulted was recrystallized from dichloromethane/hexanes to give green crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2\text{S}$ (0.15 g, 11% yield) which were identified by their characteristic IR and ^1H NMR spectra:¹²⁸ IR(hexanes): ν_{CO} 2000, 1960, 1932, 1924 cm^{-1} ; ^1H NMR (CDCl_3): δ 4.87 (s).

When $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]^{82}$ (0.50 g, 1.9 mmol) was treated in an analogous manner, the main product proved to be the well-known red $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2^{83}$ (0.13 g, 28% yield). IR(CH_2Cl_2): ν_{CO} 1960, 1915 cm^{-1} . ^1H NMR (CDCl_3): δ 5.20. The orange product which sublimed from the hexanes extracts in trace amounts was indentified as $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{NO})$ by its characteristic spectral properties:⁸² [IR(CH_2Cl_2): ν_{CO} 2020, 1937; ν_{NO} 1663 cm^{-1} ; ^1H NMR (CDCl_3): δ 5.53 (s)]. No thionitrosyl-containing species was isolated.

Reaction of "NSBF₄" with $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{NO})$. Into an orange nitromethane (5 mL) or acetonitrile (10 mL) solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{NO})^{82}$ (0.68 g, 2.45 mmol) was filtered a nitromethane solution (10 mL) of "NSBF₄" (\sim 2.45 mmol). The reaction mixture became deep purple in colour. The solvent was removed under reduced pressure, and the residue was washed with dichloromethane (4 x 20 mL). The remaining purple black solid was redissolved in nitromethane (10 mL), and to it triphenylphosphine (0.64 g, 2.4 mmol) was

added. Once again the nitromethane was removed in vacuo, and the residue dissolved in dichloromethane (40 mL) and refluxed for one hour. The reaction solution was taken to dryness under reduced pressure and washed with toluene (3 x 15 mL). Subsequent recrystallization from dichloromethane/diethylether (25 mL/15 mL) led to the isolation of a brown solid $[(\eta^5\text{-C}_5\text{H}_5)\text{-Mo(NO)(NS)PPh}_3]\text{BF}_4$ (0.70 g, 66% yield)

Anal. Calcd for $\text{MoC}_{23}\text{H}_{20}\text{N}_2\text{OSPBF}_4$: C, 47.10; H, 3.41; N, 4.78. Found: C, 47.37; H, 3.65; N, 5.00. IR (Nujol mull): $\nu(\text{NO})$ 1636 (s, br); $\nu(\text{NS})$ 1092 (s), $\nu(\text{BF})$ 1054 (s, br); also 830 (w, br), 746 (w), 693 (m). IR (CH_2Cl_2): $\nu(\text{NO})$ 1647 (s, br); $\nu(\text{NS})$ 1069 (s); $\nu(\text{BF})$ 1030 (s). ^1H NMR (CDCl_3): 7.44 (m, 15H, $\text{P}(\text{C}_6\text{H}_5)_3$), 5.93 (br m, 5H, C_5H_5). Conductivity (CH_3NO_2): $\Lambda_0 = 77.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$; slope $\Lambda_0 - \Lambda_e$ vs $\sqrt{C} = 186$. Mp (air) 133°C dec.

Reaction of "NSBF₄" with Mo(CO)_6 . As a deep orange nitromethane (20 mL) solution of "NSBF₄" (~ 3.1 mmol) was filtered into a clear dichloromethane (25 mL) solution of Mo(CO)_6 (0.41 g, 1.5 mmol) the reaction mixture turned black and a black precipitate formed. The solvent was decanted, and the black solid was rinsed with dichloromethane (3 x 15 mL) and redissolved in nitromethane (10 mL). To this solution triphenylphosphine (1.6 g, 6.1 mmol) was added. The solvent was removed in vacuo, and the brown residue was dissolved in dichloromethane (30 mL) and refluxed one hour. The infrared spectrum of the dichloromethane solution ($\nu_{\text{NS}} \approx 1105 \text{ cm}^{-1}$) was unaffected by refluxing. Filtration of the dichloromethane mixture, addition of toluene (25 mL), and partial removal of the solvent under reduced

pressure produced a brown solid (0.40 g). Anal. Found: C, 58.05; H, 4.19; N, 5.65. IR (CH_2Cl_2): $\nu(\text{NS})$ 1105 (s); $\nu(\text{BF})$ 1057 (s); also 1555 cm^{-1} . ^1H NMR (CD_3NO_2): δ 7.28 (m). Molar conductivity: $\Lambda_m = 198 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$.

Results and Discussion

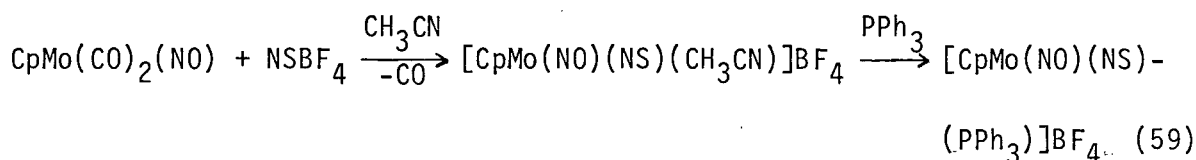
Reactions of "NSBF₄" with Transition Metal Cyclopentadienyl Carbonyl Species

A fresh solution of "NSBF₄" combined with NaCpCr(CO)₃ in nitromethane gives the same products obtained when N₃S₃Cl₃ is employed as the thionitrosylating agent, i.e. CpCr(CO)₂NS and [CpCr(CO)₂]₂S.¹²⁸ Both products are identified by their spectral properties: IR and ¹H NMR. However, like N₃S₃Cl₃, in situ "NSBF₄" fails to produce the carbonyl thionitrosyl analogues when reacted in a similar mode with Na[CpMo(CO)₃]. The major product of this reaction is [CpMo(CO)₃]₂;⁸³ a trace product is identified as CpMo(CO)₂(NO).⁸² Both are identified by their IR and ¹H NMR spectra. Observation of a nitrosyl product suggests some oxidation of the thionitrosyl.

Surprisingly, no reaction is evidenced when a fresh nitromethane solution of "NSBF₄" is filtered into an acetonitrile solution of (CH₃C₅H₄)Mn(CO)₃. This organometallic species is readily nitrosylated by NOPF₆¹⁰⁵ to produce [(CH₃C₅H₄)Mn(CO)₂(NO)]PF₆.

An orange acetonitrile solution of CpMo(CO)₂(NO) turns deep purple in colour when a nitromethane solution of "NSBF₄" is filtered into it. Addition of diethyl ether to the reaction mixture results in the precipitation of a purple solid, which from IR and ¹H NMR spectral evidence may be [CpMo(NO)(NS)(CH₃CN)]BF₄. [IR (Nujol mull): ν(CN) 2320 (w), 2350 (w); ν(NO) 1650 (s, br); ν(NS) 1065 (s); ν(BF) 1035 (s, br). ¹H NMR (CD₃CN) 6.21 (m, br).] To stabilize this cation, which appears to lose solubility in solution with the passage of time, PPh₃ is added to replace the acetonitrile ligand. The

purple product now forms a dichloromethane solution from which $[\text{CpMo}(\text{NO})(\text{NS})(\text{PPh}_3)]\text{BF}_4$ can be precipitated by addition of toluene. The overall transformation is shown in reaction 59.



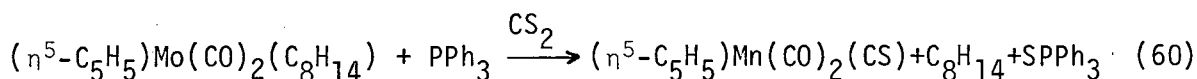
The infrared spectrum (CH_2Cl_2) confirms this formulation exhibiting a nitrosyl absorption at 1647 (s, br), a thionitrosyl absorption at 1069 (s), and an absorption at 1030 (s, br) cm^{-1} characteristic of a BF_4^- anion with tetrahedral symmetry. The proton NMR (CDCl_3) displays resonances at δ 7.44 (m, 15H) and 5.93 (br m, 5H) which are in the right range and of the correct intensity to be due to the phenyl protons of triphenylphosphine and the cyclopentadienyl protons. The puzzling feature is that instead of a sharp cyclopentadienyl resonance which is usually found in cyclopentadienyl complexes a very broad signal is observed. No satisfactory explanation has been found for this phenomenon. Conductivity measurements of a nitromethane solution ($\sim 10^{-3}\text{M}$) of the cation are consistent with its being a 1:1 electrolyte (see Table V). A similar reaction occurs when a nitromethane "NSBF₄" solution is added to $(\eta^5\text{C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NO})$.⁸² The infrared and ^1H NMR spectra are analogous to the molybdenum thionitrosyl cation. The IR spectrum (CH_2Cl_2) exhibits a ν_{NO} at 1630 (s), a ν_{NS} at ~ 1100 (s), and a ν_{BF} at ~ 1055 (s, br) cm^{-1} ; the ^1H NMR spectrum has a multiplet at δ 7.58 assignable

to the phenyl protons of PPh_3 and the same strange broad resonance at δ 6.12. The ^{19}F NMR spectrum (CD_3CN) shows a singlet at δ 148 which is characteristic of BF_4^- . However, a satisfactory elemental analysis has not been obtained to substantiate the formulation $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})(\text{NS})\text{PPh}_3]\text{-BF}_4$.

Reactions of "NSBF₄" with $\text{Mo}(\text{CO})_6$.

In hopes of isolating a $[\text{Mo}(\text{NS})_2\text{L}_4](\text{BF}_4)_2$ species analogous to the dinitrosyl dications discussed earlier in this work, a nitromethane solution of "NSBF₄" is filtered into a clear dichloromethane solution of $\text{Mo}(\text{CO})_6$. The solution turns dark purple in colour, and a black precipitate forms. This solid is dissolved in nitromethane and treated with a Lewis base, L. When L is acetonitrile or isobutyronitrile the product can be precipitated by dropwise addition of CH_2Cl_2 . In each case the isolated product appears to be hydrolyzed, despite handling in a dry dinitrogen atmosphere. The Nujol mull IR spectra show bands at ~ 2300 (w) (CN) and ~ 1050 (s, br) (NS and/or BF), and 3300 (s) (OH) cm^{-1} . If the mull of the purple isobutyronitrile product is exposed to the atmosphere for two hours, it becomes completely green in colour; the OH stretching band increases in intensity, while the CN band disappears. The elemental analyses are not consistent with there being four nitriles around the molybdenum centre. The carbon, nitrogen, and hydrogen contents are low; this taken with the IR data suggests nitrile ligands are readily replaced by water. Further attempts to characterize these species have been abandoned due to their extreme moisture sensitivity.

When PPh_3 is used as the Lewis base instead of a nitrile, a dichloromethane-soluble, purple solid can be isolated. Spectral data is not inconsistent with the formulation $[\text{Mo}(\text{NS})_2(\text{PPh}_3)_4](\text{BF}_4)_2$; [IR (CH_2Cl_2): $\nu(\text{NS})$ 1105 (s); $\nu(\text{BF})$ 1057 (s); also 1555 cm^{-1} ; ^1H NMR (CD_3NO_2): δ 7.28 (m)]. A conductance measurement of a nitromethane solution ($\sim 10^{-3}\text{M}$) of this thionitrosyl dication confirms it as a 2:1 electrolyte. However, the elemental analysis of C, H, and N is not consistent with the formulation $[\text{Mo}(\text{NS})_2(\text{PPh}_3)_4](\text{BF}_4)_2$ ($\text{MoN}_2\text{S}_2\text{C}_{72}\text{H}_{60}\text{P}_4\text{B}_2\text{F}_8$) which requires a C:H:N ratio of 36:30:1 while the one obtained is 12:10:1. The tendency of phosphines to react with coordinated nitrosyl ligands has already been discussed (see reaction 55). Phosphines are such strong thiophiles that triphenylphosphine is sometimes employed to abstract sulfur as in reaction 60.¹³¹



It is possible that the reaction of $\text{Mo}(\text{CO})_6$ with in situ "NSBF₄" produces the thionitrosyl analogue of the molybdenum dinitrosyl dication, but because NS^+ is a strong oxidizing agent further reactions occur in the presence of phosphine.

Use of triphenylphosphine oxide as the coordinating ligand instead of PPh_3 does not appear to alleviate the problem. No satisfactory elemental analysis has been obtained for the green product formed though its spectral properties were those expected for $[\text{Mo}(\text{NS})_2(\text{OPPh}_3)_4](\text{BF}_4)_2$: [IR (CH_2Cl_2):

$\nu(\text{NS}) \sim 1120$ (s); $\nu(\text{BF}) \sim 1055$ (s, br). ^1H NMR (CDCl_3): δ 7.3]. Use of the nitrogen ligand 2,2'-bipyridine produces a red solid which is only soluble in nitromethane or acetonitrile, thus, making separation from the residual "NSBF₄" difficult.

Although NOCl reacts with a variety of Lewis acids to form NO^+ , $(\text{SNCl})_3$ reacts with Lewis acids to form numerous products.¹³² Further, chloride abstraction from $\text{P}_3\text{N}_3\text{Cl}_6$ does not form PN^+ cleanly though reaction with silver salts results in the precipitation of silver chloride.¹³³ Therefore, it appears that the reaction of $(\text{SNCl})_3$ with AgBF_4 yields a complex mixture which does not provide a clean source of NS^+ . Moreover, if thionitrosyl species are produced they may be prone to form thio rather than thionitrosyl complexes. It should be noted that the principal product of the attempted thionitrosylation of $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]$ with $\text{N}_3\text{S}_3\text{Cl}_3$ or "NSBF₄" is not the thionitrosyl $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2\text{NS}$ but the bridging sulfur complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2\text{S}$. Thus, thionitrosyl organometallic complexes remain a rarity.

C. Reaction of Acetonitrile with NOPF_6 .

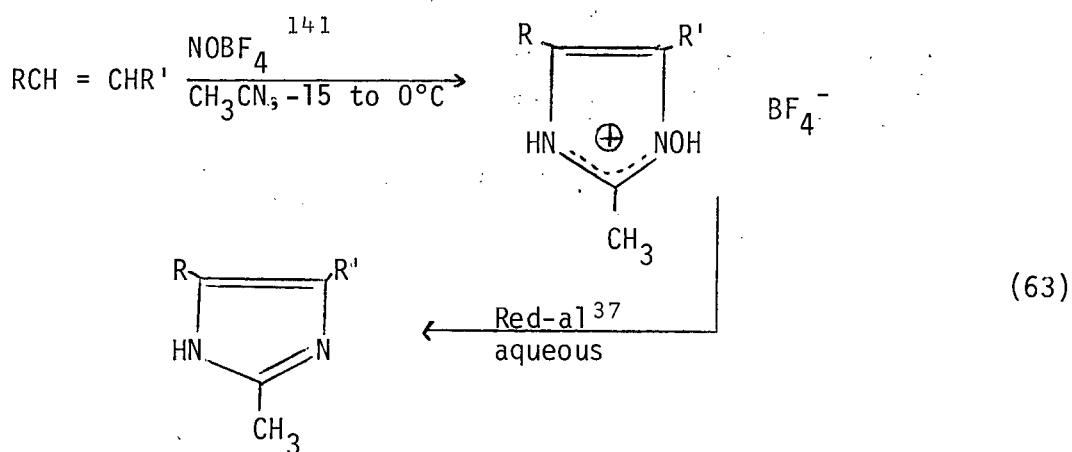
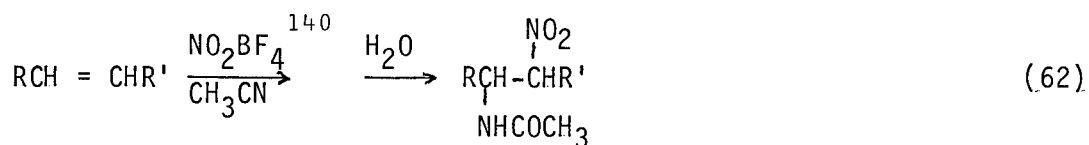
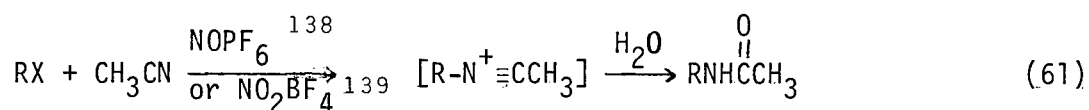
Recently Herberhold¹³⁴ has reported that a binary nitrosyl dication $[\text{Fe}_2(\text{NO})_6](\text{PF}_6)_2$ can be formed from the reaction of NOPF_6 with iron powder in nitromethane media. It would seem that both the solvent and the nitrosylating agent are critical in this reaction since in acetonitrile NOBF_4 with any of the metals Mn, Fe, Co, Ni, Zn, Cu,¹³⁵ or Pd¹³⁶ forms the dipositive metal acetonitrile species $[\text{M}(\text{CH}_3\text{CN})_n]^{2+}(\text{BF}_4)_2$; and nitrosyl metal chlorides are produced from the action of NOCl on certain metals Al, Ga, In, Pt, Au.¹³⁷

In an attempt to form simple, binary nitrosyl complexes of the group VIB elements, tungsten beads were treated with NOCl in THF or dichloromethane or with NOPF_6 in nitromethane; no nitrosyl species formed. However, when tungsten beads and NOPF_6 were stirred in acetonitrile for one day the clear solution over the tungsten acquired a pinkish tint and bands began to appear in the $1850 - 1650 \text{ cm}^{-1}$ region of the IR spectrum. After three days the solution over the tungsten beads was deep red purple in colour and the ν_{NO} IR band of NOPF_6 had disappeared. The purple solution was decanted from the tungsten; dichloromethane was added dropwise; and a purple brown solid was isolated. Conventional wet analysis methods¹²⁰ determined that the solid contained no tungsten. Subsequently, it was found that the same reaction could be effected by using chromium powder or with no metal present at all would proceed slowly, initiating after seven days. However, the purple colour was only produced if the $\text{NOPF}_6/\text{CH}_3\text{CN}$ solution were in a dry nitrogen atmosphere. If acetonitrile was replaced by isobutyronitrile, no reaction with NOPF_6 was evidenced even in the presence of tungsten.

The purple brown solid is difficult to characterize as it is extremely hygroscopic. It is soluble in polar and donating solvents: butanol, acetone, water, acetonitrile, nitromethane, tetrahydrofuran, methanol, and ethylacetate. It is insoluble in all hydrocarbon solvents and in dichloromethane and diethylether. Aqueous solutions have a pH of 2.1. The physical and spectral properties of this purple brown solid are reported below.

IR (Nujol mull): 3328 (s, br), 1751 (m), 1690 (m), 1634 - 1575 (m, vbr), 1267 (m, br), 1203 (m, br), 1137 (m, br), 1039 (m, vbr), 844 (s, br), 743 (m) cm^{-1} . (Fluorolube mull: 3320 (s, br), 2947 (w), 1755 (m), 1696 (s), 1627 (m, br), 1526 (s, br), 1425 (m), 1377 (m), 842 (s, br) cm^{-1} . NMR (CD_3NO_2): ^1H : δ 12.8 - 11.1 (br, 1H), 9.0 - 8.0 (br, 1H), 2.08 - 2.05 (m, 8H); ^{19}F : δ 71.5 (d, PF_6 , $^1J_{^{19}\text{F}-^{31}\text{P}}$ = 696 Hz). Mass spectrum (common peaks of three): 117 ($\text{C}_2\text{HN}_3\text{PF}$, $\text{CH}_4\text{O}_2\text{PF}_2$); 107 (PF_4); 104 (OPF_3); 101 ($\text{CH}_4\text{-OPF}_2$); 88 (PF_3); 85 (OPF_2); 59 (C_2NOH_5); 51 (CHF_2); 45 ($\text{C}_2\text{H}_5\text{O}$); 43 (CH_3N_2); 41 (C_3H_5). Elemental analysis (average of four): C, 21.7; H, 2.74; N, 16.4 (C:H:N = 1.54/2.34/1.00).

When the polymerization of THF by NOPF_6 was studied by Eckstein and Dreyfuss,¹⁰⁰ they noted that lower yields of polymeric THF were obtained when CH_3CN was the solvent, suggesting some side reaction involving CH_3CN . Acetonitrile has been known to participate in reactions with nitrosonium and nitronium salts:



It is known that commercial acetonitrile often contains traces of acrylonitrile which are difficult to remove.¹⁴² If acrylonitrile reacts with NOPF_6 as an olefin, a reaction such as 62 or 63 might occur. Indeed, addition of acrylonitrile to an acetonitrile solution of NOPF_6 causes initial colouration to appear in one day. Since this is about the same rate of colour formation observed when tungsten is present, it is possible that the metal catalyzes the decomposition of acetonitrile to acrylonitrile.

This intriguing purple solid, although apparently a PF_6^- salt of some sort of oligomerized acetonitrile, is definitely not the desired binary metal nitrosyl; therefore, further attempts to ascertain its identity have been abandoned. It is evident, however, since NOPF_6 reacts with tetrahydrofuran, acetonitrile, and methanol, that nitromethane is the only solvent in which NOPF_6 can dissolve and maintain its integrity; it should be the solvent of choice in reactions involving nitrosonium salts.

This study has shown the feasibility of preparing the $\text{Mo}(\text{NO})_2^{2+}$ unit both with and without coordinated solvent molecules and of reducing it to a monocationic Mo centre. Both the neutral " $\text{Mo}(\text{NO})_2$ " unit and analogous thionitrosyl species remain elusive. The role of the solvent in reactions involving nitrosonium salts has been demonstrated. Since both tetrahydrofuran and acetonitrile are capable of reacting with NOPF_6 , nitromethane and dichloromethane are the only innocent solvents which are presently employed in NO^+ reactions, and of these two only the former dissolves NOPF_6 .

References and Notes

1. Schutzenberger, M.P. Annales Chim. Phy. 1868, 15, 100.
2. a. Orgel, L.E. "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory"; Wiley: New York, 1960, pp 135-143.
 b. Pauling, L. "The Nature of the Chemical Bond"; 3rd ed.; Cornell Univ. Press: New York, 1960, pp 331-336.
3. a. Wender, I.; Pino, P., Eds. "Organic Synthesis via Metal Carbonyls"; Vols I and II, Wiley: New York, 1968 and 1977.
 b. Abel, E.W.; Stone, F.G.A. "The Chemistry of Transition-Metal Carbonyls: Synthesis and Reactivity"; Quart. Rev. 1970, 24, 498.
 c. King, R.B. in "Methodicum Chemicum"; Niedenzu, K.; Zimmer, H., Eds.; Academic Press: New York, 1976, 8, 421.
4. a. Griffiths, W.P. Adv. Organomet. Chem., 1968, 7, 211.
 b. Pierpont, C.G.; Van Derveer, D.G.; Durland, W.; Eisenberg, R. J. Am. Chem. Soc. 1970, 92, 4760.
5. Candlin, J.P.; Janes, W.H. J. Chem. Soc. C, 1968, 1856.
6. Ballivet-Tkatchenko, D.; Riveccie, M.; El Murr, N. Inorg. Chim. Acta 1978, 30, L289.
7. Kolthammer, B.W.S.; Legzdins, P. J. Chem. Soc., Dalton Trans. 1978, 31.
8. Kolthammer, B.W.S.; Legzdins, P.; Martin, D.T. Tetrahedron Let. 1978, 4, 323.
9. Hieber, W.; Leutert, F. Naturwissenschaften 1931, 19, 360.
10. Wilkinson, G.; Birmingham, J.M. J. Am. Chem. Soc. 1955, 77, 3421.
11. a. Fischer, E.O.; Hafner, W. Z. Naturforsch. 1955, 10b, 140.
 b. Fischer, E.O.; Hafner, W.; Stahl, H.O. Z. Anorg. Allg. Chem. 1955, 282, 47.
 c. Fischer, E.O. Inorg. Synth. 1963, 7, 136.

12. Chatt, J.; Duncanson, L.A.; Shaw, B.L.; Proc. Chem. Soc. 1957, 343.
13. a. Ibers, J.A. Annu. Rev. Phys. Chem. 1965, 16, 389.
b. Bau, R., Ed., "Transition-Metal Hydrides", Adv. in Chem. Series, 167; American Chemical Society: Washington, D.C., 1978.
14. For general reviews of the properties of transition-metal hydride complexes:
a. Ginsberg, A.P. In "Transition Metal Chemistry", vol. 1; Carlin, R.L., Ed.; Marcel Dekker: New York, 1965, pp 111-237.
b. Green, M.L.H.; Jones D.J. Adv. Inorg. Chem. Radiochem. 1965, 7, 115.
c. Schunn, R.A. In "The Hydrogen Series", Vol. 1; Muetterties, E.L., Ed.; Marcel Dekker: New York, 1971; pp 203-269.
d. Kaesz, H.D.; Saillant R.B. Chem. Rev. 1972, 72, 231.
15. a. Wengrovius, J.H.; Schrock, R.R.; Churchill, M.R.; Wasserman, H.J. J. Am. Chem. Soc. 1982, 104, 1739.
b. Belmonte, P.A.; Schrock, R.R.; Day C.S. J. Am. Chem. Soc. 1982, 104, 3082.
c. Gell, K.I.; Posin, B.; Schwartz, J.; Williams, G.M. J. Am. Chem. Soc. 1982, 104, 1846; and references therein.
16. Jesson, J.P. In "The Hydrogen Series", vol. 1; Muetterties, E.L., Ed.; Marcel Dekker: New York, 1971; pp 75-201.
17. Hieber, W.; Lindner, E. Chem. Ber. 1961, 94, 1417.
18. Hieber, W.; Duchatscher, H. Chem. Ber. 1965, 98, 2933.
19. Hieber, W.; Hübel, W. Z. Elektrochem. 1953, 57, 235.
20. Chatt, J.; Coffey, R.S.; Shaw, B.L. J. Chem. Soc. 1965, 7391.
21. Heck, R.F.; Breslow, D.S. J. Am. Chem. Soc. 1961, 83, 4023.
22. L'Éplattenier, F.; Calderazzo, F. Inorg. Chem. 1968, 7, 1290.
23. Slater, S.G.; Lusk, R.; Schumann, B.F.; Darensbourg, M. Organometallics 1982, 1, 1662.
24. Chatt, J.; Johnson, N.P.; Shaw, B.L. J. Chem. Soc. A 1967, 604.

25. Vaska, L.; Diluzio, J.W. J. Am. Chem. Soc. 1962, 84, 679.
26. Vaska, L.; J. Chem. Soc., Chem. Commun. 1966, 614.
27. Treichel, P.M.; Shubkin, R.L. Inorg. Chem. 1967, 6, 1328.
28. a. Hayter, R.G. J. Am. Chem. Soc. 1966, 88, 4376.
 b. Anders, U.; Graham, W.A.G. J. Chem. Soc., Chem. Commun. 1965, 499.
29. Keim, W. J. Organometal. Chem. 1968, 14, 179; 1967, 8, C25.
30. King, R.B.; Pannell, K.H. Inorg. Chem. 1968, 7, 2356.
31. Vaska, L.; DiLuzio, J.W. J. Am. Chem. Soc. 1962, 84, 4989.
32. James, B.R.; Preece, M.; Robinson, S.D. Inorg. Chim. Acta, 1979, 34, L219.
33. Stewart, R.P.; Okamoto, N.; Graham, W.A.G. J. Organomet. Chem. 1972, 42, C32.
34. Tam, W.; Lin, G.Y.; Wong, W.K.; Kiel, W.A.; Wong, V.K.; Gladysz, J.A. J. Am. Chem. Soc. 1982, 104, 141.
35. Legzdins, P.; Martin, D.T. Inorg. Chem. 1979, 18, 1250.
36. Johnson, B.F.G.; Raithby, P.R.; Zuccaro, C. J. Chem. Soc., Dalton Trans. 1980, 99.
37. Red-al is a trade name of the Aldrich Chemical Co. for $\text{NaH}_2\text{Al}(\text{OCH}_2\text{-CH}_2\text{OCH}_3)_2$.
38. Shriver, D.F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.
39. Perrin, D.D.; Armarego, W.L.F.; Perrin, D.R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: Oxford, 1980.
40. Crutchfield, M.M.; Dungan, C.H.; Letcher, J.H.; Mark V.; VanWazer, J.R. "Topics in Phosphorus Chemistry", vol. 5; Grayson, M.; Griffith, E.J., Eds.; Wiley-Interscience: New York, 1967, p 227.
41. Kolthammer, B.W.S.; Legzdins, P. Inorg. Chem. 1979, 18, 889.
42. Kolthammer, B.W.S. Ph.D. Dissertation, The University of British Columbia, 1979.

43. Legzdins, P.; Martin, D.T.; Nurse, C.R. Inorg. Chem. 1980, 19, 1560.
44. Connelly, N.G. Inorg. Chim. Acta Rev. 1972, 6, 47.
45. Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970, p 110.
46. Weast, R.C., Ed. "Handbook of Chemistry and Physics", 52nd ed., Chemical Rubber Co.: Cleveland, 1972, pp B-440.
47. Pregosin, P.S.; Kunz, R.W. "³¹P and ¹³C NMR of Transition Metal Phosphine Complexes", Springer-Verlag: New York, 1979.
48. Dungan, C.H.; VanWaze, J.R. "Compilation of Reported ¹⁹F NMR Chemical Shifts", Wiley-Interscience: New York, 1970.
49. Legzdins, P.; Martin, D.T.; manuscript in preparation.
50. Graham, W.A.G.; Sweet, J.R. J. Am. Chem. Soc. 1982, 104, 2811.
51. Letts, J.B.; Mazanec, T.J.; Meek, D.W. J. Am. Chem. Soc. 1982, 104, 3898.
52. Hames, B.W.; Legzdins, P.; Oxley, J.C. Inorg. Chem. 1980, 19, 1565.
53. Piper, T.S.; Wilkinson, G. J. Inorg. Nucl. Chem. 1956, 3, 104.
54. a. Becker, E.D. "High Resolution NMR", 2nd ed.; Academic Press: New York, 1980, Chp 7.
b. Pople, J.A.; Schneider, W.G.; Bernstein, H.J. "High-resolution Nuclear Magnetic Resonance"; McGraw-Hill: New York, 1959, pp 132-138.
c. Leyden, D.E.; Cox, R.H. "Analytical Applications of NMR"; Wiley-Interscience: New York, 1977, Chp. 4.
55. James, T.A.; McCleverty, J.A. J. Chem. Soc. (A) 1971, 1068.
56. a. Tolman, C.A. J. Am. Chem. Soc. 1970, 92, 2956.
b. Tolman, C.A. Chem. Rev. 1977, 77, 313.
57. Druliner, J.D.; English, A.D.; Jesson, J.P.; Meakin, P.; Tolman, C.A. J. Am. Chem. Soc. 1976, 98, 2156.
58. Faller, J.W.; Anderson, A.S. J. Am. Chem. Soc. 1970, 92, 5852 and references therein.

59. a. Kalck, P.; Poilblanc, R. J. Organomet. Chem. 1969, 19, 115.
b. Kalck, P.; Pince, R.; Poilblanc, R.; Roussel, J. J. Organomet. Chem. 1970, 24, 445.
60. Meek, D.W.; Mazanec, T.J. Acc. Chem. Res. 1981, 14, 266.
61. McNeese, T.J.; Wreford, S.S.; Foxman, B.M. J. Chem. Soc., Chem. Commun. 1978, 500.
62. Giusto, G.; Ciani, G.; Manassero, M. J. Organomet. Chem. 1976, 105, 91.
63. Chen, H.W.; Jolly, W.L.; Xiang, S.F.; Legzdins, P. Inorg. Chem. 1981, 20, 1779 and references contained therein.
64. Sabherwal, I.H.; Burg, A.B. J. Chem. Soc., Chem. Commun. 1970, 1001.
65. a. Swanson, B.I.; Satija, S.K. J. Chem. Soc., Chem. Commun. 1973, 40.
b. Herberhold, M.; Razavi, A. Angew. Chem. Int. Ed. Engl. 1972, 11, 1092.
c. Herberhold, M.; Razavi, A. J. Organomet. Chem. 1974, 67, 81.
66. Griffith, W.P.; Lewis, J.; Wilkinson, G. J. Chem. Soc. 1958, 3993.
67. a. Addison, C.C.; Lewis, J. Q. Rev., Chem. Soc. 1955, 9, 115.
b. Lewis, J. Sci. Prog. (London) 1959, 47, 506.
68. Green, M.; Taylor, S.H. J. Chem. Soc., Dalton Trans. 1972, 2629.
69. Clamp, S.; Connelly, N.G.; Taylor, G.E.; Louttit, T.S. J. Chem. Soc., Dalton Trans. 1980, 2162.
70. Johnson, B.F.G.; Khair, A.; Savory, C.G.; Walter, R.H.; Al-Obaidi, K.H.; Al-Hassam, T.J. Transition Met. Chem. 1978, 3, 81.
71. Johnson, B.F.G.; Bhaduri, S.; Connelly, N.G. J. Organomet. Chem. 1972, 40, C36.
72. Mocella, M.T.; Okamoto, M.S.; Barefield, E.K. Synth. React. Inorg. Met. Org. Chem. 1974, 4(1), 69.
73. Connelly, N.G.; Davies, J.D. J. Organomet. Chem. 1972, 38, 385.
74. Tatsumi, T.; Sekizawa, K.; Tominaga, H. Bull. Chem. Soc. Jpn. 1980, 53, 2297.

75. Connelly, N.G.; Kelly, R.L. J. Chem. Soc., Dalton Trans. 1974, 2334.
76. Drago, R.S. Pure Appl. Chem. 1980, 52, 2261.
77. a. Cotton, F.A.; Johnson, B.F.G. Inorg. Chem. 1964, 3, 1609.
b. Johnson, B.F.G.; Al-Obadi, K.H. Inorg. Synth. 1970, 12, 264.
78. Hewertson, W.; Watson, H.R. J. Chem. Soc. 1962, 1490.
79. Johnson, B.F.G.; Khair, A.; Savory, C.G.; Walter, R.H. J. Chem. Soc., Chem. Commun. 1974, 744.
80. Okamoto, N. Ph.D. Dissertation, The University of Alberta, 1971.
81. Sarkar, S.; Subramanian, P. J. Inorg. Nucl. Chem. 1981, 43, 202.
82. a. Hoyano, J.K.; Legzdins, P.; Malito, J.T. Inorg. Synth. 1978, 18, 126.
b. Botto, R.E.; Kolthammer, B.W.S.; Legzdins, P.; Roberts, J.D. Inorg. Chem. 1979, 18, 2049.
83. Ginley, D.S.; Bock, C.R.; Wrighton, M.S. Inorg. Chim. Acta 1977, 23, 85.
84. a. Gladysz, J.A.; Williams, G.M.; Tam, W.; Johnson, D.L.; Parker, D.W.; Selover, J.C. Inorg. Chem. 1979, 18, 553.
b. Plotkin, J.S.; Shore, S.G. Inorg. Chem. 1981, 20, 284.
85. Hoyano, J.K.; Legzdins, P.; Malito, J.T. J. Chem. Soc., Dalton Trans. 1975, 1022.
86. Regina, F.J.; Wojcicki, A. Inorg. Chem. 1980, 19, 3803.
87. Ashford, P.K.; Baker, P.K.; Connelly, N.G.; Kelly, R.L.; Woodley, V.A. J. Chem. Soc., Dalton Trans. 1982, 477.
88. Dolphin, D.; Wick, A.E. "Tabulation of Infrared Spectral Data"; Wiley-Interscience: New York, 1977, p 488.
89. Beck, W.; Schlöter, K. Z. Naturforsch., B. 1978, 33B, 1214.
90. Morrison, R.M.; Thompson, R.C.; Trotter, J. Can. J. Chem. 1980, 58, 238.
91. Horn, E.; Snow, M.R. Aust. J. Chem. 1980, 33, 2369.

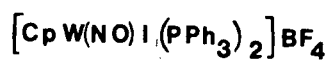
92. Smith, G.; Cole-Hamilton, D.J.; Gregory, A.C.; Gooden, N.B. Polyhedron 1982, 1, 97.
93. Thompson, S.J.; Bailey, P.M.; White, C.; Maitlis, P.M. Angew. Chem., Int. Ed. Engl. 1976, 15, 490.
94. Tan, T.H.; Dalziel, J.R.; Yeats, P.A.; Sams, J.R.; Thompson, R.C.; Aubke, F. Can. J. Chem. 1972, 50, 1843.
95. For example $\text{Me}_2\text{Sn}(\text{O}_2\text{PF}_2)_2$ exhibits IR bands: $\nu_{\text{PO}}^{\text{asym}} = 1258$; $\nu_{\text{PO}}^{\text{sym}} = 1168$; $\nu_{\text{PF}}^{\text{asym}} = 928$; $\nu_{\text{PF}}^{\text{sym}} = 888 \text{ cm}^{-1}$ (ref. 94).
96. Thompson, R.C.; Reed, W. Inorg. Nucl. Chem. Let. 1969, 5, 581.
97. a. Gebala, A.E.; Jones, M.M. J. Inorg. Nucl. Chem. 1969, 31, 771.
b. Clark, H.R.; Jones, M.M. J. Am. Chem. Soc. 1970, 92, 816.
98. Connelly, N.G.; Gardner, C. J. Chem. Soc., Dalton Trans. 1979, 609.
99. Hames, B.W.; Legzdins, P. Organometallics 1982, 1, 116.
100. Eckstein, Y.; Dreyfuss, P. J. Polym. Sci. Polym. Chem. Ed. 1979, 17, 4115.
101. Dreyfuss, P. "Poly(tetrahydrofuran)"; Gordon and Breach: New York, 1982.
102. Klendworth, D.D.; Walters, W.W., III; Walton, R.A. J. Organomet. Chem. 1981, 213, C13.
103. Hoyano, J.K.; Graham, W.A.G. Organometallics 1982, 1, 783.
104. Stewart, R.P., Jr.; Moore, G.T. Inorg. Chem. 1975, 14, 2699.
105. Connelly, N.G. Inorg. Synth. 1974, 15, 91.
106. Sen, A.; Thomas, R.R. Organometallics 1982, 1, 1251.
107. Geary, W.J. Coord. Chem. Rev. 1971, 7, 81.
108. Feltham, R.D.; Hayter, R.G. J. Chem. Soc. 1964, 4587 and references therein.
109. Feltham, R.D.; Nyholm, R.S. Inorg. Chem. 1965, 4, 1334.
110. Castellano, S.; Gunther, H.; Ebersole, S. J. Phys. Chem. 1965, 69, 4166.

111. Lytle, F.E.; Petrosky, L.M.; Carlson, L.R. Anal. Chim. Acta. 1971, 57, 239.
112. Overton, C.; Connor, J.A. Polyhedron 1982, 1, 53.
113. Connor, J.A.; McEwen, G.K.; Rix, C.J. J. Chem. Soc., Dalton Trans. 1974, 589.
114. George, T.A.; Seibold, C.D. Inorg. Chem. 1973, 12, 2548.
115. Kan, C.T.; Hitchcock, P.B.; Richard, R.L. J. Chem. Soc., Dalton Trans. 1982, 79.
116. King, F.; Leigh, G.J. J. Chem. Soc., Dalton Trans. 1977, 429.
117. Olah, G.A.; Gupta, B.G.B.; Narang, S.C. J. Am. Chem. Soc. 1979, 101, 5317.
118. a. Ballivet, D.; Tkatchenko, I. Inorg. Chem. 1977, 16, 945.
b. Hieber, W.; Heinicke, K. Z. Anorg. Allg. Chem. 1962, 316, 305.
119. Sold by Aldrich under the trade name "Super-Hydride" as a 1M THF solution.
120. Vogel, A.I. "A Textbook of Practical Organic Chemistry, Including Organic Analysis", 3rd ed.; Longman: London, 1956; p. 194.
121. a. McWhinnie, W.R.; Miller, J.D. Adv. Inorg. Chem. Radiochem. 1969, 12, 135.
b. Herzog, S.; Aul, H. Z. Naturforsch. 1960, 15b, 617.
122. Mukaida, M.; Nomura, T.; Ishimori, T. Bull. Chem. Soc. Jpn. 1975, 48, 1443.
123. King, R.B. Inorg. Chem. 1968, 7, 90.
124. Legzdins, P.; Malito, J.T. Inorg. Chem. 1975, 14, 1875.
125. a. Alich, A.; Nelson, N.J.; Strobe, D.; Shriver, D.F. Inorg. Chem. 1972, 11, 2976.
b. Nelson, N.J.; Kime, N.E.; Shriver, D.F. J. Am. Chem. Soc. 1969, 91, 5173.
c. Kotz, J.C.; Turnipseed, C.D. J. Chem. Soc., Chem. Commun. 1970, 41.
d. Kotz, J.C.; Pedrotty, D.C. Organomet. Chem. Rev. A 1969, 4, 479.

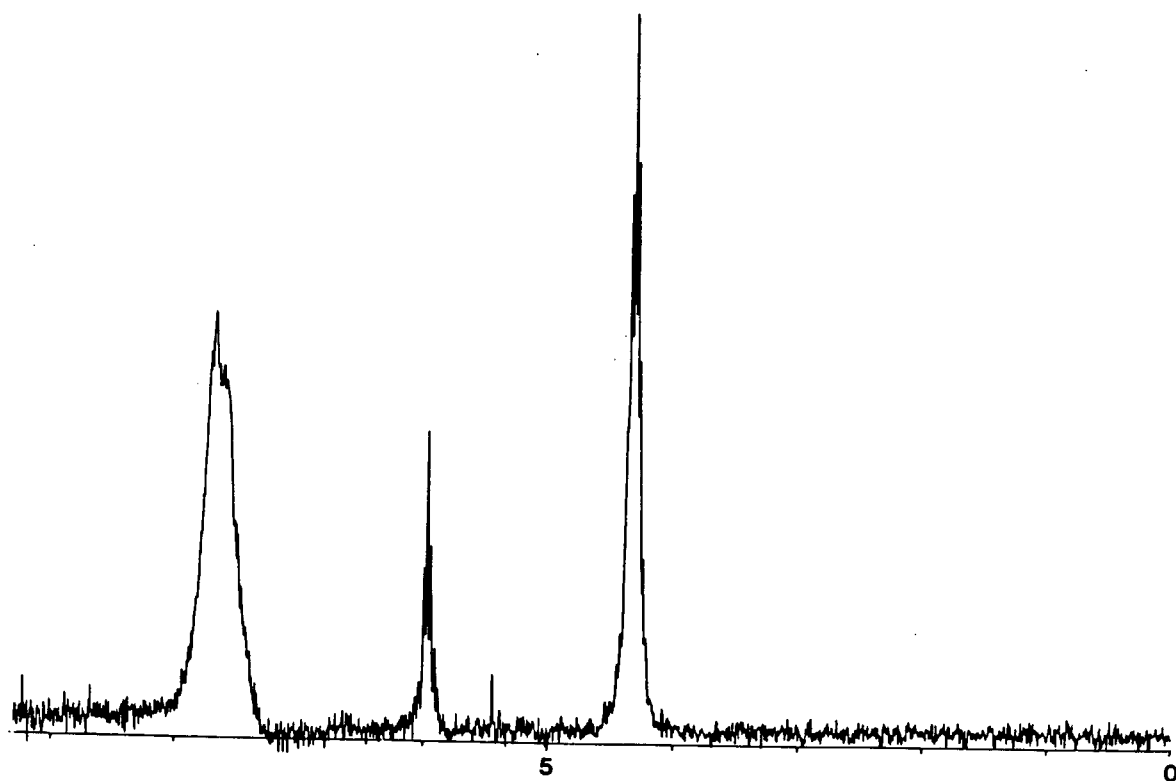
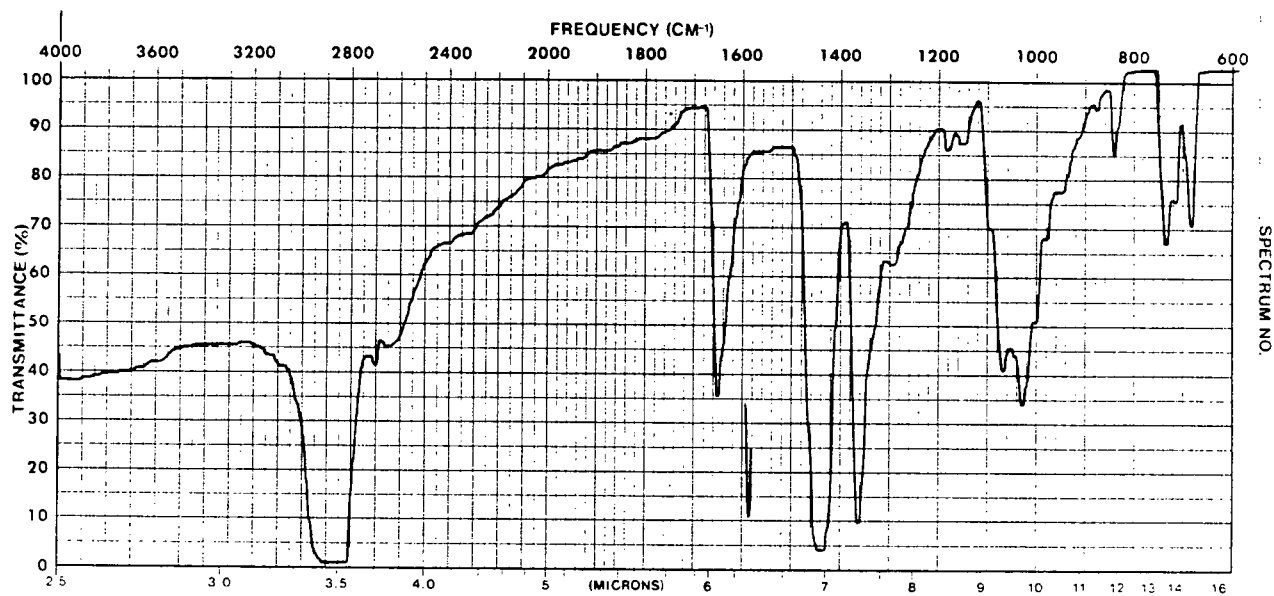
126. a. Stevens, R.E.; Yanta, T.J.; Gladfelter, W.L. J. Am. Chem. Soc. 1981, 103, 4981.
b. Hieber, W.; Beutner, H. Z. Anorg. Allg. Chem. 1963, 320, 101.
127. Bishop, M.W.; Chatt, J.; Dilworth, J.R. J. Chem. Soc., Dalton Trans. 1979, 1 and references therein.
128. a. Kolthammer, B.W.S.; Legzdins, P. J. Am. Chem. Soc. 1978, 100, 2247.
b. Greenhough, T.J.; Kolthammer, B.W.S.; Legzdins, P.; Trotter, J. J. Chem. Soc., Chem. Commun. 1978, 1036.
c. Greenhough, T.J.; Kolthammer, B.W.S.; Legzdins, P.; Trotter, J. Inorg. Chem. 1979, 18, 3548.
d. Greenhough, T.J.; Kolthammer, B.W.S.; Legzdins, P.; Trotter, J. Inorg. Chem. 1979, 18, 3543.
129. Jolly, W.L.; Maguire, K.D. Inorg. Synth. 1967, 9, 102.
130. Herberhold, M.; Haumaier, L. Z. Naturforsch. 1980, 35b, 1277.
131. Fenster, A.E.; Butler, I.S. Inorg. Chem. 1974, 13, 915.
132. a. Woolf, A.A. Adv. Inorg. Chem. Radiochem. 1966, 9, 217.
b. Gillespie, R.J.; Sawyer, J.F.; Slim, D.R.; Tyrer, J.D. Inorg. Chem. 1982, 21, 1296.
133. Paddock, N.L.; private communication.
134. Herberhold, M.; Klein, R. Angew. Chem. Int. Ed. Engl. 1978, 17, 454.
135. Hathaway, B.J.; Holah, D.G.; Underhill, A.E. J. Chem. Soc. 1962, 2444.
136. Schramm, R.F.; Wayland, B.B. J. Chem. Soc., Chem. Commun. 1968, 898.
137. a. Partington, J.R.; Whynes, A.L. J. Chem. Soc. 1948, 1952.
b. Partington, J.R.; Whynes, A.L. J. Chem. Soc. 1949, 3135.
138. Olah, G.A.; Gupta, B.G.B.; Narang, S.C. Synthesis 1979, 274.
139. a. Bach, R.D.; Holubka, J.W.; Taaffee, T.A. J. Org. Chem. 1979, 44, 1739.
b. Bach, R.D.; Taaffee, T.H.; Rajan, S.J. J. Org. Chem. 1980, 45, 165.

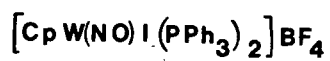
140. Scheinbaum, M.L.; Dines, M.B. J. Org. Chem. 1971, 36, 3641.
141. Scheinbaum, M.L.; Dines, M.B. Tetrahedron Lett. 1971, 24, 2205.
142. a. Coetzee, J.F.; Cunningham, G.P.; McGuire, D.K.; Padmanabhan, G.R. Anal. Chem. 1962, 34, 1139.
- b. O'Donnell, J.F.; Ayres, J.T.; Mann, C.K. Anal. Chem. 1965, 37, 1161.
- c. Walter, M.; Ramaley, L. Anal. Chem. 1973, 45, 165.

SPECTRAL APPENDIX

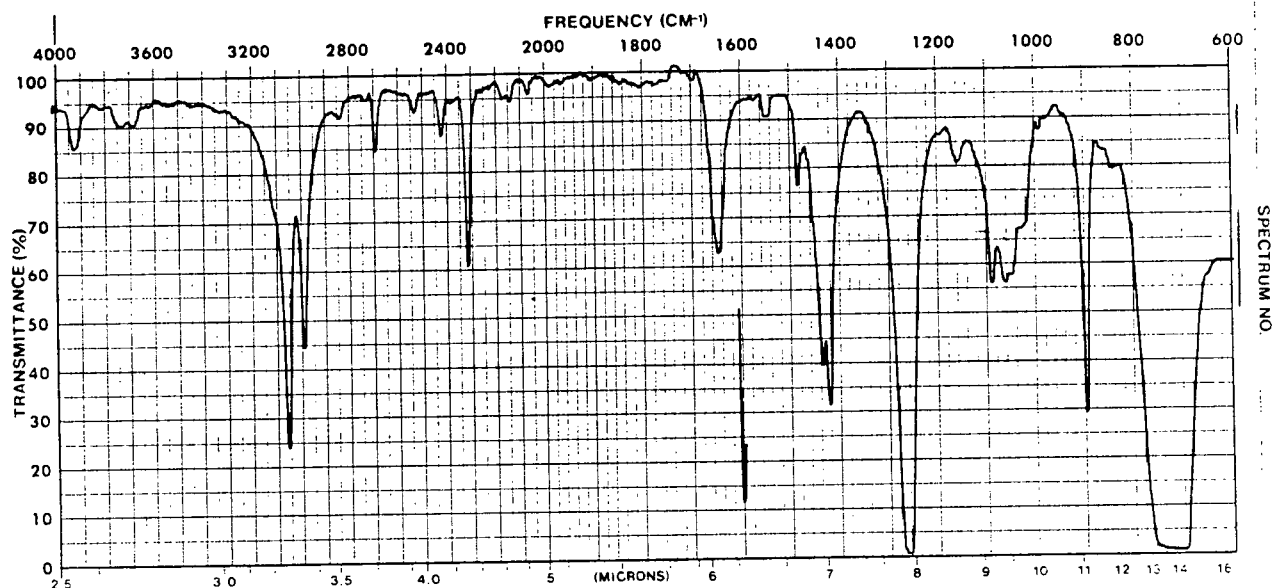


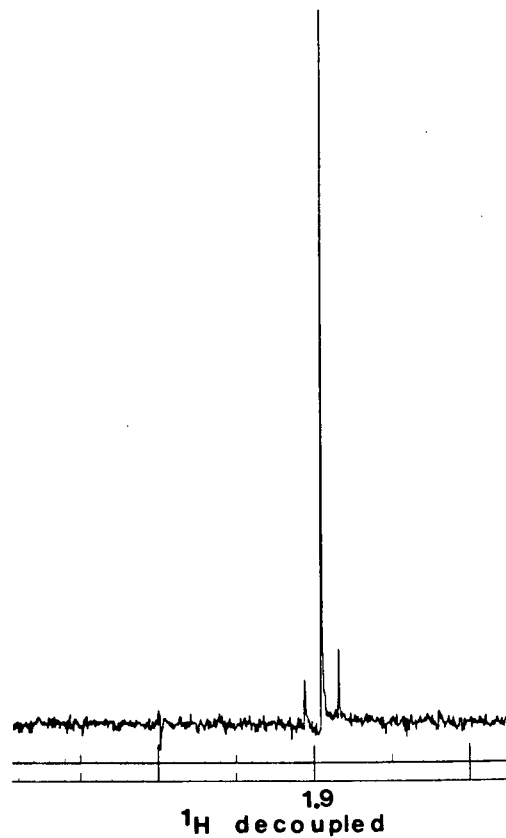
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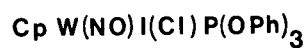
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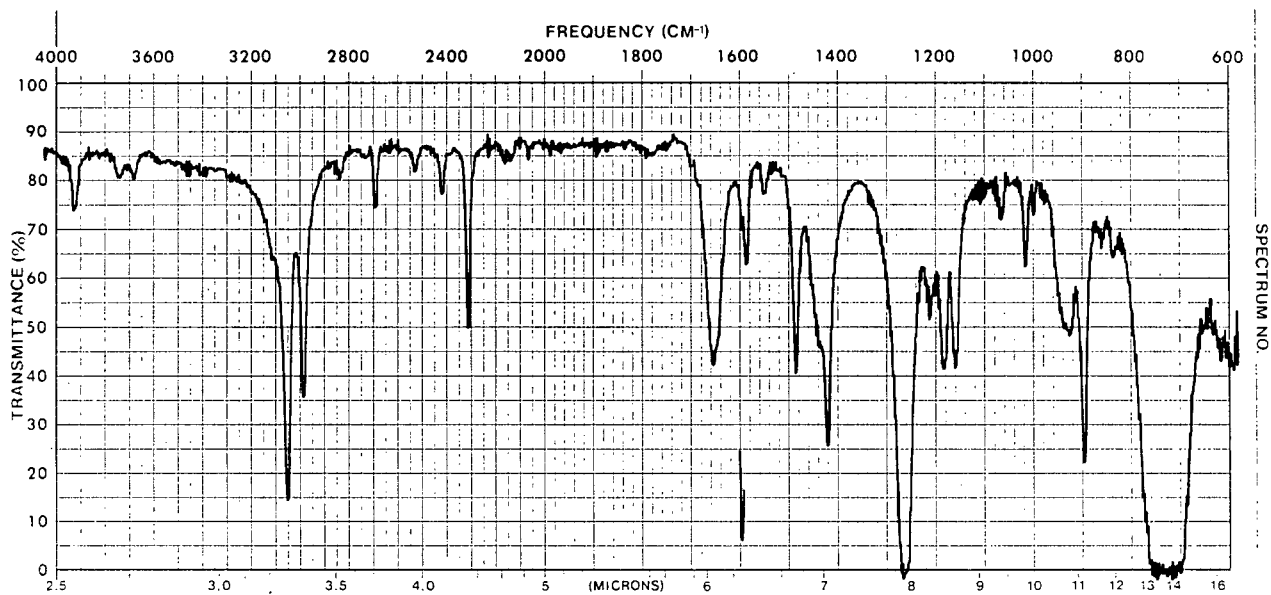
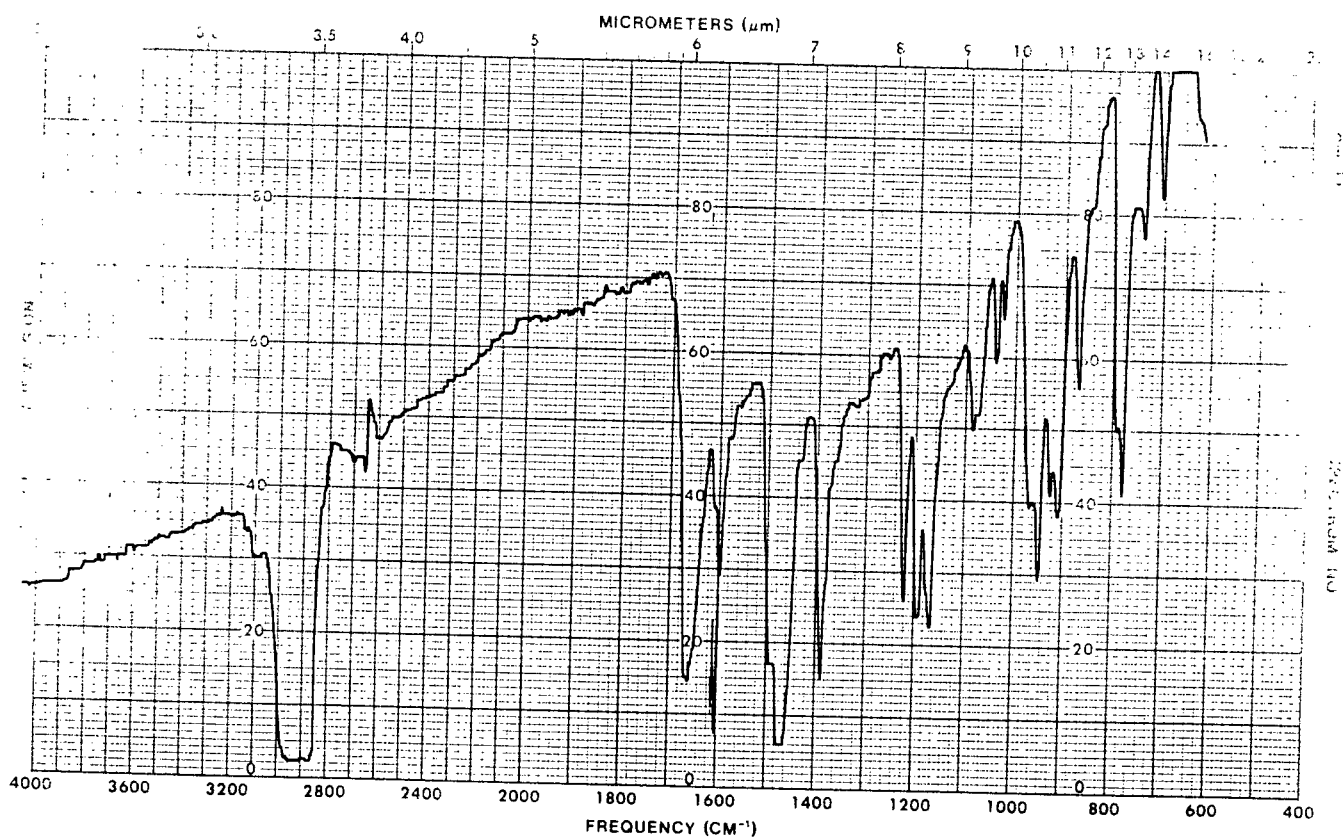
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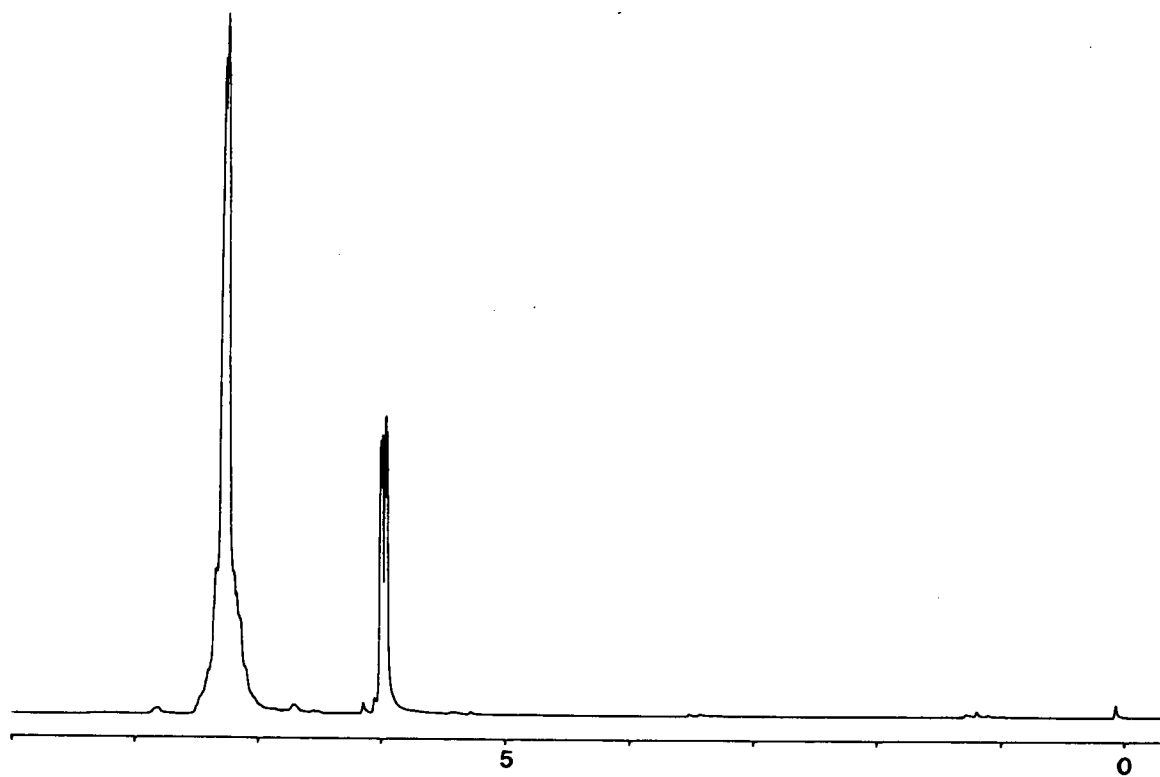
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 ^{19}F NMR

 MeNO_2

 ^{31}P NMR

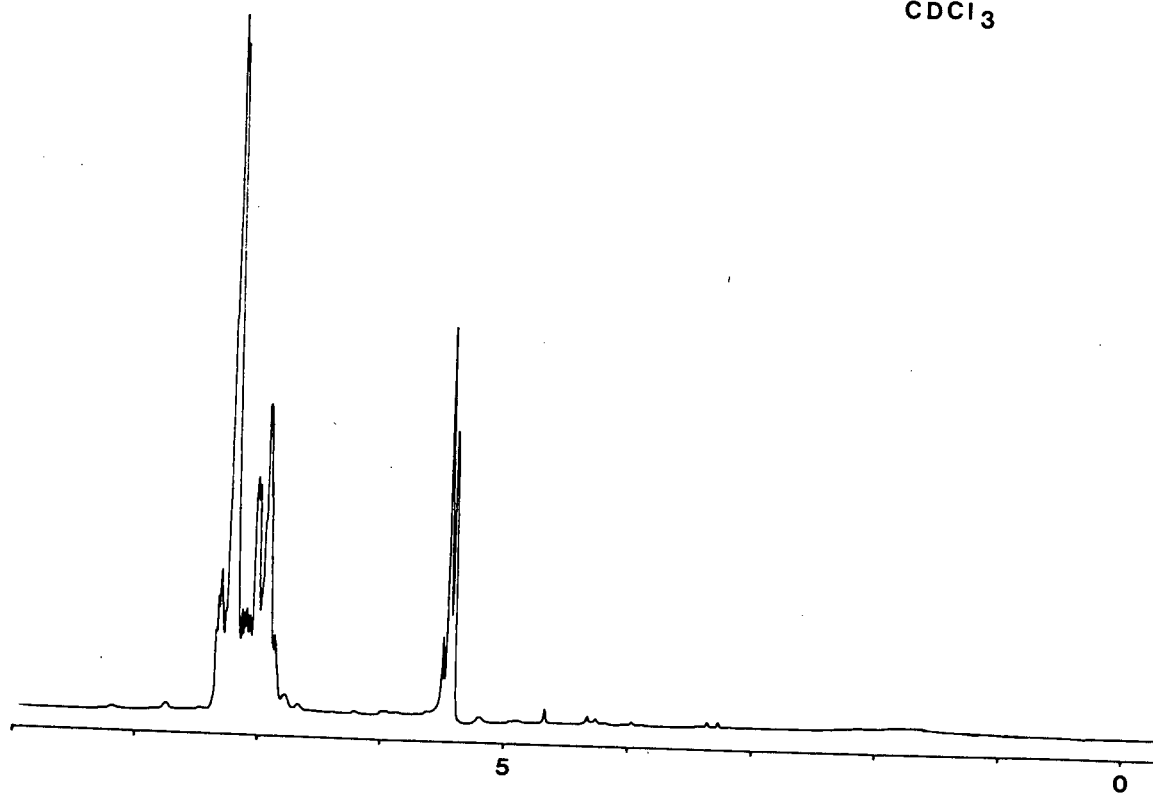


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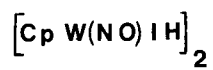
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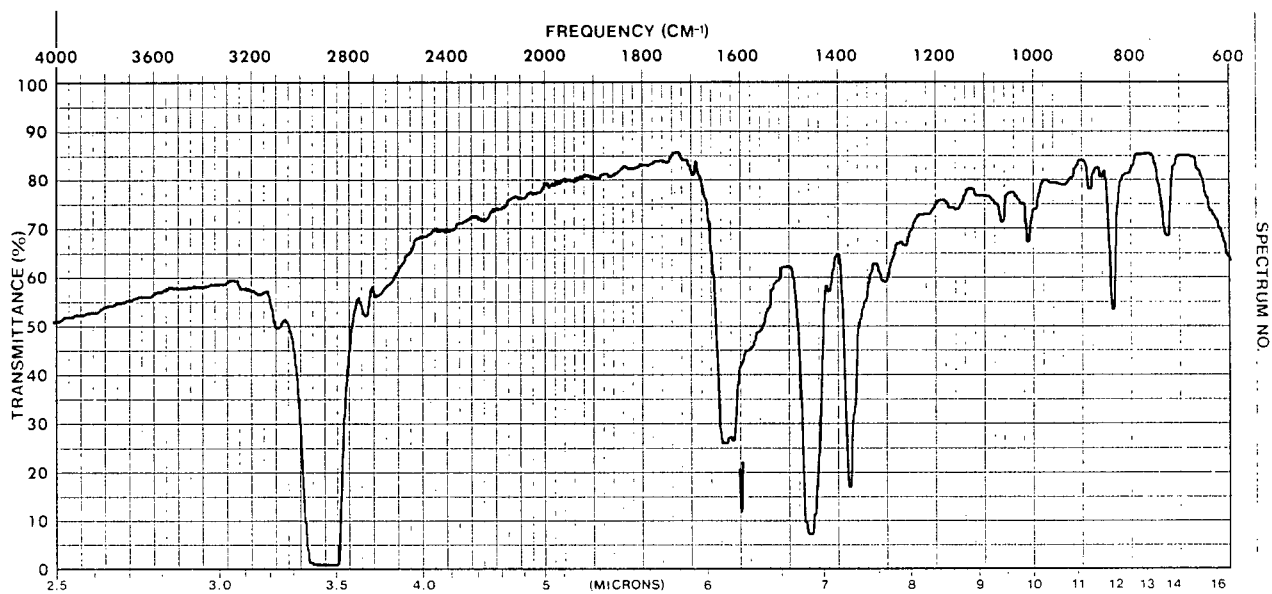
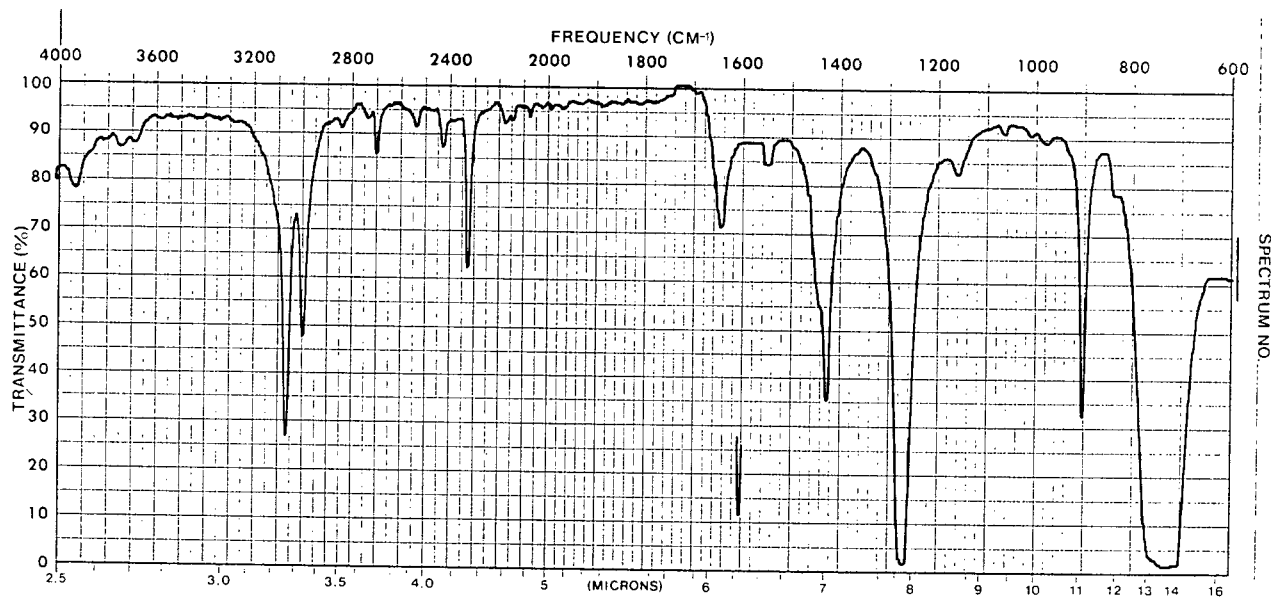
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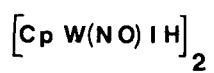


C₆D₆



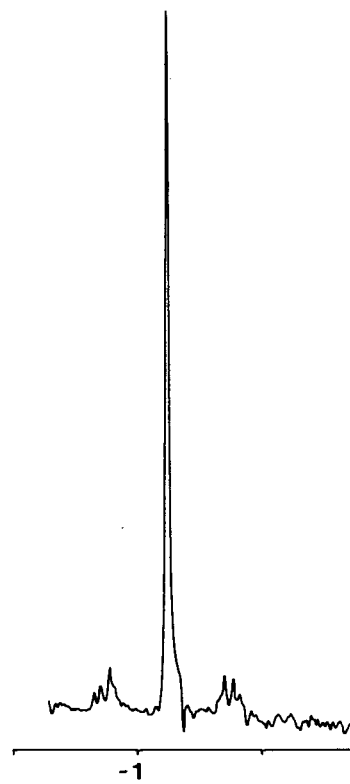
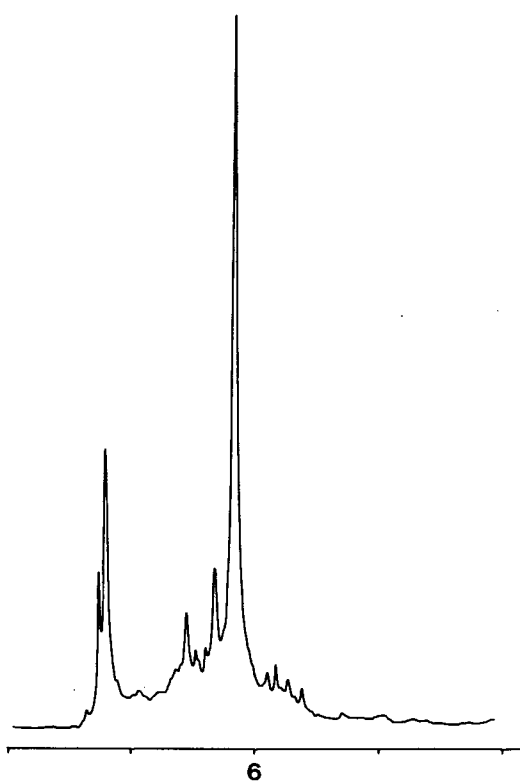
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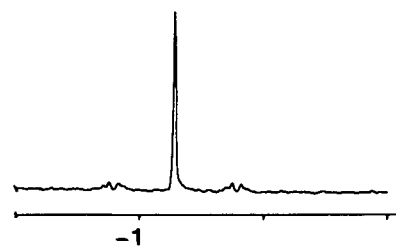
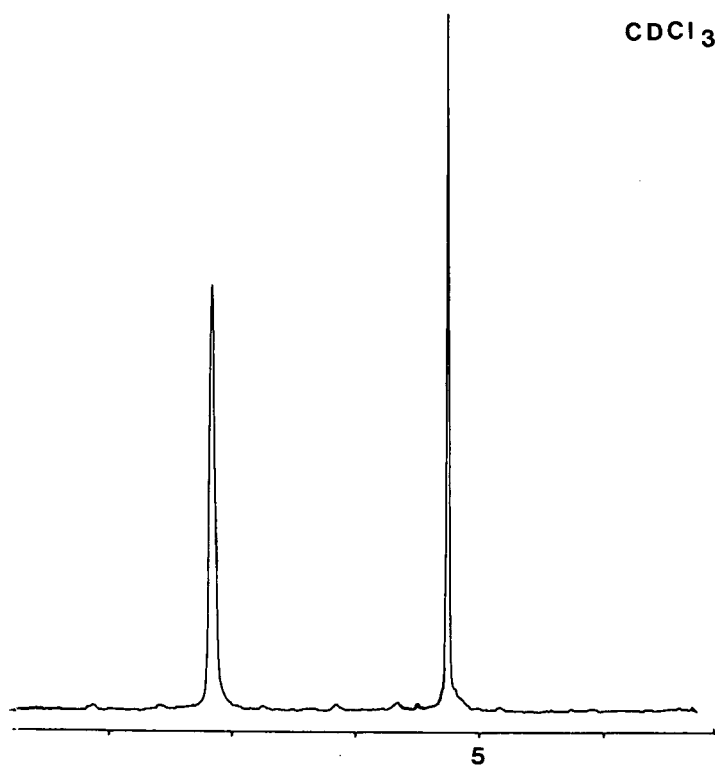


^1H NMR

163



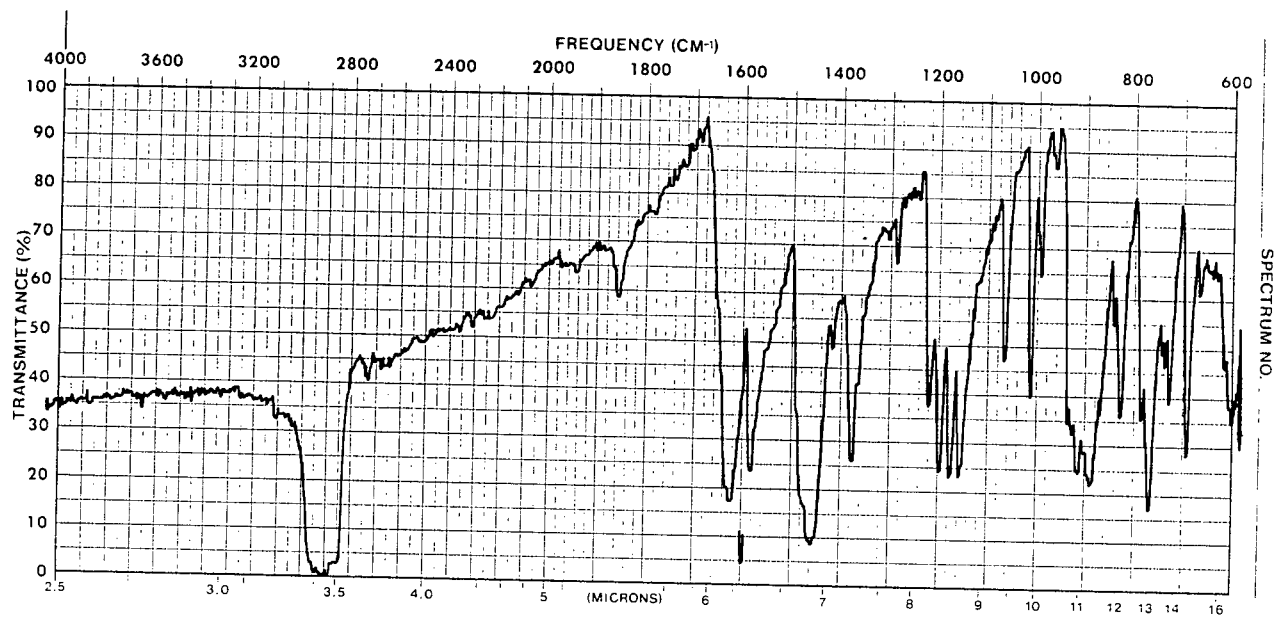
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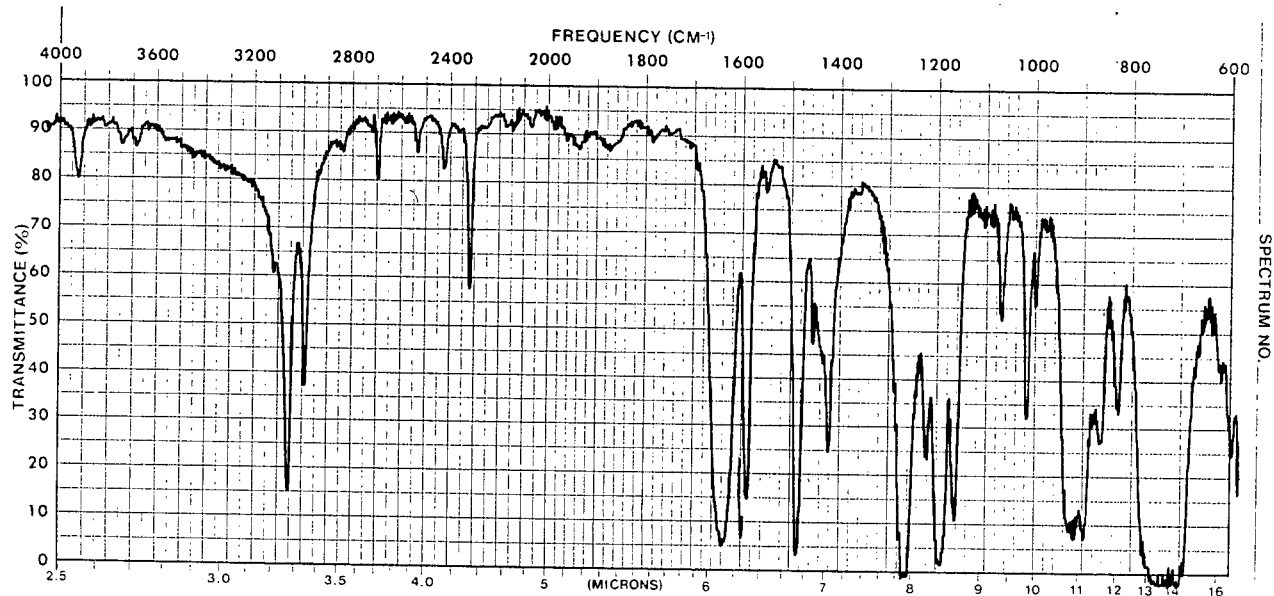
C_6D_6

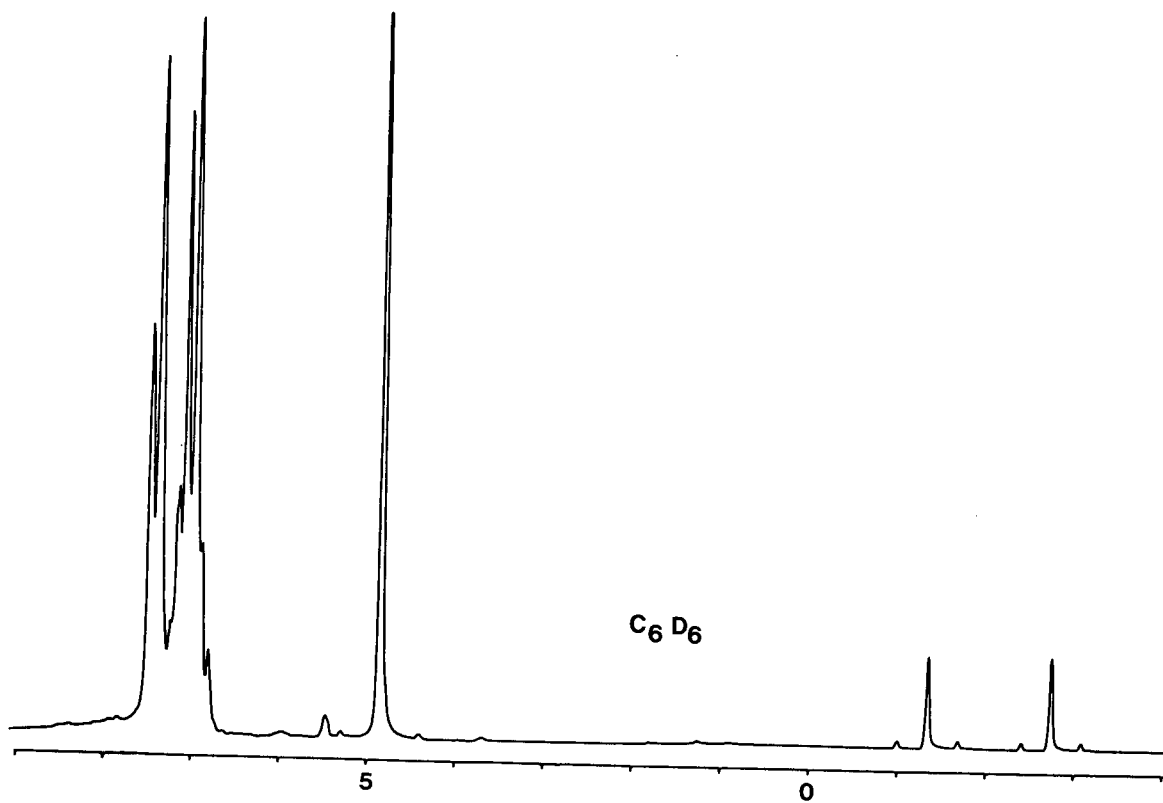
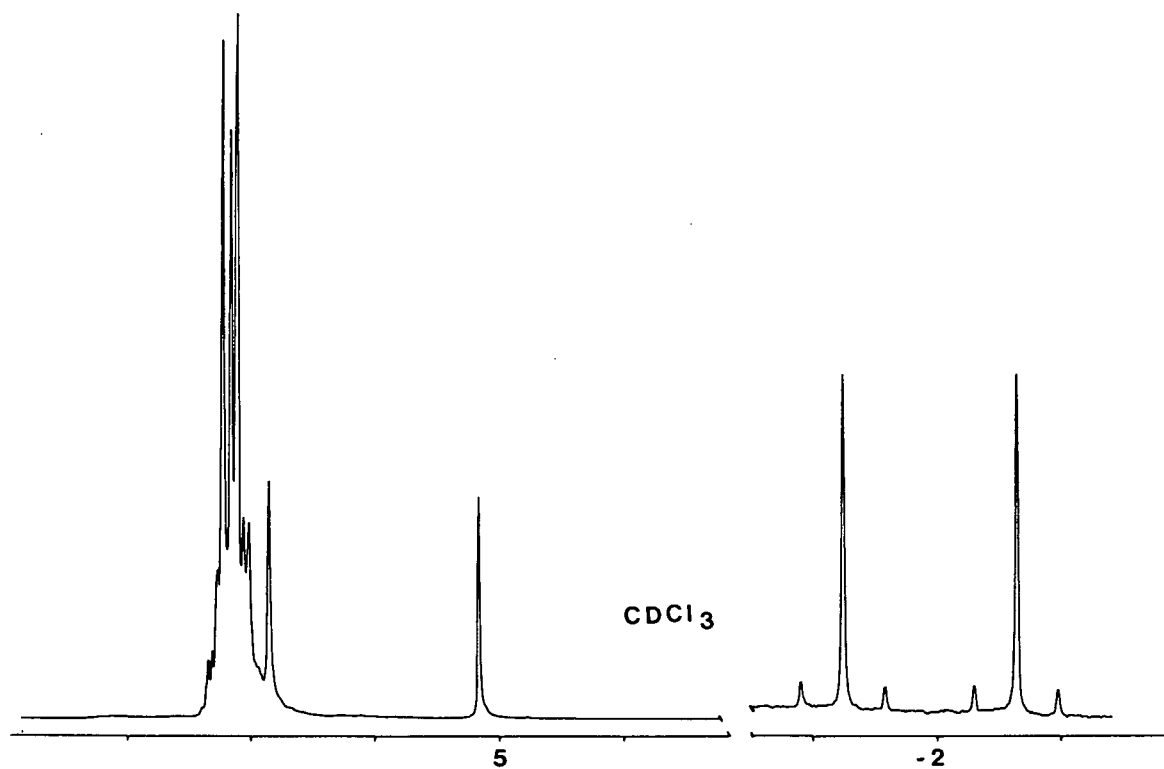
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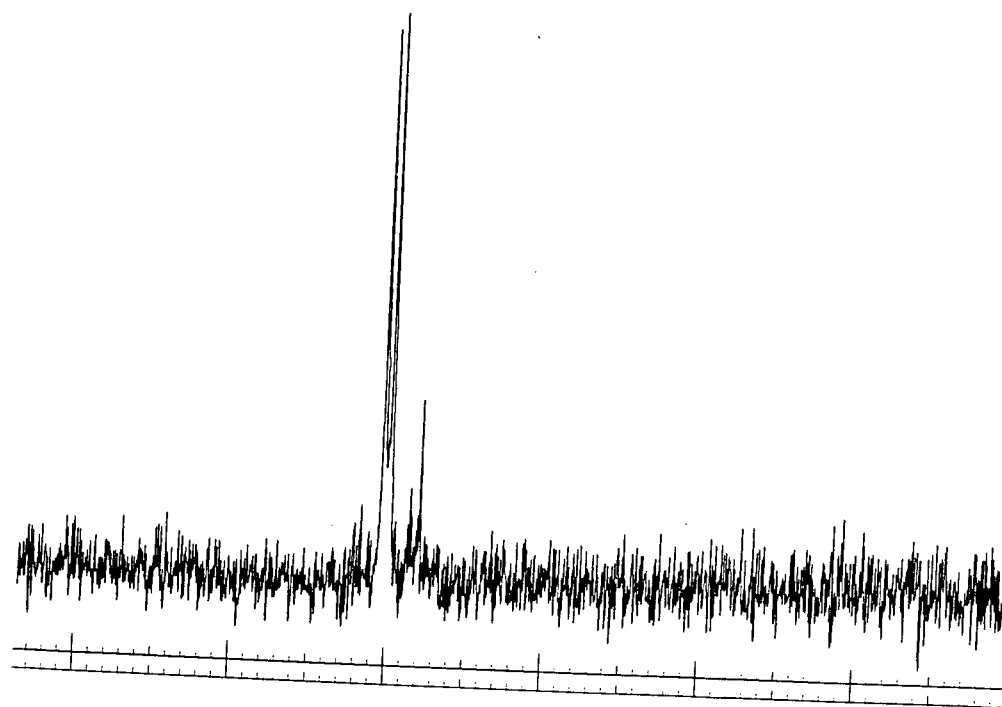
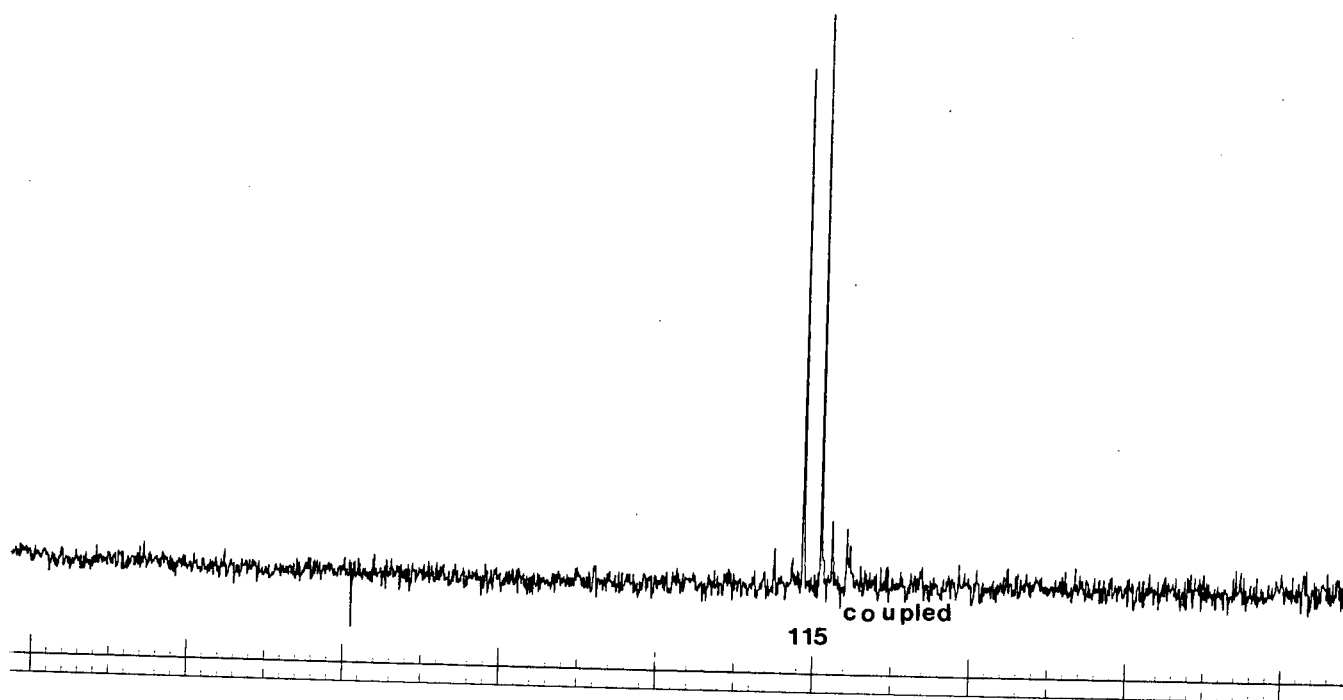
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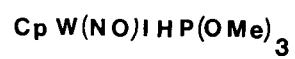


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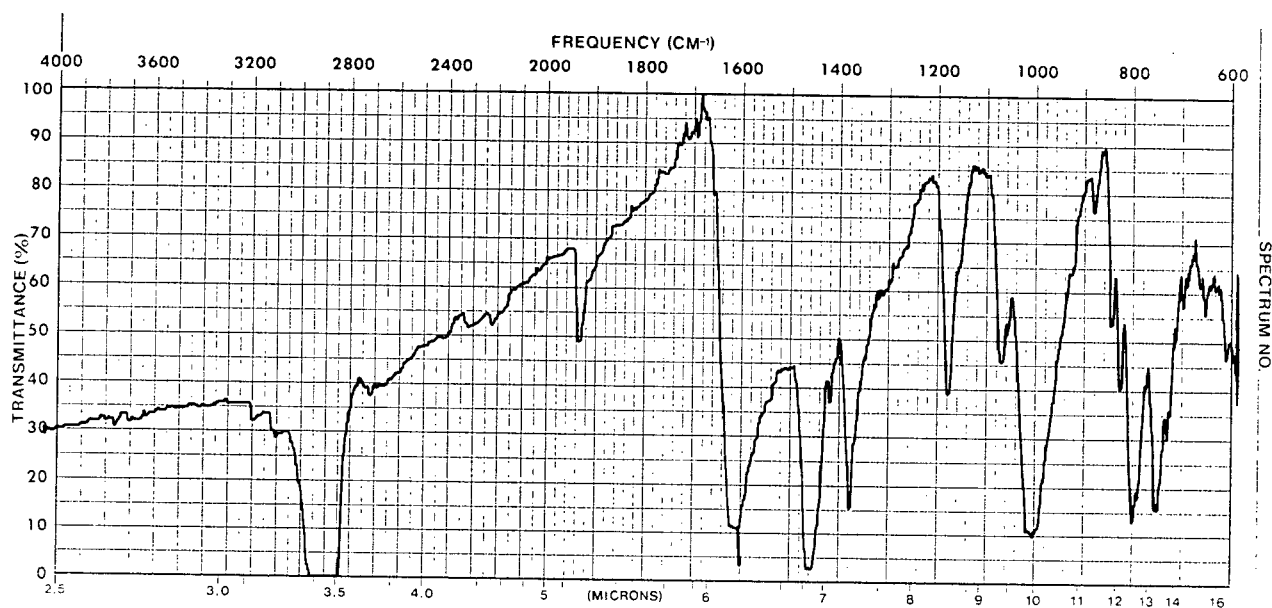
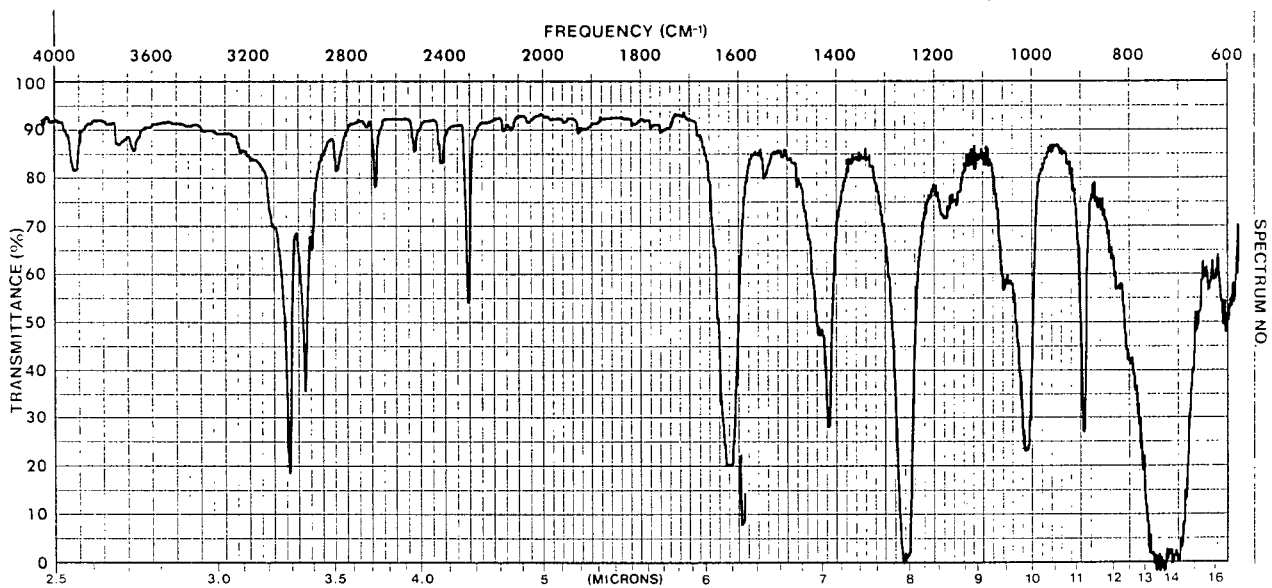


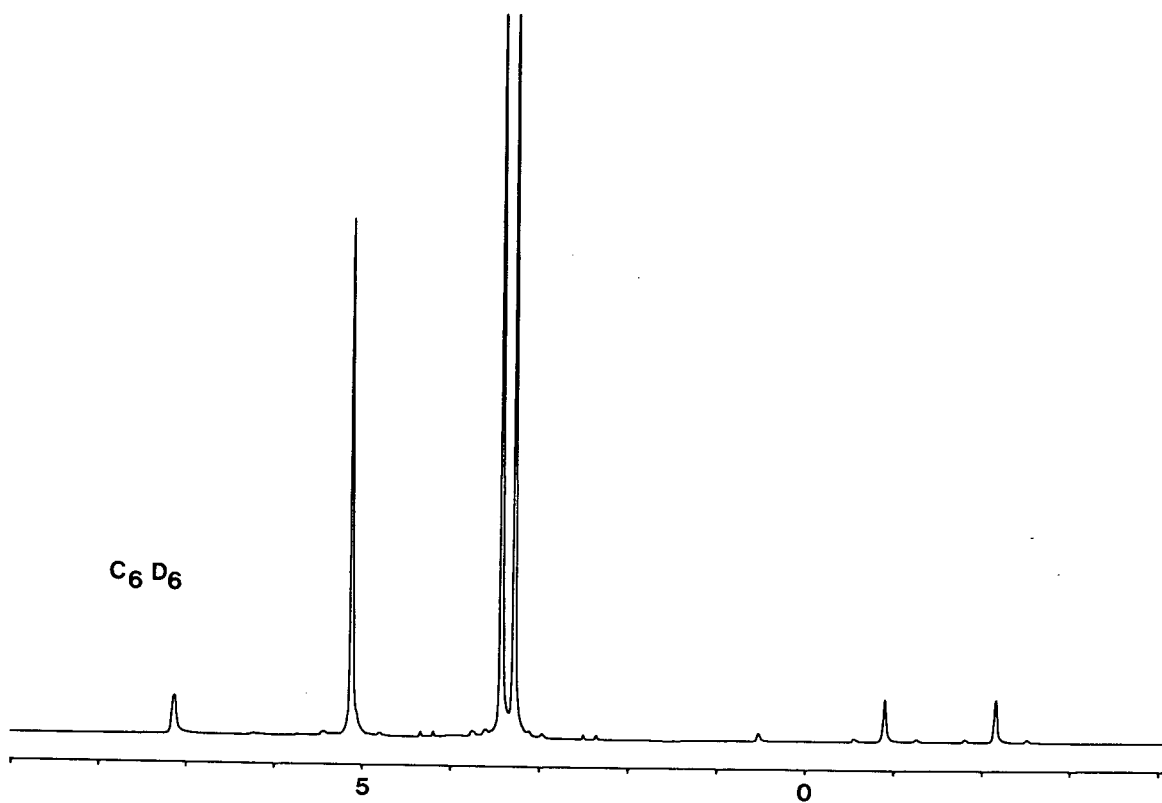
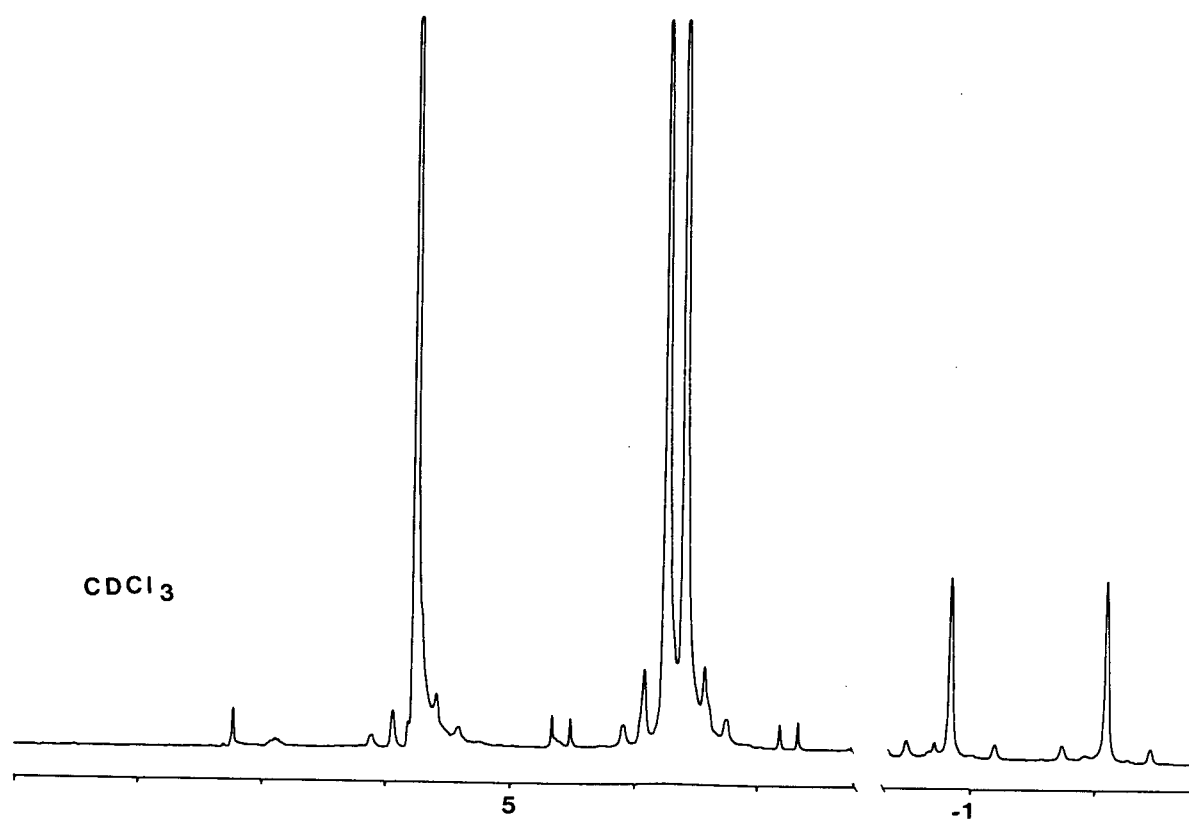


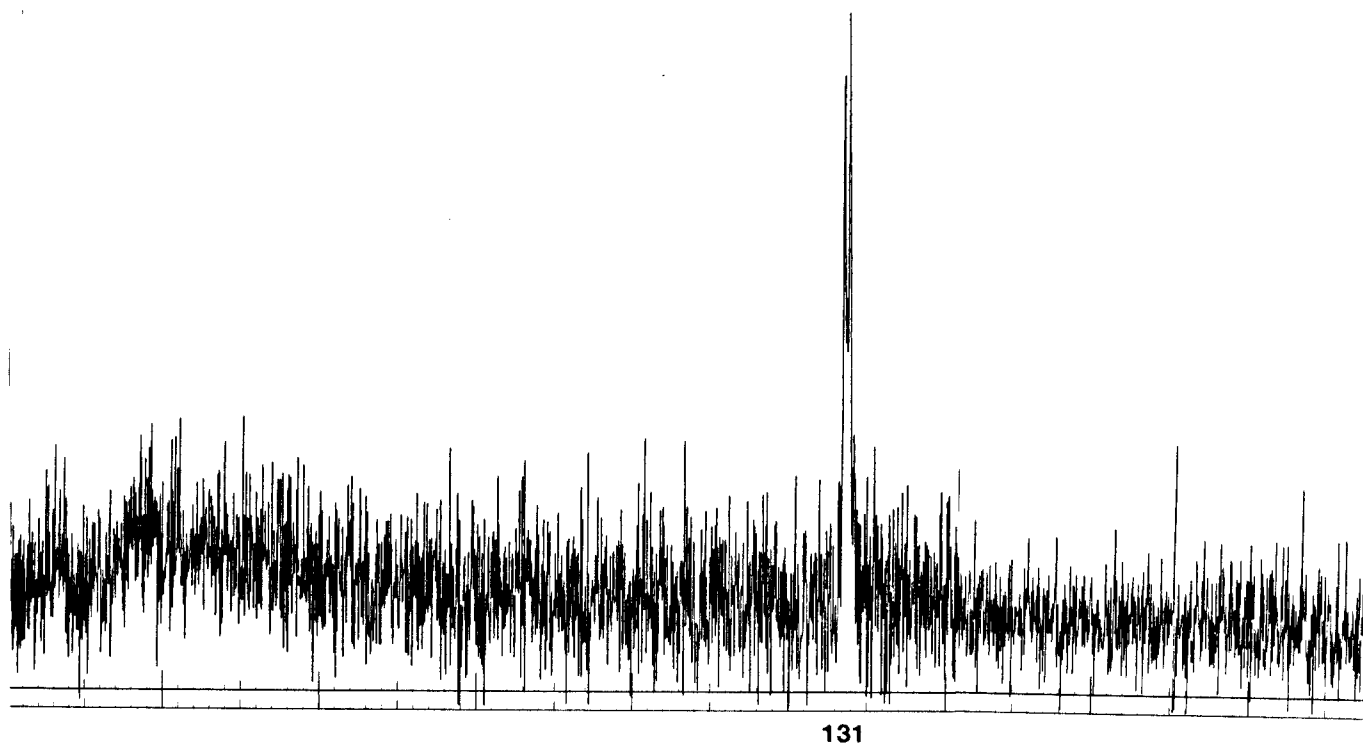
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IR NUJOL MULL

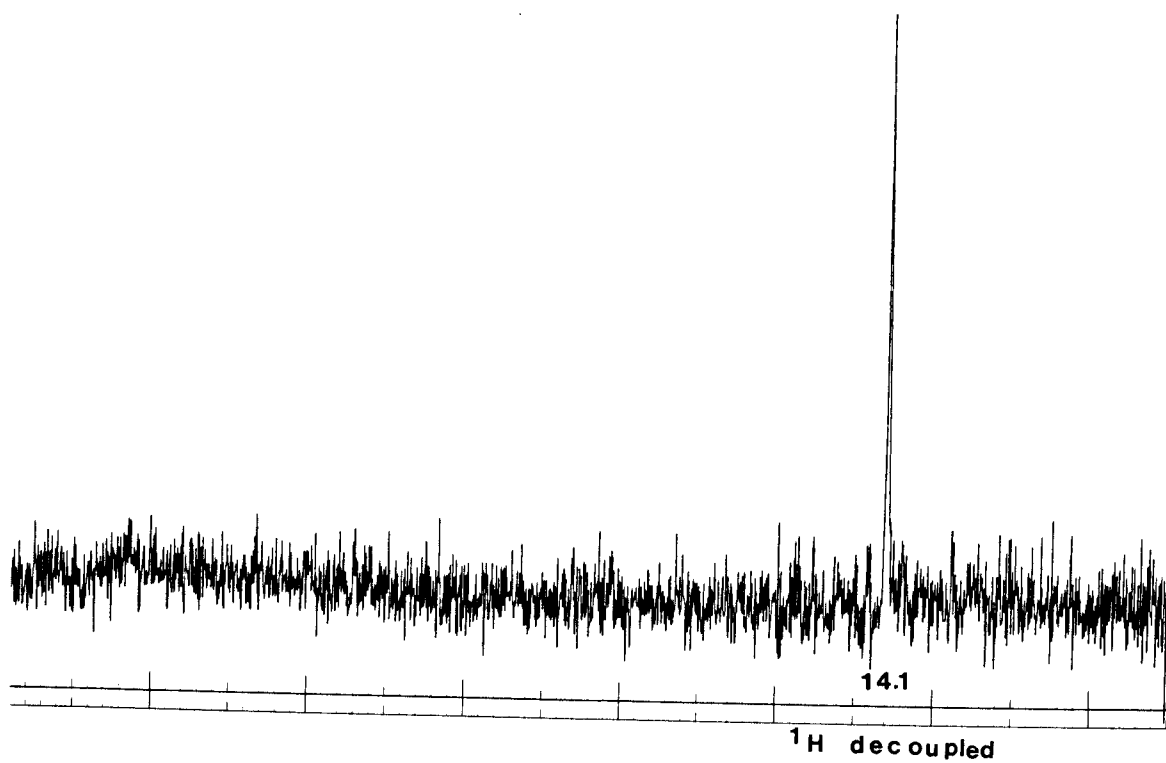
IR CH_2Cl_2 





$\text{CpW}(\text{NO})\text{IHP}(\text{OMe})_3$

off resonance ^1H decoupled

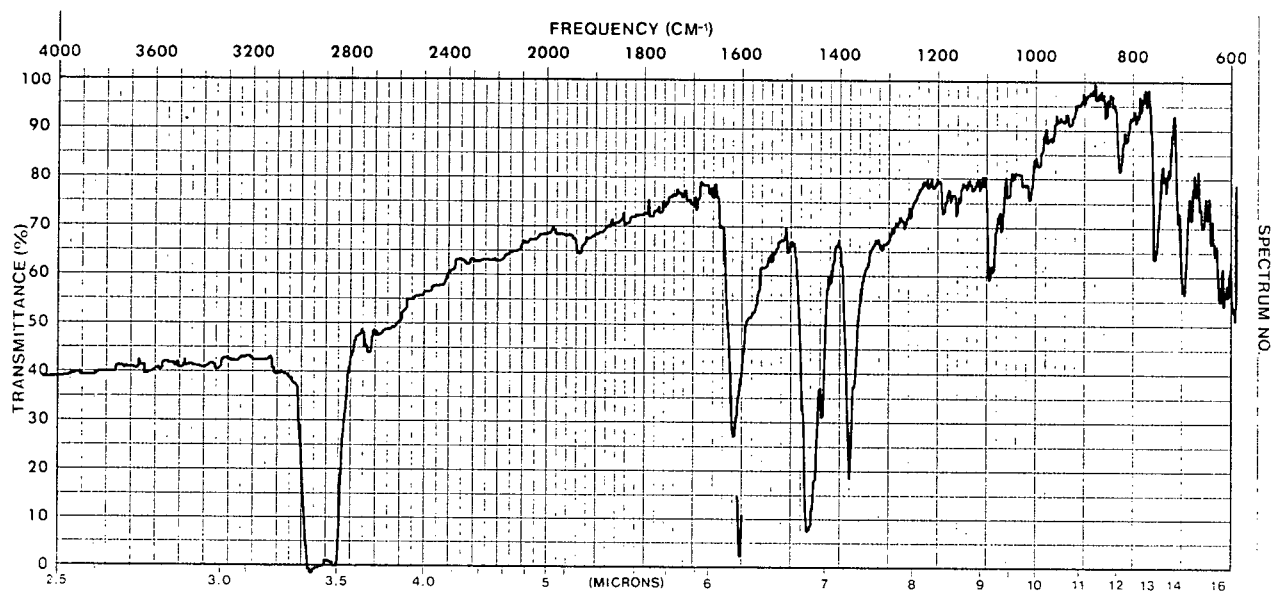


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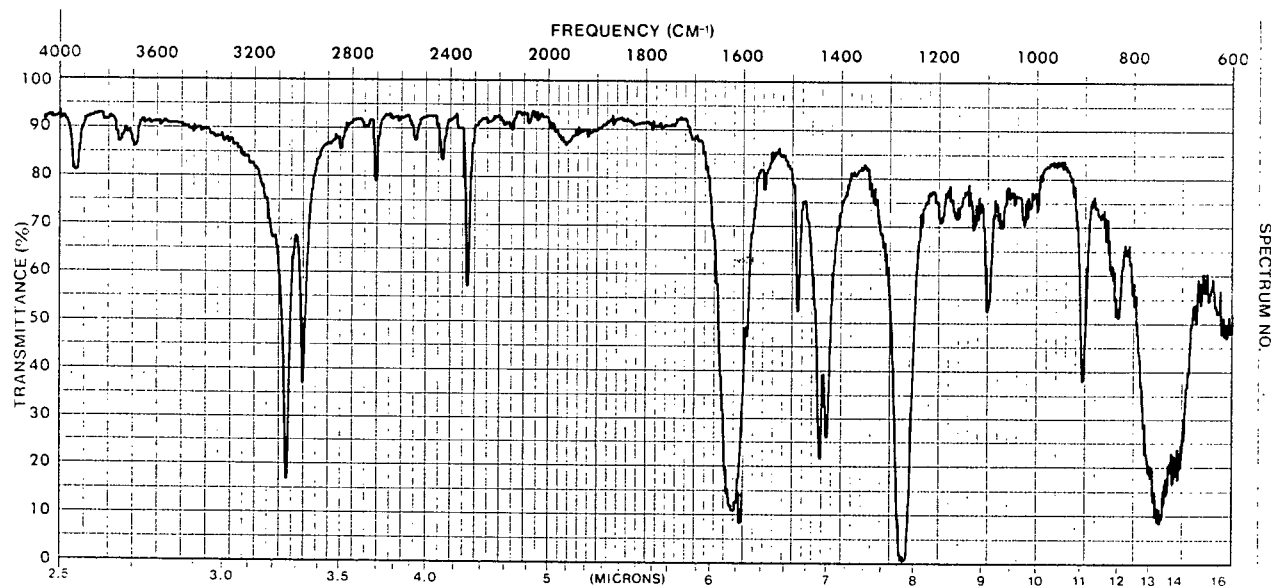
^1H decoupled

Cp W(NO)HPPPh₃

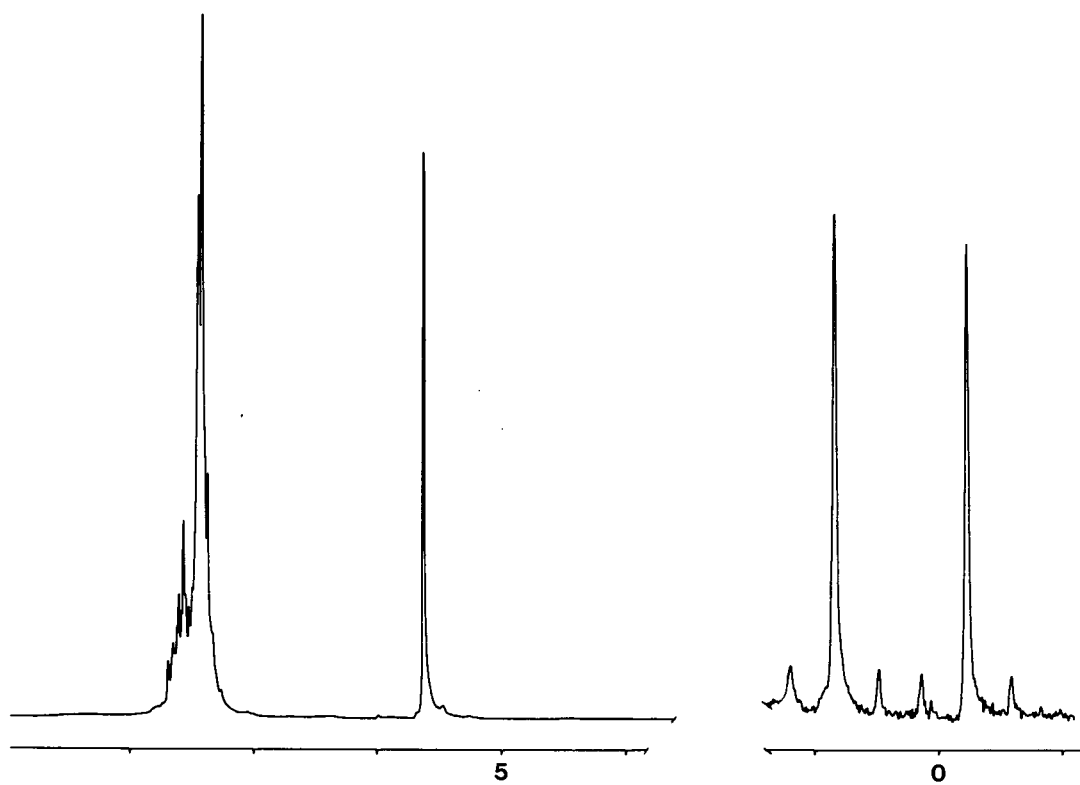
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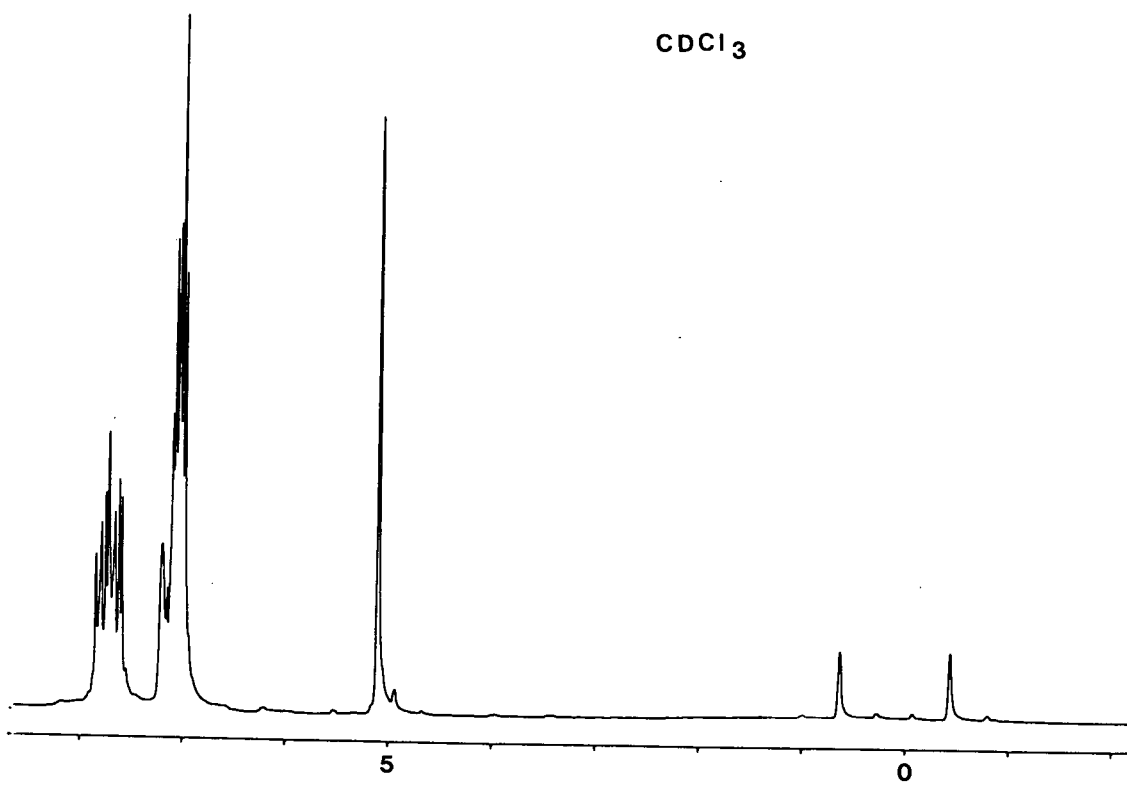
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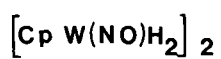
Cp W(NO)H PPh_3 ^1H NMR



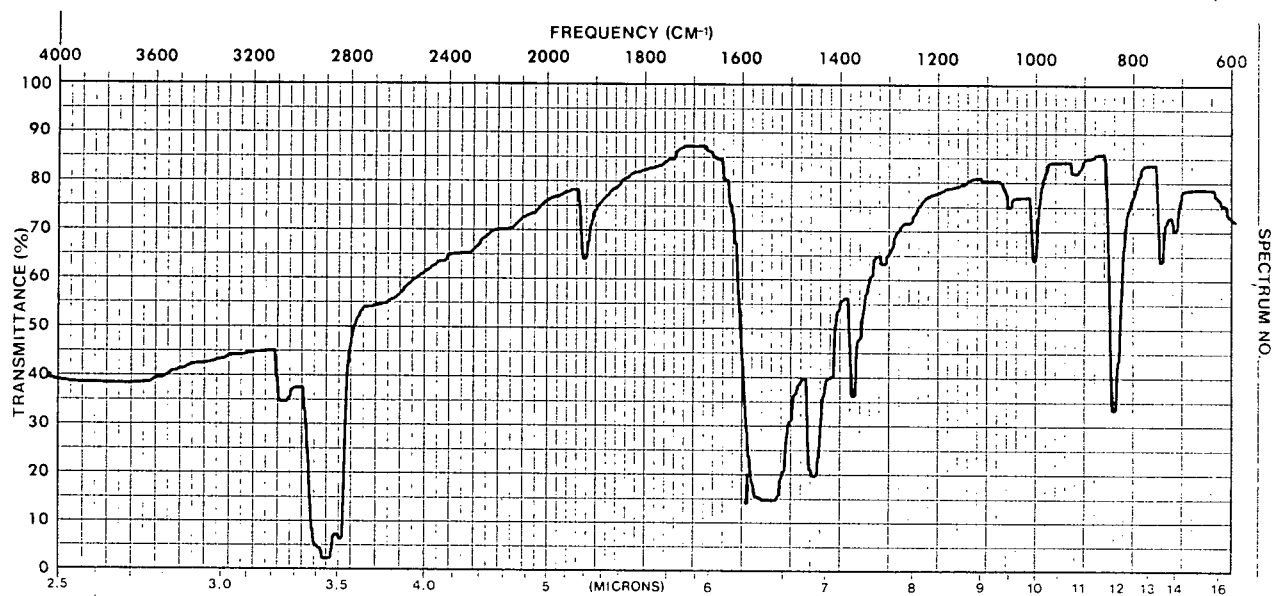
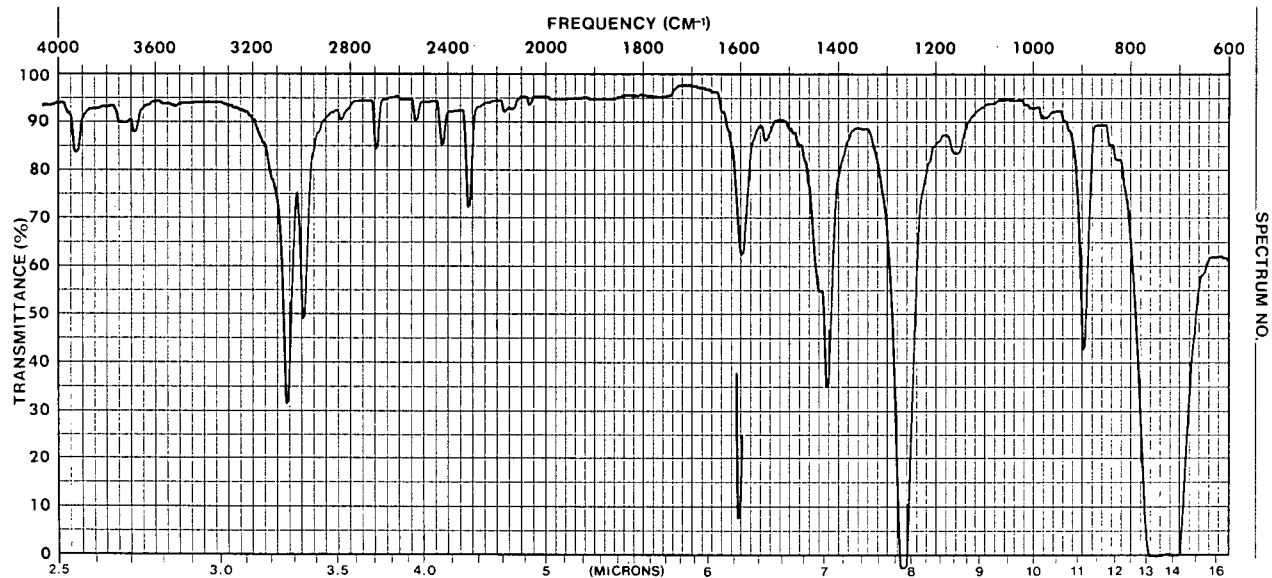
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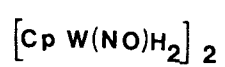
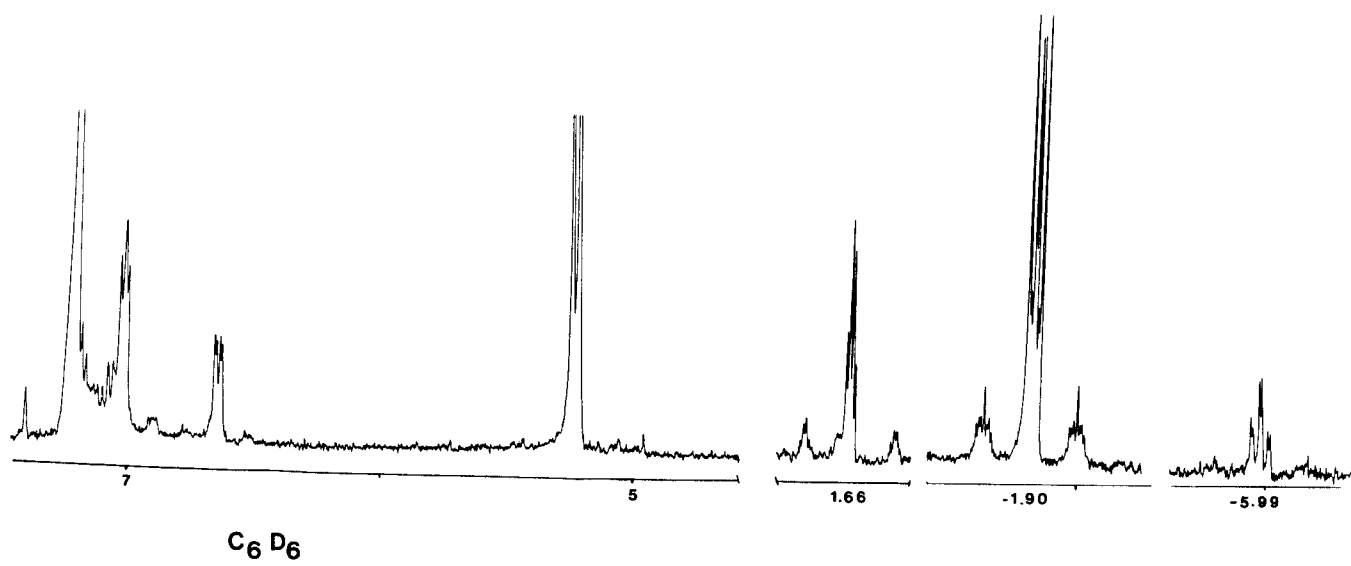
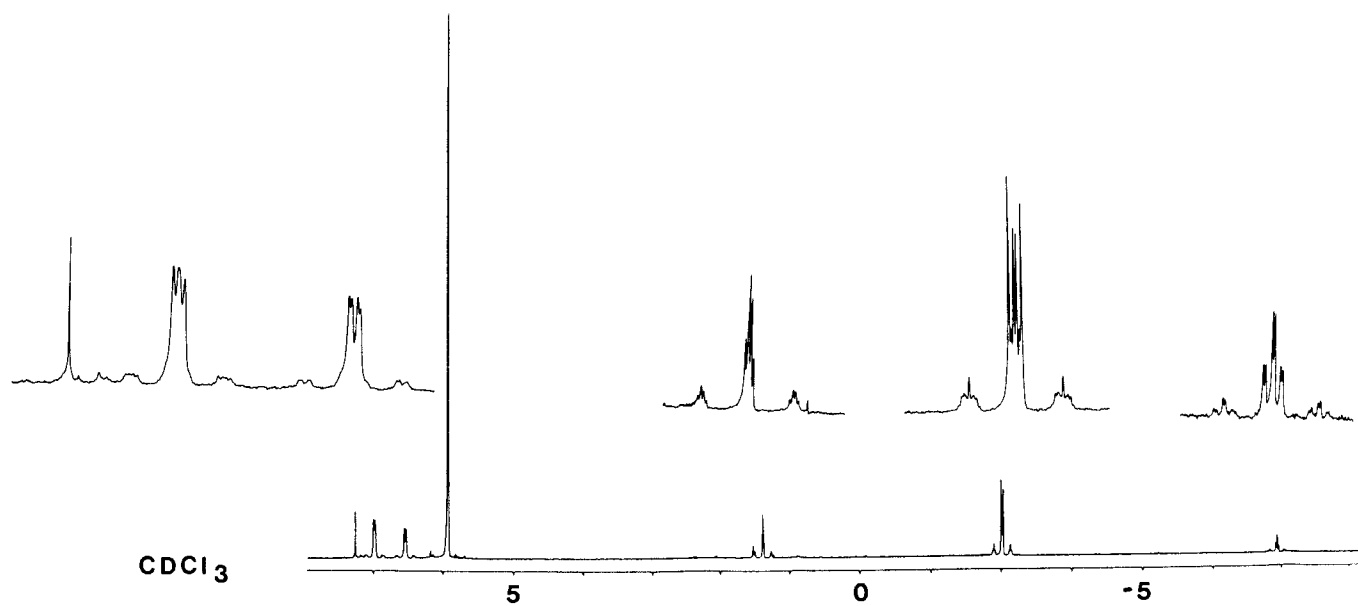


C_6D_6



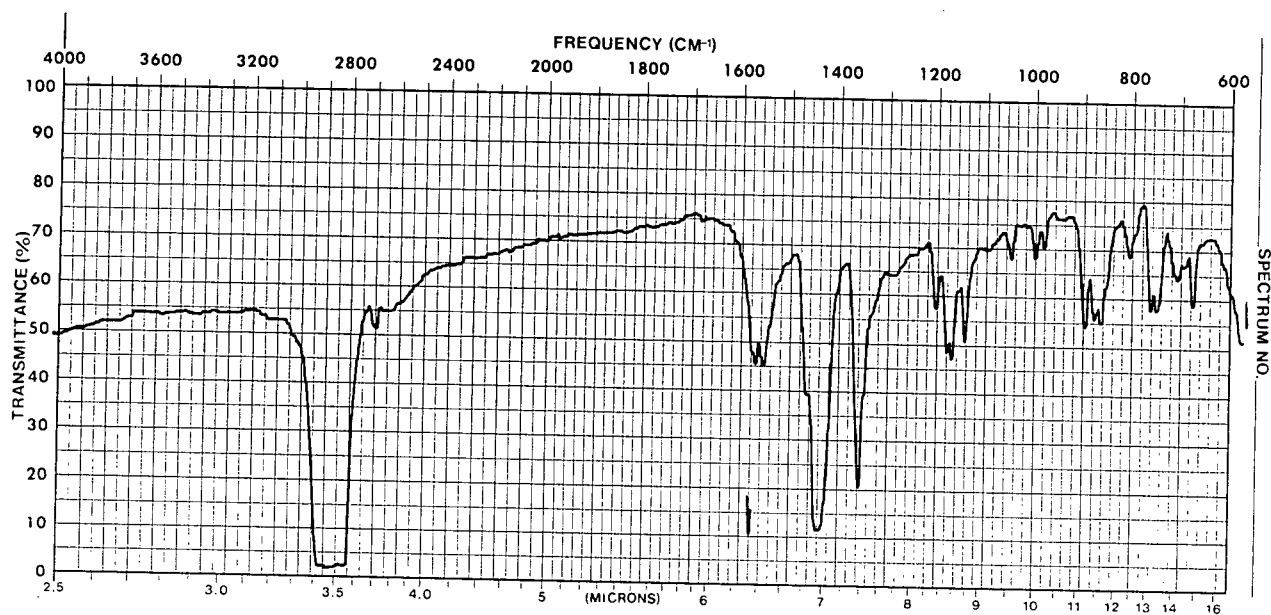
IR NUJOL MULL

IR CH_2Cl_2 

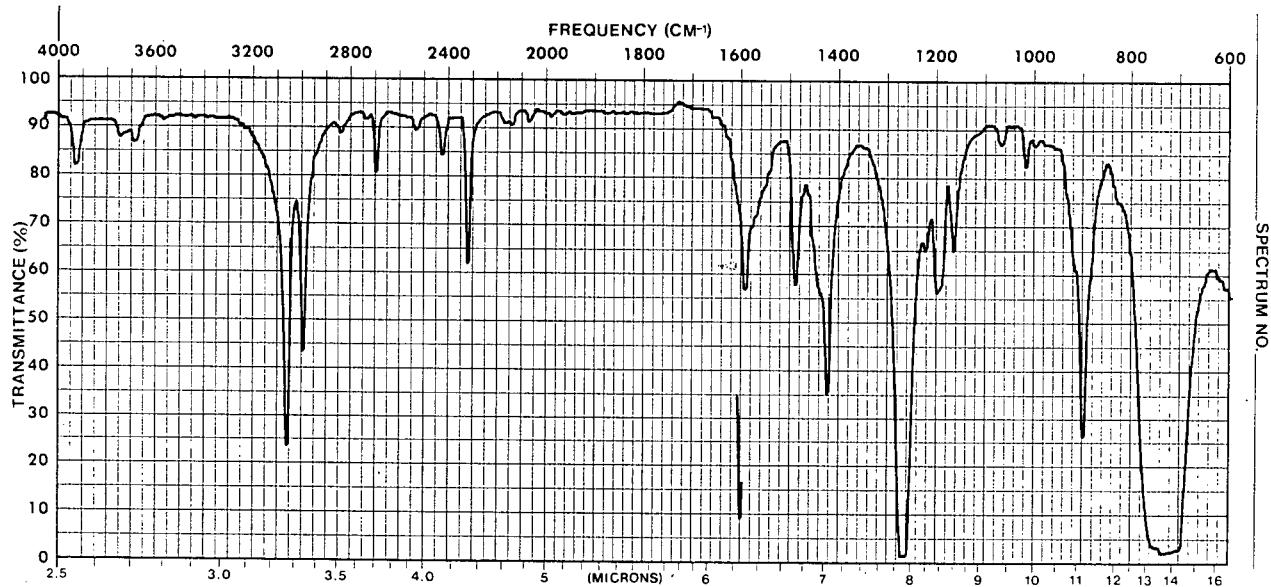
 ^1H NMR

cis $\text{Cp W(NO)H}_2\text{P(OPh)}_3$

IR NUJOL MULL

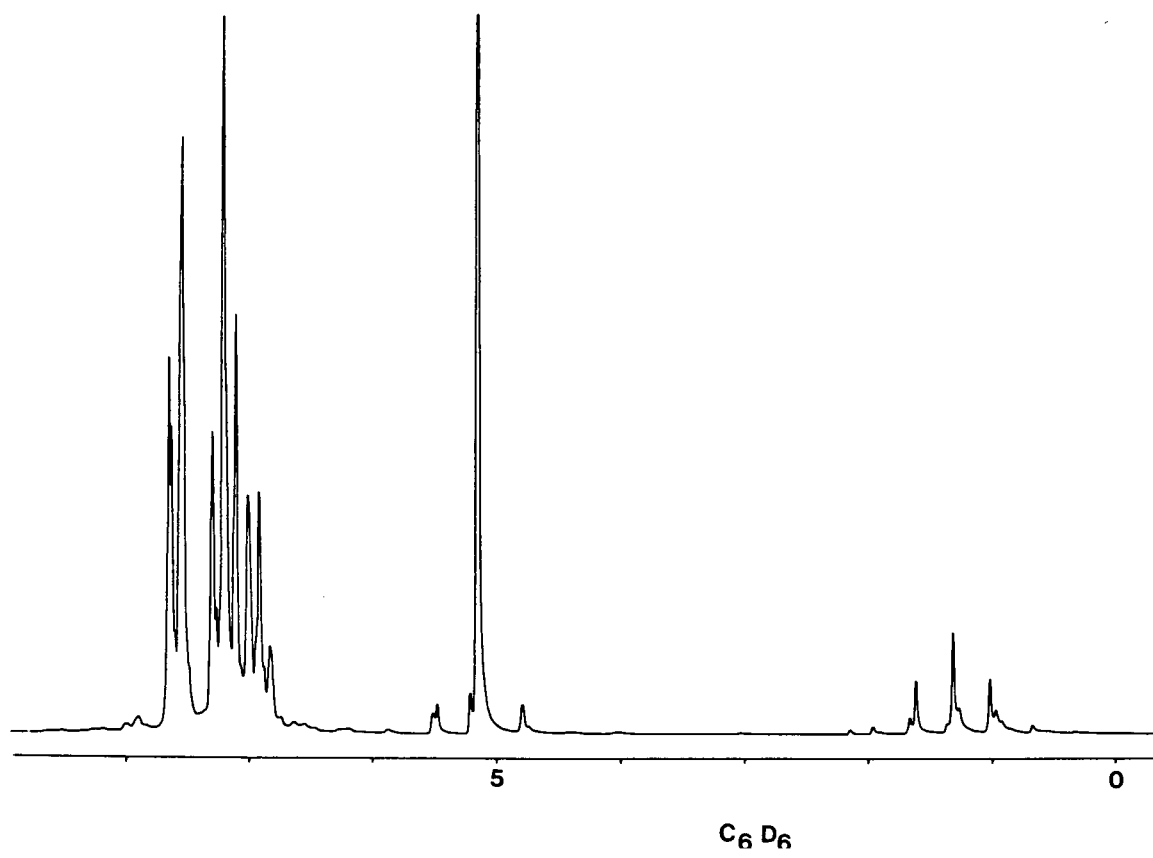
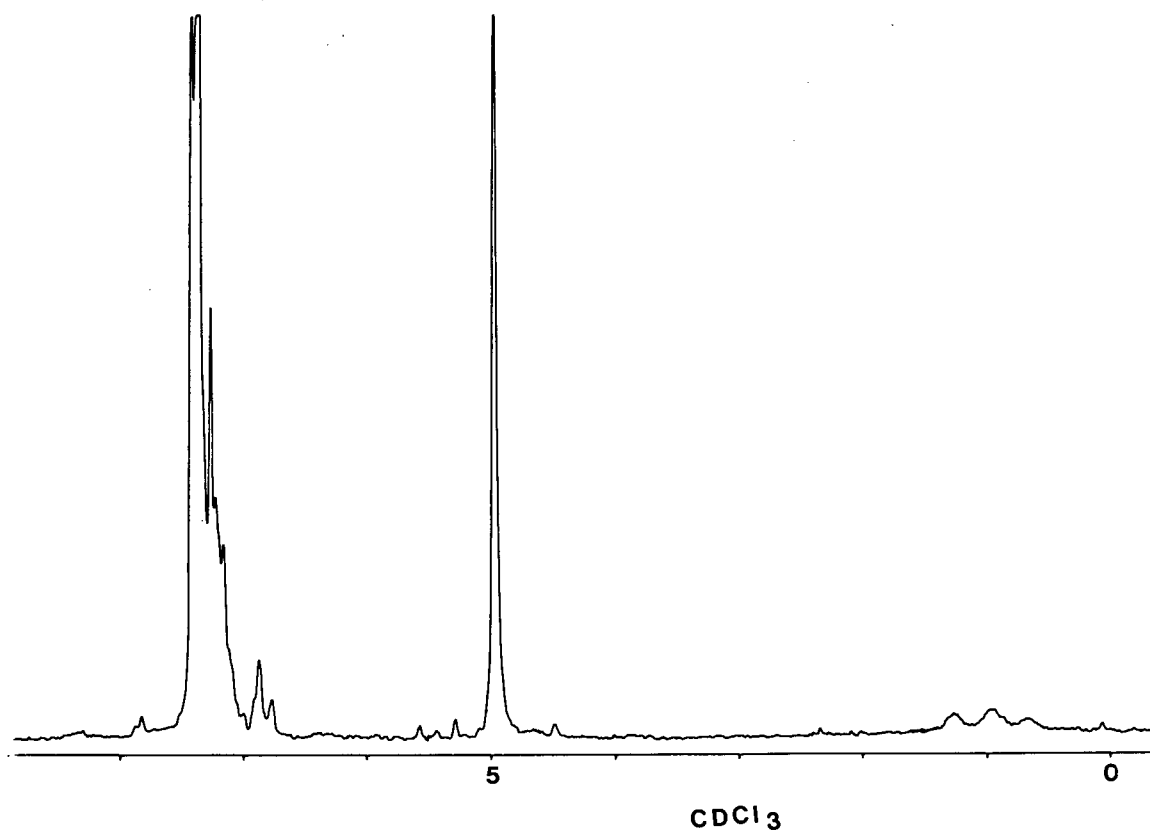


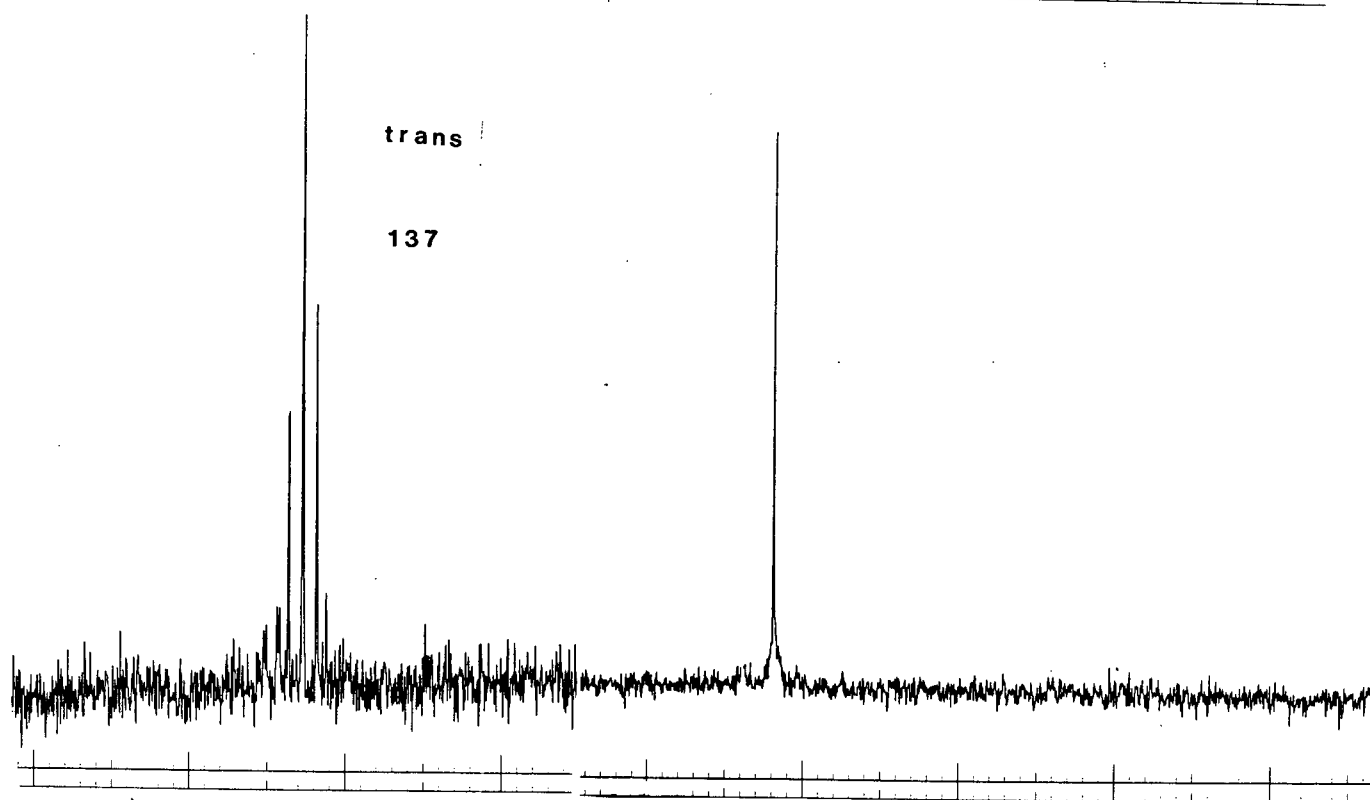
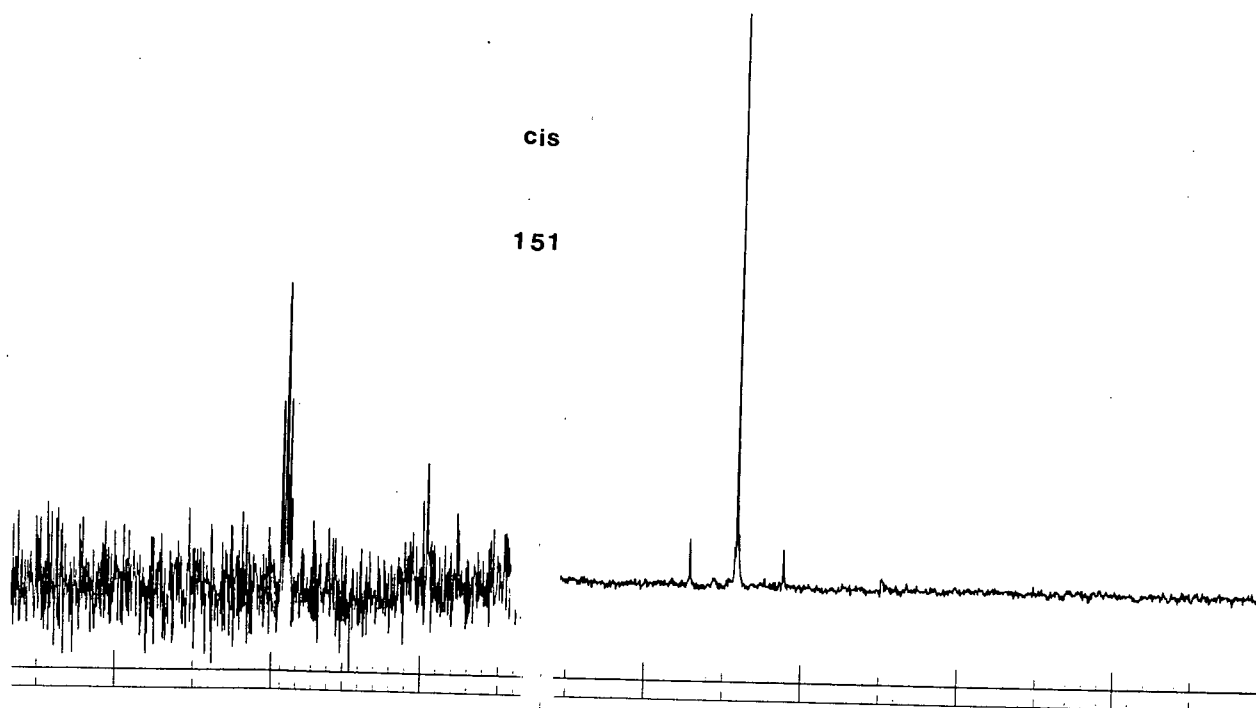
IR CH_2Cl_2



cis $\text{Cp W(NO)H}_2\text{P(OPh)}_3$

^1H NMR



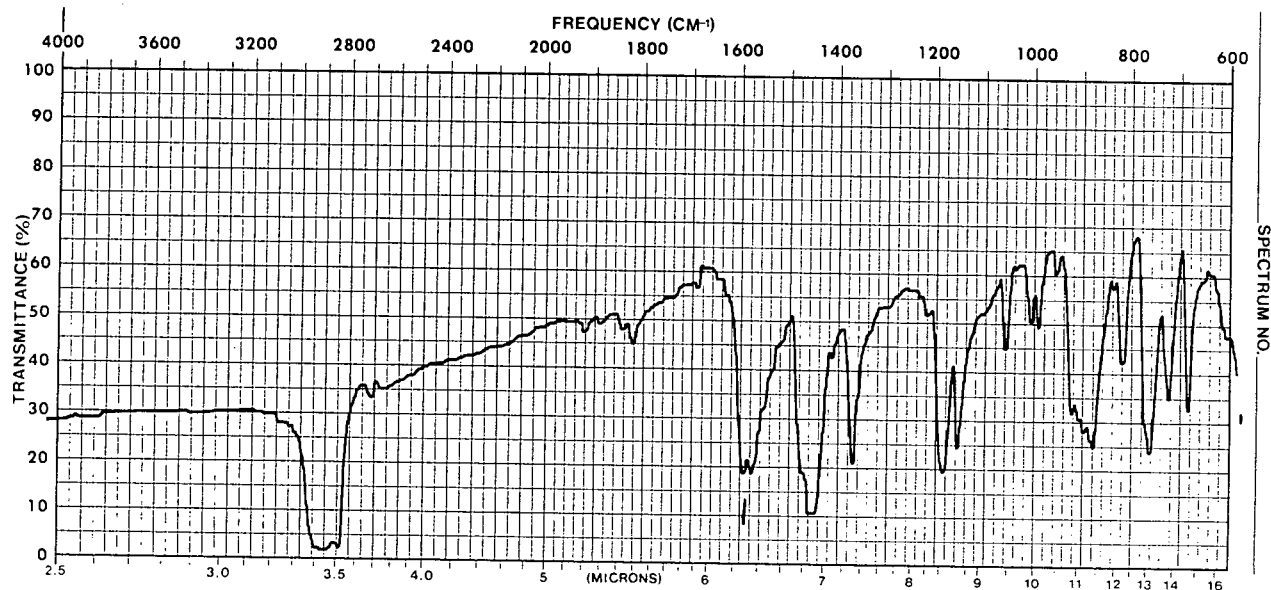


coupled

^1H decoupled

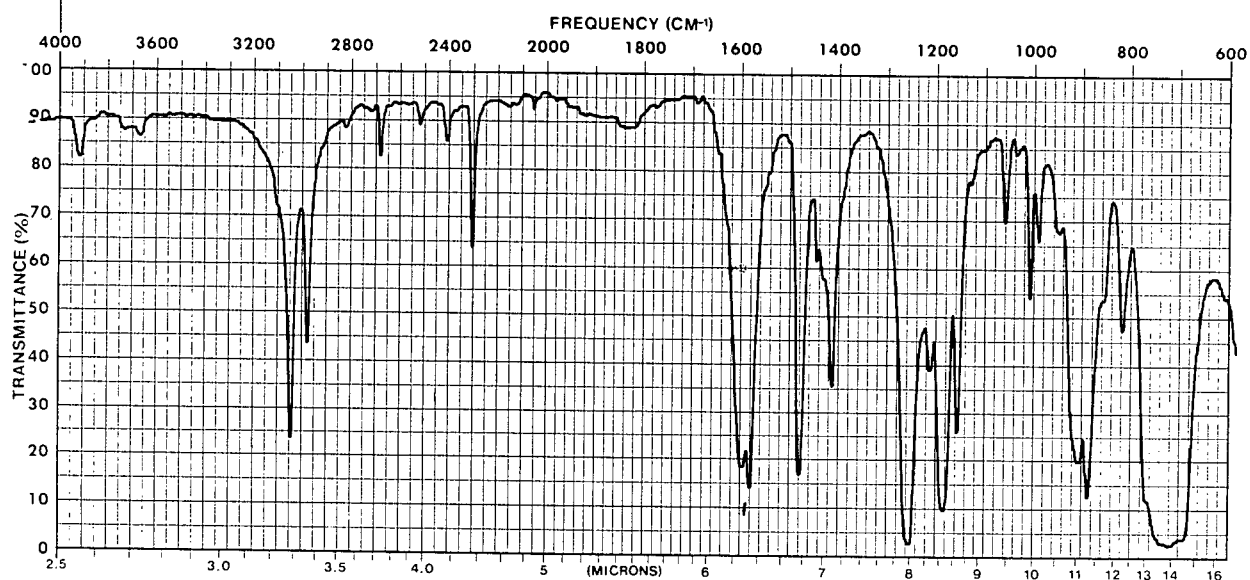
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IR NUJOL MULL



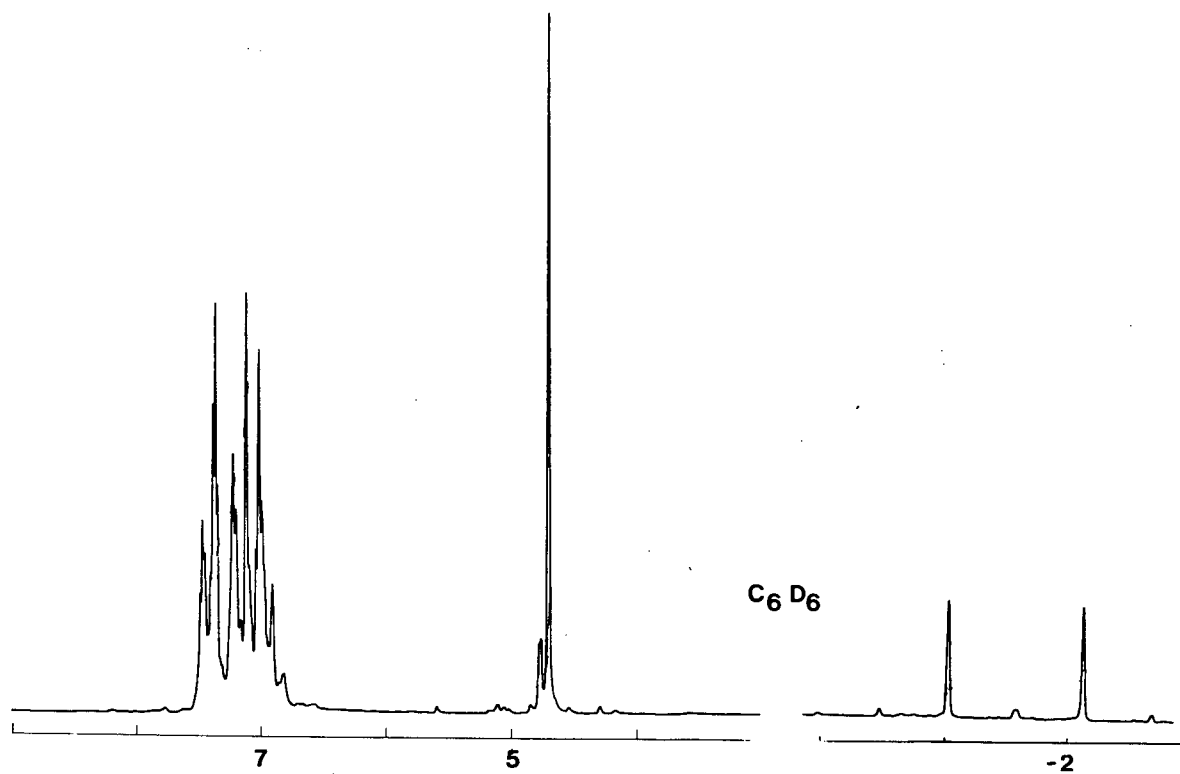
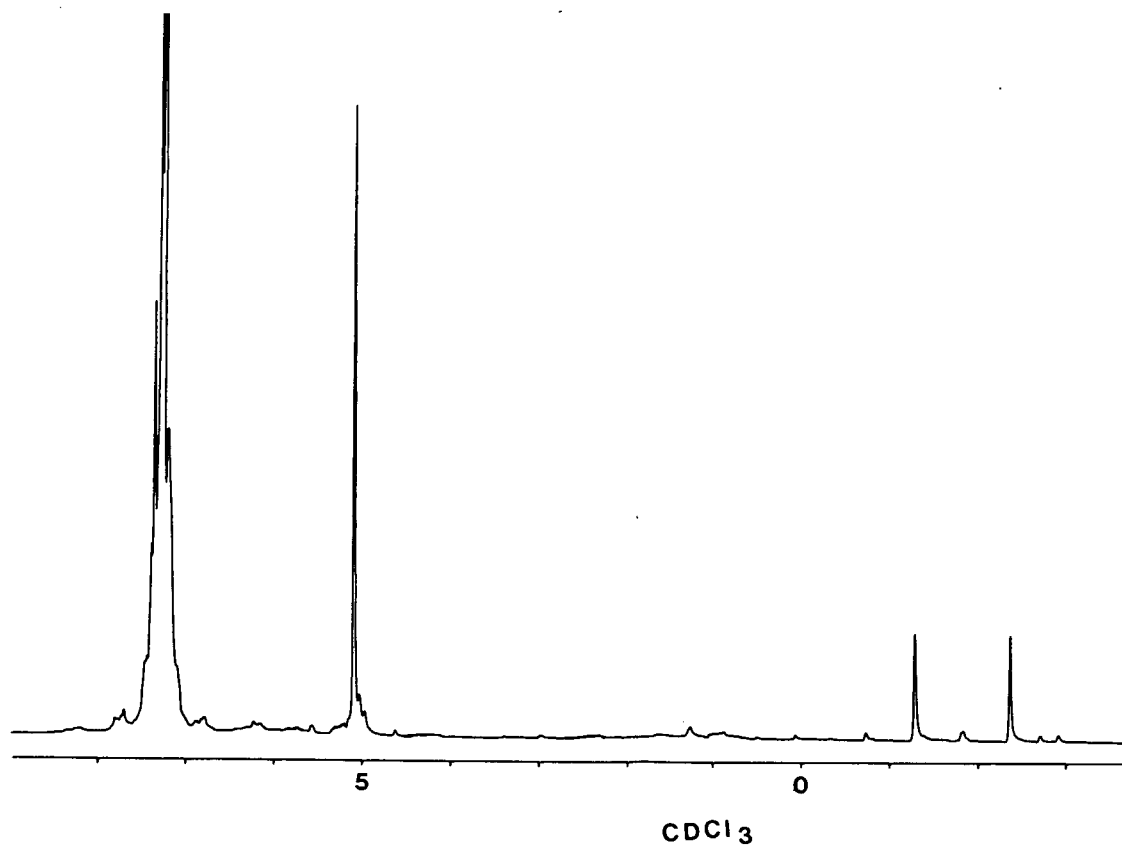
SPECTRUM NO.

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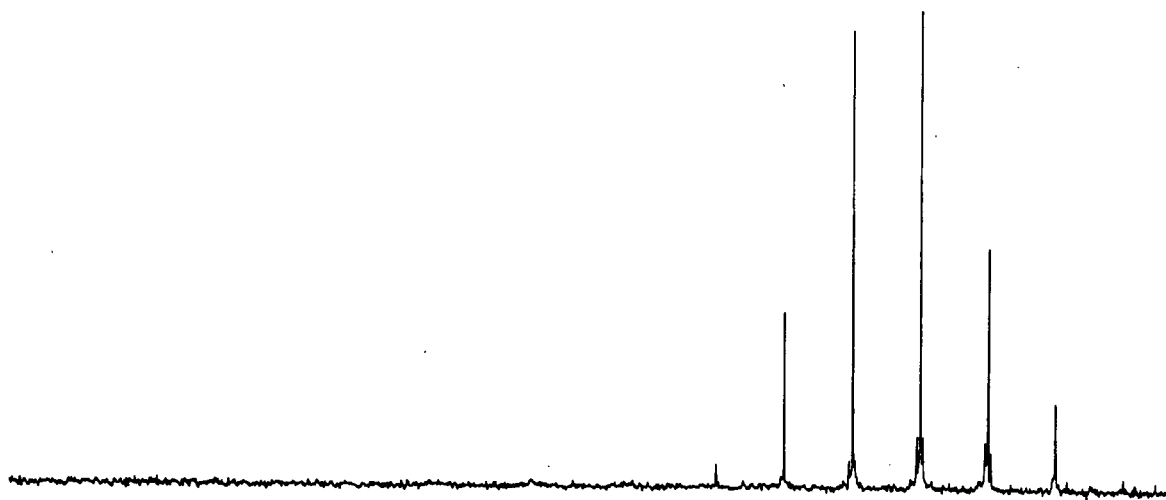
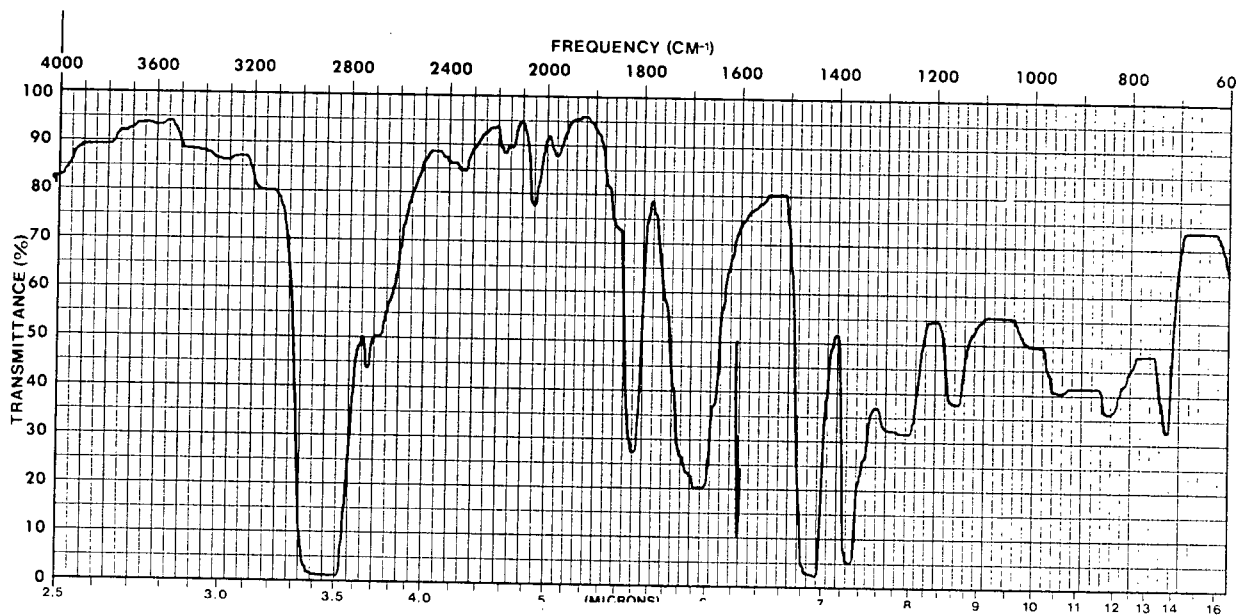


SPECTRUM NO.

trans $[\text{Cp W}(\text{NO})\text{H}_2\text{P}(\text{OPh})_3]$ ^1H NMR



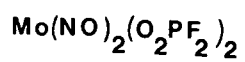
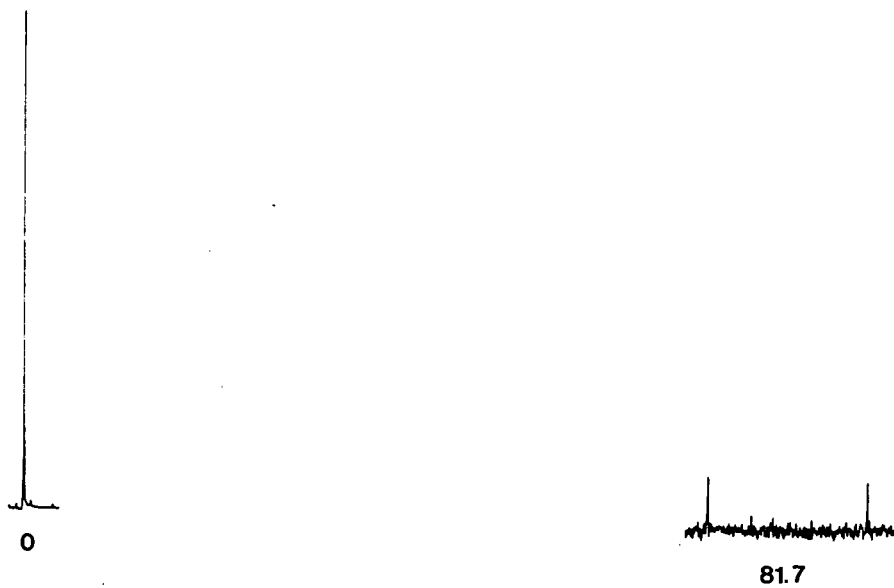
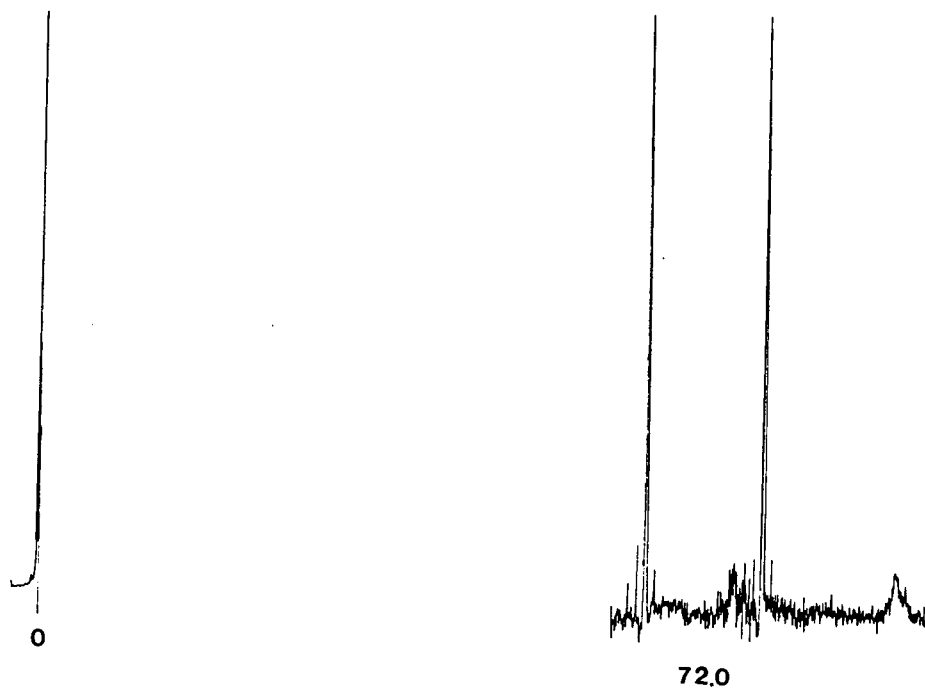
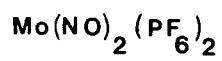
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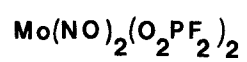


- 144

³¹P NMR

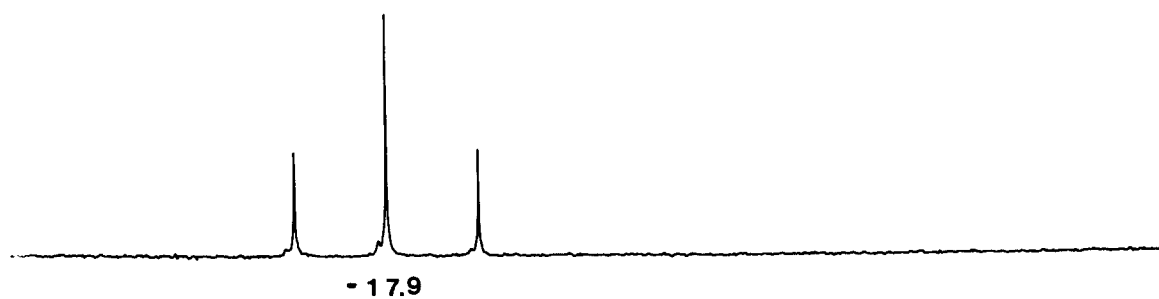
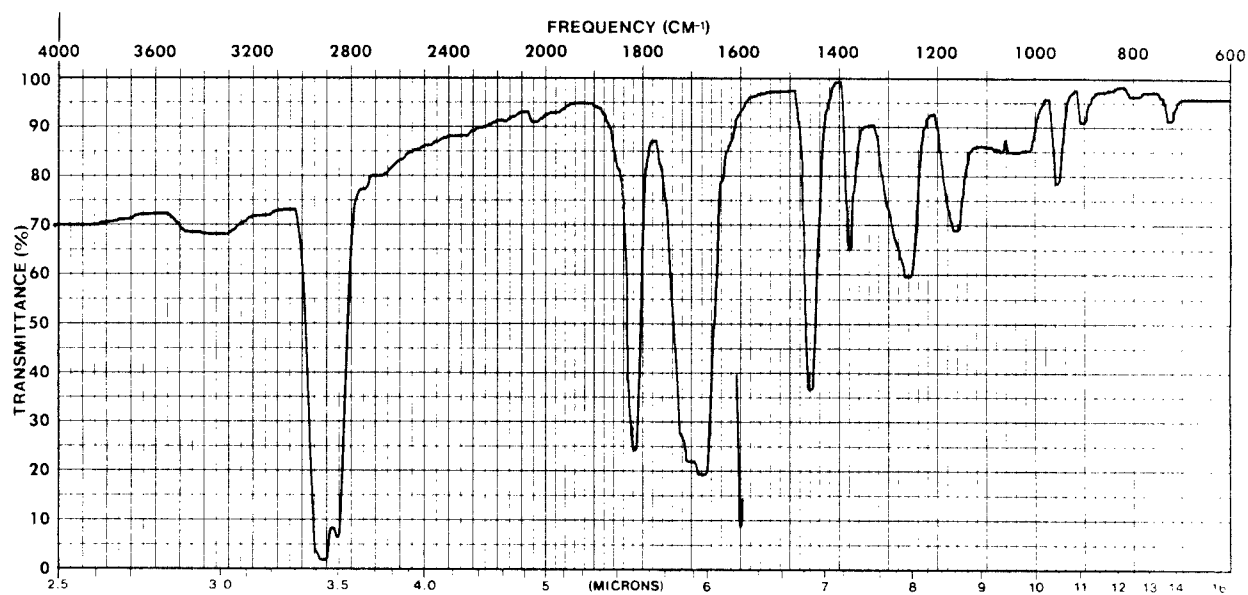
MeCN





181

IR NUJOL MULL



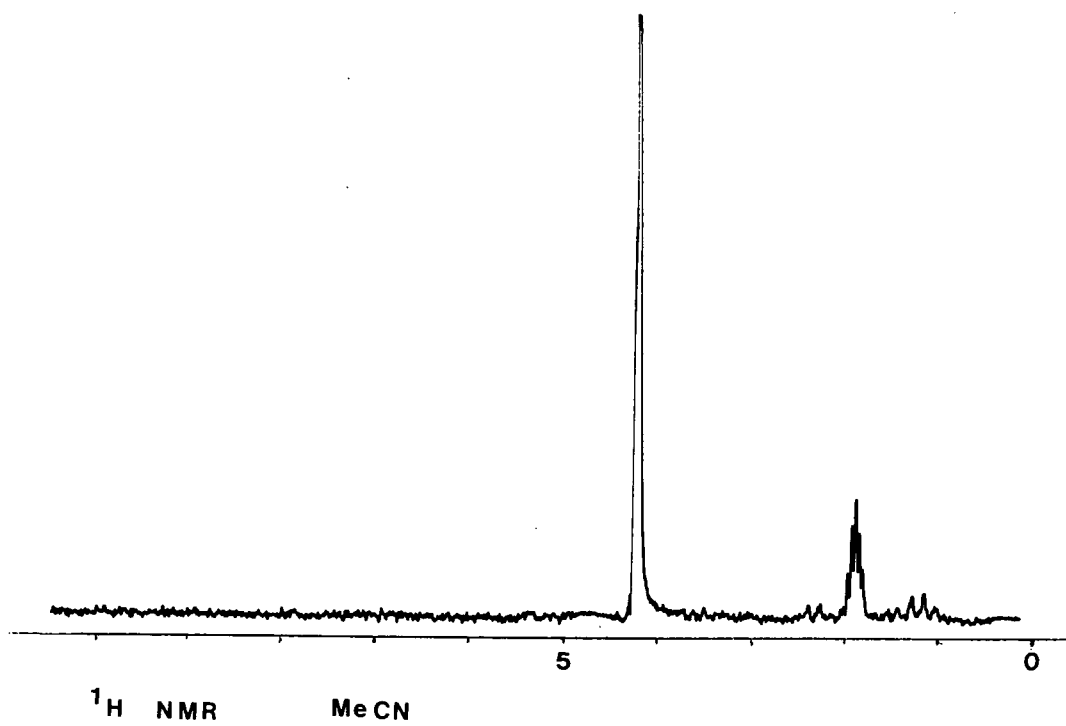
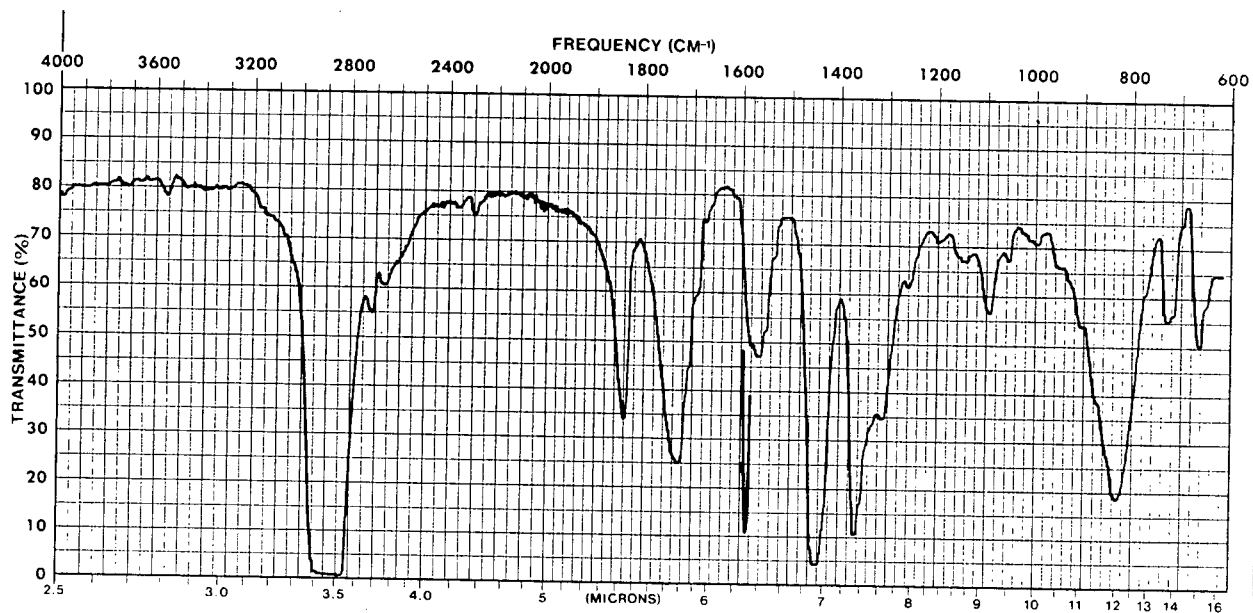
³¹P NMR

MeCN



182

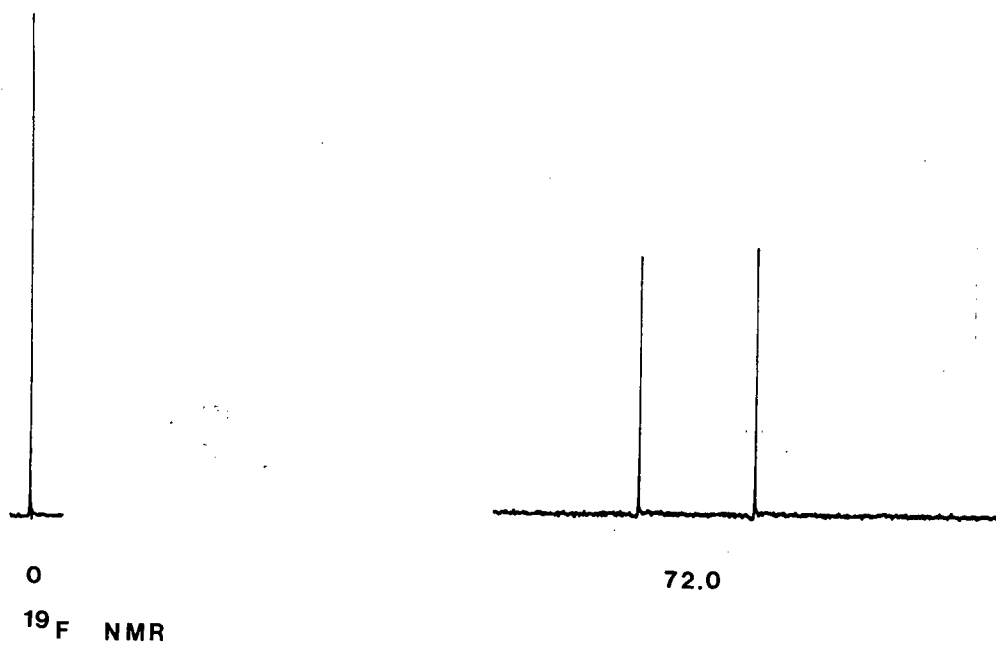
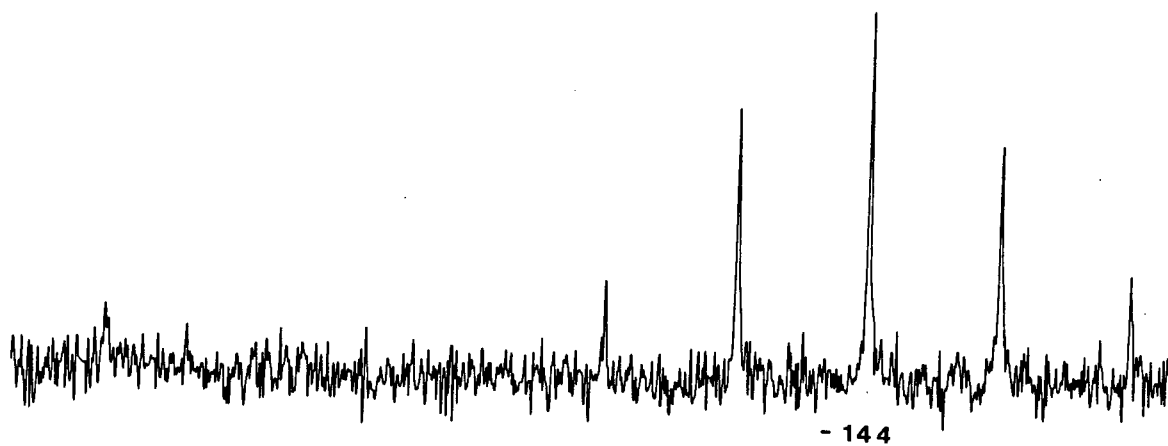
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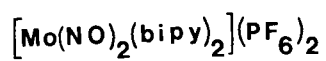




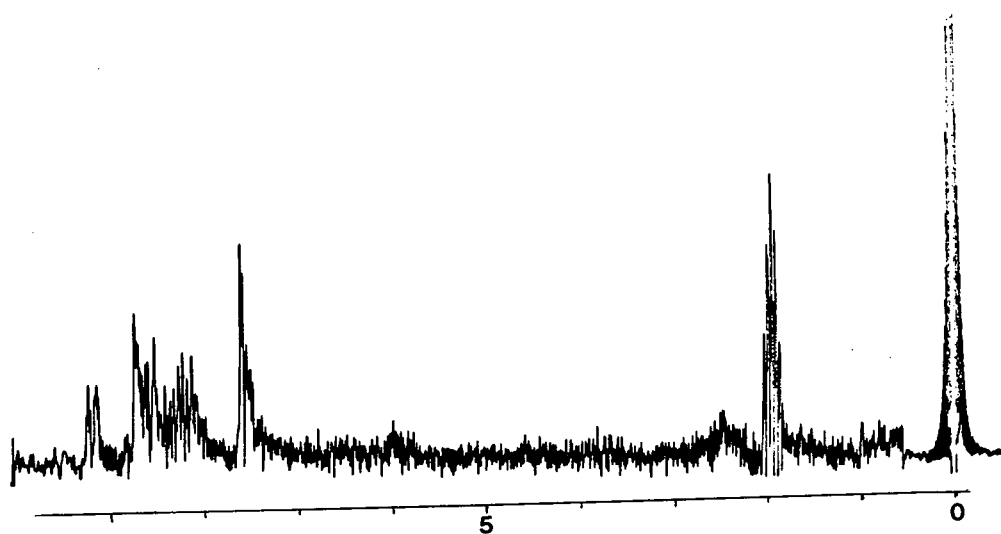
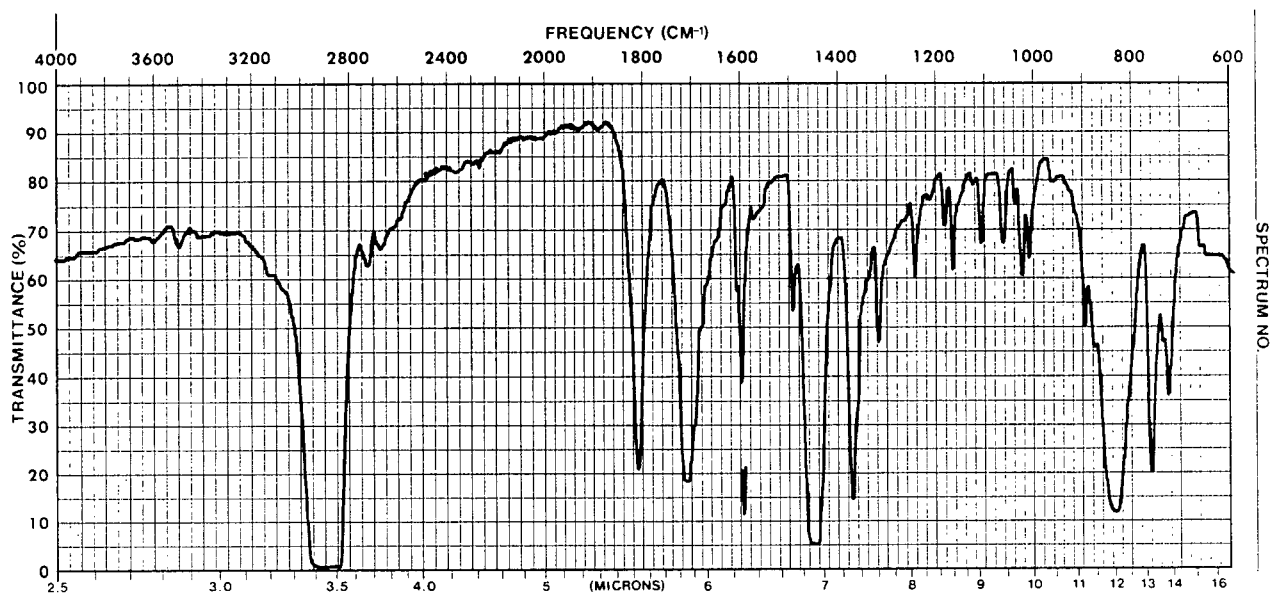
183

^{31}P NMR MeCN

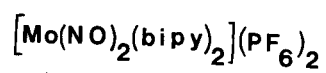




IR NUJOL MULL

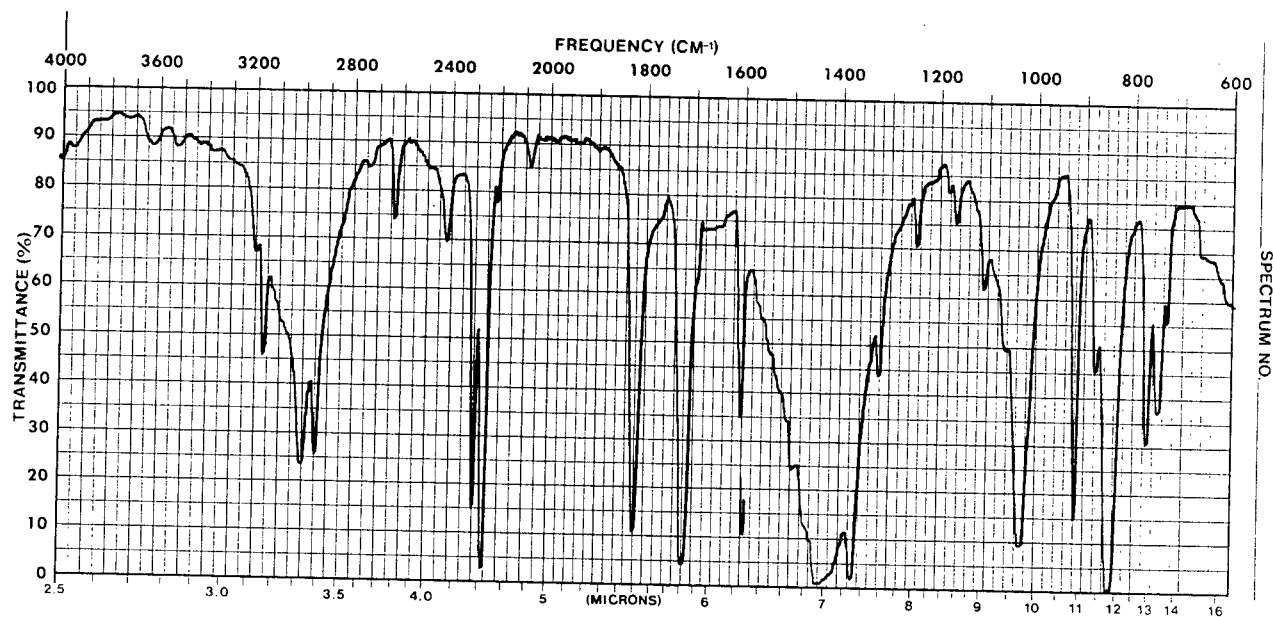
¹H NMR

MeCN

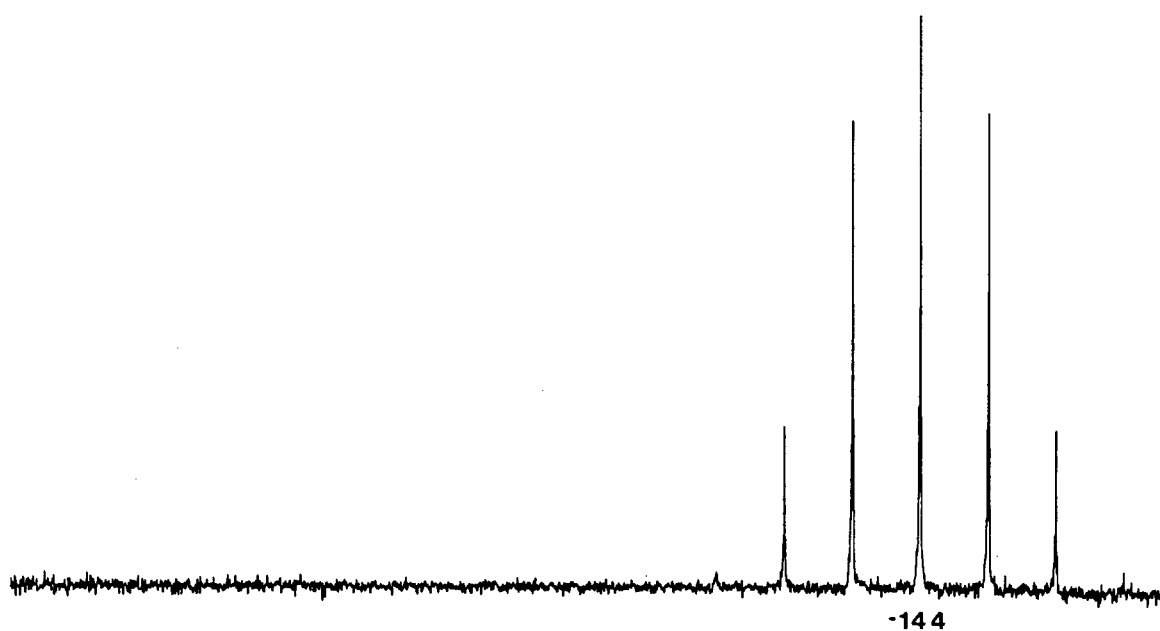


185

IR CH_3CN

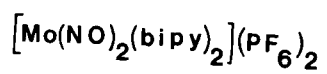
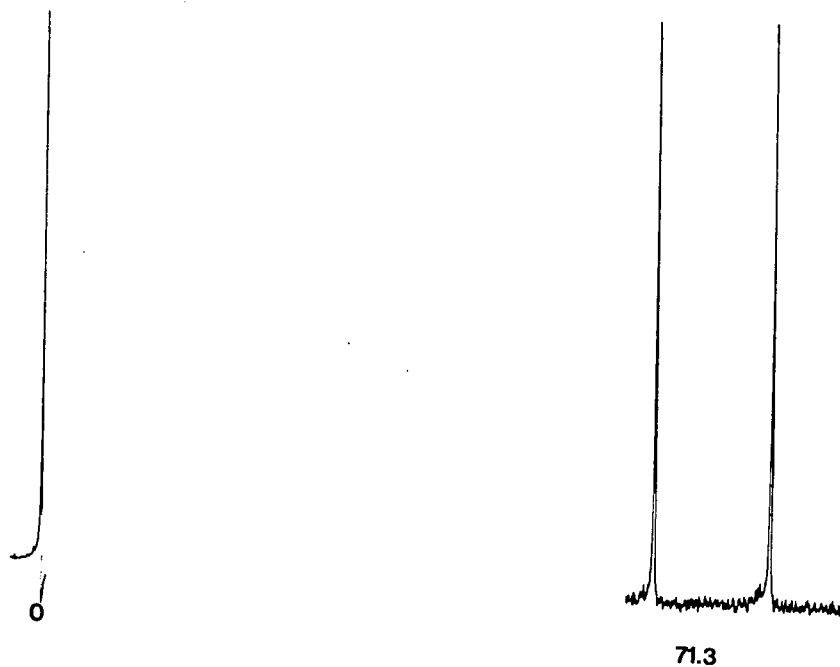
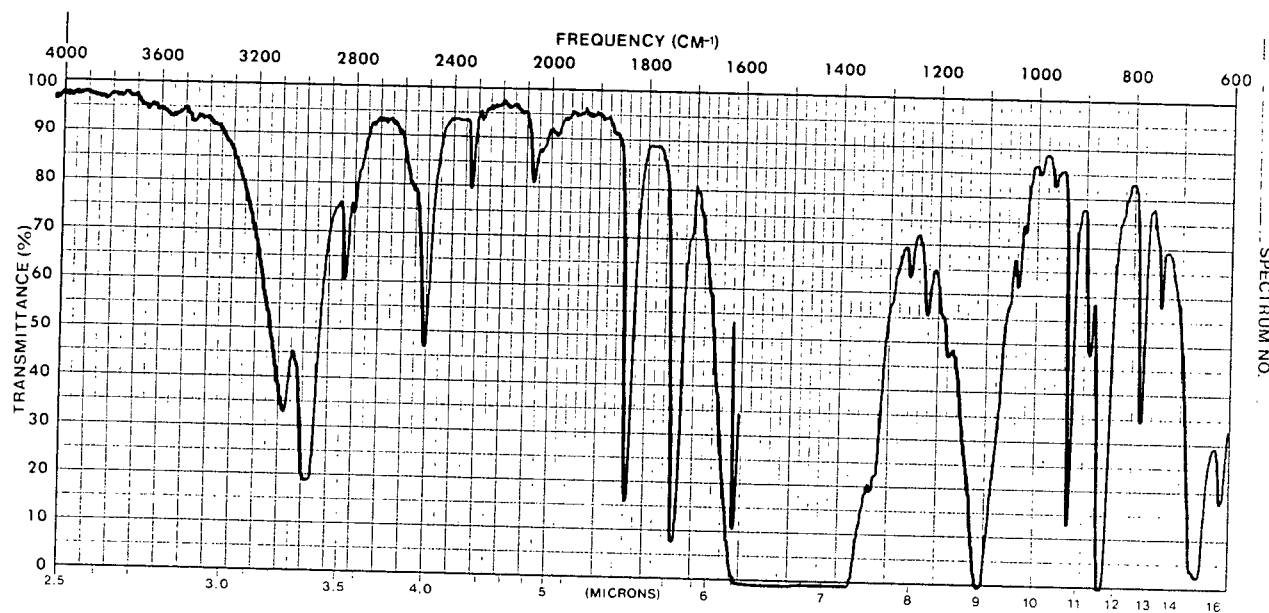


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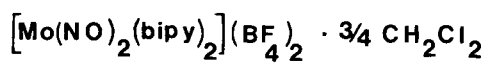


³¹P NMR

MeCN

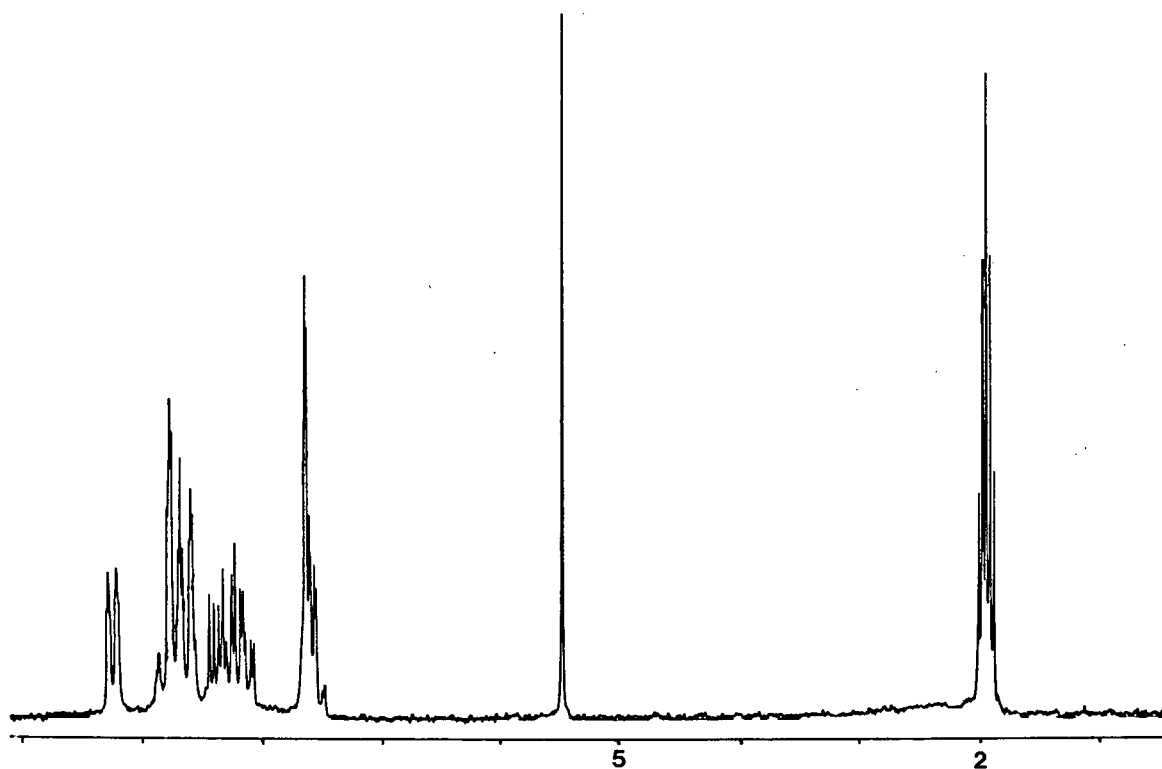
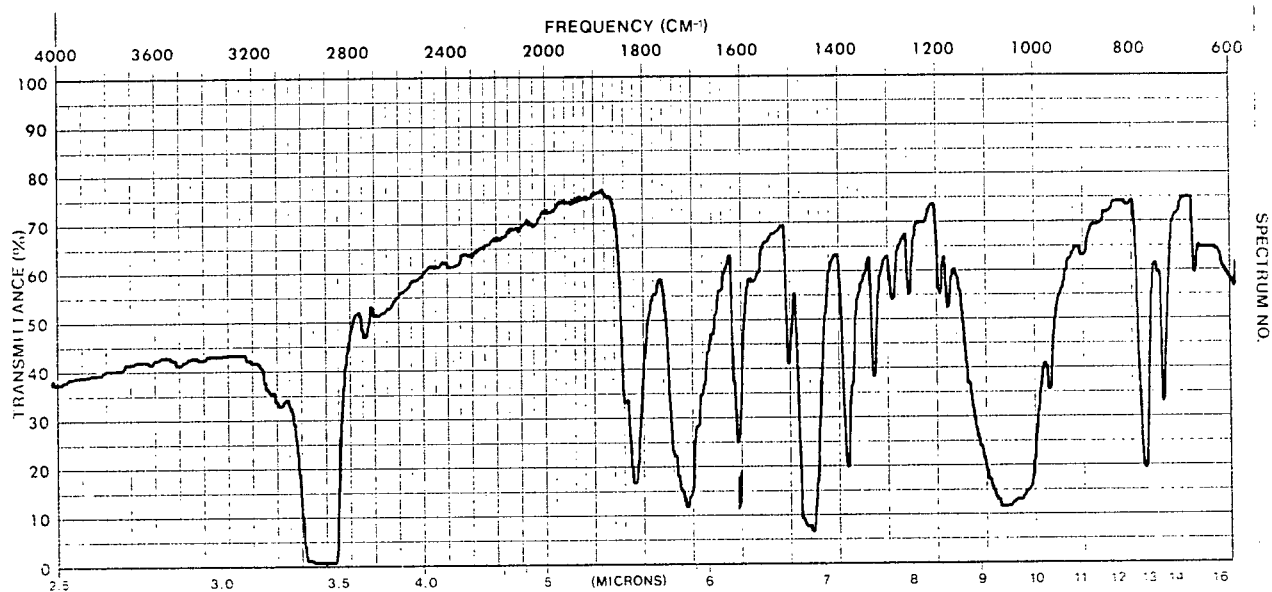
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MeCN

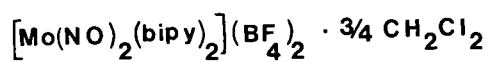
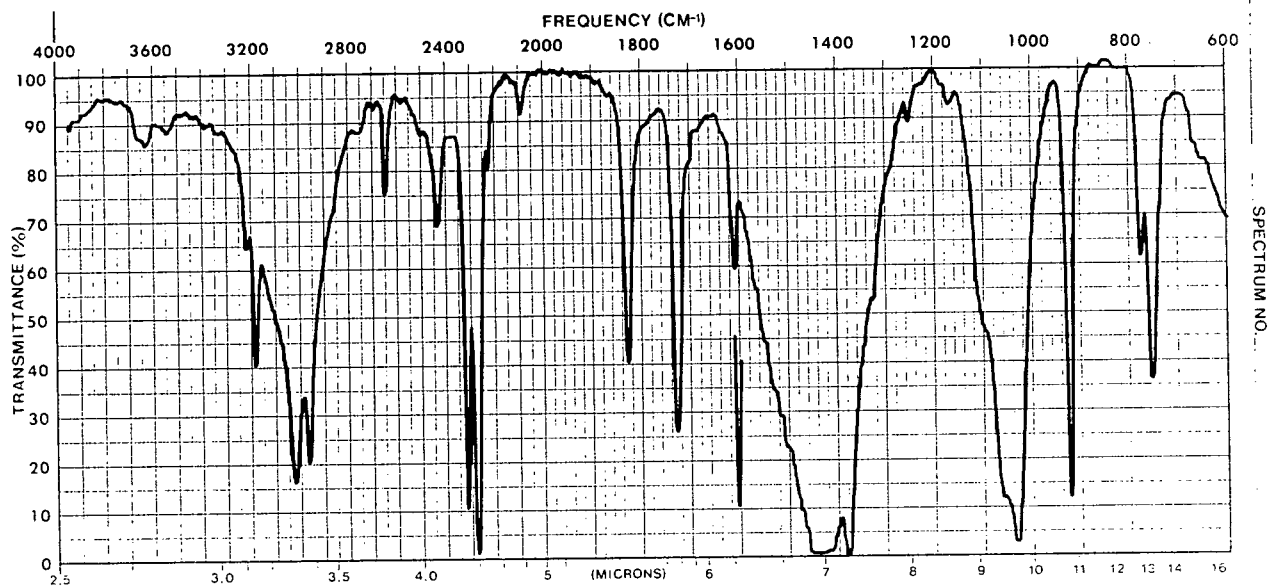
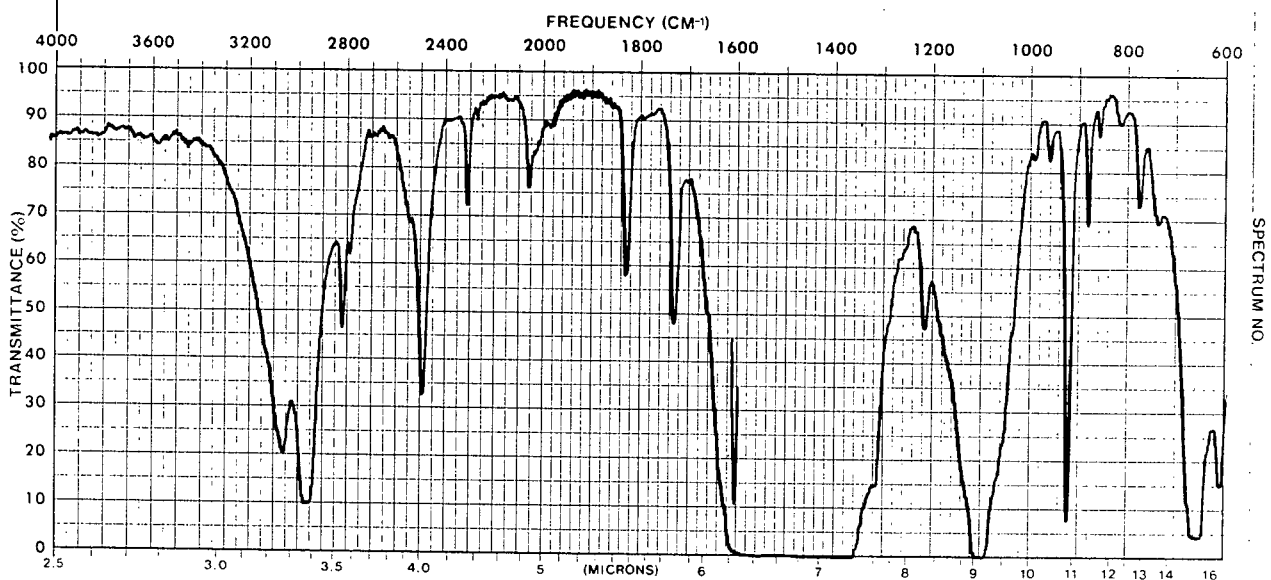


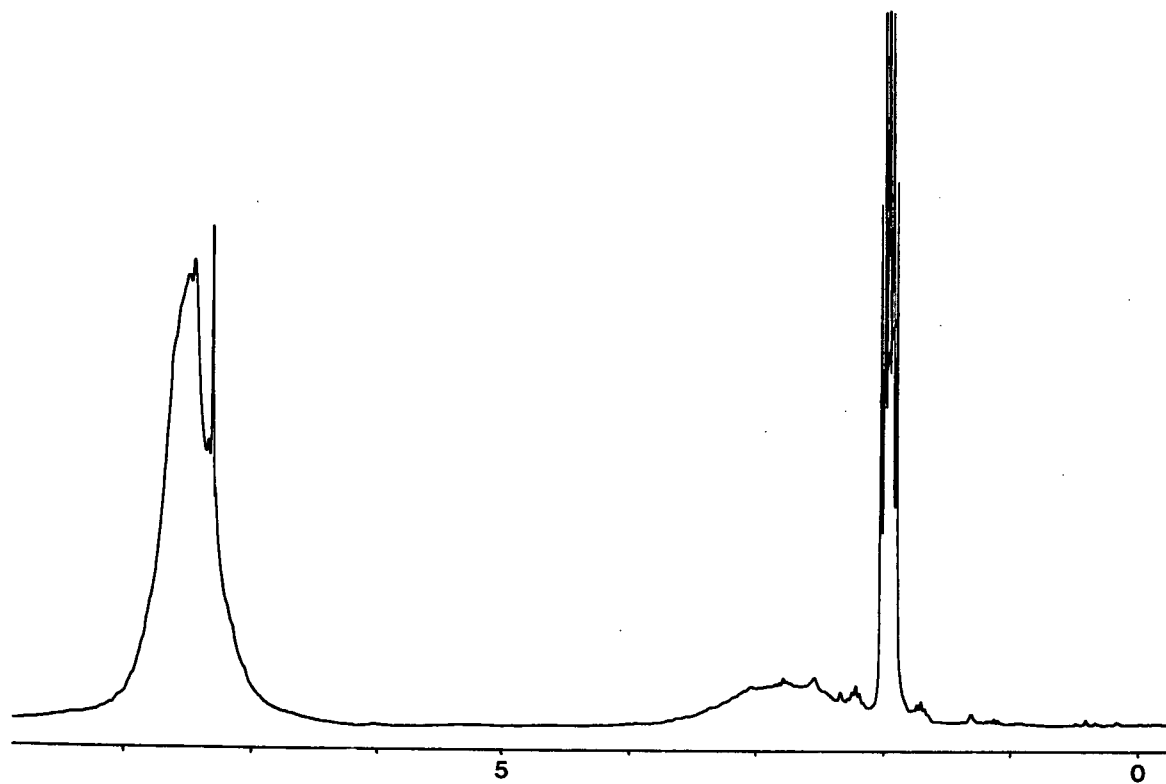
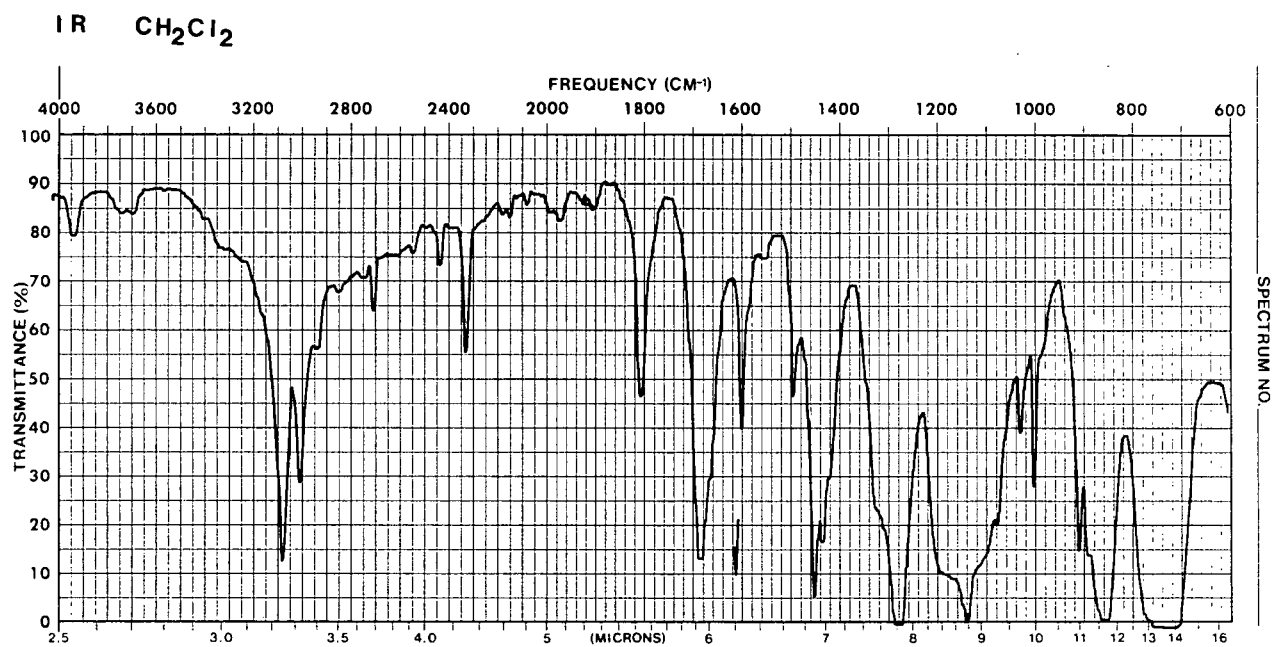
187

IR NUJOL MULL


 ^1H NMR

MeCN

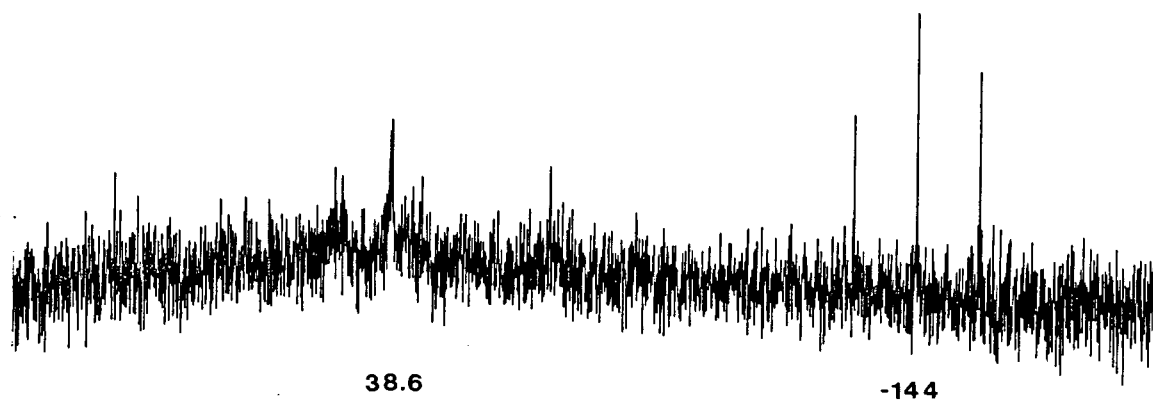
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 ^1H NMR

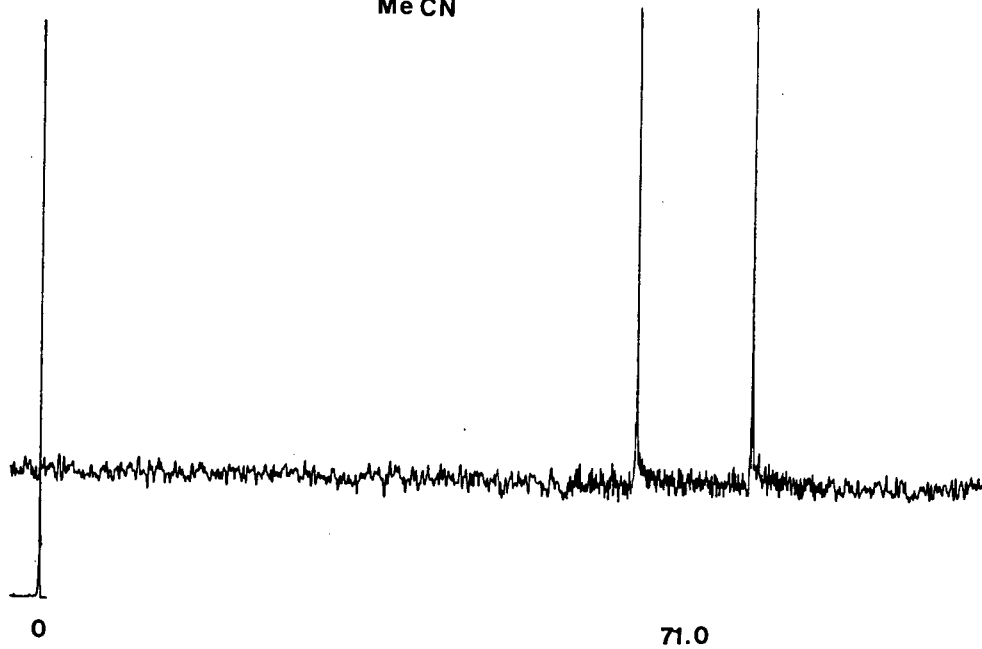
MeCN



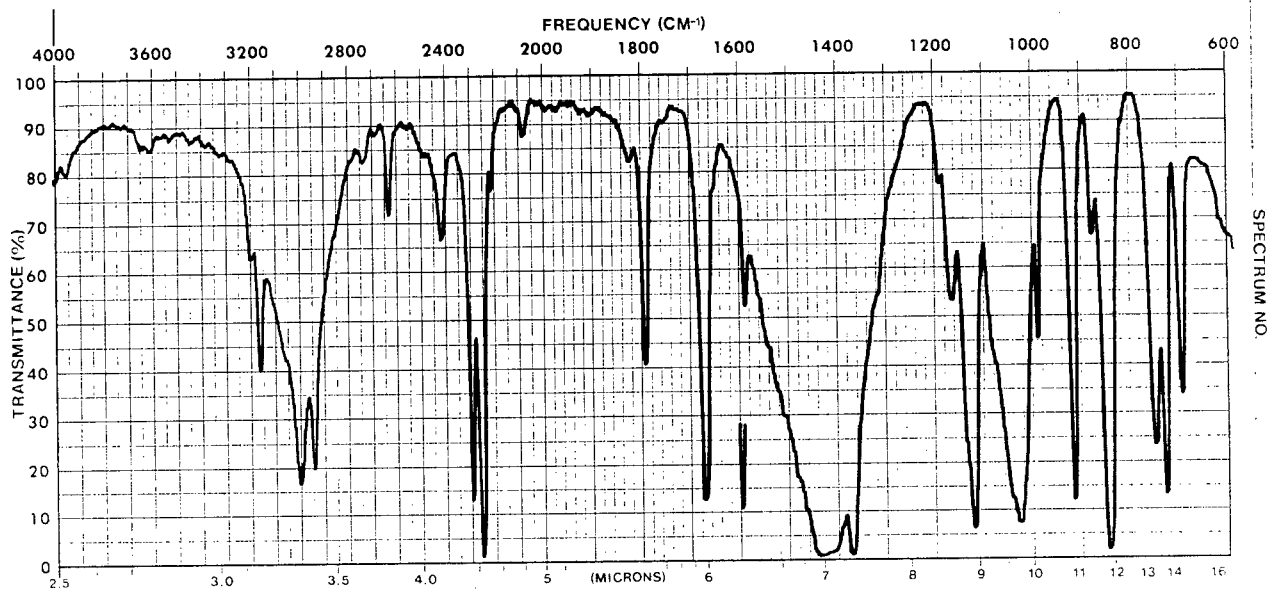
^{31}P NMR



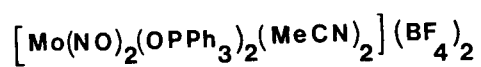
MeCN



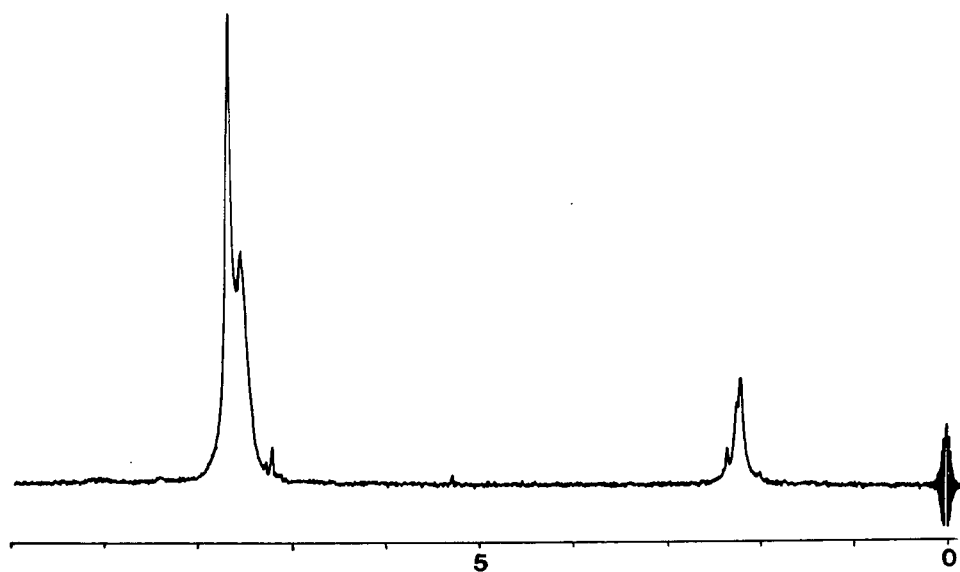
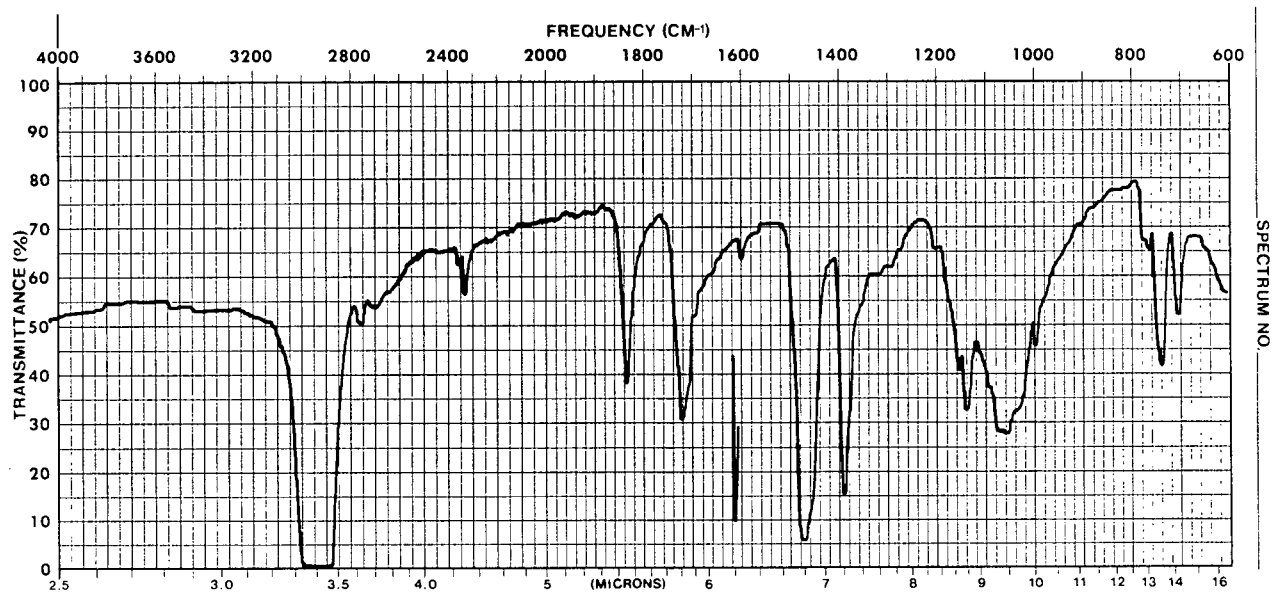
^{19}F NMR

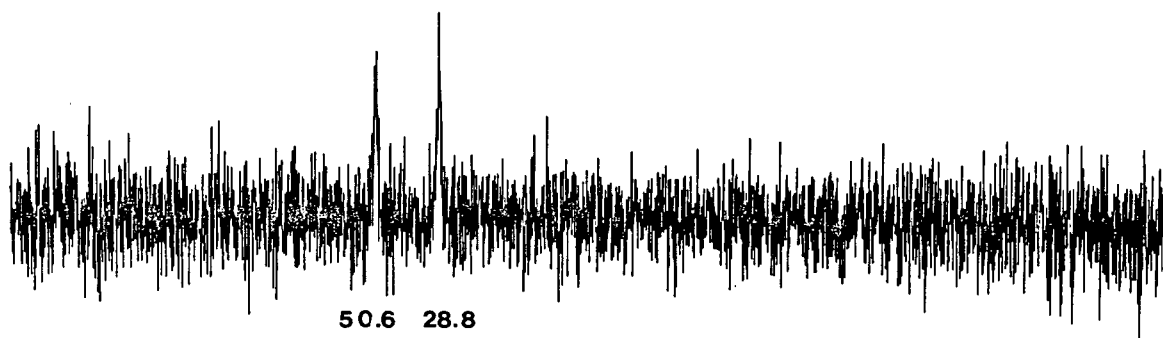
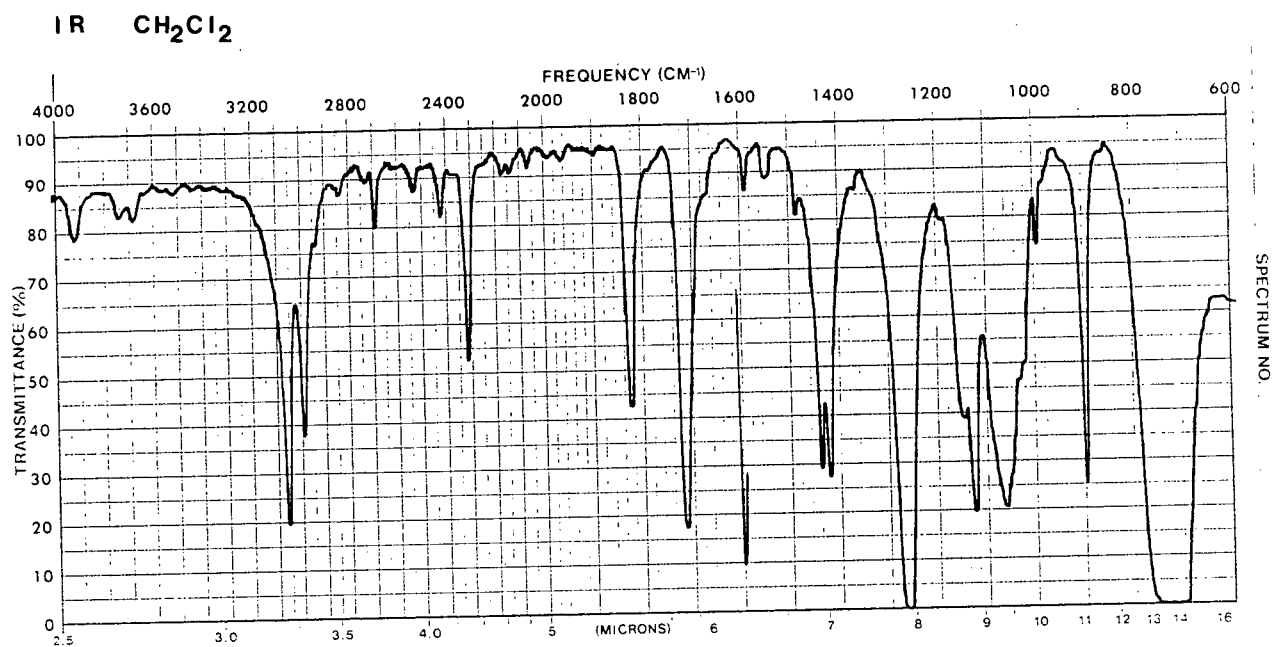
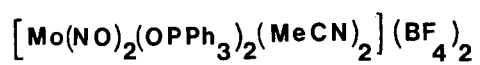
IR CH_3CN  ^1H NMR

MeCN



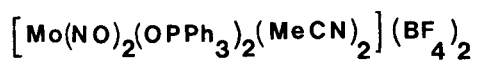
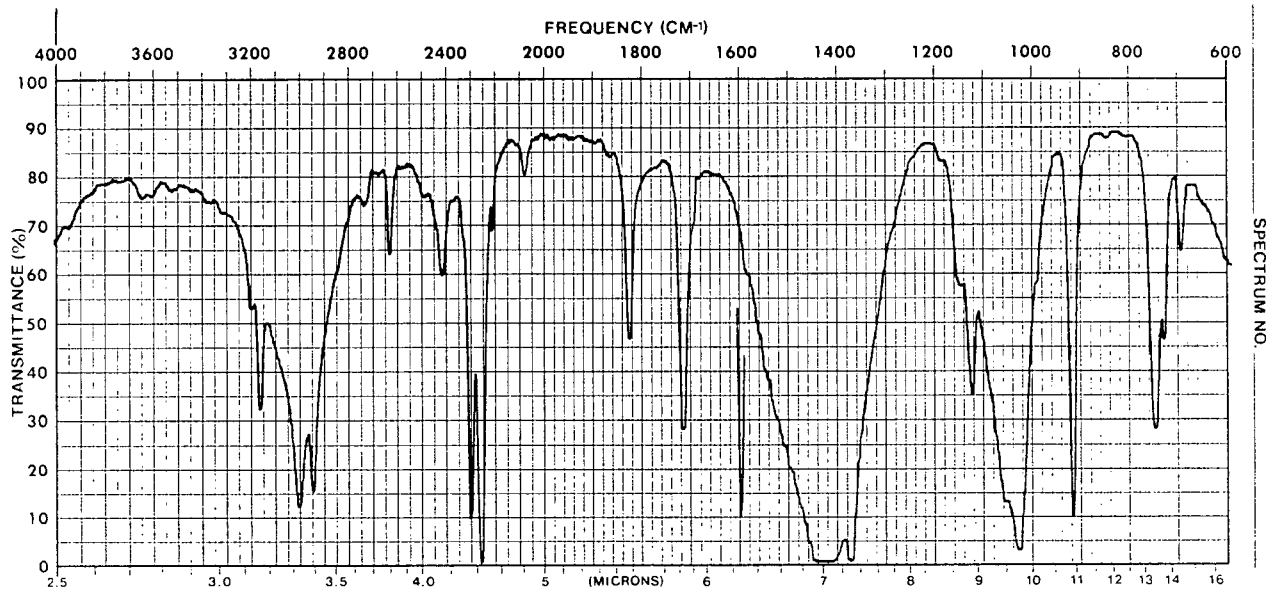
IR NUJOL MULL

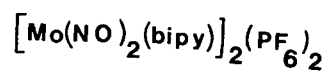
 ^1H NMR CDCl_3



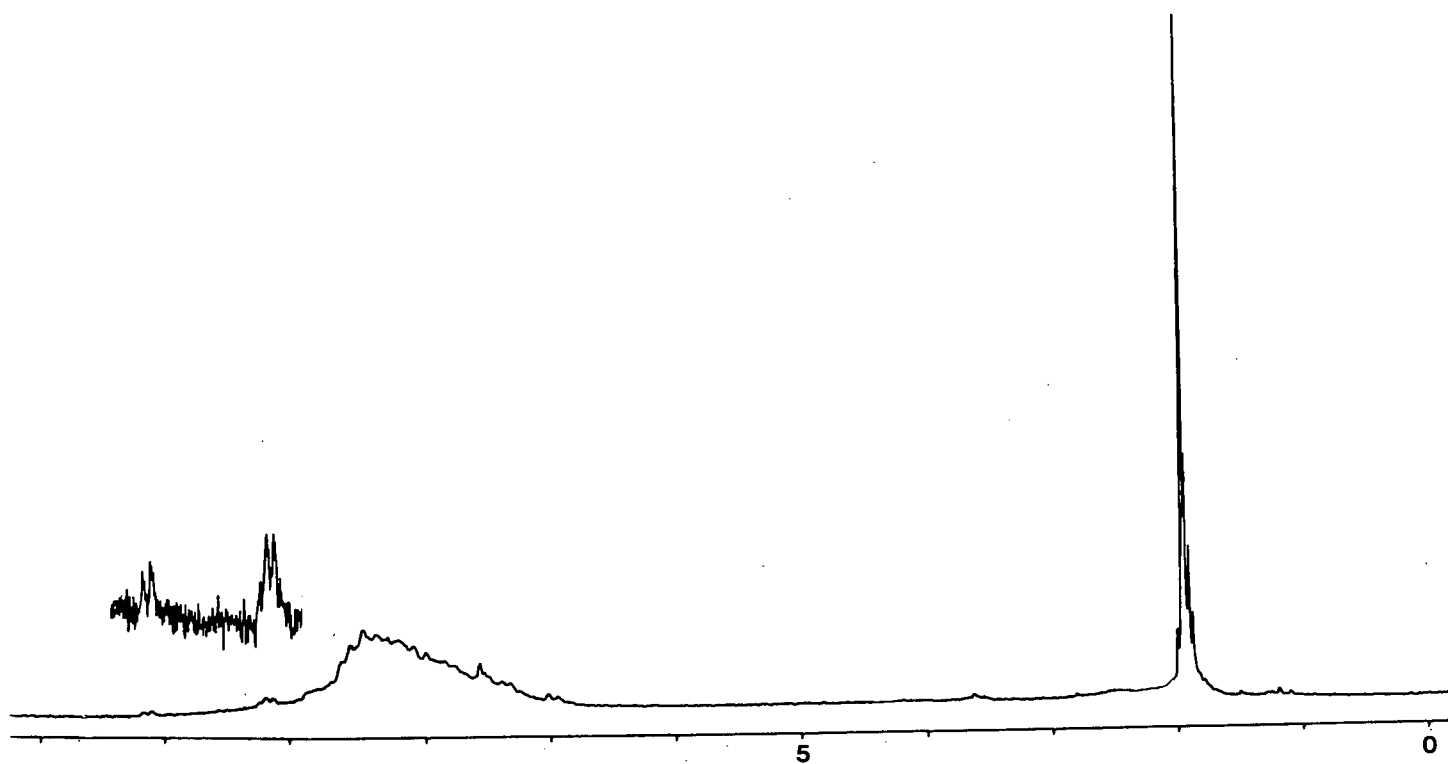
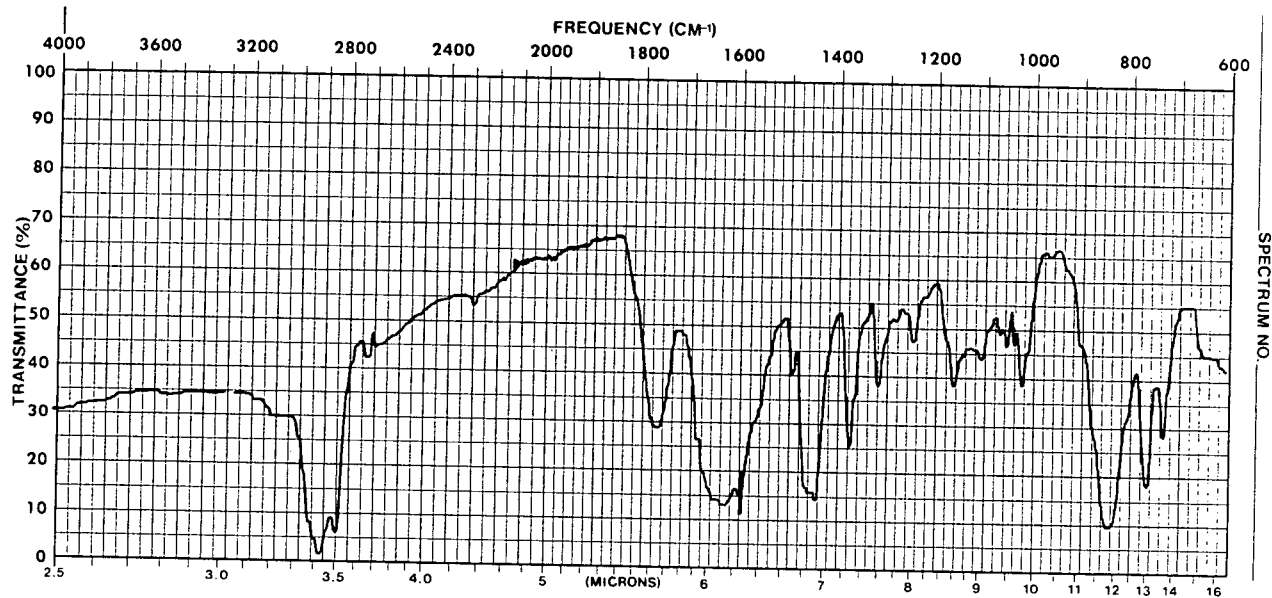
³¹P NMR

MeCN

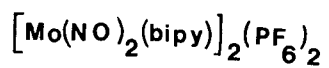
IR CH_3CN ¹⁹F NMR CDCl_3



IR NUJOL MULL

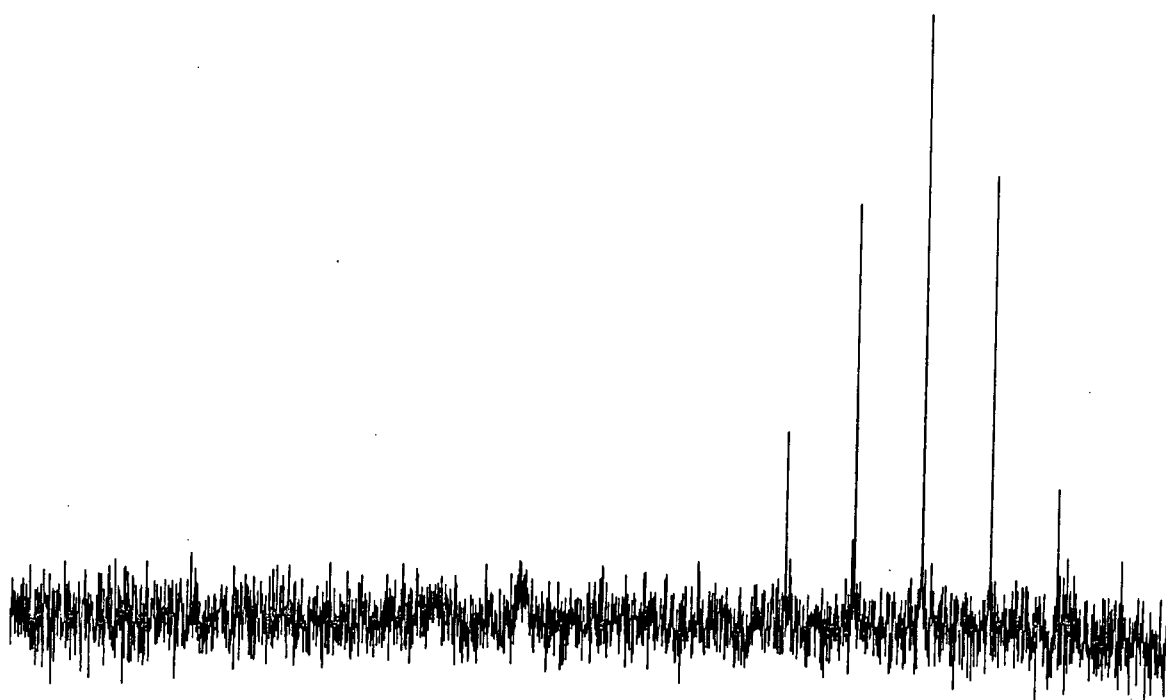
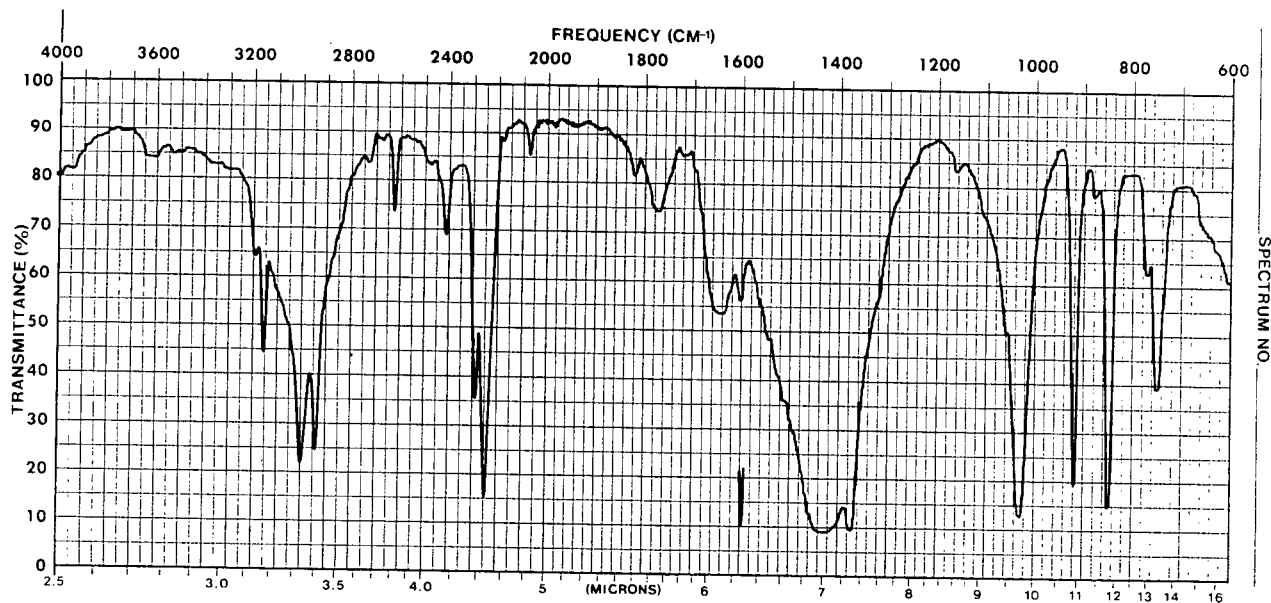
¹H NMR

MeCN



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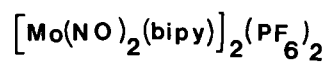
IR CH_3CN



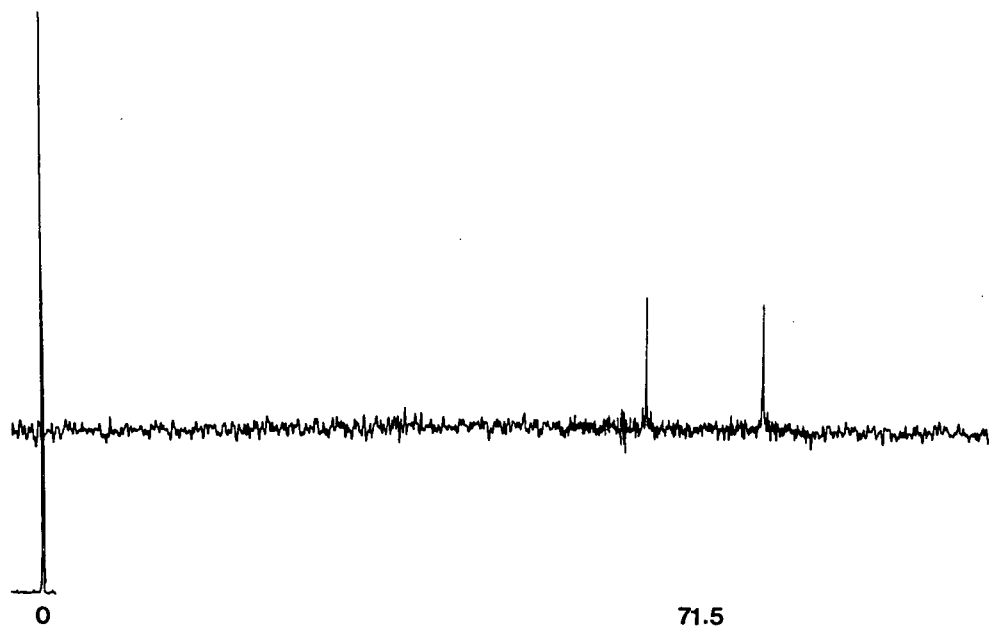
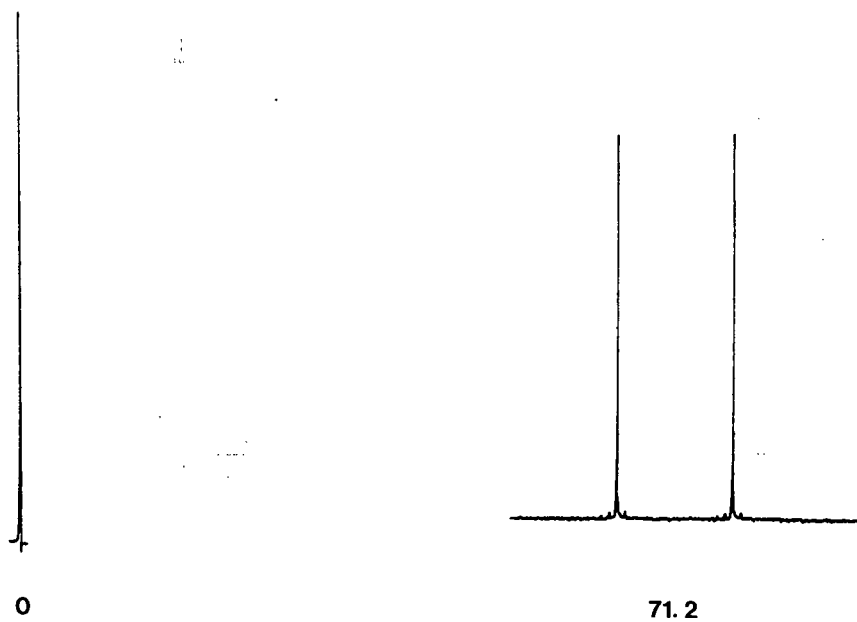
-144

³¹P NMR

MeCN



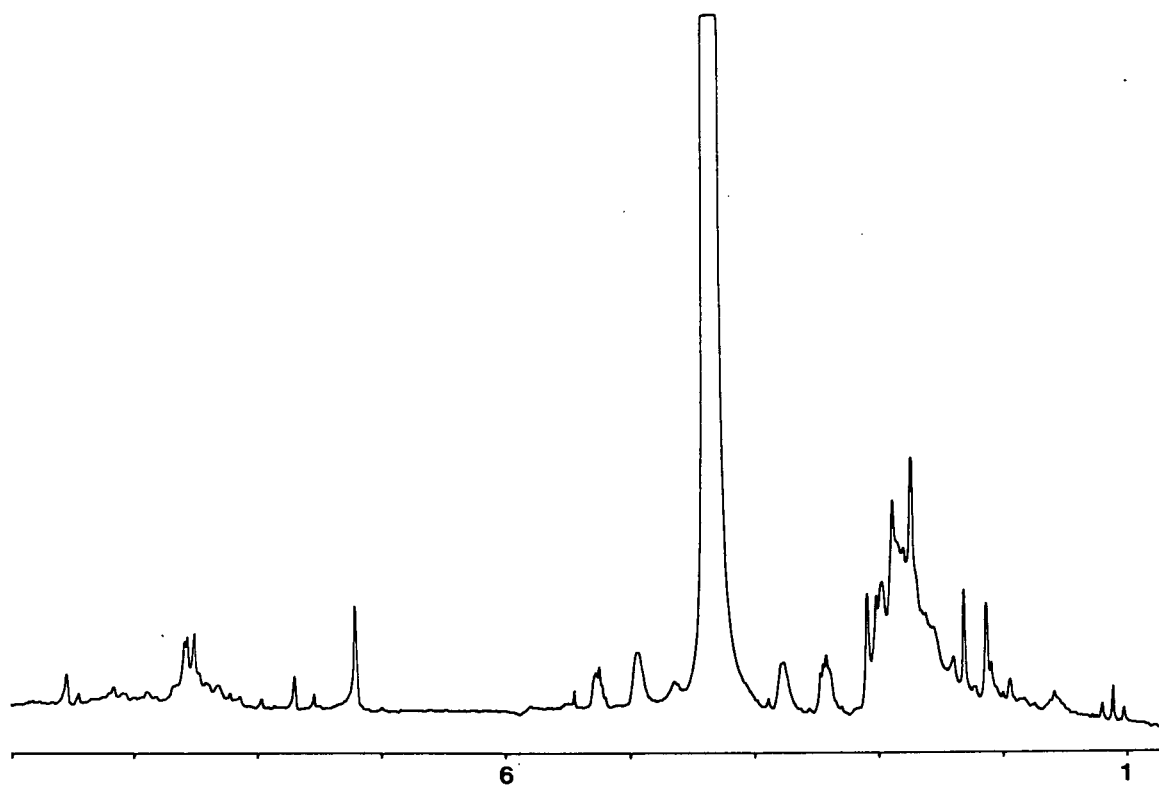
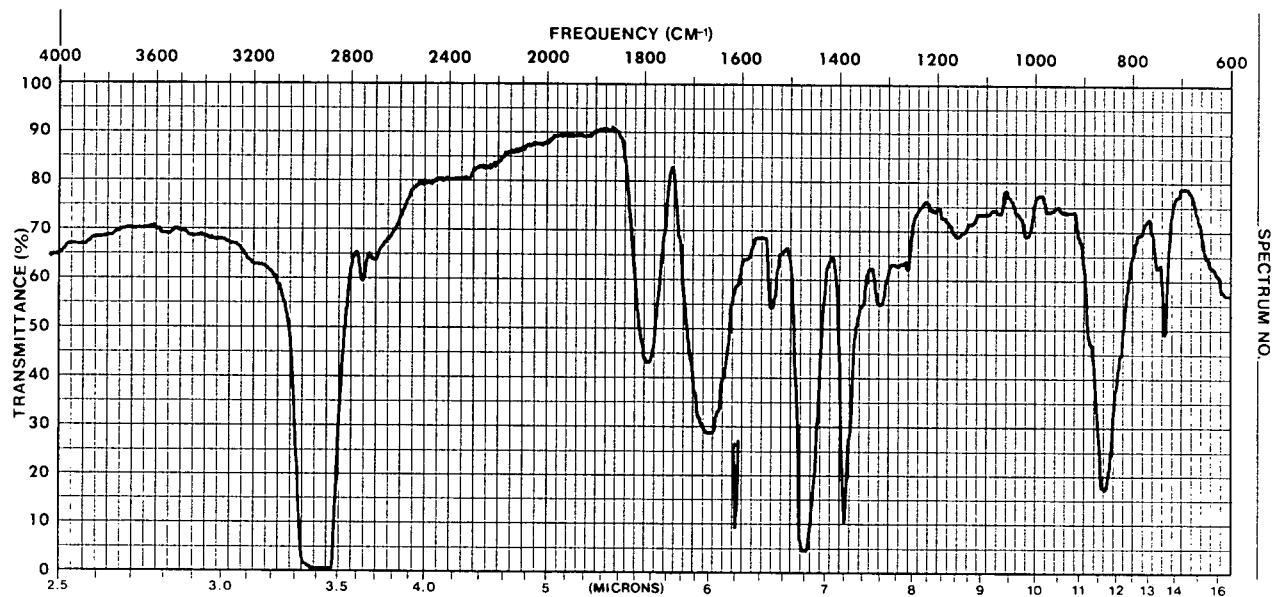
MeCN



CD_2Cl_2

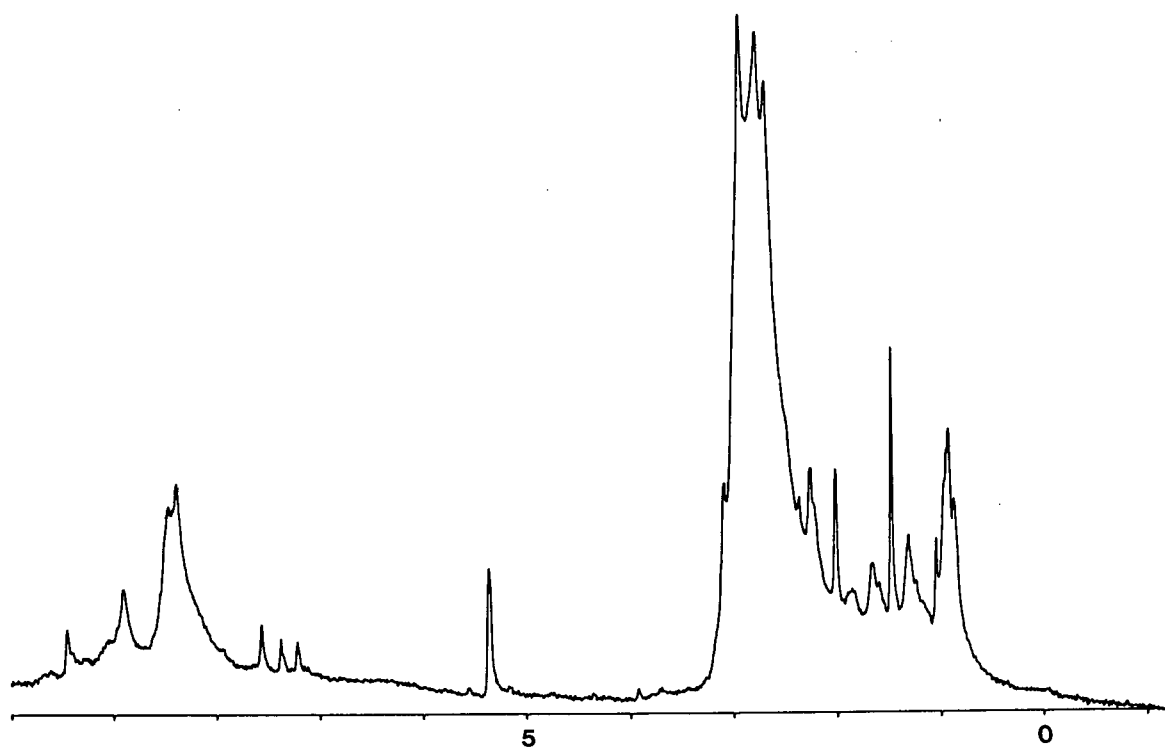
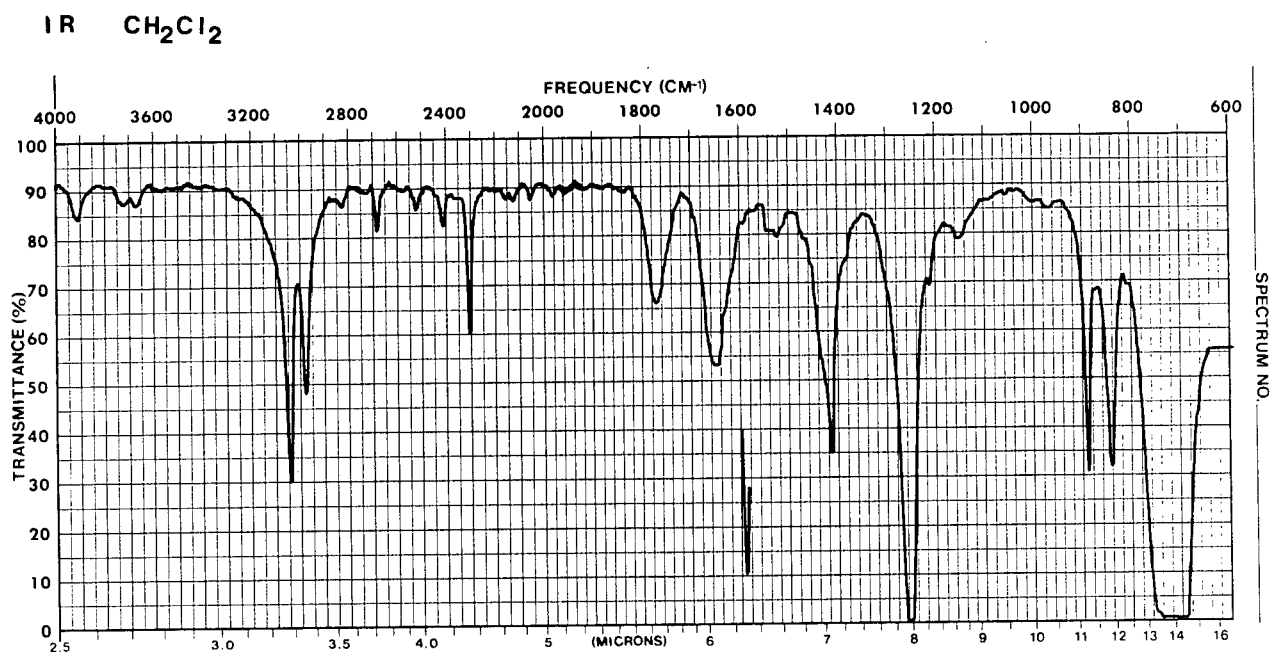


IR NUJOL MULL

¹H NMRMeNO₂



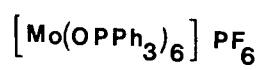
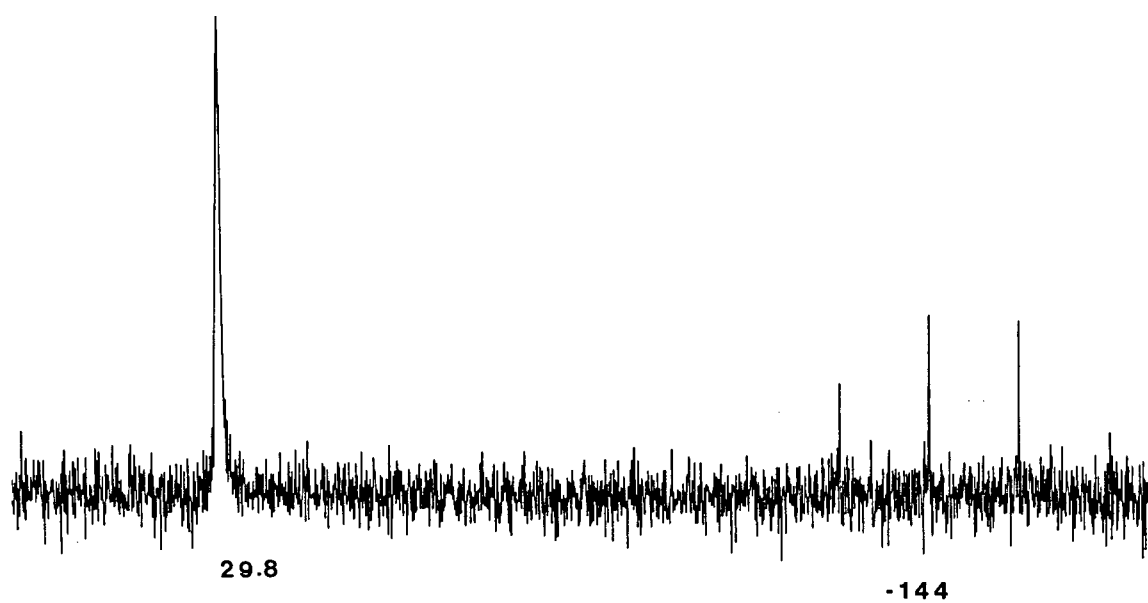
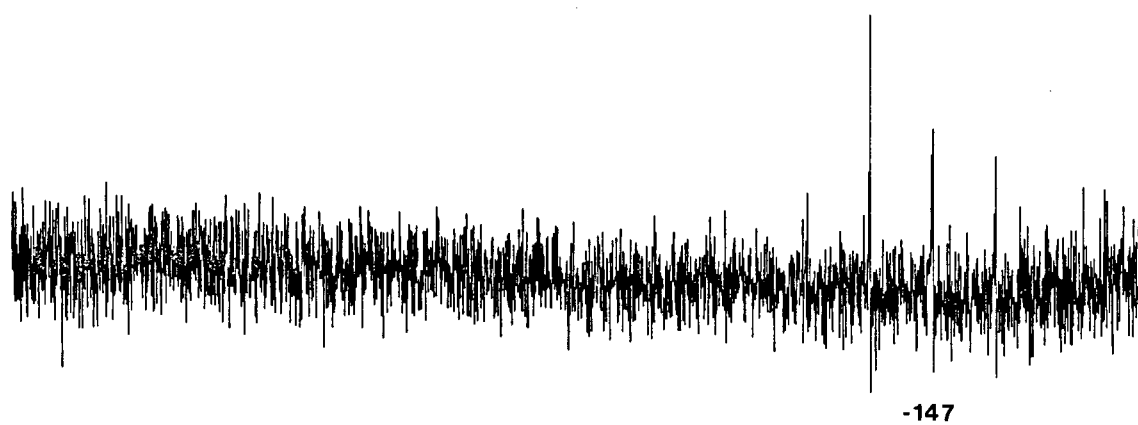
199



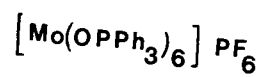


MeNO₂

200

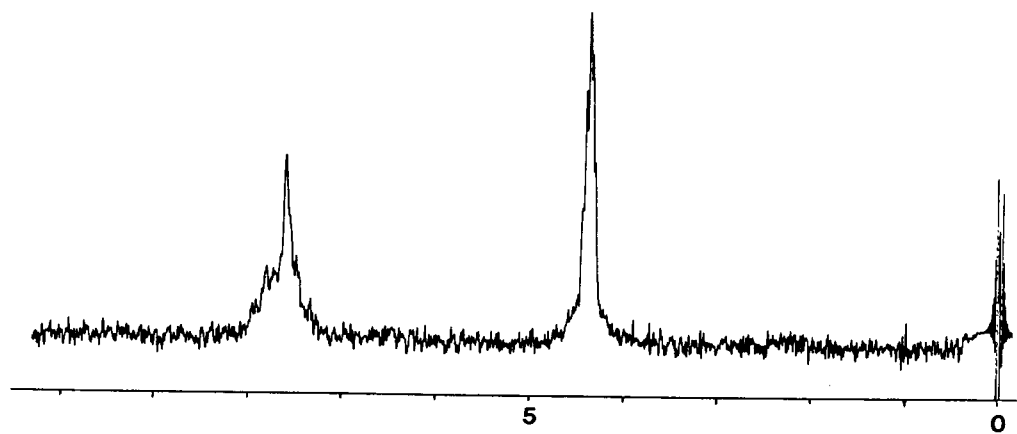
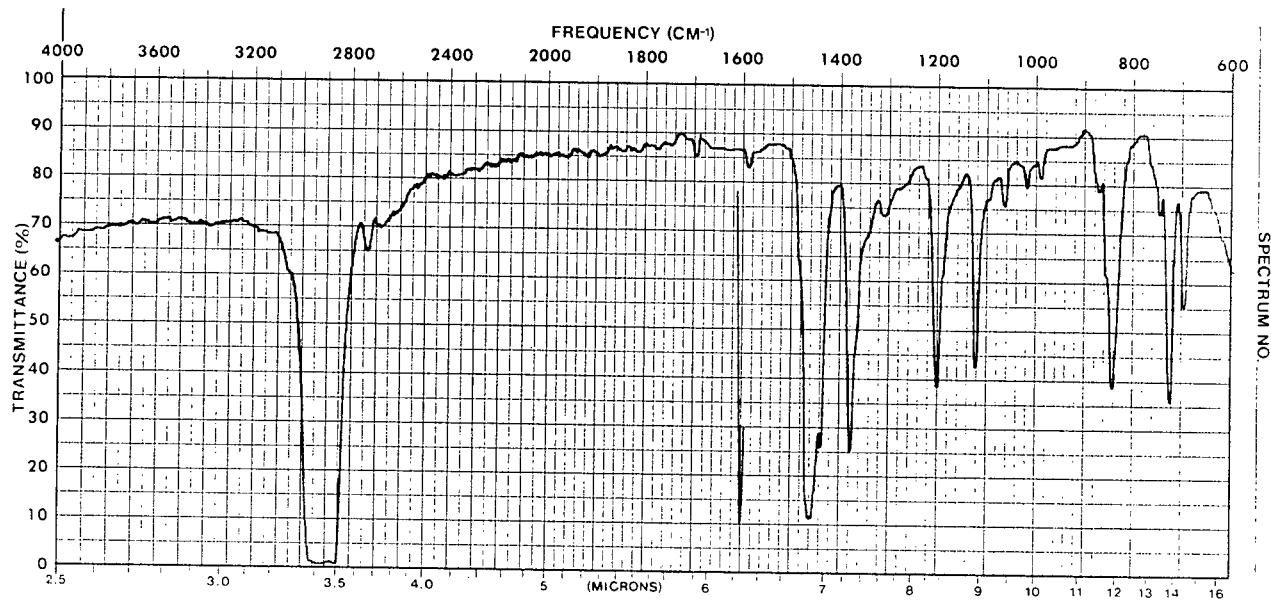


MeCN



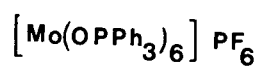
201

IR NUJOL MULL



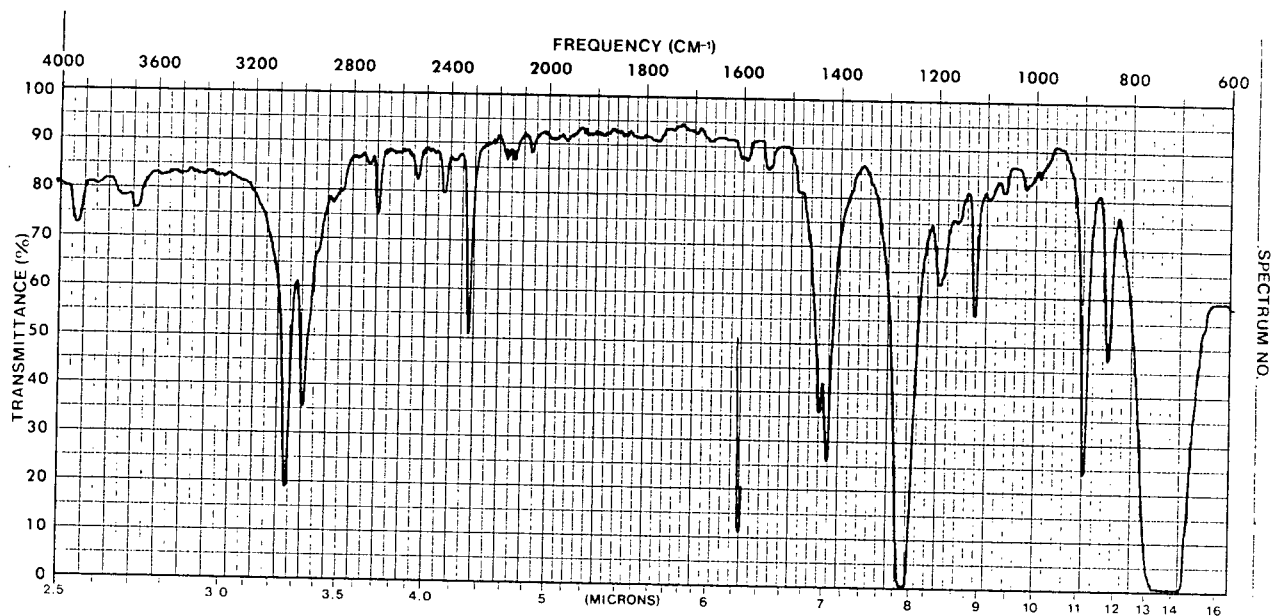
¹H NMR

MeNO₂



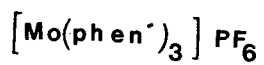
202

IR CH_2Cl_2



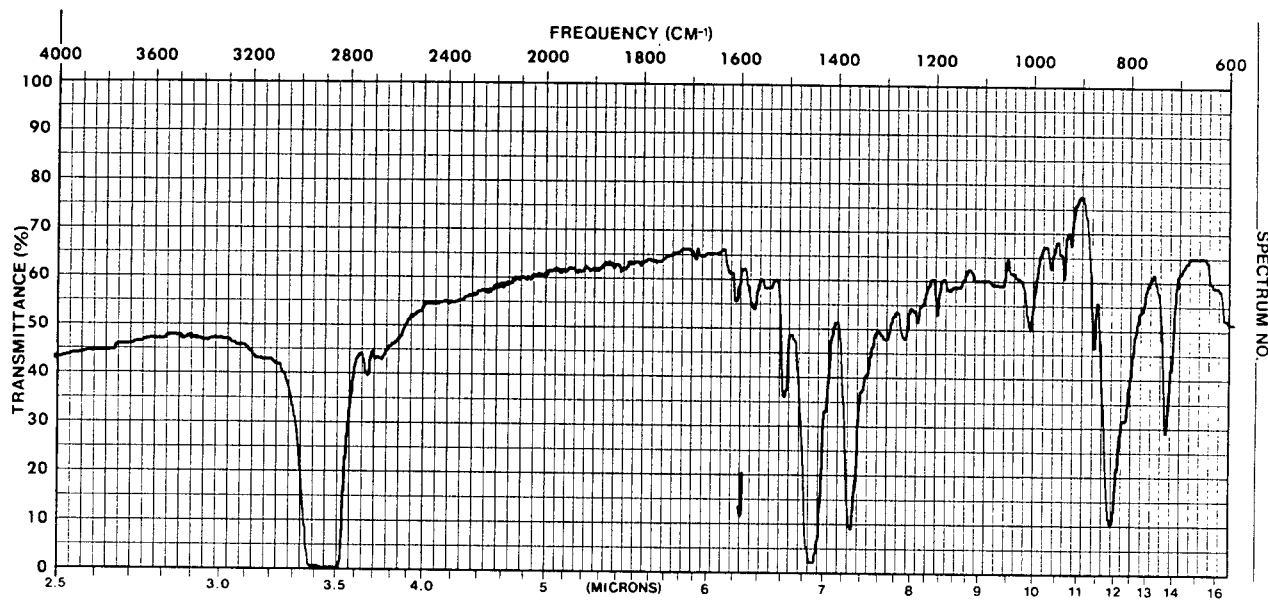
¹⁹F NMR

MeNO_2



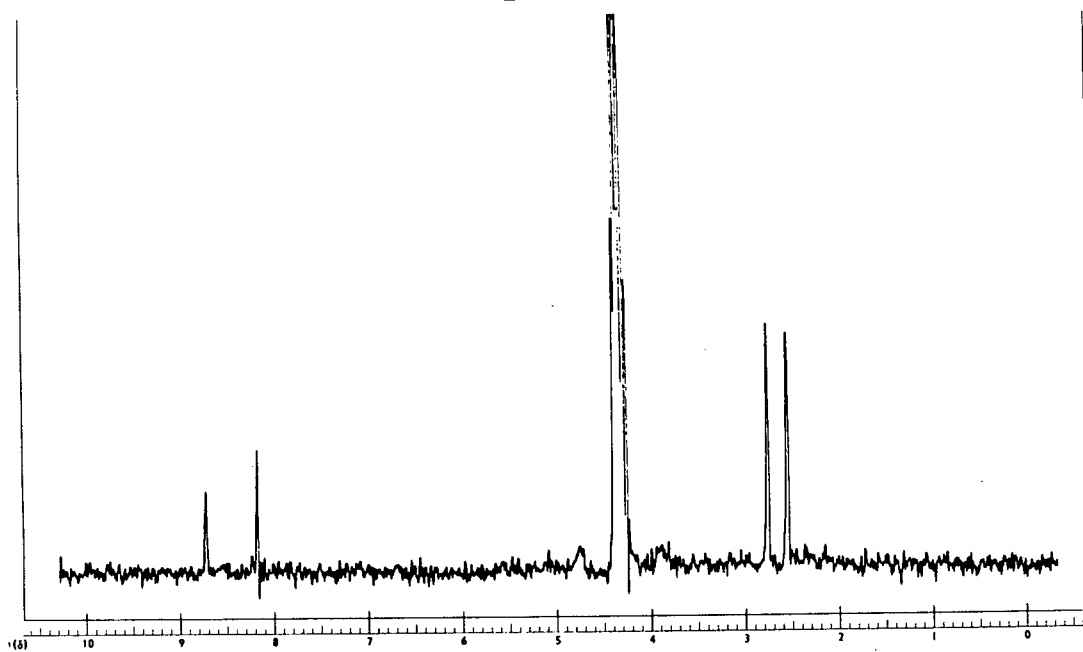
203

IR NUJOL MULL

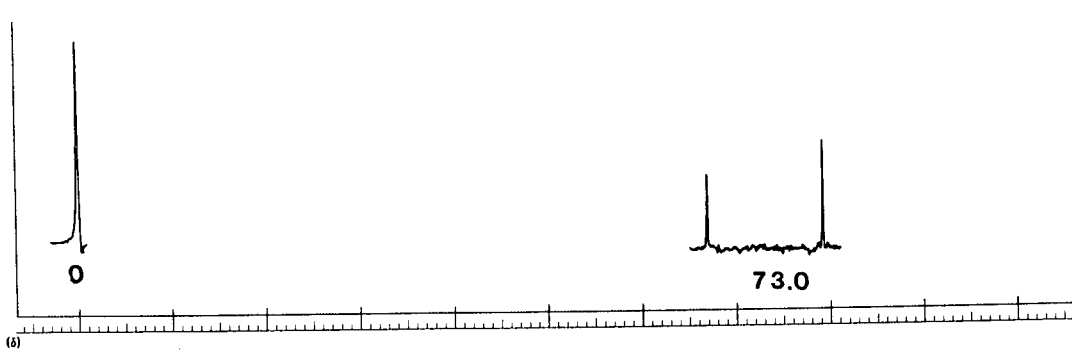


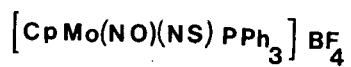
¹H NMR

MeNO₂



¹⁹F NMR





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