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Chemistry of Coordinated Dinitrogen. II.[1] Reactions of Bis(dinitrogen) Complexes of Molybdenum

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The reactions of $Mo(N_2)_2(dppe)_2$, $Mo(N_2)_2(arphos)_2$, $Mo(N_2)_2(PPh_2Me)_4$, and $Mo(N_2)_2(PMe_2Ph)_4$ (where dppe = $Ph_2PCH_2CH_2PPh_2$ and arphos = $Ph_2AsCH_2CH_2PPh_2$) with iodine and carbon monoxide are reported. Iodine oxidizes *trans*-$Mo(N_2)_2(dppe)_2$ and *trans*-$Mo(N_2)_2(arphos)_2$ to the molybdenum(I) complexes $[Mo(N_2)_2(dppe)_2]I_3$ and $[Mo(N_2)_2(arphos)_2]I_3$, which can be reduced with sodium amalgam to give the original dinitrogen complexes. Cyclic voltammetry studies support the reversibility of this oxidation reaction. Iodine decomposes *trans*-$Mo(N_2)_2(PPh_2CH_3)_4$ with loss of dinitrogen. Carbon monoxide reacts slowly at room temperature with *trans*-$Mo(N_2)_2(dppe)_2$ to give *cis*-$Mo(CO)_2(dppe)_2$. Infrared and phosphorus-31 nmr spectral data provide evidence for the formation of *trans*-$Mo(CO)_2(dppe)_2$ during this reaction which could not be isolated stereochemically pure. Carbon monoxide reacts analogously with *trans*-$Mo(N_2)_2(arphos)_2$. Carbon monoxide reacts rapidly with *trans*-$Mo(N_2)_2(PPh_2Me)_4$ to give *mer*-$Mo(CO)_3(PPh_2Mo)_3$ at −78° and *cis*-$Mo(CO)_4(PPh_2Me)_2$ at ambient temperature. Carbon monoxide reacts slowly with *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ at room temperature to give *fac*-$Mo(CO)_3(PMe_2Ph)_3$. The reduction of $MoCl_4(PPh_2Me)_2$ with sodium amalgam in the presence of excess PPh_2Me under carbon monoxide yields *mer*-$Mo(CO)_3(PPh_2Me)_3$.

Of all the stable, isolatable dinitrogen complexes of the transition metals, *trans*-$Mo(N_2)_2(dppe)_2$ and its tungsten analog have shown some of the most interesting chemistry. Typically, reactions of dinitrogen complexes result in the loss of dinitrogen.[2] However, Chatt, *et al.*,[3,4] have carried out reactions at the nitrogen-nitrogen multiple bond of coordinated dinitrogen in $Mo(N_2)_2(dppe)_2$ with the formation of both C–N and N–H bonds. Carbon monoxide has been reported[5,6] to react with *trans*-$Mo(N_2)_2(dppe)_2$ to form *cis*-$Mo(CO)_2(dppe)_2$. Dihydrogen and $CoH_3(PPh_3)_3$ have been reported[5] to react with $Mo(N_2)_2(dppe)_2$ to form *trans*-$MoH_2(dppe)_2$ in benzene and [*trans*-$MoH_2(dppe)]_2$-*μ*-(dppe) in toluene, respectively. However, more recent work[7] suggests that $MoH_4(dppe)_2$ is the sole product from the reaction of $Mo(N_2)_2(dppe)_2$ and dihydrogen. Trimethylaluminum forms a 1:1 adduct with $Mo(N_2)_2(dppe)_2$.[8] The most recent mention[9] of $Mo(N_2)_2(dppe)_2$ involves an iron-molybdenum model for nitrogenase whereby ammonia is formed upon treatment of a sodium naphthalide-$Mo(N_2)_2(dppe)_2$-$Fe_4S_4(S_2C_2Ph_2)_4$ mixture with aqueous HCl. The authors[9] suggest that $Mo(N_2)_2(dppe)_2$ is acting as the source of dinitrogen for the subsequent reduction.

In this paper, we describe the reaction of iodine[10] and carbon monoxide with a series of bis(dinitrogen) complexes of molybdenum. Cyclic voltammetry, magnetic susceptibility, infrared, and phosphorus-31 nmr data are used to help establish the structures of the reaction products.

Experimental Section

General Data. All reactions, work-up, and storage of products were carried out in an oxygen-free argon, carbon monoxide, or dinitrogen atmosphere using standard inert-atmosphere techniques. All reactions with the bis(dinitrogen) complexes and reduction reactions were carried out in a flat-bottomed Schlenk tube with a magnetic stirrer.

Reagents. All solvents were freshly distilled under an argon or dinitrogen atmosphere immediately before use. Tetrahydrofuran (THF) and diethyl ether were distilled from lithium aluminum hydride. Benzene, toluene, and diglyme were distilled from calcium hydride. Methanol was distilled from magnesium turnings. Acetonitrile, carbon tetrachloride, and dichloromethane were distilled from phosphorus(V) oxide. Dimethylformamide (DMF) was distilled from barium oxide.

The following compounds were prepared by published procedures: $Mo(N_2)_2(dppe)_2$,[1] $Mo(N_2)_2(arphos)_2$,[1] $Mo(N_2)_2(PPh_2Me)_4$,[1] $Mo(N_2)_2(PMe_2Ph)_4$,[1] $MoCl_4(PPh_2Me)_2$,[11] and $Mo(CO)_3(C_7H_8)$[12] (C_7H_8 = cycloheptatriene).

Chemicals were purchased from the following sources and used without further purification: molybdenum(V) chloride and molybdenum(0) hexacarbonyl (Alfa); $Ph_2PCH_2CH_2PPh_2$, PPh_2Me, and PMe_2Ph (ROC/RIC); $Ph_2AsCH_2CH_2PPh_2$ (Pressure Chemical Co.); carbon monoxide (Matheson Air Products).

Physical Measurements. Infrared spectra were run on a Perkin-Elmer Model 621 spectrophotometer. Solid samples were run as Nujol mulls or as pellets in CsBr or KBr. All solution spectra were run in deoxygenated reagent grade solvents and the samples were prepared and the cells filled and sealed in an inert atmosphere. Phosphorus-31 nmr spectra were run at 40.5 MHz on a Varian 620-I computer. The samples were 3% by weight solutions in 12-mm o.d. nmr tubes with benzene-d_6 as the solvent. All samples were prepared and sealed in an inert atmosphere. The chemical shift values (y (ppm), x (Hz)) with reference to 85% H_3PO_4 were calculated by reference to the value of $P(OCH_3)_3$ (−144 ppm, 95,626 Hz) in benzene-d_6 using the following conversion: $y(\text{ppm}) = \{[95{,}626 - x(\text{Hz})]/40.5\} - 144$. Molecular weights were measured on a Hewlett-Packard Model 302 B vapor pressure osmometer. The compounds were run at 26° in dichloromethane. Concentrations ranged from 10 to 50 m*M*.

Cyclic voltammograms were run using a Wenking potentiostat coupled to a Hewlett-Packard function generator and a Mossley Model 7030 AM X-Y recorder. The potentials were measured *vs.* a saturated calomel electrode. The dinitrogen-flushed solutions were about 10^{-3} *F* in DMF with 10^{-1} *F* tetraethylammonium perchlorate as supporting electrolyte. Additional cyclics were run at 10^{-3} *F* in THF with 10^{-1} *F* tetrabutylammonium perchlorate as electrolyte. Scans were run in the range of +0.45 to −0.65 V with a scan rate of 10.00 Hz. The cyclic voltammetry was run by Mr. Robert Hargens of this department. Coulometry was run at 0.00 V *vs.* a saturated calomel electrode on a platinum electrode. The DMF solution, 10^{-1} *F* in complex, contained 10^{-1} *F* tetraethylammonium perchlorate as electrolyte. The coulometry was performed by Mr. Terry Sprieck of this department.

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Magnetic susceptibility measurements were run using an Alpha Scientific Co. Gouy balance with a Model 7500 electromagnet and a 7500R series current regulator. $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ were used for calibration. The equipment was assembled by Mr. Harry Kellenbarger of this department. Melting points were determined in capillaries sealed under dinitrogen with a Mel-Temp apparatus.

Analyses were performed by Schwarzkopf Analytical Laboratories, Woodside, N. Y.

Reaction of $Mo(N_2)_2$(dppe)$_2$ with Iodine. Solid $Mo(N_2)_2$(dppe)$_2$ (0.96 g, 1.0 mmol) was added to 0.96 g (3.8 mmol) of iodine dissolved in methanol (60 ml). The mixture was stirred magnetically. The red precipitate that formed was filtered immediately and washed with methanol and then benzene. The fine red solid was dried *in vacuo* to give 1.3 g (91%) of product, mp 130° dec, $\mu_{eff} = 1.97$ BM (25°, uncorrected for diamagnetism). *Anal.* Calcd for $C_{52}H_{48}I_3MoN_4P_4$: C, 46.7; H, 3.64; N, 4.21; I, 28.6. Found: C, 47.3; H, 3.71; N, 3.41; I, 28.9.

Reaction of $Mo(N_2)_2$(arphos)$_2$ with Iodine. To a solution of 0.062 g (0.24 mmol) of iodine in methanol (30 ml) was added 0.11 g (0.11 mmol) of solid $Mo(N_2)_2$(arphos)$_2$. A red precipitate formed almost immediately. The precipitate was filtered immediately, washed with methanol and benzene, and then dried *in vacuo*. The product, mp 130-135 dec, was obtained in low yield. *Anal.* Calcd for $C_{52}H_{48}As_2I_3MoN_4P_2$: C, 44.0; H, 3.38; N, 3.94. Found: C, 45.1; H, 4.06; N, 2.32.

Reduction of $[Mo(N_2)_2(dppe)_2]I_3$. (1) A suspension of 0.55 g (0.41 mmol) of $[Mo(N_2)_2(dppe)_2]I_3$ in benzene (40 ml) was reduced with 25 g (11 mmol of Na) of 1% Na-Hg under dinitrogen. The mixture was stirred for 4 hr until the dark solid had disappeared and the solution became yellow-green. The solution was poured from the excess amalgam and filtered. The filtrate was concentrated under vacuum (0.1 mm) and then cold methanol (0°) was added to precipitate 0.16 g of $Mo(N_2)_2$(dppe)$_2$ (44%).

(2) The previous reaction was carried out under an argon atmosphere using benzene that had been thoroughly degassed with argon. After 4 hr, the yellow-green solution was worked up as described above. However, the yellow product contained no dinitrogen.

(3) Solid $[Mo(N_2)_2(dppe)_2]I_3$ (0.91 g, 0.69 mmol) was added slowly with stirring to 25 g (11 mmol Na) of 1% Na-Hg in THF (50 ml) under dinitrogen. An initial evolution of gas was observed. After 2 hr, the yellow-green solution was filtered and solvent removed under vacuum. The amorphous solid was crystallized from benzene-methanol. The yield of crystalline $Mo(N_2)_2$(dppe)$_2$ was 0.29 g (48%).

Reaction of $Mo(N_2)_2$(dppe)$_2$ with Carbon Monoxide. (1) Carbon monoxide was bubbled through a THF solution of $Mo(N_2)_2$(dppe)$_2$ (0.42 g, 0.44 mmol) for 9 hr. During this time the loss of $\nu(N{\equiv}N)$ was monitored by infrared spectroscopy and the appearance of $\nu(C{\equiv}O)$ bands at 1854, 1816, and 1786 cm^{-1} (CH_2Cl_2 solution) was noted. Solvent was removed and the yellow solid crystallized from benzene-methanol to give the known *cis*-$Mo(CO)_2$(dppe)$_2$.[13]

(2) Carbon monoxide was bubbled through a solution of 0.6 g (0.63 mmol) of $Mo(N_2)_2$(dppe)$_2$ in THF (40 ml) for 12 hr at ambient temperature. The solvent was removed while the solution was maintained at 0°. The solid was crystallized from chilled benzene-methanol (1:10). The orange-yellow product (0.3 g, 50%) was a mixture of *cis*- and *trans*-$Mo(CO)_2$(dppe)$_2$. *Anal.* Calcd for $C_{54}H_{48}MoO_2P_4$: C, 68.4; H, 5.10. Found: C, 68.3; H, 5.17. Attempts to prepare the stereochemically pure trans isomer by carrying out the reaction at 0° produced only the cis isomer together with a significant amount of decomposition.

Reaction of $Mo(CO)_2$(dppe)$_2$ with Dinitrogen. Dinitrogen was bubbled through a THF solution containing *ca.* 0.1 g of *cis*-$Mo(CO)_2$(dppe)$_2$ for 12 hr. Removal of solvent recovered unreacted starting material. No decomposition had occurred.

Reaction of $Mo(N_2)_2$(arphos)$_2$ with Carbon Monoxide. Carbon monoxide was bubbled through a solution of 0.50 g (0.48 mmol) of $Mo(N_2)_2$(arphos)$_2$ in THF (30 ml). The infrared spectrum was recorded at 4, 9, and 21 hr, respectively, at which time the reaction was judged to be complete. After 9 hr, $\nu(C{\equiv}O)$ bands at 1848, 1812, and 1778 cm^{-1} (CH_2Cl_2 solution) were noted. The solvent was removed and the solid crystallized from benzene-methanol to give a yellow product (*ca.* 60%), mp 210° dec. *Anal.* Calcd for $C_{54}H_{46}As_2MoO_2P_2$: C, 62.5; H, 4.64; mol wt 1036. Found: C, 61.5; H, 5.23; mol wt 1053.

Reaction of $Mo(N_2)_2(PPh_2Me)_4$ with Carbon Monoxide. Carbon monoxide was bubbled for 30 min through a solution of 0.10 g (0.1 mmol) of $Mo(N_2)_2(PPh_2Me)_4$ dissolved in THF (30 ml) that had been precooled to *ca.* −78°. Solvent was removed leaving an oil that resisted attempts to crystallize at room temperature. An infrared spectrum (CH_2Cl_2 solution) of the oil showed the following bands attributable to $\nu(C{\equiv}O)$: 1957, 1940, and 1851 cm^{-1}. Further work (see below) suggested that this oil was impure *mer*-$Mo(CO)_3(PPh_2Me)_3$ contaminated with displaced phosphine. About half of the oil was dissolved in THF and bubbled with carbon monoxide for 1 hr. A colorless oil was recovered after removal of solvent that could not be crystallized in our hands. The infrared spectrum (hexane solution) showed $\nu(C{\equiv}O)$ bands at 2032, 1950, 1903, and 1850 cm^{-1}, suggesting an impure mixture of *cis*-$Mo(CO)_4(PPh_2Me)_2$ (see below) and *mer*-$Mo(CO)_3(PPh_2Me)_3$.

Preparation of *mer*-$Mo(CO)_3(PPh_2Me)_3$. Under an atmosphere of carbon monoxide, a mixture of 1.88 g (2.95 mmol) of $MoCl_4(PPh_2Me)_2$ and 2.6 g (11.8 mmol) of PPh_2Me in THF (50 ml) was reduced with 50 g (22 mmol of Na) of 1% Na-Hg. The mixture was stirred for 4 hr. The yellow-green solution was poured from the mercury and filtered to give a yellow-orange solution. Solvent was removed to give an oil which was dissolved in benzene (3 ml). Addition of methanol (50 ml) and chilling (0°) precipitated fine yellow crystals. The crystals were filtered, washed with methanol, and dried *in vacuo* to give 1.11 g (48%) of pure *mer*-$Mo(CO)_3(PPh_2Me)_3$, mp 159-163°. *Anal.* Calcd for $C_{42}H_{39}MoO_3P_3$: C, 64.6; H, 5.00; mol wt 780. Found: C, 64.0; H, 5.04; mol wt 794.

Preparation of *fac*-$Mo(CO)_3(PPh_2Me)_3$. A benzene solution (25 ml) of $Mo(CO)_3(C_7H_8)$ (0.5 g, 1.82 mmol) and PPh_2Me (1.5 g, 6.83 mmol) was refluxed for 1 hr. After an initial filtration through a medium frit, the dark suspension was mixed with *ca.* 0.5 g of alumina and filtered again to give a clear yellow solution. The solution was concentrated by removing benzene under vacuum. Methanol (50 ml) was added and the solution chilled (0°) to give a white precipitate. The solid was filtered, washed with methanol, and dried *in vacuo* to give 0.83 g (59%) of white crystalline *fac*-$Mo(CO)_3(PPh_2Me)_3$, mp 110-111°. *Anal.* Calcd for $C_{42}H_{39}MoO_3P_3$: C, 62.6; H, 5.00. Found: C, 62.9; H, 5.05.

Preparation of *cis*-$Mo(CO)_4(PPh_2Me)_2$. A solution of $Mo(CO)_6$ (0.55 g, 2.16 mmol) and PPh_2Me (0.50 g, 3.6 mmol) in diglyme (40 ml) was refluxed for 4 hr. After cooling, the yellow suspension was filtered through a 1-in. layer of alumina. The filtrate was evaporated to dryness under vacuum yielding a yellow oil. The oil was dissolved in dichloromethane (*ca.* 1 ml) and methanol (20 ml) added. The solution was concentrated on a rotary evaporator (water aspiration) until crystals formed. The light yellow crystals were filtered off, washed with methanol, and dried *in vacuo* to give 0.59 g (56%) of pure *cis*-$Mo(CO)_4(PPh_2Me)_2$, mp 171-173°. *Anal.* Calcd for $C_{30}H_{26}MoO_4P_2$: C, 59.1; H, 4.28; mol wt 650. Found: C, 58.7; H, 4.38; mol wt 660.

Reaction of *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ with Carbon Monoxide. Carbon monoxide was bubbled for 30 min through a solution of *ca.* 0.1 g of $Mo(N_2)_2(PMe_2Ph)_4$ in THF precooled to −78°. A solution infrared spectrum indicated that no reaction had occurred after this time. The reaction was continued at room temperature for 1 hr. Solvent was removed to give a colorless oil. An infrared spectrum (CH_2Cl_2 solution) showed bands in the $\nu(C{\equiv}O)$ region at 1936, 1834, and 1824 cm^{-1}. This agrees very well with the reported infrared spectrum ($CHCl_3$ solution) of *fac*-$Mo(CO)_3(PMe_2Ph)_3$[14] (1936, 1832, and 1824 cm^{-1}). The reaction with carbon monoxide was continued for a further 24 hr. The infrared spectrum showed no change in the carbonyl stretching region.

Results and Discussion

Solid *trans*-$Mo(N_2)_2$(dppe)$_2$ reacted with a methanol solution of iodine under an atmosphere of dinitrogen to produce a red precipitate I that was shown to be $[trans\text{-}Mo(N_2)_2(dppe)_2]^+,I_3^-$. Compound I was produced rapidly and was filtered off immediately and washed with methanol and then benzene. In the solid state, I is stable in dry air. However, in solvents such as acetone, dichloromethane, and THF I decomposes rapidly with the loss of dinitrogen. Compound I is stable for short periods of time in DMF (*ca.* 10^{-3} *F*) that had been thoroughly flushed with dinitrogen. The high dielectric constant of DMF may be stabilizing the ions and slowing down the decomposition and/or further oxidation of $[Mo(N_2)_2(dppe)_2]^+$. Attempts to exchange the triiodide

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ion with the perchlorate ion were unsuccessful. The formation of I is very dependent upon the reaction conditions. When the reaction time was extended, extensive decomposition occurred. A homogeneous reaction with iodine in benzene produced no dinitrogen-containing species.

The infrared spectrum (Table I) of I shows a strong absorption at 2047 cm^{-1} (Nujol) due to the A_{2u} N≡N stretching vibration. An increase in the value of A_{2u} N≡N (from 1976 cm^{-1} for $Mo(N_2)_2(dppe)_2$ to 2047 cm^{-1} for I) is to be expected upon going from a d^6 (Mo^0) to a d^5 (Mo^+) system. These data support the belief that a formal oxidation has occurred. This is further substantiated by the magnetic susceptibility measurements. Compound I gave a spin-only value of μ_{eff} at 25° of 1.97 BM. The value is comparable to the 1.66-BM value reported for the isoelectronic $[Mo(CO)_2(dppe)_2]I_3$[15] and indicates a spin of $^1/_2$ expected for d^5 Mo^+.

The cyclic voltammogram of *trans*-$Mo(N_2)_2(dppe)_2$ is shown in Figure 1. The voltammogram was run in 10^{-3} *F* DMF solution at a platinum electrode with tetraethylammonium perchlorate (10^{-1} *F*) as the supporting electrolyte. In a scan from +0.43 to −0.65 V, $Mo(N_2)_2(dppe)_2$ showed a curve characteristic of a reversible oxidation. On the forward scan the complex gave an anodic peak at −0.20 V, and on the reverse scan a cathodic peak at −0.27 V. There was a slight shoulder on the anodic peak in the region of −0.05 V which seemed to be independent of scan speed and number of scans. On a wider scan, −1.3 to +0.9 V, a more complicated curve was observed. On the forward scan the peak at −0.20 V was still present but at +0.71 V a nonreversible peak of much greater intensity appeared. Cyclic voltammetry in THF solution gave no reproducible results. Controlled-potential coulometry measurements, to determine the number of electrons involved in the oxidation step, were unsuccessful as a result of extensive decomposition occurring in solution during the time of the experiment. Similarly, conductivity measurements were unsuccessful.

The cyclic voltammetry data support the ability of $Mo(N_2)_2(dppe)_2$ to undergo a reversible oxidation and in conjunction with the magnetic susceptibility data strongly support the one-electron oxidation of *trans*-$Mo(N_2)_2(dppe)_2$ to [*trans*-$Mo(N_2)_2(dppe)_2]I_3$. The cyclic voltammetry data almost certainly rule out the alternative structure proposed[10] for I, namely, $[\mu\text{-}N_2\text{-}[Mo(N_2)_2(dppe)_2]_2]^{2+}, 2I_3^-$. The formation of the latter species would require the loss of one dinitrogen ligand from every other molecule of complex with subsequent association. This reaction is unlikely to be a reversible oxidation under the conditions of the cyclic voltammetry studies.

The reduction of I with sodium amalgam in benzene or THF under dinitrogen produced $Mo(N_2)_2(dppe)_2$ in 40 and 45% yields, respectively. However, under an argon atmosphere, no dinitrogen-containing product was isolated.

Chlorine and bromine reacted with $Mo(N_2)_2(dppe)_2$ with loss of dinitrogen. At −78°, bromine in methanol reacted with $Mo(N_2)_2(dppe)_2$ to produce an impure dark red material that had a band at 2047 cm^{-1} in the infrared spectrum which suggests the presence of the $[Mo(N_2)_2(dppe)_2]^+$ ion. Previously,[15] metal ions have been shown to oxidize some dinitrogen-containing species. However, Ag(I) and Cu(II) reacted with $Mo(N_2)_2(dppe)_2$ with the loss of dinitrogen.

Iodine reacts analogously with *trans*-$Mo(N_2)_2(arphos)_2$ to form purple [*trans*-$Mo(N_2)_2(arphos)_2]I_3$ that shows a strong absorption in the infrared spectrum at 2043 cm^{-1} (Nujol) due to the ν(N≡N) stretching vibration. The cyclic voltammogram of $Mo(N_2)_2(arphos)_2$ (Figure 2) shows a curve characteristic of a one-step reversible oxidation. On the forward scan there was a peak at −0.19 V and on the reverse scan a peak at −0.26 V. These values are similar to those observed for $Mo(N_2)_2(dppe)_2$.

Table I. Selected Infrared Data for New Compounds of Molybdenum

Compd	$\nu_{N\equiv N}$, cm^{-1}	$\nu_{C\equiv O}$, cm^{-1}
$[Mo(N_2)_2(dppe)_2]I_3$	2047s[a]	
$[Mo(N_2)_2(arphos)_2]I_3$	2043s[a]	
$Mo(CO)_2(arphos)_2$[b]		1851 s, 1779 s[c]
fac-$Mo(CO)_3(PPh_2Me)_3$		1941 s, 1835 s[c]
mer-$Mo(CO)_3(PPh_2Me)_3$		1960 w, 1940 w, 1845 vs[d]
$Mo(CO)_4(PPh_2Me)_2$[b]		2028 m, 1931 m, 1906 vs[d]

[a] Nujol mull. [b] Cis isomer. [c] CH_2Cl_2 solution. [d] Hexane solution.

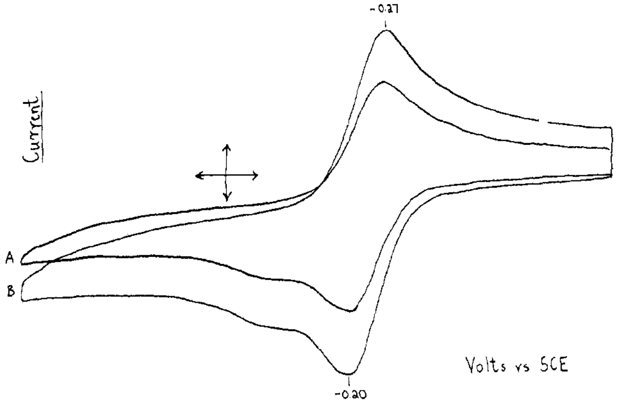

Figure 1. Cyclic voltammogram of *trans*-$Mo(N_2)_2(dppe)_2$ in DMF (10^{-3} *F*) at a Pt electrode with tetraethylammonium perchlorate (10^{-1} *F*) as supporting electrolyte; scan rates of 5.0 Hz (curve A) and 10.0 Hz (curve B).

Iodine reacted with *trans*-$Mo(N_2)_2(PPh_2Me)_4$ but all dinitrogen was lost. The cyclic voltammogram (Figure 3) in the range −0.8 to +0.2 V was quite complicated. On the forward scan there were anodic peaks at −0.48 and −0.16 V and an extremely intense peak at +0.5 V. On the reverse scan only a weak cathodic peak was seen at −0.58 V. The complexity of these data may in part be due to dissociation of the phosphine ligands in solution that was observed[1] in the ^{31}P nmr spectrum of *trans*-$Mo(N_2)_2(PPh_2Me)_4$. *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ decomposes in DMF and therefore no scan was run.

Hidai, *et al.*,[5] have reported that the reaction of *trans*-$Mo(N_2)_2(dppe)_2$ with carbon monoxide in toluene produced *cis*-$Mo(CO)_2(dppe)_2$ over a 4-day period at ambient temperature. Darensbourg[6] carried out the same reaction photochemically, for 15 min, and isolated *cis*-$Mo(CO)_2(dppe)_2$ as well as an unidentified product. We bubbled carbon monoxide through a THF solution of *trans*-$Mo(N_2)_2(dppe)_2$ at ambient temperature and monitored the extent of reaction by observing the loss of ν(N≡N) in the infrared spectrum. The reaction was observed to be complete after 9 hr and the pale yellow product was characterized as *cis*-$Mo(CO)_2(dppe)_2$.[13] However, during the reaction three bands were observed in the carbonyl region: 1853 and 1785 cm^{-1} (due to *cis*-$Mo(CO)_2(dppe)_2$) and 1820 cm^{-1}. The reaction was repeated both in THF (9 hr) and in benzene (9 hr) and the solvent-removal and crystallization steps were carried out below room temperature. The orange product exhibited three bands of particular interest in the infrared spectrum: 1853, 1816, and 1785 cm^{-1}. When

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[15] J. Chatt, J. R. Dilworth, H. P. Gunz, G. J. Height, and J. R. Sanders, *Chem. Commun.*, 90 (1970).

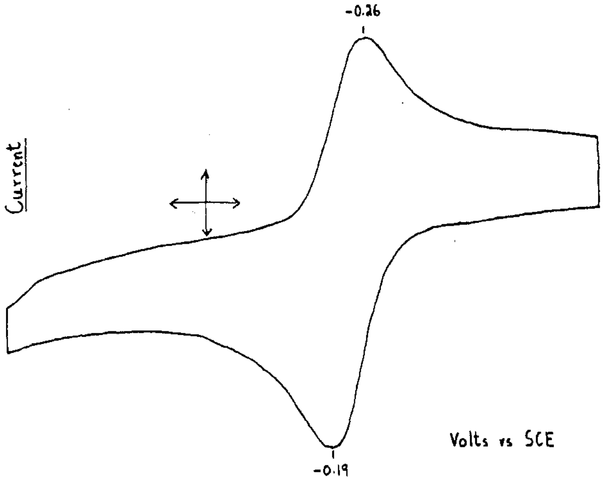

Figure 2. Cyclic voltammogram of *trans*-$Mo(N_2)_2(arphos)_2$ in DMF (10^{-3} *F*) at a Pt electrode with tetraethylammonium perchlorate (10^{-1} *F*) as supporting electrolyte; scan rate of 10.0 Hz.

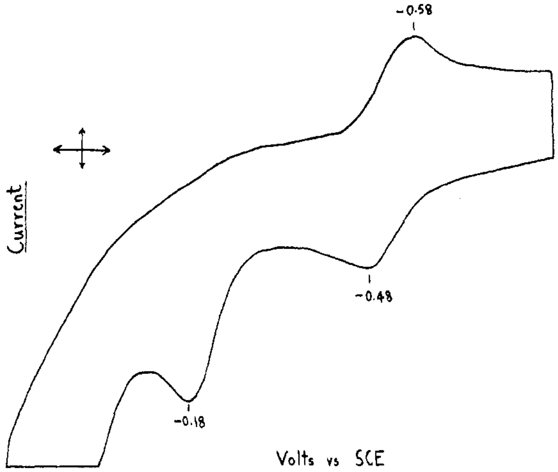

Figure 3. Cyclic voltammogram of *trans*-$Mo(N_2)_2(PPh_2Me)_4$ in DMF (10^{-3} *F*) at a Pt electrode with tetraethylammonium perchlorate (10^{-1} *F*) as supporting electrolyte; scan rate of 10.0 Hz.

the orange solid was heated at reflux in dichloromethane, pale yellow *cis*-$Mo(CO)_2(dppe)_2$ was isolated quantitatively.

The ^{31}P nmr spectrum of the orange solid was studied in C_6D_6 solution over the temperature range 6-40° with all protons decoupled. At 6° a multiplet was observed at −50.9 ppm and a singlet at −71 ppm. The multiplet is due to *cis*-$Mo(CO)_2(dppe)_2$ which was confirmed by running an authentic sample of *cis*-$Mo(CO)_2(dppe)_2$. The singlet is assigned to the four equivalent phosphorus nuclei of *trans*-$Mo(CO)_2(dppe)_2$. By comparison, *trans*-$Mo(N_2)_2(dppe)_2$ exhibits a singlet in the proton-decoupled ^{31}P nmr spectrum at −69 ppm. As the temperature was increased, the relative intensity of the singlet decreased while that of the multiplet increased. After the sample was held at 40° for 2 hr, the pale yellow cis isomer began to crystallize out in the nmr tube. An infrared spectrum of the sample from the nmr tube showed two carbonyl stretching bands at 1853 and 1785 cm^{-1} characteristic of the cis isomer.

Attempts to prepare a pure sample of the trans isomer by bubbling carbon monoxide through a THF solution of *trans*-$Mo(N_2)_2(dppe)_2$ at 0° were unsuccessful. A significant amount of decomposition occurred during the reaction and only *cis*-$Mo(CO)_2(dppe)_2$ was identified.

Clearly, *trans*-$Mo(N_2)_2(dppe)_2$ is losing dinitrogen and reacting to form *trans*-$Mo(CO)_2(dppe)_2$ which isomerizes in solution to *cis*-$Mo(CO)_2(dppe)_2$. It is uncertain whether or not *cis*-$Mo(CO)_2(dppe)_2$ is also formed directly as a result of the isomerization of possible intermediates such as $Mo(N_2)(dppe)_2$ and $Mo(dppe)_2$ prior to the incorporation of carbon monoxide. During the monitoring of the reactions by infrared spectroscopy, no evidence was found for mixed carbon monoxide-dinitrogen complexes such as $Mo(CO)(N_2)(dppe)_2$.

The cyclic voltammogram of *cis*-$Mo(CO)_2(dppe)_2$ in the region from +0.43 to −0.65 V is shown in Figure 4. On the forward scan two anodic peaks were seen at −0.16 and +0.17 V, while on the reverse scan only one cathodic peak at −0.24 V was observed. The peak at −0.16 V represents the oxidation of *trans*-$Mo(CO)_2(dppe)_2$ to [*cis*-$Mo(CO)_2(dppe)_2]^+$ and/or [*trans*-$Mo(CO)_2(dppe)_2]^+$. The peak at −0.24 V is due to the reduction of [*trans*-$Mo(CO)_2(dppe)_2]^+$ to *cis*- and/or *trans*-$Mo(CO)_2(dppe)_2$. The similarity of these two electrode potentials with those for the reversible oxidation of *trans*-$Mo(N_2)_2(dppe)_2$ suggests that they are indeed due to the reversible oxidation of the trans isomer of $Mo(CO)_2(dppe)_2$. The oxidation of *cis*-$Mo(CO)_2(dppe)_2$ is believed to occur at +0.17 V. The absence of a cathodic peak corresponding to *ca.* +0.17 V implies that either during or subsequent to the oxidation of *cis*-$Mo(CO)_2(dppe)_2$ isomerization to [*trans*-$Mo(CO)_2(dppe)_2]^+$ occurs. The cis and trans isomers of $[Mo(CO)_2(dppe)_2]^+$ have been isolated[16] by the oxidation of *cis*-$Mo(CO)_2(dppe)_2$ with $NOPF_6$. However, the particular isomer formed was very dependent upon the reaction solvent.

Only *cis*-$Mo(CO)_2(arphos)_2$ was isolated from the reaction of carbon monoxide with *trans*-$Mo(N_2)_2(arphos)_2$ in THF. The reaction was monitored by following the loss of $\nu(N\equiv N)$ in the infrared spectrum. The reaction was observed to be complete after 21 hr. Although the infrared spectrum during the reaction showed three bands in the carbonyl region (1848, 1812, and 1778 cm^{-1} after 9 hr), after 21 hr only two bands were present in the carbonyl region of the product (1851 and 1779 cm^{-1}). Evidently, the apparent longer reaction time allowed complete isomerization to occur under these reaction conditions.

The reaction of carbon monoxide with *trans*-$Mo(N_2)_2(PPh_2Me)_4$ and *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ caused the loss of dinitrogen and one or more of the phosphine ligands, the presence of which prevented analytically pure samples of the products from being isolated. At −78°, carbon monoxide reacts with a THF solution of *trans*-$Mo(N_2)_2(PPh_2Me)_4$ to produce an oil. An infrared spectrum of the oil (hexane solution) showed three bands in the infrared spectrum attributable to $\nu(CO)$ at 1957 (w), 1940 (w), and 1851 (s) cm^{-1}. The infrared spectrum suggested the presence of *mer*-$Mo(CO)_3(PPh_2Me)_3$. In order to confirm this the previously unknown *mer*- and *fac*-$Mo(CO)_3(PPh_2Me)_3$ were prepared. The reduction of $MoCl_4(PPh_2Me)_2$ with sodium amalgam in THF in the presence of excess PPh_2Me, under an atmosphere of carbon monoxide, gave pure yellow *mer*-$Mo(CO)_3(PPh_2Me)_3$: $\nu(CO)$ 1960 (w), 1940 (w), and 1845 (vs) cm^{-1} (CH_2Cl_2 solution). The reaction of $Mo(CO)_3(C_7H_8)$ with 3 equiv of PPh_2Me yielded pure white *fac*-$Mo(CO)_3(PPh_2Me)_3$: $\nu(CO)$ 1941 (s) and 1835 (s) cm^{-1} (CH_2Cl_2 solution). The infrared data support the presence of *mer*-$Mo(CO)_3(PPh_2Me)_3$ in the oil formed in the carbon monoxide reaction at −78° reported above.

At ambient temperature, carbon monoxide reacts with a

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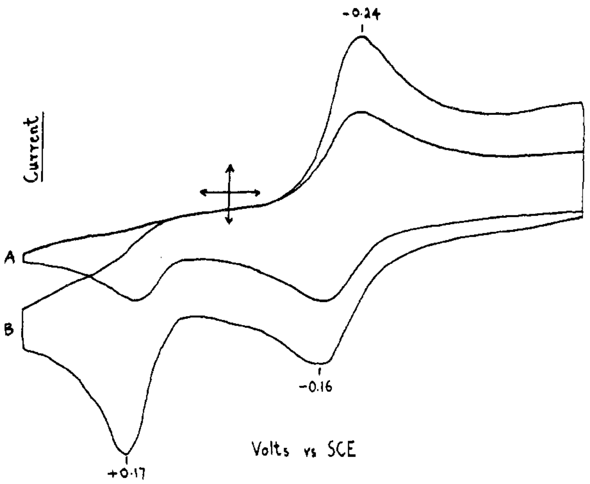

Figure 4. Cyclic voltammogram of $Mo(CO)_2(dppe)_2$ in DMF (10^{-3} *F*) at a Pt electrode with tetraethylammonium perchlorate (10^{-1} *F*) as supporting electrolyte; scan rates of 5.0 Hz (curve A) and 20.0 Hz (curve B).

THF solution of *trans*-$Mo(N_2)_2(PPh_2Me)_4$ (30 min) to produce an oil which could not be crystallized. The infrared spectrum showed four bands in the carbonyl region at 2032 (m), 1950 (s), 1903 (vs), and 1850 (m) cm^{-1} (hexane solution). In order to gain an insight into the nature of the carbonyl-containing species in the oil the previously unknown *cis*-$Mo(CO)_4(PPh_2Me)_2$ was prepared from $Mo(CO)_6$ and PPh_2Me. The infrared spectrum in hexane solution exhibited bands due to $\nu(CO)$ at 2028 (m), 1931 (m), and 1906 (vs) cm^{-1}. A mixture of *cis*-$Mo(CO)_4(PPh_2Me)_2$ and *mer*-$Mo(CO)_3(PPh_3Me)_3$ appears to constitute the carbonyl-containing part of the oil formed at ambient temperature. In a separate experiment carbon monoxide was bubbled through a THF solution of a pure sample of *mer*-$Mo(CO)_3(PPh_2Me)_3$ for 1 hr. The product was identified as *cis*-$Mo(CO)_4(PPh_2Me)_2$, by infrared spectroscopy.

Carbon monoxide did not react with *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ at −78° in THF. However, at ambient temperature *fac*-$Mo(CO)_3(PMe_2Ph)_3$ was formed slowly after several hours. This isomer was identified by infrared spectroscopy.[14] No evidence for further substitution was observed when the reaction was allowed to continue for 24 hr at ambient temperature.

In no case did dinitrogen appear to react with the carbonyl complexes of molybdenum.

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Registry No. $[Mo(N_2)_2(dppe)_2]I_3$, 38887-40-0; $[Mo(N_2)_2(arphos)_2]I_3$, 41375-70-6; *cis*-$Mo(CO)_2(arphos)_2$, 41367-49-1; *fac*-$Mo(CO)_3(PPh_2Me)_3$, 41367-50-4; *mer*-$Mo(CO)_3(PPh_2Me)_3$, 41367-51-5; *cis*-$Mo(CO)_4(PPh_2Me)_2$, 37438-49-6; $Mo(N_2)_2(dppe)_2$, 25145-64-6; $Mo(N_2)_2(arphos)_2$, 37138-36-6; *cis*-$Mo(CO)_2(dppe)_2$, 17523-42-1; $Mo(N_2)_2(PPh_2Me)_4$, 33248-03-2; $MoCl_4(PPh_2Me)_2$, 30411-57-5; phosphorus-31; 7723-14-0; iodine, 7553-56-2.

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Electron Spin Resonance Study of Coordination of Lewis Bases to Vanadyl Dithiophosphinate Complexes

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The results of an esr study of the five-coordinate vanadyl complexes, bis(dimethyldithiophosphinato)oxovanadium(IV), bis(diphenyldithiophosphinato)oxovanadium(IV), and bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV), in the noncoordinating solvents toluene and CS_2 are presented. The esr spectra correspond to the interaction of the unpaired electron with the ^{51}V nucleus and two equivalent ^{31}P nuclei. Addition of 1–5% by volume of the strongly coordinating ligands pyridine, dimethylformamide, or hexamethylphosphoramide results in esr spectra indicative of hyperfine interactions with the ^{51}V nucleus and a single ^{31}P nucleus. It is shown that, in this vanadyl species, the added ligand coordinates at an equatorial site, resulting in a five-coordinate species in which one of the dithiophosphinate groups is monodentate and a six-coordinate species in which one of the chelating dithiophosphinates is rearranged so that one sulfur atom occupies an equatorial position and the other the axial position. The equilibrium constants and heats of adduct formation for the equatorial ligand addition were determined from the esr spectra. At higher ligand concentrations, the esr spectra show no ^{31}P hyperfine interactions which indicate that both chelating dithiophosphinate groups become monodentate. Infrared and conductivity measurements indicated that the vanadyl dithiophosphinate dissociates completely in solutions with still higher ligand concentrations but that several vanadyl species containing one or two dithiophosphinate moieties coordinated to the vanadium atom are present in these solutions.

Introduction

Four- and five-coordinate compounds of vanadium(IV) are known to undergo substitution at vacant coordination sites.[1-5] The formation of adducts of vanadyl complexes with many Lewis bases in dilute solutions in noncoordinating solvents has been studied by electronic,[5-10] vibrational,[11-13] and

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