

THF solution was made by reduction of IIa with 3% sodium amalgam. This reaction yielded only a clear solution that showed no $\nu(\text{NO})$ absorptions. Both the first and the second reduction potentials become more negative with changes in L in the order $\text{P}(\text{OPh})_3 > \text{P}(\text{OMe})_3 > \text{PPh}_3$. This is also the order of decreasing π -acceptor: σ -donor ratios for these ligands, which is consistent with the most strongly electron-withdrawing phosphorus ligands giving the most easily reduced species.

Reactions of $\text{CpW}(\text{NO})_2(\text{P}(\text{OPh})_3)$. The $\text{CpW}(\text{NO})_2(\text{P}(\text{OPh})_3)$ complex (IIa) is easily oxidized to the cation $\text{CpW}(\text{NO})_2(\text{P}(\text{OPh})_3)^+$ (Ia) by a variety of oxidizing agents (Scheme I). The purple CH_2Cl_2 solution of IIa becomes the characteristic green of Ia within 1 min upon treatment with AgBF_4 . Oxidation of IIa by $\text{Ph}_3\text{C}^+\text{BF}_4^-$ occurs immediately; the organic product, $\text{Ph}_3\text{COOCPh}_3$, is isolated in 13% yield, presumably formed from $\text{Ph}_3\text{C}^\cdot$ during workup of the reaction mixture in air.¹³

The reaction of IIa with $\text{CH}_3\text{OSO}_2\text{F}$ is complete within 1 min and yields Ia and the reduction product ethane, which was detected by gas chromatography. An immediate reaction occurs between IIa and $\text{CF}_3\text{SO}_3\text{H}$ to give 75% Ia; the other product is presumably H_2 . When HCl gas is slowly bubbled into a CH_2Cl_2 solution of IIa, $\text{CpW}(\text{NO})_2\text{Cl}$ is the only NO-containing product identified by IR in the reaction solution. The formation of $\text{CpW}(\text{NO})_2\text{Cl}$ presumably occurs by Cl^- substitution of $\text{P}(\text{OPh})_3$ in Ia generated by acid oxidation.

When I_2 is added to a CH_2Cl_2 solution of IIa, the purple solution gradually turns green over a 15-min period; at this stage both Ia and $\text{CpW}(\text{NO})_2\text{I}$ are present. When the solution stands an additional 15 min, only $\text{CpW}(\text{NO})_2\text{I}$ is present in 75% yield; presumably Ia is converted to the iodo complex by substitution of the $\text{P}(\text{OPh})_3$ in Ia.

To examine the possibility that the $\text{CpW}(\text{NO})_2(\text{P}(\text{OPh})_3)$ radical initiates the polymerization of styrene, we added IIa to a CH_2Cl_2 solution of styrene; no reaction occurred.

Acknowledgment. We thank James Richardson for assistance with the X-ray studies and Professor Glen A. Russell for helpful discussions. We sincerely appreciate Dr. M. B. Hall's comments on the MO interpretation of structural features of IIa.

Note Added in Proof. The extra electron in the dithiocarbamate complexes $\text{M}(\text{R}_2\text{dth})_2(\text{NO})_2^-$, $\text{M} = \text{Mo}$ or W , is also delocalized over both NO groups: Budge, J. R.; Broomhead, J. A.; Boyd, P. D. *Inorg. Chem.* 1982, 21, 1031.

Registry No. Ia, 53419-13-9; Ib, 53419-05-9; Ic, 53419-11-7; IIa, 82044-72-2; IIb, 82044-73-3; IIc, 82044-74-4; $\text{CpW}(\text{NO})_2\text{I}$, 53419-16-2; $\text{Ph}_3\text{COOCPh}_3$, 596-30-5; $[\text{Ph}_3\text{C}]\text{BF}_4$, 341-02-6.

Supplementary Material Available: Tables of calculated hydrogen atom positions, additional bond distances and angles, thermal parameters, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Organometallic Nitrosyl Chemistry. 17.¹ Solvent Control of the Reactions of Dicyclopentadienyliodonitrosylmolybdenum with Some Silver(I) Salts

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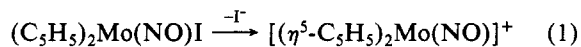
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Stoichiometric reactions between $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$ and equimolar amounts of AgY ($\text{Y} = \text{BF}_4$ or SbF_6) produce different organometallic nitrosyl complexes depending upon the solvent employed. In acetonitrile, the monomeric cation $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{CH}_3\text{CN})]^+$ results and can be isolated as its Y^- salt in good yields. In aqueous acetone, the final isolable products are the trimetallooxonium salts, $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})(\text{OH})_3]\text{OY}$, which probably result from initial formation of the aquo cation $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{OH}_2)]^+$. [The iodo analogue of the trimetallic hydroxo species can be prepared by treatment of an aqueous acetone solution of $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})\text{I}_2]$ with AgY in 1:2 stoichiometry.] In dichloromethane, the Lewis acid-base adducts $(\text{C}_5\text{H}_5)_2\text{M}(\text{NO})\text{I}\cdot\text{AgY}$ form and precipitate in high yields for both $\text{M} = \text{Mo}$ or W . These adducts react with the donor solvents in which they dissolve, converting in acetonitrile to the $[(\text{C}_5\text{H}_5)_2\text{M}(\text{NO})(\text{CH}_3\text{CN})]^+$ cations and in aqueous acetone to the trimetallooxonium salts. In none of the solvents investigated do the AgY salts transform $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$ to $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})]^+$, this novel cation only being formed in low yield when an excess of AlCl_3 in CH_2Cl_2 is used as the iodide-abstracting reagent. The physical properties of all new compounds prepared are presented and discussed in relation to possible molecular structures.

Introduction

Since the first report of its existence in 1968,² $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$ has attracted considerable attention.^{3,4} In particular, the molecular structure of the complex in solutions and the mode of attachment of the cyclopentadienyl rings to the metal center have been the subjects of much speculation. Static structures such as $(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}^2$ and $(\eta^4\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}^3$ have been proposed for this stereochemically nonrigid compound, and it has also been suggested that the complex might exist transitionally as $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}$ (possibly solvated) with the η^1 - and

$\eta^5\text{-C}_5\text{H}_5$ rings rapidly exchanging their electronic roles.⁴ In any event, it is clear from the previous studies that not all of the available electron density on the cyclopentadienyl ligands is being utilized by the metal. Consequently, it should be possible to effect the iodide-abstractation reaction



a process that would be facilitated by the concomitant linkage of both C_5H_5 rings to the molybdenum atom in an η^5 fashion in order that the metal center may retain the favored 18-electron configuration.

One of the principal methods for accomplishing conversions of the type (1) involves treatment of the organometallic halide with various silver(I) salts. Generally, the cationic complexes thus produced are 18-electron species in which either a donor solvent (e.g., CH_3CN , THF, acetone, etc.) or a ligated counterion (e.g., BF_4^- , PF_6^- , SbF_6^- , etc.) has replaced the halide in the metal's coordination sphere, the latter situation occurring

(1) Part 16: Hames, B. W.; Legzdins, P. *Organometallics* 1982, 1, 116.

(2) King, R. B. *Inorg. Chem.* 1968, 7, 90.

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in weakly coordinating solvents.⁵ During our investigations of the reactions of $(C_5H_5)_2Mo(NO)I$ with AgY ($Y = BF_4$ or SbF_6), we discovered a more pronounced influence of the solvent on the outcome of these transformations. In this paper we describe in detail this solvent control.

Experimental Section

General procedures routinely employed in these laboratories have been described previously.¹ Proton-decoupled carbon-13 NMR spectra were recorded on a Varian Associates CFT-20 spectrometer with reference to the solvent used, but all ¹³C chemical shifts are reported in ppm downfield from Me_4Si . Conductivities of 10^{-3} M solutions of the complexes were measured with a YSI Model 31 conductivity bridge at ambient temperatures.

Reaction of $(C_5H_5)_2Mo(NO)I$ with AgY ($Y = BF_4$ or SbF_6) in CH_3CN . To a rapidly stirred green-brown solution of $(C_5H_5)_2Mo(NO)I^2$ (0.77 g, 2.0 mmol) in CH_3CN (40 mL) was added solid $AgBF_4$ (0.39 g, 2.0 mmol). A white precipitate formed immediately, and the supernatant solution became red-black. After being stirred for 1 h to ensure completion of the reaction, the reaction mixture was filtered through a column of Celite (3×3 cm) supported on a medium-porosity frit. The filtrate was concentrated under reduced pressure to a volume of 10 mL. Addition of diethyl ether (40 mL) induced the crystallization of black $[(C_5H_5)_2Mo(NO)(CH_3CN)]BF_4$: (0.54 g, 71% yield).

Anal. Calcd for $C_{12}H_{13}MoN_2OBF_4$: C, 37.53; H, 3.41; N, 7.30. Found: C, 37.58; H, 3.43; N, 7.26. IR (Nujol mull): ν_{CN} 2319, 2297; ν_{NO} 1666 (br) cm^{-1} . IR (CH_3CN): ν_{NO} 1651 cm^{-1} . ¹H NMR (CD_3CN): δ 6.36 (s). ¹H NMR (CD_3NO_2): δ 6.34 (10 H, br), 2.70 (3 H, s). ¹³C NMR (CD_3CN): δ 114.6 (s). Mp: 125 °C dec.

Analytically pure $[(C_5H_5)_2Mo(NO)(CH_3CN)]SbF_6$ can be obtained similarly in 85% yield from $(C_5H_5)_2Mo(NO)I$ and $AgSbF_6$.

Anal. Calcd for $C_{12}H_{13}MoN_2OSbF_6$: C, 27.04; H, 2.46; N, 5.26. Found: C, 27.14; H, 2.40; N, 5.20. IR (Nujol mull): ν_{CN} 2320, 2298; ν_{NO} 1665 (br); ν_{SbF} 650 (br) cm^{-1} . IR (CH_3CN): ν_{NO} 1651; ν_{SbF} 663 cm^{-1} . ¹H NMR (CD_3CN): δ 6.37 (s). ¹H NMR (CD_3NO_2): δ 6.40 (10 H, br), 2.70 (3 H, s). Mp: 117 °C dec.

Reaction of $(C_5H_5)_2Mo(NO)I$ with AgY ($Y = BF_4$ or SbF_6) in Aqueous $(CH_3)_2CO$. Solid $AgBF_4$ (0.59 g, 3.0 mmol) was added to a stirred dark green solution of $(C_5H_5)_2Mo(NO)I$ (1.15 g, 3.0 mmol) in acetone (125 mL) containing H_2O (2 mL). Immediately the solution became red-black, and white AgI precipitated. The reaction mixture was stirred at ambient temperature for 3 h, whereupon the solution gradually became bright orange. The final mixture was filtered through Celite (vide supra), and the volume of the filtrate was reduced to ~25 mL in vacuo. Diethyl ether (40 mL) was then slowly added to induce the crystallization of 0.37 g (48% yield) of orange, microcrystalline $[(\eta^5-C_5H_5)Mo(NO)(OH)]_3O[B(C_6H_5)_4]_2 \cdot 2H_2O$.

Anal. Calcd for $C_{15}H_{22}Mo_3N_3O_9BF_4$: C, 23.61; H, 2.91; N, 5.51; Mo, 37.72. Found: C, 23.60; H, 2.45; N, 5.06; Mo, 37.83. IR (Nujol mull): ν_{OH} 3460 cm^{-1} ; ν_{NO} 1662 (br) cm^{-1} ; ν_{BF} 1082, 1049, 1020, 999 cm^{-1} . ¹H NMR ($(CD_3)_2CO$): δ 6.27 (15 H, s), 2.77 (7 H, s). ¹³C NMR (D_2O): δ 112.3 (s). Mp: 192 °C dec.

The reaction of $(C_5H_5)_2Mo(NO)I$ with $AgSbF_6$ was effected similarly except that 15 mL of H_2O was employed. The final orange filtrate was taken to dryness in vacuo, and the resulting residue was recrystallized from acetone-diethyl ether to obtain $[(\eta^5-C_5H_5)Mo(NO)(OH)]_3O[SbF_6](CH_3)_2CO$ as an orange solid in 18% yield.

Anal. Calcd for $C_{18}H_{24}Mo_3N_3O_8SbF_6$: C, 23.15; H, 2.59; N, 4.50. Found: C, 23.29; H, 2.64; N, 4.26. IR (Nujol mull): ν_{OH} 3510 cm^{-1} ; ν_{NO} 1666 (br) cm^{-1} ; ν_{SbF} 655 cm^{-1} . IR (THF): ν_{NO} 1673 cm^{-1} . ¹H NMR (CD_3CN): δ 6.17 (15 H, s), 2.08 (6 H, s), 1.67 (3 H, s). Mp: 203 °C dec.

Preparation of $[(\eta^5-C_5H_5)Mo(NO)(OH)]_3O[B(C_6H_5)_4]_2 \cdot 2H_2O$. A saturated solution of $NaB(C_6H_5)_4$ (~0.2 g) in H_2O (10 mL) was added dropwise to an orange solution of $[(\eta^5-C_5H_5)Mo(NO)-$

$(OH)]_3O[B(C_6H_5)_4]_2 \cdot 2H_2O$ (0.15 g, 0.20 mmol) in H_2O (100 mL). A yellow precipitate formed immediately, and the mixture was stirred for 0.5 h to ensure complete precipitation. The solid was then collected by filtration and recrystallized from acetone-water to isolate 0.1 g (50% yield) of $[(\eta^5-C_5H_5)Mo(NO)(OH)]_3O[B(C_6H_5)_4]_2 \cdot 2H_2O$ as a yellow solid.

Anal. Calcd for $C_{39}H_{42}Mo_3N_3O_9B$: C, 47.06; H, 4.25; N, 4.22; Mo, 28.92. Found: C, 47.00; H, 4.00; N, 4.45; Mo, 29.50. IR (Nujol mull): ν_{NO} 1661 (br) cm^{-1} . IR (THF): ν_{NO} 1673 cm^{-1} . ¹H NMR ($(CD_3)_2CO$): δ 7.00 (20 H, m), 6.20 (15 H, s), 2.77 (7 H, s). Mp: 176 °C dec.

Reaction of $[(C_5H_5)_2Mo(NO)(CH_3CN)]BF_4$ with H_2O . To a stirred dark red solution of $[(C_5H_5)_2Mo(NO)(CH_3CN)]BF_4$ (0.34 g, 0.90 mmol) in acetone (50 mL) was added H_2O (1 mL). The mixture gradually became orange over a period of 2 h. It was then concentrated under reduced pressure to a volume of 15 mL, and diethyl ether (30 mL) was added dropwise to induce the crystallization of 0.08 g (35% yield) of orange $[(\eta^5-C_5H_5)Mo(NO)(OH)]_3O[B(C_6H_5)_4]_2 \cdot 2H_2O$, which was identified by its characteristic physical properties (vide supra).

Reaction of $[(\eta^5-C_5H_5)Mo(NO)I_2]$ with $AgBF_4$ in Aqueous $(C_5H_5)_2CO$. Solid $AgBF_4$ (0.39 g, 2.0 mmol) was added to a stirred red solution containing $[(\eta^5-C_5H_5)Mo(NO)I_2]^6$ (0.89 g, 1.0 mmol) in acetone (80 mL). A white precipitate formed, and the solution became orange-red over a period of 15 min. The mixture was then filtered through Celite (vide supra), and H_2O (20 mL) was added to the filtrate. After being stirred for 1 h at room temperature, the orange solution was taken to dryness in vacuo. Recrystallization of the residue from acetone-diethyl ether afforded 0.3 g (40% yield) of $[(\eta^5-C_5H_5)Mo(NO)I_2]O[B(C_6H_5)_4]_2 \cdot 2H_2O$ as an orange solid.

Anal. Calcd for $C_{18}H_{21}Mo_3N_3O_5I_3BF_4$: C, 19.37; H, 1.88; N, 3.77; I, 34.17. Found: C, 19.39; H, 2.10; N, 3.94; I, 34.00. IR (Nujol mull): ν_{NO} 1669 (m), 1645 (sh) cm^{-1} . ¹H NMR (CD_3CN): δ 6.39, 6.36, 6.30, 6.28 (total of 15 H, all s), 2.12 (6 H, s). Mp: 142 °C dec.

Reaction of $[(\eta^5-C_5H_5)Mo(NO)I_2]O[B(C_6H_5)_4]_2$ with $NaB(C_6H_5)_4$ in Aqueous $(CH_3)_2CO$. An orange solution of $[(\eta^5-C_5H_5)Mo(NO)I_2]O[B(C_6H_5)_4]_2$ in aqueous acetone (prepared as described in the preceding section) was treated with an aqueous solution (25 mL) of $NaB(C_6H_5)_4$ (0.68 g, 2.0 mmol). The resulting mixture was stirred for 1 h at ambient temperature. Concentration of the final orange solution under reduced pressure induced the crystallization of 0.65 g (98% yield) of $[(\eta^5-C_5H_5)Mo(NO)(OH)]_3O[B(C_6H_5)_4]_2 \cdot 2H_2O$, which was identified by its characteristic spectral properties (vide supra).

Reaction of $(C_5H_5)_2M(NO)I$ ($M = Mo^2$ or W^2) with AgY ($Y = BF_4$ or SbF_6) in CH_2Cl_2 . These experiments were all performed in the same manner. The procedure, using the reaction of $(C_5H_5)_2Mo(NO)I$ with $AgBF_4$ as a typical example, was as follows.

Solid $AgBF_4$ (0.59 g, 3.0 mmol) was added to a dark green solution of $(C_5H_5)_2Mo(NO)I$ (1.15 g, 3.0 mmol) in CH_2Cl_2 (100 mL), and the mixture was stirred for 16 h. During this time the reaction mixture became red and a dark red solid slowly precipitated. This solid was collected by filtration, washed thoroughly with CH_2Cl_2 (3×40 mL), and dried in vacuo to obtain 1.30 g (75% yield) of analytically pure $(C_5H_5)_2Mo(NO)I \cdot AgBF_4$.

The other red-brown adducts were isolated analogously in yields of 60% ($M = Mo$, $Y = SbF_6$), 74% ($M = W$, $Y = BF_4$), and 95% ($M = W$, $Y = SbF_6$).

Anal. Calcd for $C_{10}H_{10}MoNOI \cdot AgBF_4$: C, 20.79; H, 1.74; N, 2.42; Mo, 16.61; Ag, 18.68; I, 21.96. Found: C, 20.61; H, 1.98; N, 1.99; Mo, 16.28; Ag, 18.50; I, 21.90. IR (Nujol mull): ν_{NO} 1644 (br); ν_{BF} 1083 (sh), 1053 (m), 1018 (sh), 1003 (sh) cm^{-1} . ¹H NMR (CD_3NO_2): δ 5.86–6.88 (multiple signals). Mp: 75 °C dec.

Anal. Calcd for $C_{10}H_{10}MoNOI \cdot AgSbF_6$: C, 16.53; H, 1.39; N, 1.93; I, 17.46. Found: C, 16.76; H, 1.60; N, 1.66; I, 17.29. IR (Nujol mull): ν_{NO} 1658 (br); ν_{SbF} 659 (s), 639 (sh) cm^{-1} . ¹H NMR (CD_3NO_2): δ 5.60–7.00 (multiple signals). Mp: 58 °C dec.

Anal. Calcd for $C_{10}H_{10}WNOI \cdot AgBF_4$: C, 18.02; H, 1.50; N, 2.10; I, 19.07. Found: C, 17.35; H, 1.70; N, 1.99; I, 18.88. IR (Nujol mull): ν_{NO} 1618; ν_{BF} 1091 (m), 1059 (m), 1024 (sh), 1009 (sh) cm^{-1} . Mp: 61 °C dec.

Anal. Calcd for $C_{10}H_{10}WNOI \cdot AgSbF_6$: C, 14.72; H, 1.23; N, 1.72; I, 15.58. Found: C, 15.20; H, 1.51; N, 1.48; I, 15.26. IR (Nujol mull): ν_{NO} 1616 cm^{-1} ; ν_{SbF} 658 (s) cm^{-1} . Mp: 58 °C dec.

(5) For representative examples see: (a) Mews, R.; Glemser, O. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 186. (b) Uson, R.; Riera, V.; Gimena, J.; Laguna, M.; Gamasa, M. P. *J. Chem. Soc., Dalton Trans.* **1979**, 996. (c) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73. (d) White, C.; Thompson, S. J.; Maitlis, P. M. *Ibid.* **1977**, *134*, 319. (e) Regina, F. J.; Wojcicki, A. *Inorg. Chem.* **1980**, *19*, 3803. (f) Klein, H. P.; Thewalt, U. *J. Organomet. Chem.* **1981**, *206*, 69. (g) Mattson, B. M.; Graham, W. A. *G. Inorg. Chem.* **1981**, *20*, 3186.

(6) King, R. B. *Inorg. Chem.* **1967**, *6*, 30.

(7) Legzdins, P.; Martin, D. T.; Nurse, C. R. *Inorg. Chem.* **1980**, *19*, 1560.

Reactions of $(C_5H_5)_2Mo(NO)I \cdot AgBF_4$ with Donor Solvents. (A) **With Acetonitrile.** $(C_5H_5)_2Mo(NO)I \cdot AgBF_4$ (100 mg) was added to CH_3CN (5 mL) with stirring to obtain a dark red-brown solution and a small amount of an off-white solid. An infrared spectrum of the supernatant solution displayed a ν_{NO} absorption at 1651 cm^{-1} , characteristic of $[(C_5H_5)_2Mo(NO)(CH_3CN)]BF_4$.

Repetition of the experiment with CD_3CN as solvent afforded a red-brown supernatant solution whose 1H NMR spectrum exhibited a single strong resonance at δ 6.36 in addition to several weak signals in the region δ 6.0–6.6.

(B) **With Acetone–Water.** Attempted dissolution of $(C_5H_5)_2Mo(NO)I \cdot AgBF_4$ (50 mg) in 2:1 $(CD_3)_2CO-D_2O$ (2 mL) produced an orange-brown solution and an off-white solid. A 1H NMR spectrum of the orange-brown solution contained a strong signal at δ 6.36 and weaker, sharp signals at δ 6.48, 6.20, and 6.10. After 2 days, the resonance at δ 6.36 was unaltered, but the less intense peaks had diminished in intensity by $\sim 50\%$.

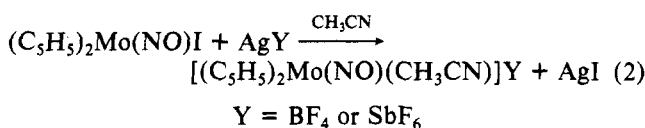
A 1H NMR spectrum of an authentic sample of $[(\eta^5-C_5H_5)Mo(NO)(OH)_3O]BF_4 \cdot 2H_2O$ in the same solvent mixture displayed a sharp signal at δ 6.36.

Reaction of $(C_5H_5)_2Mo(NO)I$ with $AlCl_3$. To a stirred dark green solution of $(C_5H_5)_2Mo(NO)I$ (0.77 g, 2.0 mmol) in CH_2Cl_2 (40 mL) was added an excess of solid $AlCl_3$ (0.54 g, 4.0 mmol). The solution became dark red immediately, and a brown precipitate formed. The reaction mixture was stirred at ambient temperature for 10 min and was then filtered through a short Celite column (3×2 cm) supported on a medium-porosity frit. The filtrate was concentrated under reduced pressure to ~ 10 mL and was filtered into a flask containing diethyl ether (100 mL) to induce the precipitation of 0.13 g (13% yield) of dark red $[(\eta^5-C_5H_5)_2Mo(NO)]AlCl_3I$.

Anal. Calcd for $C_{10}H_{10}MoNOAlCl_3I$: C, 23.26; H, 1.95; N, 2.71; Cl, 20.60; I, 24.58. Found: C, 23.34; H, 2.12; N, 2.66; Cl, 20.50; I, 24.33. IR (CH_2Cl_2): ν_{NO} 1690 cm^{-1} . IR (CH_3CN): ν_{NO} 1678 cm^{-1} . 1H NMR ($(CD_3)_2CO$): δ 6.27 (s). Mp: 95°C dec. Δ_M (CH_3NO_2): $57.5\text{ } \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$.

Results and Discussion

Reactions of Silver(I) Salts with $(C_5H_5)_2Mo(NO)I$. (a) **In Acetonitrile.** The addition of a stoichiometric amount of $AgBF_4$ or $AgSbF_6$ to a solution of $(C_5H_5)_2Mo(NO)I$ in CH_3CN results in the rapid precipitation of silver iodide and the formation of the new organometallic cation $[(C_5H_5)_2Mo(NO)(CH_3CN)]^+$ (eq 2). The organometallic



products from these conversions can be isolated in good yields (71–85%). Their formation indicates that under these conditions the metal center prefers to attain the 18e configuration by coordination of a molecule of the donor solvent rather than by altering the nature of its linkages to the C_5H_5 rings from that which exists in the iodide reactant.

The black salts $[(C_5H_5)_2Mo(NO)(CH_3CN)]Y$ ($Y = BF_4$ or SbF_6) are diamagnetic solids that can be handled in air for short periods of time without the occurrence of noticeable decomposition. They are freely soluble in most polar organic solvents to produce red-black, air-sensitive, and moisture-sensitive solutions. Their spectral properties are consistent with the cation having a monomeric molecule structure. Thus, their Nujol mull infrared spectra exhibit single strong absorptions in the region normally associated with terminal nitrosyl ligands⁸ (e.g., $\nu_{NO} = 1665\text{ cm}^{-1}$ for $Y = SbF_6$) as well as weaker bands attributable to the acetonitrile ligand (e.g., $\nu_{CN} = 2320$ and 2298 cm^{-1} for $Y = SbF_6$; cf. 2298 and 2258 cm^{-1} for free acetonitrile). The presence of the CH_3CN ligand is also confirmed by their 1H NMR spectra, those of the SbF_6 salt being presented in Figure 1. The 1H NMR spectrum of the salt in CD_3NO_2 displays a broad resonance at δ 6.4 due to the

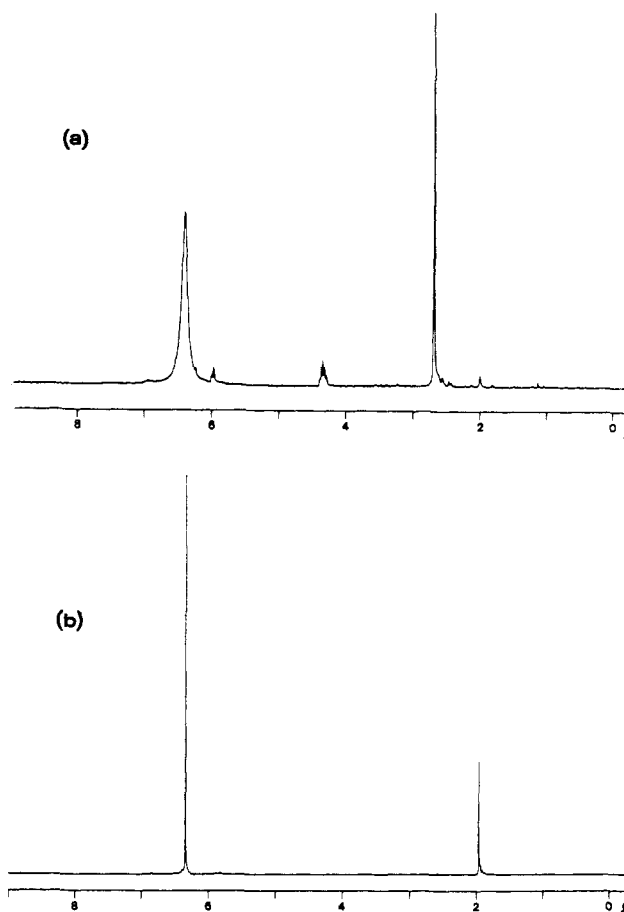
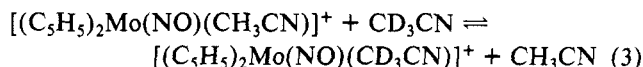


Figure 1. 80-MHz 1H NMR spectra of $[(C_5H_5)_2Mo(NO)(CH_3CN)]SbF_6$ in (a) CD_3NO_2 and (b) CD_3CN .

cyclopentadienyl protons⁹ and a sharp singlet at δ 2.70 due to the protons of the coordinated CH_3CN (cf. δ 2.00 for free CH_3CN). In CD_3CN , the peak due to the C_5H_5 protons is a sharp singlet⁹ while the resonance due to the coordinated acetonitrile is superimposed on the residual solvent signal. These observations, taken in conjunction with ^{13}C NMR data,¹⁰ indicate that in solution there is rapid chemical exchange (on the NMR time scale) between free and coordinated CH_3CN (eq 3).

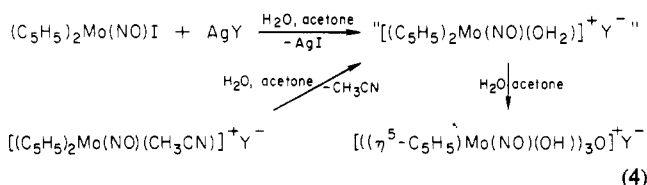


(b) **In Aqueous Acetone.** The initial reaction between AgY ($Y = BF_4$ or SbF_6) and an equimolar amount of $(C_5H_5)_2Mo(NO)I$ in aqueous acetone proceeds as in acetonitrile, precipitation of AgI and formation of a red-black solution occurring rapidly. However, over a period of several hours, the solution becomes bright orange; salts of the trimetallic cation $[(\eta^5-C_5H_5)Mo(NO)(OH)_3O]^+$ can be isolated in moderate yields from the final reaction mixture. Since the same products result when acetone solutions of the $[(C_5H_5)_2Mo(NO)(CH_3CN)]Y$ compounds are treated with water, it seems likely that the first step in both conversions involves the formation of the aquo cation $[(C_5H_5)_2Mo(NO)(OH_2)]^+$

(9) The broadness of the cyclopentadienyl resonance in the 1H NMR spectrum of $[(C_5H_5)_2Mo(NO)(CH_3CN)]SbF_6$ in CD_3NO_2 probably reflects the existence of a fluxional process analogous to that believed to occur for the parent $(C_5H_5)_2Mo(NO)I$.^{3,4} However, the fact that this resonance becomes sharp when the salt is dissolved in CD_3CN indicates some dependence of the rearrangement processes on the solvent.

(10) A ^{13}C NMR spectrum of $[(C_5H_5)_2Mo(NO)(CH_3CN)]BF_4$ in CD_3CN only displays a single sharp resonance due to the C_5H_5 carbons at δ 114.6 and signals at δ 118.5 and 1.3 due to CH_3CN .

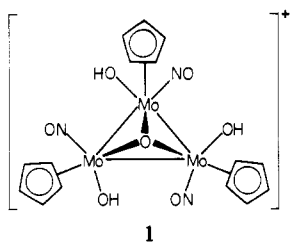
(eq 4). Once isolated, the hexafluoroantimonate or tetra-



fluoroborate salts of $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})(\text{OH})_3\text{O}]^+$ can be converted to the tetraphenylborate salt by simple metathesis with $\text{NaB}(\text{C}_6\text{H}_5)_4$ in H_2O .

The tris $[(\eta^5\text{-cyclopentadienyl})\text{hydroxynitrosylmolybdenio}]$ oxonium salts are yellow ($\text{Y} = \text{B}(\text{C}_6\text{H}_5)_4$) or orange ($\text{Y} = \text{BF}_4$ or SbF_6) air-stable solids that crystallize from solution with one or two molecules of the solvent of crystallization. Their trimetallic nature can be determined from elemental analyses and confirmed by careful integration of the ^1H NMR spectrum of the tetraphenylborate salt. They are soluble in strongly solvating solvents to afford bright orange, air-stable solutions. The spectral properties of the SbF_6^- salt, isolable as the acetone solvate, are typical of this class of compounds. Its Nujol mull infrared spectrum exhibits a strong ν_{NO} at 1666 cm^{-1} and a weaker ν_{OH} at 3510 cm^{-1} . Its ^1H NMR spectrum in CD_3CN consists of single sharp peaks at δ 6.17, 2.08, and 1.67 of relative intensity 5:2:1, which are assignable to the protons of the C_5H_5 , $(\text{CH}_3)_2\text{CO}$, and OH groups, respectively. The addition of a small quantity of D_2O to this CD_3CN solution causes the resonance at δ 1.67 to shift downfield to δ 3.73, thereby indicating rapid H-D chemical exchange, a feature typical of hydroxyl groups.¹¹

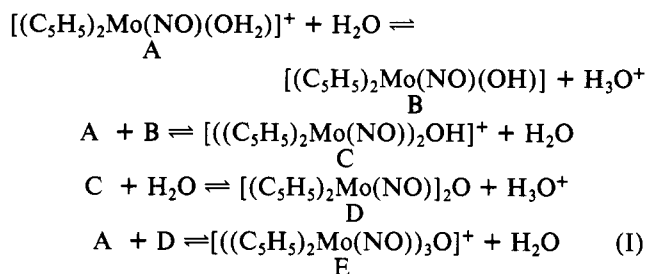
These properties are in accord with the trimetallic cation possessing the basic structure 1, an arrangement having overall



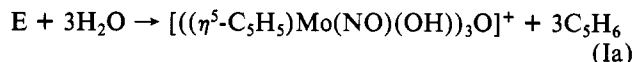
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C_{3v} symmetry. Such an arrangement also satisfies the effective atomic number rule, the capping oxygen atom functioning as a formal four-electron donor.¹² The latter structural feature has ample precedence in the literature [e.g., $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_2(\mu_3\text{-O})]^+$,¹⁴ $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Co}(\mu_3\text{-CO})(\mu_3\text{-O})]$,¹⁵ $[(\text{OC})_3\text{Re}(\mu\text{-H})(\mu_3\text{-O})]^2$,¹⁶ and $[(\text{F}_3\text{W}(\mu_2\text{-O}))_3(\mu_3\text{-O})]^5$], the molybdenum complex¹⁴ being of particular relevance since it is valence isoelectronic with the hydroxynitrosyl cation depicted above. $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_2\text{O}]^+$ can be synthesized by the reactions of $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_3]^+$ or $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_3(\text{C}_6\text{H}_5\text{O})]^+$ with water via the intermediate aquo complex, $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_3(\text{OH}_2)]^+$.¹⁴ By analogy, the for-

mation of $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})(\text{OH})_3\text{O}]^+$ could involve the decomposition of the initially formed $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{OH}_2)]^+$ cation (cf. eq 4) by a series of Lowry-Brønsted acid-base equilibria (eq 1) to give $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})_3\text{O}]^+$



in a fashion similar to that proposed¹⁴ for the carbonyl derivative. The final step to form the observed product would then require an irreversible hydrolysis of one of the cyclopentadienyl ligands (eq 1a). Support for the involvement of



such a mechanism is provided by the fact that, whereas $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{CH}_3\text{CN})]\text{BF}_4$ readily converts to $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})(\text{OH})_3\text{O}]\text{BF}_4$ in aqueous acetone, it is stable to hydrolysis in CH_3CN where the bulk solvent competes as a ligand, thereby suppressing the formation of the requisite aquo cation. Furthermore, when reaction mixtures that ultimately afford the trimetallooxonium salts are quenched prematurely with hexanes, they precipitate a brown solid whose ^1H NMR spectrum in various solvents displays multiple resonances in the cyclopentadienyl region (δ 6.0–6.5).

In a related reaction, treatment of an aqueous acetone solution of $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})\text{I}_2]_2$ with AgBF_4 in 1:2 stoichiometry affords $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})\text{I}_3\text{O}]\text{BF}_4 \cdot (\text{CH}_3)_2\text{CO}$, the iodo analogue of the hydroxo species discussed above. Again, the formation of this trimetallic cation can be rationalized in terms of initial formation of an aquo complex, i.e., $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})\text{I}(\text{OH}_2)_2]^+$. Subsequent Lowry-Brønsted acid-base equilibria would lead to $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})\text{I}(\text{OH}_2)_3\text{O}]^+$, which could then irreversibly lose H_2O to give the final product. Tris $[(\eta^5\text{-cyclopentadienyl})\text{iodonitrosylmolybdenio}]$ oxonium tetrafluoroborate is an orange, air-stable solid which is less soluble in strongly solvating solvents than its hydroxo analogue. Its ^1H NMR spectrum in CD_3CN exhibits four sharp resonances in the cyclopentadienyl region at δ 6.28, 6.30, 6.36, and 6.39. This feature contrasts with the spectra of the valence isoelectronic species $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{CO})_2\text{O}]\text{BF}_4$ ¹⁴ and $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})(\text{OH})_3\text{O}]\text{BF}_4$ in $(\text{CD}_3)_2\text{CO}$, which display single resonances at δ 6.10 and 6.27, respectively, and indicates the existence in solution of more than one isomer of the basic trimetallic structure.¹⁸ This inference is supported by the Nujol mull infrared spectrum of the complex, which exhibits two nitrosyl absorption at 1669 and 1645 cm^{-1} .

(c) In Dichloromethane. Since iodide abstraction from $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$ in coordinating solvents apparently leads to $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{solvent})]^+$ cations rather than $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})]^+$, we next attempted reaction 1 in CH_2Cl_2 , a noncoordinating solvent. Under these conditions, the desired

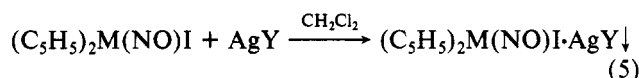
- (11) The ^1H NMR spectra of the BF_4^- and $\text{B}(\text{C}_6\text{H}_5)_4^-$ salts (both diaquo solvates) in $(\text{CD}_3)_2\text{CO}$ display a resonance at δ 2.77, which integrates for seven protons. Upon the addition of D_2O , this signal also shifts to δ 4–5.
- (12) Alternatively, the OH groups may bridge the edges of the Mo_3 triangle in a manner analogous to that found for the MeO groups¹³ in $[\text{Na}(\text{Mo}_3(\text{CO})_6(\text{NO})_3(\mu\text{-OMe})_3(\mu_3\text{-O}))_2]^3$. In this case, formal Mo-Mo linkages would not have to be invoked to satisfy the 18-electron rule.
- (13) Kirtley, S. W.; Chanton, J. P.; Love, R. A.; Tipton, D. L.; Sorrell, T. N.; Bau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3451.
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- (17) Mennemann, K.; Mattes, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 118.

- (18) Attempts to form the $\text{B}(\text{C}_6\text{H}_5)_4^-$ salt of $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})\text{I}_3\text{O}]^+$ by metathesis in aqueous acetone result in the quantitative formation of $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}(\text{NO})(\text{OH})_3\text{O}]\text{B}(\text{C}_6\text{H}_5)_4$. This transformation is consistent with the putative trimetallic nature of the iodo cation.
- (19) (a) McCleverty, J. A.; Murray, A. J. *Transition Met. Chem. (Weinheim Ger.)* **1979**, *4*, 273. (b) Faller, J. W.; Shvo, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5396.
- (20) Greenhough, T. J.; Legzdins, P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3268.

Table I. Nitrosyl Stretching Frequencies of Some Molybdenum and Tungsten Complexes

complex	medium	ν_{NO} , cm^{-1}	ref
$(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$	CH_2Cl_2	1642	2
	Nujol	1621	this work
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\eta^3\text{-C}_3\text{H}_5)\text{I}$	KBr	1651	19
$(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I} \cdot \text{AgBF}_4$	Nujol	1644	this work
$(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I} \cdot \text{AgSbF}_6$	Nujol	1658	this work
$[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{CH}_3\text{CN})]\text{BF}_4$	Nujol	1666	this work
$[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{CH}_3\text{CN})]\text{SbF}_6$	Nujol	1665	this work
$(\text{C}_5\text{H}_5)_2\text{W}(\text{NO})\text{I}$	CH_2Cl_2	1622	7
	Nujol	1581	this work
$(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{NO})(\eta^3\text{-C}_3\text{H}_5)\text{I}$	CH_2Cl_2	1636	20
$(\text{C}_5\text{H}_5)_2\text{W}(\text{NO})\text{I} \cdot \text{AgBF}_4$	Nujol	1618	this work
$(\text{C}_5\text{H}_5)_2\text{W}(\text{NO})\text{I} \cdot \text{AgSbF}_6$	Nujol	1616	this work

conversion again does not occur in the presence of silver(I) salts as the adducts $(\text{C}_5\text{H}_5)_2\text{M}(\text{NO})\text{I} \cdot \text{AgY}$ precipitate instead in high yields for $\text{M} = \text{Mo}$ or W (see eq 5). The adducts are

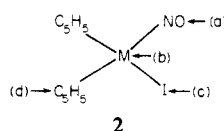


$\text{M} = \text{Mo}$ or W ; $\text{Y} = \text{BF}_4$ or SbF_6

red-brown, air-stable (but light-sensitive) solids, which only dissolve in solvents with which they react at varying rates. For instance, decomposition of $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I} \cdot \text{AgBF}_4$ in CH_3NO_2 is only significant after more than 10 min. Nevertheless, its initial solubility in this solvent precludes its being a physical mixture of $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{BF}_4$ and AgI .

The Nujol infrared spectra of the adducts display broad absorptions attributable to terminal nitrosyl ligands in the range 1615–1660 cm^{-1} (Table I). Furthermore, these spectra show strong absorptions due to the anions, which indicate some degree of coordination of these species. Thus, instead of displaying the characteristic single ν_{BF} absorption at 984 cm^{-1} assignable to the T_2 stretching mode of the free BF_4^- anion, the spectrum of $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I} \cdot \text{AgBF}_4$ displays ν_{BF} bands at 1083, 1053, 1018, and 1003 cm^{-1} . The appearance of these bands may be attributed to a lowering of the local symmetry of the BF_4^- anions from T_d to C_{2v} , a change which produces four infrared-active vibrations due to the $2A_1$, B_1 , and B_2 stretching modes.¹⁴ Similarly, the infrared spectrum of $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I} \cdot \text{AgSbF}_6$ exhibits two ν_{SbF} bands at 659 and 639 cm^{-1} , a feature which indicates a lowering of the local symmetry at the hexafluoroantimonate anion from O_h to C_{4v} or C_{2v} .²¹

The mull infrared spectra also provide some insight into the nature of the adducts produced by reaction 5. The reactant $(\text{C}_5\text{H}_5)_2\text{M}(\text{NO})\text{I}$ molecules contain four potential Lewis base sites with which the soft Lewis acid Ag^+ may interact (see structure 2). That sites a and b are not involved in linkages



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to Ag^+ is indicated by the ν_{NO} data presented in Table I which reveal a shift to higher frequency of ~ 25 –40 cm^{-1} upon adduct formation. Typically, the formation of isonitrosyl linkages results in the diminution of ν_{NO} by 100–200 cm^{-1} ,^{22,23} and

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- (22) (a) Crease, A. E.; Legzdins, P. *J. Chem. Soc., Chem. Commun.* **1972**, 268. (b) Crease, A. E.; Legzdins, P. *J. Chem. Soc., Dalton Trans.* **1973**, 1501.

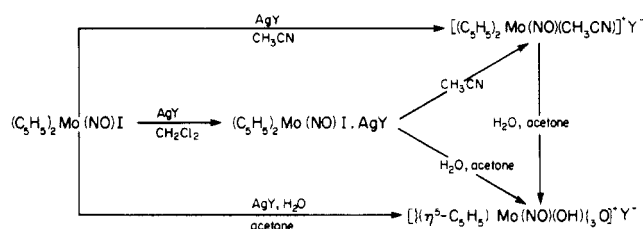
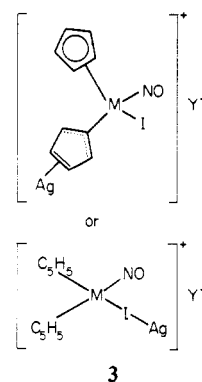


Figure 2. The reactions of $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$ with silver(I) salts in various solvents.

studies with related carbonyl complexes²⁴ suggest that formation of an $\text{M}-\text{Ag}$ bond should be reflected by an increase in ν_{NO} of at least 100 cm^{-1} .²⁵ However, the infrared data are not sufficient to permit a differentiation between the two other possible structures, the site of attachment of the anions being indeterminate (see illustration 3). For both arrangements a



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slight increase in the nitrosyl stretching frequency from that displayed by the parent $(\text{C}_5\text{H}_5)_2\text{M}(\text{NO})\text{I}$ complex is to be expected.^{23,26}

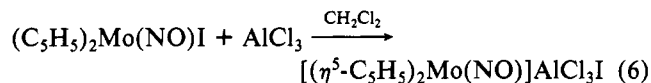
The ^1H NMR spectra of the adducts do not provide any further insight as to their structures. For instance, the spectrum of $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I} \cdot \text{AgBF}_4$ in CD_3NO_2 contains multiple signals in the region δ 5.86–6.88, which cannot be readily assigned. Consequently, definitive resolution of this question must await a single-crystal X-ray diffraction analysis of one of the adducts.

As stated earlier, the molybdenum adducts react with the donor solvents in which they dissolve, the solvents being better Lewis bases than $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$ and complexing the silver cation preferentially. Thus, in acetonitrile the adducts convert to the $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{CH}_3\text{CN})]^+$ cation and AgI , and in aqueous acetone they transform to the metalloxonium salts $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{OH})_2\text{O}]^+\text{Y}^-$. The interrelationship of these reactions and those described earlier in this paper is presented schematically in Figure 2. Clearly, the solvent exerts a pronounced influence on the outcome of these transformations. In a nondonor solvent, the silver cation acts as a Lewis acid and forms an adduct with the organometallic complex. However, in a donor solvent that is a stronger Lewis base than the complex, the Ag^+ ion reverts to its more common

- (23) (a) Lokshin, B. V.; Ginzburg, A. G.; Nazarova, E. B. *Russ. Chem. Rev. (Engl. Transl.)* **1980**, *49*, 115. (b) Lokshin, B. V.; Rusach, E. B.; Kolobova, N. E.; Makarov, Y. V.; Ustynyuk, N. A.; Zdanovich, V. I.; Zhakaeva, A. Z.; Setkina, V. N. *J. Organomet. Chem.* **1976**, *108*, 353.
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- (25) A study of the interaction of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\text{NO})(\text{PPh}_3)$ ($\text{M} = \text{Mo}$ or W) with AlCl_3 and SnCl_4 shows that both the carbonyl and nitrosyl absorptions increase by 120–170 cm^{-1} upon adduct formation via the transition metal.²³
- (26) The first structure, involving adduct formation at site d, would be expected to display a ν_{NO} resembling those of the well-known $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})(\eta^3\text{-C}_3\text{H}_5)\text{I}$ complexes (Table I).

mode of reactivity, namely, halide abstraction.

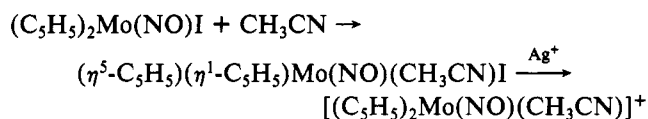
Reaction of AlCl_3 with $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$ in CH_2Cl_2 . In view of the solvent control of the reactions of $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$ with silver(I) salts (Figure 2), it thus appears that reaction 1 cannot be effected when Ag^+ is employed as the iodide acceptor. Mindful of our results with the AgY species, we then attempted the desired conversion with AlCl_3 (a harder Lewis acid than Ag^+) as the halide abstractor in CH_2Cl_2 , a noncoordinating solvent. In this manner we discovered that the anticipated transformation (eq 6) does indeed occur, albeit in



low yield. An excess of AlCl_3 is required to drive the reaction to completion, and the new organometallic salt isolated is a dark red, moisture-sensitive solid, which is fairly soluble in polar organic solvents. An infrared spectrum of a dichloromethane solution of the complex exhibits a strong absorption at 1690 cm^{-1} attributable to the terminal nitrosyl ligand. This band is at a significantly higher frequency than the corresponding absorptions of the $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$ precursor ($\nu_{\text{NO}} = 1642\text{ cm}^{-1}$) and the $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{CH}_3\text{CN})]^+$ cation ($\nu_{\text{NO}} = 1673\text{ cm}^{-1}$ for the SbF_6^- salt in CH_2Cl_2). Not surprisingly, the ^1H NMR spectrum of the complex in $(\text{CD}_3)_2\text{CO}$ consists of a single sharp resonance at δ 6.27 due to the equivalent $\eta^5\text{-C}_5\text{H}_5$ ligands.

The molar conductance of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})]\text{AlCl}_3\text{I}$ in CH_3NO_2 is $57.5\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, a value which is in the range associated with 1:1 electrolytes.²⁷ Interestingly, the 18-electron $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})]^+$ cation retains its identity in

CH_3CN (i.e., $\nu_{\text{NO}} = 1678\text{ cm}^{-1}$) and does not convert to the $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{CH}_3\text{CN})]^+$ species ($\nu_{\text{NO}} = 1651\text{ cm}^{-1}$ in CH_3CN). Both of these observations are consistent with the complex being an ionic species rather than a Lewis acid-base adduct via a $\text{Mo}-\text{I} \rightarrow \text{Al}$ linkage. Furthermore, the second observation also indicates that $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})]^+$ is not an intermediate either during the formation of the acetonitrile cation by reaction 2 or during the exchange process shown in eq 3. A plausible mechanism for reaction 2 is thus



a sequence of steps in accord with McCleverty's proposal concerning the transitional structure of $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$.⁴ Similarly, the exchange reaction (3) must be associative.

We are currently endeavoring to optimize the yields of the $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})]^+$ cation and are investigating its reactivity toward a variety of nucleophiles.

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Registry No. $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})\text{I}$, 53449-96-0; $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{CH}_3\text{CN})]\text{BF}_4$, 81857-41-2; $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{OH})_3\text{O}]\text{BF}_4$, 81898-50-2; $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{OH})_3\text{O}]\text{SbF}_6$, 81875-62-9; $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{OH})_3\text{O}]\text{B}(\text{C}_6\text{H}_5)_4$, 81857-43-4; $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}_2]$, 12203-25-7; $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}_3\text{O}]\text{BF}_4$, 81875-64-1; $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{NO})(\text{CH}_3\text{CN})]\text{SbF}_6$, 81875-65-2; $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NO})]\text{AlCl}_3\text{I}$, 81875-67-4; AgBF_4 , 14104-20-2; AgSbF_6 , 26042-64-8; AlCl_3 , 7446-70-0.

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Catalytic Hydrogenation and Isomerization of 1-Hexene with $[\text{RhCl}(\text{CO})(1,4\text{-(CN)}_2\text{C}_6\text{H}_4)]_n$ in the Dark and under Irradiation

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The insoluble matrix of $[\text{RhCl}(\text{CO})(1,4\text{-(CN)}_2\text{C}_6\text{H}_4)]_n$ was prepared by the reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with an equimolar amount of 1,4-diisocyanobenzene. This matrix was observed to display chemocatalytic activity under heterogeneous conditions with respect to the hydrogenation and isomerization of 1-hexene. Catalysis experiments with this matrix carried out under irradiation have led to the characterization of photoretarded catalytic 1-hexene hydrogenation and isomerization processes, photoretarded catalytic hydrogenation of 2-hexene isomers, and photoassisted catalytic initiation of hydrogenation and isomerization processes.

Introduction

Much attention has been focused in recent years on the study of the photocatalytic¹⁻³ and chemocatalytic⁴⁻⁷ behavior of various transition-metal complexes anchored to inert support matrices. A different approach to heterogenized homogeneous catalysis may be suggested to involve insoluble coordination polymers or oligomers where the metal constitutes an integral

part of the matrix. This new strategy toward catalysis is exemplified in the current study by the preparation of an insoluble matrix of the type $[\text{RhCl}(\text{CO})(1,4\text{-(CN)}_2\text{C}_6\text{H}_4)]_n$ and the investigation of its activity with respect to the hydrogenation and isomerization of 1-hexene in the dark as well as under irradiation.

Results and Discussion

Nonchelating bidentate ligands capable of forming stereochemically rigid linkages between metal nuclei are of interest from the standpoint of the molecular design of some rather unusual coordination polymers. This approach has recently been demonstrated⁸⁻¹⁰ by the preparation of numerous rho-

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