Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

Mono- and Bimetallic Cationic Dinitrosylmolybdenum Complexes[1]

PETER LEGZDINS* and JIMMIE C. OXLEY

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Treatment of a CH_2Cl_2 solution of $Mo(CO)_6$ with solid $NOPF_6$ in differing stoichiometries under varying, but rigorously anhydrous, experimental conditions results in the precipitation of *cis*-$Mo(NO)_2(PF_6)_2$ in moderate yields. When the same reactants are mixed in CH_3NO_2 at room temperature, the final product formed is *cis*-$[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$, which can be isolated in ~60% yield. Similar solvated products, i.e. *cis*-$[Mo(NO)_2(\text{solvent})_4](BF_4)_2$, result from the abstraction of chloride from $Mo(NO)_2Cl_2$ by 2 equiv of $AgBF_4$ in either CH_3NO_2 or THF. These cationic dinitrosylmolybdenum complexes readily incorporate relatively hard and strong Lewis bases into the metal's coordination sphere and form a variety of *cis*-$[Mo(NO)_2L_4]X_2$ salts, where L = a monodentate ligand such as CH_3CN or $OPPh_3$ or L_2 = a bidentate ligand such as 2,2′-bipyridine or $Ph_2PCH_2CH_2PPh_2$ and X = PF_6^- or BF_4^-. The *cis*-$[Mo(NO)_2L_4]^{2+}$ cations are generally quite electrophilic and facilitate both the hydrolysis of PF_6^- and the polymerization of THF. Furthermore, they can be reduced by employing 1 equiv of reducing agents such as Na/Hg, $Li[Et_3BH]$, or $Na[Ph_2CO]$ in CH_3CN or THF to the bimetallic cations $[Mo(NO)_2L_2]_2^{2+}$, which may be isolated as their PF_6^- salts in ~50% yields when L_2 = 2,2′-bipyridine or 3,4,7,8-tetramethyl-1,10-phenanthroline. Further reduction, however, leads to loss of the NO ligands. The *cis*-$[Mo(NO)_2L_4]^{2+}$ cations also function as two-electron oxidants toward neutral (e.g. $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$) or anionic (e.g. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$) organometallic reactants. The physical properties of all new compounds prepared are presented and discussed in relation to possible molecular structures.

Introduction

We recently described the preparation and properties of the bimetallic cations $[(\eta^5\text{-}C_5H_5)_2M_2(NO)_4H]^+$ (M = Mo or W).[2] The physical and chemical properties of these cations indicated that they could be viewed as adducts between the Lewis bases, $(\eta^5\text{-}C_5H_5)M(NO)_2H$, and the Lewis acids, $[(\eta^5\text{-}C_5H_5)M(NO)_2]^+$. In subsequent work, we have demonstrated that the $[(\eta^5\text{-}C_5H_5)W(NO)_2]^+$ cation is indeed quite acidic in nature and interacts strongly with Lewis bases capable of good σ donation.[3] This pronounced electrophilicity of the 16-electron cation probably reflects the generally acknowledged good π-acceptor ability of the nitrosyl ligands.[4] Nevertheless, these earlier observations suggested to us the desirability of investigating in a complementary fashion the chemical properties of the precursor $[M(NO)_2]^{2+}$ cations from which the $[(\eta^5\text{-}C_5H_5)M(NO)_2]^+$ species may be considered, at least in a formal sense, to be derived. Specifically, at the outset of this research, we wished to determine (a) the Lewis acid properties of the binary nitrosyl cations and their modification by the presence of ancillary ligands, and (b) the feasibility of forming neutral nitrosyl complexes by reduction of $M(NO)_2{}^{2+}$-containing compounds.

It has been known for some time that solvated derivatives of the $[M(NO)_2]^{2+}$ cations may be synthesized by reactions such as

$$Mo(CO)_3(CH_3CN)_3 \xrightarrow[CH_3CN]{NOPF_6} [Mo(NO)_2(CH_3CN)_4](PF_6)_2 \quad (1)^5$$

$$Mo(CO)_6 \xrightarrow[CH_3CN]{NOPF_6} [Mo(NO)_2(CH_3CN)_4](PF_6)_2 \quad (2)^6$$

$$Mo(NO)_2Cl_2 + 2AgPF_6 \xrightarrow[reflux]{CH_3CN} [Mo(NO)_2(CH_3CN)_4](PF_6)_2 + 2AgCl \quad (3)^7$$

Consequently, our expectation was that transformations of types 2 and 3 when effected in solvents of poor coordinating and good solvating abilities[8] would afford the desired binary nitrosyl cations. In this paper we report the successful synthesis of the "$[Mo(NO)_2]^{2+}$" cation and describe in detail its characteristic chemistry, which provides some insight concerning points a and b outlined above.

Experimental Section

General procedures routinely employed in these laboratories have been described previously.[2] ^{31}P NMR spectra were recorded at 32.31 MHz on a Bruker WP-80 spectrometer with reference to external $NaPF_6$ in CD_3CN (δ −144, i.e. upfield from H_3PO_4), but all ^{31}P chemical shifts are reported in ppm downfield from H_3PO_4. ^{19}F NMR spectra were obtained on a Varian EM-360 spectrometer at 56.45 MHz with reference to external $CFCl_3$, and the observed chemical shifts are reported upfield from this standard.[9] The conductivities of solutions of various complexes were measured with a YSI Model 31 conductivity bridge at ambient temperatures. A micro solution cell with platinized electrodes (cell constant 1.08 cm^{-1}) and nitromethane (specific conductance $4.3 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$) were employed for these measurements. If necessary, the conductance data obtained were treated in the manner described by Feltham and Hayter.[10] ESR spectra of ~10^{-3} M nitromethane solutions of several complexes were recorded on a Varian E-3 spectrometer at room temperature.

Reactions of $Mo(CO)_6$ with $NOPF_6$. (a) In CH_2Cl_2 (Procedure A). To a rapidly stirred, colorless solution of $Mo(CO)_6$ (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 coloration. 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 ν_{CO} at ~1980 cm^{-1} characteristic of $Mo(CO)_6$. 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 $Mo(NO)_2(PF_6)_2$. (Unreacted $Mo(CO)_6$ (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 $MoN_2O_2P_2F_{12}$: 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): ν_{NO} 1811 (s), 1683 (s, br) cm^{-1}; also 1265 (m, br), 1154 (m), 948 (m), 885 (m), 843 (m, br), 565 (s) cm^{-1}. ^{19}F NMR (CD_3CN): δ 72 (d, $J_{^{19}F-^{31}P}$ = 707 Hz). ^{31}P NMR (CD_3CN): δ −144 (sept). Mp: 110 °C dec.

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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, and (c) refluxing the initial reaction mixture for 2–6 h under either an N_2 or NO atmosphere. If rigorously anhydrous conditions were not maintained throughout, though, the green solid isolated in comparable yields from the final reaction mixtures was not $Mo(NO)_2(PF_6)_2$ but rather $Mo(NO)_2(O_2PF_2)_2$.

Anal. Calcd for $MoN_2O_6P_2F_4$: C, 0.00; H, 0.00; N, 7.82. Found: C, 0.64; H, 0.36; N, 8.02. IR (Nujol mull): ν_{NO} 1821 (s), 1693 (s, br) cm^{-1}; also 1265 (m, br), 1163 (m), 955 (m), 901 (m), 569 (m) cm^{-1}. ^{19}F NMR (CD_3CN): δ 82 (d, $J_{^{19}F-^{31}P}$ = 957 Hz). ^{31}P NMR (CD_3CN): δ −17.9 (t). Mp: >220 °C.

(b) In CH_3NO_2 (Procedure B). To a stirred suspension of $Mo(CO)_6$ (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 half of the $NOPF_6$ solution had been added, the supernatant solution was red-brown in color 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 $Mo(CO)_6$ 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 ν_{NO}'s at ~1860 and ~1750 cm^{-1}. The solution was then concentrated to 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 × 20 mL) and dried in a stream of dinitrogen for 0.5 h to obtain 2.41 g (61% yield) of $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$.

Anal. Calcd for $MoN_6O_{10}C_4H_{12}P_2F_{12}$: C, 6.96; H, 1.74; N, 12.17. Found: C, 7.43; H, 1.77; N, 11.70. IR (Nujol mull): ν_{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 (d, $J_{^{19}F-^{31}P}$ = 706 Hz). ^{31}P NMR (CD_3CN): δ −144 (sept). Λ_M (CH_3NO_2): 202 Ω^{-1} cm^2 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. Consequently, during subsequent chemical transformations in which these complexes serve as reactants, they are represented as $[Mo(NO)_2(CH_3NO_2)_x](PF_6)_2$ with the molar equivalents being calculated on the assumption that $x \simeq 4$.

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 $Mo(NO)_2Cl_2$ with $AgBF_4$. (a) In CH_3NO_2 (Procedure C). To a stirred green suspension of partially dissolved $Mo(NO)_2Cl_2$[11] (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 color 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 ~1695 cm^{-1} and the concomitant growth of new absorptions at ~1860 and ~1750 cm^{-1}. After 2 h, 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 $[Mo(NO)_2(THF)_4](BF_4)_2$ 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 throughout at ~1795 and ~1675 cm^{-1}.

Preparation of $[Mo(NO)_2(CH_3CN)_4](PF_6)_2$. A sample of $[Mo(NO)_2(CH_3NO_2)_x](PF_6)_2$ (0.45 g, ~0.65 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 (~70% yield) of $[Mo(NO)_2(CH_3CN)_4](PF_6)_2$ as bright green crystals, which were collected by filtration.

Anal. Calcd for $MoN_6O_2C_8H_{12}P_2F_{12}$: 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): ν_{NO} 1863 (s), 1754 (s, br) cm^{-1}; ν_{PF} 844 (s, br) cm^{-1}; also 2333 (m), 2305 (m) cm^{-1}. Mp: 95 °C dec.

$Mo(NO)_2(PF_6)_2$ (prepared by procedure A) afforded the same product in comparable yield when subjected to the identical experimental procedure.

Preparation of $[Mo(NO)_2(bpy)_2](PF_6)_2$. To a bright green solution of $[Mo(NO)_2(CH_3NO_2)_x](PF_6)_2$ (1.00 g, ~2.24 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′-bipyridine (bpy, $C_{10}H_8N_2$). The resulting solution was stirred for 18 h, whereupon it became darker green. 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 $[Mo(NO)_2(bpy)_2](PF_6)_2$ as a green solid (0.47 g, ~28% yield), which was collected by filtration, washed with CH_2Cl_2 (2 × 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): ν_{NO} 1816 (s), 1716 (s, br) cm^{-1}; ν_{PF} 840 (s, br) cm^{-1}; also 1603 (m), 1497 (w), 1321 (m), 881 (m), 765 (s), 730 (m) cm^{-1}. IR (CH_3NO_2): ν_{NO} 1825 (s), 1726 (s) cm^{-1}; ν_{PF} 849 (s) cm^{-1}; also 878 (w) cm^{-1}. IR (CH_3CN): ν_{NO} 1824 (s), 1724 (s) cm^{-1}; ν_{PF} 847 (s) cm^{-1}; also 1605 (m), 1500 (w), 1323 (m), 880 (m), 752 (m), 733 (w) cm^{-1}. ^1H NMR (CD_3CN): δ 9.2–7.5 (m). ^{19}F NMR (CD_3CN): δ 71 (d, $J_{^{19}F-^{31}P}$ = 707 Hz). ^{31}P NMR (CD_3CN): δ −144 (sept). Mp: 182 °C dec.

Preparation of $[Mo(NO)_2(bpy)_2](BF_4)_2 \cdot 0.75CH_2Cl_2$. 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 colorless THF solution (10 mL) of 2,2′-bipyridine (bpy, $C_{10}H_8N_2$; 0.69 g, 4.4 mmol). As the addition proceeded, the solution darkened to green-black, 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 $[Mo(NO)_2(bpy)_2](BF_4)_2 \cdot \sim 0.75CH_2Cl_2$ was obtained as a green solid.

Anal. Calcd for $MoN_6O_2C_{20.75}H_{17.5}B_2F_8Cl_{1.5}$: C, 35.28; H, 2.48; N, 11.90. Found: C, 35.39; H, 2.67; N, 11.92. IR (Nujol mull): ν_{NO} 1816 (s), 1707 (s, br) cm^{-1}; ν_{BF} 1057 (s, br) cm^{-1}; also 1603 (m), 1503 (w), 1329 (w), 775 (m), 737 (m) cm^{-1}. IR (CH_3NO_2): ν_{NO} 1828 (s), 1727 (s) cm^{-1}; also 771 (m), 733 (m) cm^{-1}. IR (CH_3CN): ν_{NO} 1828 (s), 1727 (s) cm^{-1}; ν_{BF} 1059 (s) cm^{-1}; also 1606 (m), 750 (m), 731 (w) cm^{-1}. ^1H NMR (CD_3CN): δ 9.2–7.5 (m, 16 H), 5.44 (s, 1.6 H). Λ_M (CH_3NO_2): 191 Ω^{-1} cm^2 mol^{-1}. Mp: 194 °C dec.

The analogous reaction between $[Mo(NO)_2(CH_3NO_2)_x](BF_4)_2$ (generated by procedure C) and bpy in CH_3NO_2 afforded the same product in comparable yield.

Preparation of $[Mo(NO)_2(diphos)_2](PF_6)_2$. A stirred green suspension of $Mo(NO)_2(PF_6)_2$ (0.60 g, 1.35 mmol, prepared by procedure A) in CH_2Cl_2 (20 mL) was treated with solid $Ph_2PCH_2CH_2PPh_2$[12] (diphos, 1.07 g, 2.69 mmol), whereupon the supernatant solution became slightly darker green. The reaction mixture was refluxed for 18 h and then stirred at ambient temperature for 14 days until all

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visible traces of the nitrosyl reactant had disappeared. The final red-brown solution (displaying ν_{NO}'s at ~1800 and ~1675 cm^{-1} in its IR spectrum) was taken to dryness in vacuo, and the remaining brown oil was washed with benzene (3 × 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 × 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 $[Mo(NO)_2(diphos)_2](PF_6)_2$.

Anal. Calcd for $MoN_2O_2C_{52}H_{48}P_6F_{12}$: C, 50.24; H, 3.86; N, 2.25. Found: C, 50.00; H, 4.00; N, 2.24. IR (CH_2Cl_2): ν_{NO} 1800 (m), 1676 (s) cm^{-1}; ν_{PF} 845 (s, br) cm^{-1}; also 1593 (m), 1481 (w), 1437 (s), 1310 (m), 1127 (s, br), 1029 (m), 1000 (m) cm^{-1}. ^{1}H NMR (CD_3CN): δ 7.59–7.37 (m, 40 H, C_6H_5), 2.78 (br, 8 H, CH_2). ^{19}F NMR (CD_3CN): δ 71 (d, $J_{^{19}F-^{31}P}$ = 707 Hz). ^{31}P NMR (CD_3CN): δ −144 (sept), 38.6 (br). Mp: 150–151 °C.

On occasion, this reaction proved to be difficult to repeat reproducibly, the final brown solid isolated (mp 170 °C dec) being slightly lower in carbon and slightly higher in nitrogen content than the authentic material described above.

Preparation of $[Mo(NO)_2(OPPh_3)_4](PF_6)_2$. A stirred green suspension of $[Mo(NO)_2(CH_3NO_2)_x](PF_6)_2$ (0.5 g, ~1.1 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 × 2 mL), and dried in vacuo (5 × 10^{-3} mm) to obtain 0.40 g (46% yield based on Ph_3PO) of $[Mo(NO)_2(OPPh_3)_4](PF_6)_2$ as a lime green solid.

Anal. Calcd for $MoN_2O_6C_{72}H_{60}P_6F_{12}$: C, 55.46; H, 3.85; N, 1.80. Found: C, 55.09; H, 4.15; N, 1.63. IR (CH_3CN): ν_{NO} 1800 (s), 1680 (s) cm^{-1}; ν_{PF} 847 (s) cm^{-1}; also 1594 (w), 1125 (s), 1000 (m), 731 (s), 697 (m) cm^{-1}. ^{1}H NMR (CD_3CN): ν 7.8–7.0 (m). Mp (in air): >220 °C.

Preparation of $[Mo(NO)_2(CH_3CN)_2(OPPh_3)_2](BF_4)_2$. To a stirred green solution of $[Mo(NO)_2(CH_3CN)_4](BF_4)_2$ (3.06 g, 6.20 mmol) in CH_3CN (20 mL) was added solid $OPPh_3$ (3.00 g, 10.8 mmol). No color change in the green solution was apparent, but its IR spectrum showed a general shift of the original nitrosyl absorptions to lower frequencies (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 solution induced the formation of bright green crystals (3.10 g, 59% yield based on $OPPh_3$) of $[Mo(NO)_2(CH_3CN)_2(OPPh_3)_2](BF_4)_2$, which were collected by filtration.

Anal. Calcd for $MoN_4O_4C_{40}H_{36}P_2B_2F_8$: C, 49.59; H, 3.72; N, 5.79. Found: C, 49.33; H, 3.69; N, 5.77. IR (Nujol mull): ν_{NO} 1827 (s), 1713 (s) cm^{-1}; ν_{BF} 1056 (s, br) cm^{-1}; also 2320 (w), 2300 (w), 1143 (m), 1126 (m), 1036 (m), 766 (w), 726 (m) cm^{-1}. IR (CH_3CN): ν_{NO} 1832 (s), 1721 (s) cm^{-1}; ν_{BF} 1059 (s) cm^{-1}; also 1149 (w), 1124 (m), 733 (m) cm^{-1}. IR (CH_2Cl_2): ν_{NO} 1831 (s), 1720 (s) cm^{-1}; ν_{BF} 1067 (s, br) cm^{-1}; also 1446 (m), 1125 (s), 1049 (m), 1001 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.7–7.5 (m, 30 H), 2.22 (s, 6 H). ^{19}F NMR ($CDCl_3$): δ 147 (s). ^{31}P NMR (CD_3CN): δ 50.6 (br, 1 P), 28.8 (br, 1 P). Λ_M (CH_3NO_2): 179 Ω^{-1} cm^2 mol^{-1}. Mp: 134 °C dec.

Preparation of $[Mo(NO)_2(bpy)]_2(PF_6)_2$. A sample of $[Mo(NO)_2(CH_3NO_2)_x](PF_6)_2$ (1.0 g, ~1.5 mmol) prepared by procedure B was dissolved in CH_3CN (20 mL), and the resulting green solution was stirred at room temperature for 6 h. The solution was then cooled to 0 °C, and a stoichiometric amount of sodium amalgam (1.5 mmol of Na in 7 mL of Hg) was added dropwise over a period of 15 min. During this addition, the solution darkened from bright green to olive green, and its IR spectra revealed a shift in the nitrosyl absorptions from 1828 and 1716 cm^{-1} to 1800 and 1682 cm^{-1}. After the reaction mixture had been stirred for 1 h, the supernatant solution was filtered, and solid 2,2′-bipyridine (0.46 g, 3.0 mmol) was added to the filtrate, whereupon the color of the filtrate darkened to green-brown. The solvent was removed from the final solution in vacuo, and the solid remaining was crystallized first from CH_3NO_2–THF and then from CH_3CN–CH_2Cl_2 to obtain ultimately 0.35 g (51% yield) of $[Mo(NO)_2(bpy)]_2(PF_6)_2$ as a green-brown microcrystalline solid.

Anal. Calcd for $MoN_4O_2C_{10}H_8PF_6$: C, 26.26; H, 1.75; N, 12.25. Found: C, 26.15; H, 2.00; N, 12.40. IR (Nujol mull): ν_{NO} 1775 (s), 1639 (s, br) cm^{-1}; ν_{PF} 845 (s) 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), 768 (m), 733 (m) cm^{-1}. IR (CH_3CN): ν_{NO} 1774 (s), 1650 (s, br) cm^{-1}; ν_{PF} 850 (s) cm^{-1}; also 1602 (s), 873 (w) cm^{-1}. ^{1}H NMR (CD_3CN): δ 10.2–7.0 (m). ^{19}F NMR (CD_3CN): δ 71 (d, $J_{^{19}P-^{31}P}$ = 707 Hz). ^{31}P NMR (CD_3CN): δ −144 (sept). Mp: 208 °C dec.

Preparation of $[Mo(NO)_2(phen')]_2(PF_6)_2$. A green suspension of $[Mo(NO)_2(CH_3NO_2)_x](PF_6)_2$ (1.0 g, ~1.5 mmol, prepared by procedure B) in THF (40 mL) was treated successively with solid 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 (~2 h). The olive green supernatant solution (which displayed nitrosyl absorptions at 1780 and 1673 cm^{-1} in its IR spectrum) was removed from the final reaction mixture by syringe and was filtered through a Celite column (4 × 5 cm) supported on a medium-porosity frit. The filtrate was treated dropwise with a THF–CH_2Cl_2 solution (20 mL–10 mL) of 3,4,7,8-tetramethyl-1,10-phenanthroline (phen′, 0.64 g, 2.7 mmol) whereupon a small amount of a fine, pale yellow precipitate formed. This precipitate was removed by filtration, and solvent was evaporated from the filtrate under reduced pressure to obtain a green tar. The tar was extracted with CH_3CN (3 × 5 mL), and the extracts were taken to dryness in vacuo. Crystallization of the oily residue from CH_2Cl_2–toluene afforded 0.40 g (47% yield) of $[Mo(NO)_2(phen')]_2(PF_6)_2$ as a golden green solid, which was collected by filtration and washed with toluene (3 × 8 mL) and hexanes (3 × 8 mL) before being dried in vacuo.

Anal. Calcd for $MoN_4O_2C_{16}H_{16}PF_6$: C, 35.75; H, 2.98; N, 10.43. Found: C, 35.80; H, 3.20; N, 10.12. IR (Nujol mull): ν_{NO} 1786 (s), 1660 (s, br) cm^{-1}; ν_{PF} 845 (s) cm^{-1}; also 1530 (m), 1304 (w), 1007 (w), 740 (w), 723 (m) cm^{-1}. IR (CH_2Cl_2): ν_{NO} 1782 (s), 1661 (s, br) cm^{-1}; ν_{PF} 849 (s) cm^{-1}; also 1530 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 9.5–7.2 (m, 2 H), 3.1–0.8 (m, 12 H). ^{19}F NMR (CD_2Cl_2): δ 72 (d, $J_{^{19}F-^{31}P}$ = 707 Hz). ^{31}P NMR (CD_3NO_2): δ −146.5 (sept). Mp: 187 °C dec.

Preparation of $Mo(NO)_2(acac)_2$. A quantity of solid $[Mo(NO)_2(CH_3NO_2)_x](PF_6)_2$ (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 × 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 × 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 ^{1}H NMR (($CDCl_3$): δ 5.60 (s, 2 H), 2.20 (s, 6 H), 1.98 (s, 6 H)) spectra as $Mo(NO)_2(acac)_2$.[5,7,13]

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 $Mo(NO)(acac)_2(CH_3C(O)C(NO)C(O)CH_3)$[14] as an orange-brown solid.

Anal. Calcd for $MoN_2O_8C_{15}H_{20}$: 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) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.62 (s, 2 H), 2.23 (m, 18 H).

Reaction of $Mo(NO)_2Cl_2$ with $Na[(\eta^5\text{-}C_5H_5)W(CO)_3]$. To a green solution of $Mo(NO)_2Cl_2$ (0.50 g, 2.2 mmol) in THF (10 mL) at −78 °C was added yellow $Na[(\eta^5\text{-}C_5H_5)W(nCO)_3]$[15] (1.59 g, 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

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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}. This 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 × 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 remaining 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 $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ by its IR ((CH_2Cl_2): ν_{CO} 2010 (s), 1925 (s) cm^{-1}; ν_{NO} 1655 (s) cm^{-1}), ^1H NMR (($CDCl_3$): δ 5.60 (s, C_5H_5)) and mass spectra.[15] 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 $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ (0.43 g, 29% yield) as a red solid identifiable by its characteristic spectral properties (IR (CH_2Cl_2) ν_{CO} 1958 (s), 1910 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.33 (s, C_5H_5)).[16] Finally, elution of the column with THF produced a yellow solution (ν_{CO} at ~2070 (m), ~1970 (m), ~1940 (s), and ~1880 (m) 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 $Mo(NO)_2Cl_2$ (0.23 g, 1.0 mmol) and $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$[17] (0.43 g, 2.0 mmol) in THF (35 mL) at −78 °C revealed the disappearance of the nitrosyl absorptions at ~1795 and ~1675 cm^{-1} due to $Mo(NO)_2Cl_2$ and only the appearance of carbonyl absorptions at ~1985, ~1945, and ~1780 cm^{-1} characteristic of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (determined by comparison to the IR spectrum of an authentic sample of the dimer in THF).

Analogous reactions between $[Mo(NO)_2(CH_3NO_2)_x](PF_6)_2$ and $Na[(\eta^5\text{-}C_5H_5)W(CO)_3]$ or $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ in THF resulted in products identical with those described in the preceding paragraphs. In no case were any molybdenum-containing products isolable.

Reaction of $[Mo(NO)_2(CH_3CN)_4](PF_6)_2$ with $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$. Solid green $[Mo(NO)_2(CH_3CN)_4](PF_6)_2$ (0.31 g, 0.50 mmol) was added to a red-violet CH_2Cl_2 solution (20 mL) containing $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$[18] (0.18 g, 0.50 mmol). After being stirred for 3 days at room temperature, the reaction mixture consisted of a green-brown precipitate and a brown supernatant solution. An IR spectrum of this solution did not display the absorptions characteristic of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ but did exhibit new nitrosyl absorptions at ~1845 (s) and ~1745 (s) cm^{-1}. The final mixture was filtered, and THF (15 mL) and hexanes (10 mL) were added to the filtrate. Slow concentration of the resulting solution under reduced pressure induced the crystallization of 0.15 g (83% yield) of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(CH_3CN)]PF_6$, which was identified by its spectroscopic properties (IR (Nujol mull): ν_{NO} 1862 (s), 1757 (s) cm^{-1}; ν_{CN} 2312 (m) cm^{-1}; ν_{PF} 840 (s, br) cm^{-1}) (^1H NMR (CD_3NO_2): δ 5.97 (s, 5 H, C_5H_5), 2.40 (s, 3 H, CH_3)).[19]

Results and Discussion

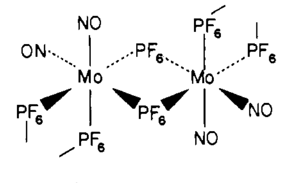
Preparation of "$[Mo(NO)_2]^{2+}$" from $Mo(CO)_6$ and $NOPF_6$. (a) In Dichloromethane. Treatment of a CH_2Cl_2 solution of $Mo(CO)_6$ with solid $NOPF_6$ in differing stoichiometries under varying, but rigorously anhydrous, experimental conditions results in the transformation

$$Mo(CO)_6 + 2NOPF_6 \xrightarrow{CH_2Cl_2} Mo(NO)_2(PF_6)_2 + 6CO \quad (4)$$

the nitrosyl-containing product precipitating from solution in moderate yields. For practical purposes, reaction 4 is best effected with a slight excess of the hexacarbonyl reactant since $NOPF_6$ is insoluble in CH_2Cl_2. In terms of its physical and chemical properties, the $Mo(NO)_2(PF_6)_2$ product resembles the well-known $Mo(NO)_2Cl_2$, which can be synthesized in a manner analogous to that depicted in eq 4, i.e.

$$Mo(CO)_6 + 2ClNO \xrightarrow{CH_2Cl_2} Mo(NO)_2Cl_2 + 6CO \quad (5)$$

Thus, $Mo(NO)_2(PF_6)_2$ is a very air-sensitive, involatile, hygroscopic, green solid (mp 110 °C dec) whose IR spectrum as a Nujol mull exhibits strong absorptions at 1811 and 1683 cm^{-1} attributable to cis-nitrosyl ligands (vs. 1805 and 1690 cm^{-1} for $Mo(NO)_2Cl_2$). Furthermore, this spectrum also does not display a strong, sharp absorption at ~840 cm^{-1}, which is characteristic of an octahedral PF_6^- anion,[20] but rather exhibits a broad band of medium intensity in this region suggestive of lowered local symmetry of the hexafluorophosphate group.[21] $Mo(NO)_2(PF_6)_2$ is insoluble in nondonor solvents such as benzene, CCl_4, $CHCl_3$, CH_2Cl_2, and alkanes. Like its chloro analogue,[11] the complex is thus best formulated as a polymer, i.e.



in which the $Mo(NO)_2^{2+}$ units are bridged by weakly ligated PF_6^- anions.[22]

In solvents with coordinating ability, the PF_6^- groups are displaced from $Mo(NO)_2(PF_6)_2$, and solvated derivatives of the $[Mo(NO)_2]^{2+}$ cation are formed, i.e.

$$Mo(NO)_2(PF_6)_2 + 4(\text{solvent}) \rightarrow [Mo(NO)_2(\text{solvent})_4](PF_6)_2 \quad (6)$$

Accordingly, the ^{19}F and ^{31}P NMR spectra of $Mo(NO)_2(PF_6)_2$ in CD_3CN only contain signals due to a PF_6^- anion having O_h symmetry, i.e. δ 72 (d, $J_{^{19}F-^{31}P}$ = 707 Hz)[9] and δ −144 (sept, $J_{^{31}P-^{19}F}$ = 707 Hz),[24] respectively. This solution, which contains $[Mo(NO)_2(CD_3CN)_4](PF_6)_2$ (vide infra), must be maintained under an inert atmosphere since the PF_6^- anions are readily hydrolyzed to $O_2PF_2^-$. Hence, exposure of the solution to moist air results in the doublet due to the PF_6^- anions in the ^{19}F NMR spectrum gradually diminishing in intensity and a new doublet due to $O_2PF_2^-$ appearing at δ 82 ($J_{^{19}F-^{31}P}$ = 957 Hz)[25] in addition to a broad resonance at δ 160. These observations are indicative of the pronounced electrophilic nature of the $[Mo(NO)_2(CD_3CN)_4]^{2+}$ cation since the hydrolysis of PF_6^- is known to be facilitated by hard Lewis acids.[26,27] Indeed, this electrophilicity of $[M(NO)_2(CH_3CN)_4]^{2+}$ (M = Mo or W) species has been recently exploited by Sen and Thomas during catalysis of the polymerization, oligomerization, and rearrangement of certain olefins.[28]

In a similar manner, if water is not completely excluded during the performance of reaction 4, the final isolated product is not $Mo(NO)_2(PF_6)_2$ but rather $Mo(NO)_2(O_2PF_2)_2$. This

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(20) Dolphin, D.; Wick, A. E. "Tabulation of Infrared Spectral Data"; Wiley-Interscience: New York, 1977; p 488.

(21) IR spectra of $Mo(NO)_2(PF_6)_2$ as a Nujol mull always display absorptions (e.g. at 1265, 1154, and 948 cm^{-1}) that reflect partial hydrolysis of the PF_6 groups to O_2PF_2 groups.

(22) PF_6^- functions as a weakly coordinated, monodentate ligand in $(\eta^5\text{-}C_5H_5)Cr(NO)_2PF_6$[19] and $(\eta^5\text{-}C_5H_5)Mo(CO)_3PF_6$.[23]

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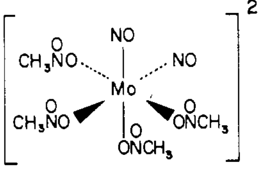
difluorophosphate complex resembles quite closely its PF_6^- analogue in terms of its physical appearance and solubility properties, but it does not show any noticeable decomposition when heated under an N_2 atmosphere to 220 °C. Its IR spectrum (Nujol mull) confirms the existence of cis-nitrosyl ligands (ν_{NO} 1821 (s), 1693 (s, br) cm^{-1}) and O_2PF_2 groups (ν_{PO_2}(as) 1265 cm^{-1}, ν_{PO_2}(s) 1163 cm^{-1}, ν_{PF_2}(as) 955 cm^{-1}, ν_{PF_2}(s) 901 cm^{-1}). These vibrational data for the O_2PF_2 groups are most consistent with the difluorophosphate ligands being coordinated in a bidentate fashion[29] to either one or two molybdenum centers. Solutions of the complex in CD_3CN exhibit ^{19}F (δ 82 (d, $J_{^{19}F-^{31}P}$ = 957 Hz)) and ^{31}P (δ −17.9 (t)) NMR signals readily attributable to the O_2PF_2 groups.

(b) In Nitromethane. When a suspension of $Mo(CO)_6$ in CH_3NO_2 is treated dropwise with a CH_3NO_2 solution containing 2 equiv of $NOPF_6$, a series of sequential substitution reactions occurs. In this case, the product complexes are soluble, and the progress of these conversions can thus be conveniently monitored by solution IR spectroscopy. Such monitoring indicates the intermediacy of several carbonylnitrosyl complexes,[30] i.e.

$$Mo(CO)_6 \xrightarrow[CH_3NO_2]{NO^+} [Mo(CO)_{5-n}(NO)(CH_3NO_2)_n]^+ \xrightarrow[CH_3NO_2]{NO^+} [Mo(CO)_{4-n}(NO)_2(CH_3NO_2)_n]^{2+} \xrightarrow[CH_3NO_2]{} [Mo(NO)_2(CH_3NO_2)_4]^{2+}$$

but the only species that persists in solution is $[Mo(NO)_2(CH_3NO_2)_4]^{2+}$, which can be conveniently isolated as its PF_6^- salt in 61% yield. $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$ is a hygroscopic, green solid that decomposes when heated to 88 °C. Its IR spectrum as a Nujol mull (ν_{NO} 1853 (s), 1743 (s, br) cm^{-1}; ν_{PF} 843 (s, br) cm^{-1}) is consistent with its formulation as a salt and with the dication possessing the octahedral structure



This formulation is also supported by the fact that CH_3NO_2 solutions of the complex exhibit a molar conductance of 202 Ω^{-1} cm^2 mol^{-1}, a value which is in the range associated with 1:2 electrolytes.[31] However, the CH_3NO_2 ligands of the cation are again only weakly coordinated (probably via a single oxygen atom in a monodentate fashion) to the $[Mo(NO)_2]^{2+}$ entity as evidenced by the fact that the complex slowly loses CH_3NO_2 when subjected to vacuum (5 × 10^{-3} mm) at ambient temperatures. Not surprisingly, therefore, dissolution of $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$ in a solvent having a better donor ability than nitromethane such as CH_3CN[8] results in the reaction

$$[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2 + 4CH_3CN \rightarrow [Mo(NO)_2(CH_3CN)_4](PF_6)_2 + 4CH_3NO_2 \quad (7)$$

A ^1H NMR spectrum of the complex dissolved in CD_3CN thus displays a singlet at δ 4.34 due to the liberated CH_3NO_2, while ^{19}F and ^{31}P NMR spectra contain the signals characteristic of octahedral PF_6^- (vide supra). As discussed above, these solutions of the complex are very moisture sensitive.

Preparation of "$[Mo(NO)_2]^{2+}$" from $Mo(NO)_2Cl_2$ and $AgBF_4$. (a) In Nitromethane. Abstraction of chloride from $Mo(NO)_2Cl_2$ by 2 equiv of $AgBF_4$ in CH_3NO_2, i.e.

$$Mo(NO)_2Cl_2 + 2AgBF_4 \xrightarrow{CH_3NO_2} [Mo(NO)_2(CH_3NO_2)_4](BF_4)_2 + 2AgCl\downarrow \quad (8)$$

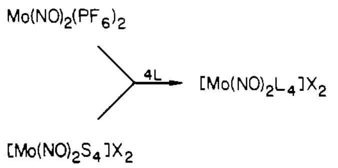
is complete at ambient temperatures in 2 h as judged by IR spectroscopy. Interestingly, it has previously been reported[7] that the related reaction in CH_3CN (eq 3) requires reflux conditions to go to completion. The properties of the soluble product resulting from reaction 8 closely resemble those exibited by its PF_6^- analogue (vide supra).

(b) In Tetrahydrofuran. Chloride abstraction also occurs readily in THF at room temperature, i.e.

$$Mo(NO)_2Cl_2 + 2AgBF_4 \xrightarrow{THF} [Mo(NO)_2(THF)_4](BF_4)_2 + 2AgCl\downarrow \quad (9)$$

but in this solvent there is no change evident in the nitrosyl absorptions in the IR spectrum of the reaction mixture as the conversion proceeds. Consequently, reaction 9 is judged to be complete in 2 h since after that interval no further precipitation of AgCl occurs. The $[Mo(NO)_2(THF)_4]^{2+}$ cation[32] generated in this fashion has not been isolated but has been employed in situ during subsequent reactions (vide infra). In this connection, it should be noted that THF is not generally the solvent of choice for conversions involving the various cationic dinitrosylmolybdenum complexes as reactants, particularly if the conversions require several hours at room temperature to reach completion. All the $Mo(NO)_2^{2+}$-containing salts when dissolved in THF are sufficiently electrophilic to initiate the polymerization of the solvent, a process that is believed to occur only by a cationic ring-opening mechanism with the propagating species being a tertiary oxonium ion.[33] This polymerization is readily evident after a few hours at ambient temperatures as the green THF solutions, presumably all containing $[Mo(NO)_2(THF)_4]^{2+}$, become quite viscous and in some instances form gels. The possibility that the polymerization process is being induced by dissociated NO^+ [33] can be excluded since the various $Mo(NO)_2^{2+}$-containing complexes do not function as nitrosylating agents in donor solvents. For instance, treatment of a CH_3CN solution of $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$ under reflux conditions with $(\eta^5-C_5H_5)Mo(CO)_2(NO)$ or $(\eta^5-C_5H_4Me)Mn(CO)_3$ does not result in the formation of any nitrosyl products even though the carbonyl complexes can both be readily nitrosylated by $NOPF_6$.[34,35]

Reactivity of "$[Mo(NO)_2]^{2+}$". (a) With Neutral Lewis Bases. In a manner analogous to that shown in eq 6 and 7, the cationic dinitrosylmolybdenum complexes readily incorporate relatively hard and strong Lewis bases into the metal's coordination sphere, i.e.



$$Mo(NO)_2(PF_6)_2 \text{ or } [Mo(NO)_2S_4]X_2 \xrightarrow{4L} [Mo(NO)_2L_4]X_2 \quad (10)$$

($X = PF_6^-$ or BF_4^-)

where S = a solvent such as CH_3NO_2, THF, or CH_3CN and

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[30] Treatment of $W(CO)_6$ or $W(CO)_3(CH_3CN)_3$ with $NOPF_6$ in CH_3CN produces *cis*-$[W(NO)_2(CO)(CH_3CN)_3](PF_6)_2$.[5,13]

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[32] The presence of four coordinated THF molecules in $[Mo(NO)_2(THF)_4]^{2+}$ is assumed by analogy to the related CH_3CN- and CH_3NO_2-containing dications, which have been isolated.

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[35] Connelly, N. G. *Inorg. Synth.* **1974**, *15*, 91.

L = a monodentate ligand such as CH_3CN or $OPPh_3$ or L_2 = a bidentate ligand such as 2,2′-bipyridine (bpy) or $Ph_2PCH_2CH_2PPh_2$ (diphos), thereby reflecting the relatively hard acidic nature of the molybdenum center in the cations. The extent of incorporation is determined largely by the relative donor abilities of S and L. Of the $[Mo(NO)_2L_4]X_2$ complexes isolated from reactions of type 10, only $[Mo(NO)_2(CH_3CN)_4]X_2$[5,7,13] and $[Mo(NO)_2(bpy)_2](PF_6)_2$[7,13] have been described previously. They are generally green, hygroscopic solids that are only freely soluble in strongly solvating solvents such as CH_3CN or CH_3NO_2. The spectroscopic properties of these salts both in the solid state and in solution are consistent with their possessing octahedral *cis*-dinitrosyl cations and normal, uncoordinated anions. Particular features of the individual complexes that are worthy of note include the following:

(1) The molar conductances of $[Mo(NO)_2(bpy)_2](BF_4)_2$ and $[Mo(NO)_2(OPPh_3)_2(CH_3CN)_2](BF_4)_2$ in CH_3NO_2 are 191 and 179 Ω^{-1} cm^2 mol^{-1}, respectively, as expected for 1:2 electrolytes.[31]

(2) $[Mo(NO)_2(diphos)_2](PF_6)_2$ is unique among the $[Mo(NO)_2L_4]X_2$ complexes isolated during this work in that it is a brown solid. Its ^{31}P NMR spectrum in CD_3CN contains the usual septet at δ −144 characteristic of octahedral PF_6^- and a broad signal at δ 38.6, which can be assigned to the inequivalent phosphorus atoms of the diphos ligands.[36,37] Interestingly, other synthetic routes that might reasonably be expected to lead to the $[Mo(NO)_2(diphos)_2]^{2+}$ cation apparently do not.[36,38]

(b) With Sodium Amalgam. Both $Mo(NO)_2(PF_6)_2$ and $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$ are reduced by 1 equiv of sodium amalgam in THF or CH_3CN, the reduction being accompanied by a shift to lower energy of the characteristic nitrosyl absorptions in the IR spectra of the reaction mixtures. The product complexes prove to be unisolable as such, but they can be derivatized by the addition of the hard Lewis bases 2,2′-bipyridine (bpy) or 3,4,7,8-tetramethyl-1,10-phenanthroline (phen′). In this manner, new complexes having the empirical composition $[Mo(NO)_2L_2]PF_6$ are formed via the sequential transformations

$$[Mo(NO)_2S_4](PF_6)_2 + Na/Hg \xrightarrow{S} [Mo(NO)_2S_n]PF_6 + NaPF_6 \xrightarrow{+L_2} [Mo(NO)_2L_2]PF_6 + nS \quad (11)$$

where S = THF or CH_3CN and L_2 = bpy or phen′. Both $[Mo(NO)_2L_2]PF_6$ complexes are isolable in yields of ~50% and have similar physical properties. They are greenish, air-stable solids whose solubilities resemble those displayed by the $[Mo(NO)_2L_4]X_2$ salts (vide supra) and whose spectroscopic properties again indicate the presence of cis-nitrosyl ligands and uncoordinated anions.[39] Nitromethane solutions of the complexes (10^{-3}–10^{-4} M) do not exhibit ESR signals at ambient temperatures but do afford conductance data that, when treated in the manner described by Feltham and Hayter[10] (see Figures 1 and 2), produce slopes for the plots of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ in the range expected for 1:2 electrolytes. These observations suggest that these compounds are thus best formulated as $[Mo(NO)_2L_2]_2(PF_6)_2$, but on the basis of the presently available data no conclusions concerning the molecular structures of these bimetallic cations may be drawn with certainty.

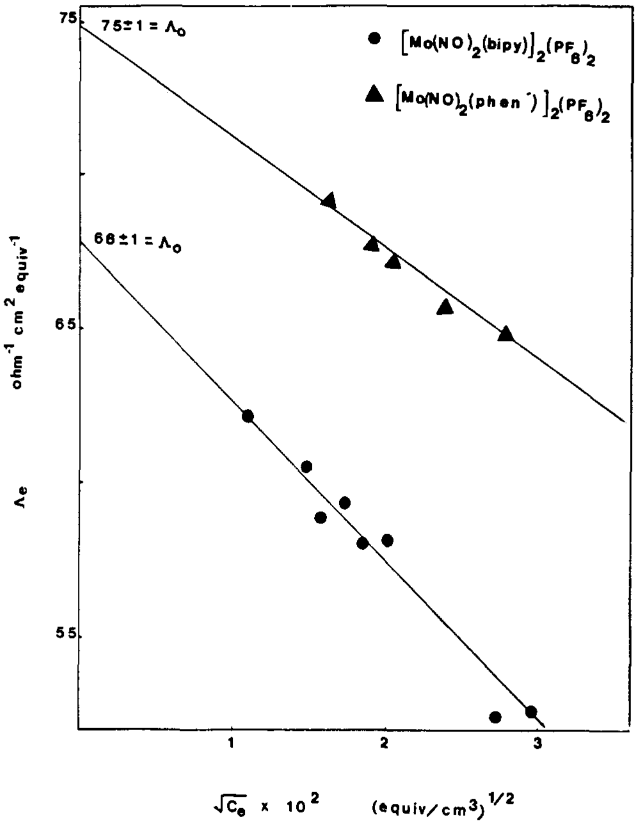

Figure 1. Plots of equivalent conductance vs. concentration for two $[Mo(NO)_2L_2]_2(PF_6)_2$ complexes.

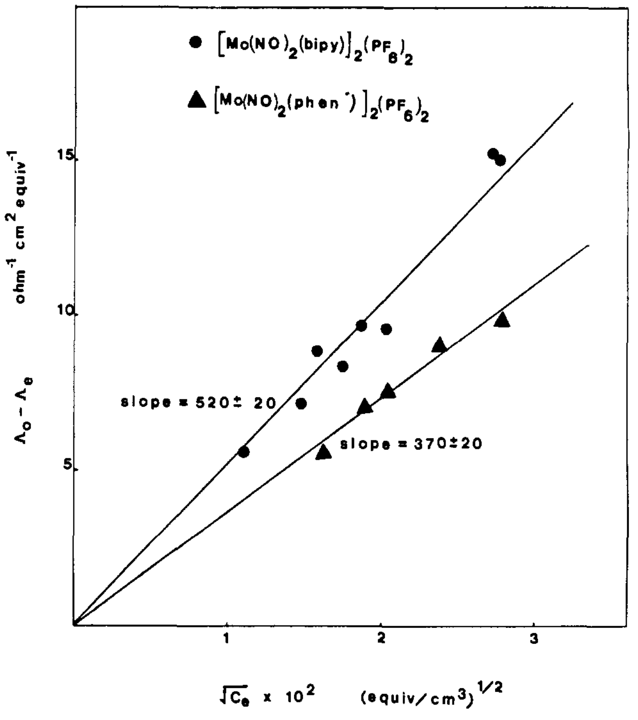

Figure 2. Plots of corrected equivalent conductance vs. concentration for two $[Mo(NO)_2L_2]_2(PF_6)_2$ complexes.

Identical products are obtained if $Li[Et_3BH]$ (at −78 °C) or $Na[Ph_2CO]$ is employed as the stoichiometric reducing agent in place of Na/Hg when conversions 11 are effected in THF. Interestingly, if a large excess of L_2 is added to the solutions containing the initial reduction products, small amounts of white solids precipitate. These hygroscopic solids appear to be slightly impure $[Mo(L_2)_3]PF_6$ complexes, and their isolation indicates that the nitrosyl ligands are labilized

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(36) Tatsumi, T.; Sekizawa, K.; Tominaga, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2297.

(37) George, T. A.; Seibold, C. D. *Inorg. Chem.* **1973**, *12*, 2548.

(38) Kan, C. T.; Hitchcock, P. B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1982**, 79.

(39) The ^1H NMR spectra of the $[Mo(NO)_2L_2]PF_6$ salts consist of a myriad of broad resonances, which are singularly uninformative.

by electron transfer to the initial dicationic reactant. Similarly, all attempts to produce a neutral molybdenum nitrosyl complex by treating $Mo(NO)_2(PF_6)_2$ or $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$ with 2 equiv of a reducing agent have resulted in failure. Although the changes in physical properties accompanying these attempted reductions are initially encouraging, e.g.

$$\begin{array}{ccccc} [Mo(NO)_2S_4]^{2+} & \xrightarrow{e^-} & \text{“}[Mo(NO)_2S_n]^{+}\text{”} & \xrightarrow{e^-} & \text{“}[Mo(NO)_2]\text{”} \\ \text{bright green} & & \text{olive green} & & \text{brown} \\ \sim 1790, \sim 1680 & & \sim 1780, \sim 1675 & & \sim 1775, \sim 1665 \end{array} \qquad (12)$$

(where the solution color and IR ν(NO) (THF, cm^{-1}) are given directly below the species), the final brown product gradually decomposes in solution (THF or CH_3CN) to a nitrosyl-free species even in the presence of added Lewis bases such as bpy or phen′.

(c) With Anionic Reagents. When treated with anionic reagents, the various $Mo(NO)_2^{2+}$-containing salts engage in either simple substitution or redox reactions. Anions that are not readily oxidized are incorporated into the coordination sphere of the molybdenum atom in the manner summarized in eq 10. Thus, treatment of $[Mo(NO)_2S_4](PF_6)_2$ (S = CH_3CN or CH_3NO_2) with acetylacetone (acacH) in the presence of Na_2CO_3 affords the well-known[5,7,13] green *cis*-$Mo(NO)_2(acac)_2$ complex as the major product. A minor product (25% yield) formed during the reaction when S = CH_3NO_2 is orange-brown $Mo(NO)(acac)_2(CH_3C(O)C(NO)C(O)CH_3)$,[14] which probably results from nucleophilic attack of $acac^-$ on the nitrogen atom of a nitrosyl ligand in the dicationic reactant.

Anions that are more potent reductants simply effect reduction of the cationic dinitrosylmolybdenum complexes in the manner depicted in eq 12. For instance, 2 equiv of $Na[C_5H_5]$ or $Na[C_5H_4Me]$ or 1 equiv of $K_2[C_8H_8]$ consumes completely $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$ or $Mo(NO)_2Cl_2$ in THF, but no organometallic nitrosyl complexes result as products. Similarly, 2 equiv of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ or $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-$ is oxidized by $Mo(NO)_2Cl_2$ or $[Mo(NO)_2(THF)_4](PF_6)_2$ in THF at −78 °C to their respective carbonyl dimer, i.e. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ or $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$. In no case are any molybdenum-containing products isolable.[40] On occasion, these oxidizing properties of the $Mo(NO)_2^{2+}$-containing species are also manifested during their reactions with neutral organometallic complexes. Thus, an equimolar mixture of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $[Mo(NO)_2(CH_3CN)_4](PF_6)_2$ in CH_2Cl_2 at room temperature ultimately results in the virtually quantitative production of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(CH_3CN)]PF_6$ as the only isolable nitrosyl complex.

Summary. This work has shown that dinitrosylmolybdenum dications are hard and strong Lewis acids that prefer to coordinate hard Lewis bases, L, capable of good σ donation. The resulting *cis*-$[Mo(NO)_2L_4]^{2+}$ cations are quite electrophilic and facilitate both the hydrolysis of PF_6^- and the polymerization of THF. Furthermore, they undergo stoichiometric reduction by a variety of reducing agents to the bimetallic $[Mo(NO)_2L_2]_2^{2+}$ cations. Further reduction does not afford neutral nitrosyl complexes but rather leads to loss of the NO ligands. The tendency of the *cis*-$[Mo(NO)_2L_4]^{2+}$ cations to function as oxidizing agents is also evident during their reactions with some neutral or anionic reagents.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of a grant to P.L. (Grant A5885) and to The University of British Columbia for the award of a University Graduate Fellowship to J.C.O.

Note Added in Proof. The syntheses of cationic dinitrosylmolybdenum complexes similar to those described in this paper have been recently reported: Ballivet-Tkatchenko, D.; Bremard, C. *J. Chem. Soc., Dalton Trans.* **1983**, 1143.

Registry No. $Mo(CO)_6$, 13939-06-5; $Mo(NO)_2(PF_6)_2$, 88887-81-4; $Mo(NO)_2(O_2PF_2)_2$, 88887-64-3; $[Mo(NO)_2(CH_3NO_2)_4](PF_6)_2$, 88887-66-5; $Mo(NO)_2Cl_2$, 44513-97-5; $[Mo(NO)_2(CH_3NO_2)_4](BF_4)_2$, 88887-67-6; $[Mo(NO)_2(CH_3CN)_4](PF_6)_2$, 39797-76-7; $[Mo(NO)_2(bpy)_2](PF_6)_2$, 88082-00-2; $[Mo(NO)_2(bpy)_2](BF_4)_2$, 88081-01-0; $[Mo(NO)_2(THF)_4](BF_4)_2$, 88887-69-8; $[Mo(NO)_2(diphos)_2](PF_6)_2$, 88887-71-2; $[Mo(NO)_2(OPPh_3)_4](PF_6)_2$, 88887-73-4; $[Mo(NO)_2(CH_3CN)_2(OPPh_3)_2](BF_4)_2$, 88887-75-6; $[Mo(NO)_2(CH_3CN)_4](BF_4)_2$, 82583-10-6; $[Mo(NO)_2(bpy)]PF_6$, 88887-77-8; $[Mo(NO)_2(phen')]PF_6$, 88887-79-0; $Mo(NO)_2(acac)_2$, 39797-78-9; $Mo(NO)(acac)_2(CH_3C(O)C(NO)C(O)CH_3)$, 77348-67-5; $Na[(\eta^5\text{-}C_5H_5)W(CO)_3]$, 12107-36-7; $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$, 12128-14-2; $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$, 12091-65-5; $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, 60039-75-0; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 38117-54-3; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, 66649-16-9; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(CH_3CN)]PF_6$, 74924-59-7; PF_6^-, 16919-18-9; THF, 109-99-9.

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[40] A minor product (4% yield) formed during the reactions involving $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-$ is $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$, which probably results from redistribution of the ligands in the substitution product, $Mo(NO)_2[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$.[41]

[41] Cf.: Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1979**, *18*, 1250.