15 mL and cooled to 0 °C. A solution of $(Ph_3P)_2C$ (1.096 g, 2.042 mmol) dissolved in 50–55 mL of THF is then added dropwise to the cold, stirring $Me_3Pt^{IV}$ solution over 65 min. The reaction mixture rapidly turns orange and then turbid as the phosphonium salt begins to precipitate. As the rest of the ylide is added, the suspension gradually deepens to red-orange. After the solution has stirred at 0 °C for 9 h, the white solid is filtered out and washed once with THF by back-distillation under reduced pressure. The vacuum-dried solid weighs 0.497 g (108% as $[HC(PPh_3)_2][PF_6]$; 97% as $[HC(PPh_3)_2][PF_6]\cdot THF$). The compound is identified by its KBr pellet infrared spectrum (identical with that of known samples). The phosphonium salt crystallizes with 1 mol of solvent as evidenced by $^1H$ NMR; the higher field THF multiplet obscures the triplet produced by the proton on the $\alpha$-carbon atom of the phosphonium salt.

The blood red filtrate is vacuum-evaporated, and the residue kept under vacuum for 15 min at room temperature. Dry $C_6H_6$ (100 mL) is then added; most of the residue dissolves to give a dark red solution. The mixture is stirred for 20 min and filtered through a medium frit, the gummy-looking residue being washed twice with benzene by distillation. The filtrate is vacuum-evaporated to give a dark red solid which slowly fades to orange under vacuum (15 min, 20 °C, $10^{-2}$ torr) (0.908 g (98%)), mp 122–124 °C dec (foams, sealed tube). Anal. Calcd for $C_{79}H_{68}OP_4Pt$: C, 70.16; H, 5.07; P, 9.16. Found: C, 69.86; H, 5.27; P, 10.41.[38] $^1H$ NMR ($C_6D_6$): $\delta$ 1.49 (m (THF)), 1.69–1.93 (small peaks (THF + impurity)), 2.32 (m, broadish (tolyl methyl)), 3.39 (s, small (THF)), 3.62 (m (THF)), 7.06 (m, major (meta and para aromatics)), 7.48 (m, minor (ortho aromatics of impurity)), 7.89 (m, major (ortho aromatics)). Molecular weight: calcd, 1352.41; found, 577 (43%), 763 (56%). For further details, see text.

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**Registry No.** **3**, 68843-05-0; **4**, 68843-06-1; **5**, 68843-07-2; $[(^{13}CH_3)(CH_3)_2PtI]_4$, 68843-08-3; (COD)$PtMe_2$, 12266-92-1; $[Me_3Pt(OSO_2CF_3)]_4$, 68950-86-7; $[HC(PPh_3)_2]PF_6$, 54807-61-3; $Ph_3P{=}C{=}PPh_3$, 7533-52-0; $[Me_3Pt(py)_3][OSO_2CF_3]$, 68833-46-5.

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# Complex Halides of the Transition Metals. 27.[1] Reactions of Nitric Oxide with Molybdenum(II) Dimers Containing Metal–Metal Quadruple Bonds. A New Route to Monomeric Dinitrosyl Derivatives of Molybdenum

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Nitric oxide reacts with the metal–metal bonded dimers $Mo_2X_4L_4$, where X = Cl or Br and L = $PEtPh_2$, $PEt_3$, or P-*n*-$Bu_3$, and $Mo_2X_4(LL)_2$, where X = Cl or NCS and LL = 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm) in dichloromethane to afford the dinitrosyls of molybdenum, $Mo(NO)_2X_2L_2$ and $Mo(NO)_2X_2(LL)$. The cleavage of the Mo–Mo quadruple bond of the starting materials is contrasted with the reaction of carbon monoxide with the rhenium(II) dimers $Re_2X_4(PR_3)_4$ to produce *trans*-$Re(CO)_2X_2(PR_3)_2$ and the lack of reactivity of $Mo_2X_4(PR_3)_4$ toward this same ligand.

## Introduction

We have recently investigated the reactivity of the metal–metal bonded dimers $Re_2X_4(PR_3)_4$, where X = Cl or Br and R = Et or *n*-Pr, toward carbon monoxide.[2,3] One of the most significant results of these studies was the synthesis of a new class of carbonyl derivatives of rhenium(II), the paramagnetic 17-electron monomers *trans*-$ReX_2(CO)_2(PR_3)_2$. In contrast, complexes of the types $Re_2Cl_6(PR_3)_2$ and

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$Mo_2Cl_4(PR_3)_4$, which possess metal–metal quadruple rather than triple bonds, do not react with CO.[2,3]

In view of these observations and because of our continuing interest in exploring those conditions under which metal–metal multiple bonds are changed or completely disrupted, it was appropriate for us to examine the effect of nitric oxide on molybdenum halide complexes, such as $Mo_2Cl_4(PR_3)_4$ and other closely related species, containing metal–metal quadruple bonds. If the Mo–Mo bonds were to be broken, then we were interested in the possibility of establishing a general procedure for the synthesis of complexes of the type $Mo(NO)_2X_2(PR_3)_2$. One of the important features of these species is their use as homogeneous catalysts for alkene metathesis (olefin disproportionation) reactions.[4-6]

In the present article we describe details of our investigations into the reactions of nitric oxide with dimers of the type $Mo_2X_4L_4$, where X = Cl, Br, or NCS and L represents a tertiary phosphine ligand. Both monodentate phosphines and the bidentates 1,2-bis(diphenylphosphino)ethane (abbreviated dppe) and bis(diphenylphosphino)methane (abbreviated dppm) were used in this study.

## Experimental Section

**Starting Materials.** The molybdenum dimers $Mo_2Cl_4(PEt_3)_4$, $Mo_2Cl_4(PEtPh_2)_4$, $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$, $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_4$, $Mo_2Cl_4(dppm)_2$, $Mo_2(NCS)_4(PEt_3)_4$, $Mo_2(NCS)_4(dppm)_2$, and $Mo_2(NCS)_4(dppe)_2$ were prepared by standard literature procedures.[7-10] $Mo_2Br_4(PEtPh_2)_4$ was synthesized using the sequence $Cs_3Mo_2Br_8H \rightarrow Mo_2Br_4(py)_4 \rightarrow Mo_2Br_4(PEtPh_2)_4$, as described by San Filippo et al.[9] to prepare the analogous complex $Mo_2Br_4(P\text{-}n\text{-}Bu_3)_4$. All solvents (analytical grade) and other reagents were obtained from commercial sources. Nitric oxide (Matheson) was purified by passing over NaOH pellets to remove nitrogen dioxide and then dried by passing through concentrated sulfuric acid. Solvents were thoroughly deoxygenated and dried over molecular sieves before use.

**General Reaction Procedure.** The apparatus employed consisted of a three-necked 100-mL round-bottom flask equipped with a Teflon-coated magnetic stirring bar. The central joint of the reaction vessel was fitted with a reflux condenser, and a second neck was capped with a rubber serum cap. The third joint was fitted with a bubbler tube to allow for entry of gases ($N_2$ or NO). The appropriate molybdenum starting material was placed in the flask and the apparatus was swept with dry nitrogen gas. This was followed by the introduction of dry deoxygenated dichloromethane through the rubber serum cap by means of a syringe. Nitric oxide was then passed through the stirred reaction solution at room temperature for 1–2 h. During this time a noticeable change in the solution color occurred. The system was again flushed with nitrogen, and the resulting solution was evaporated to a small volume (5–10 mL). Different workup procedures were then followed to isolate the nitrosyl-containing solid compounds (see later). The products were dried in vacuo for several hours and then stored under nitrogen in a refrigerator prior to their use.

**A. Reactions of Complexes of the Types $Mo_2X_4L_4$ and $Mo_2X_4(LL)_2$, Where X = Cl, Br, or NCS, L = $PEt_3$, P-*n*-$Bu_3$, or $PEtPh_2$, and LL = dppe or dppm. (i) $Mo(NO)_2Br_2(PEtPh_2)_2$.** $Mo_2Br_4(PEtPh_2)_4$ (0.40 g) was dissolved in dichloromethane (50 mL), and nitric oxide was passed through the solution for 1.5 h. The color of the reaction mixture changed from deep purple to green during this period. A major portion of the solvent was removed by rotary evaporation and the remaining solution was filtered to remove a very small amount of an unidentified brown solid. Ethanol (15 mL) was added to the filtrate and the cloudy solution was allowed to stand at 0 °C for 4 days. The bright green crystals of the nitrosyl complex which separated were filtered off, washed with ethanol, and then dried in vacuo; yield 0.10 g. Anal. Calcd for $C_{28}H_{30}Br_2MoN_2O_2P_2$: C, 45.20; H, 4.03; Br, 21.48. Found: C, 45.49; H, 4.14; Br, 21.70.

**(ii) $Mo(NO)_2Cl_2(PEtPh_2)_2{\cdot}0.5CH_2Cl_2$.** This complex was obtained following essentially the same procedure as that described for $Mo(NO)_2Br_2(PEtPh_2)_2$. Using 0.25 g of $Mo_2Cl_4(PEtPh_2)_4$ in 25 mL of dichloromethane, we isolated a crop of bright green crystals; yield ~0.08 g. Anal. Calcd for $C_{28.5}H_{31}Cl_3MoN_2O_2P_2$: C, 49.07; H, 4.44; Cl, 15.24; mol wt 697.5. Found: C, 48.63; H, 4.70; Cl, 15.30; mol wt (acetone) 690.

**(iii) $Mo(NO)_2Cl_2(PEt_3)_2{\cdot}0.25C_6H_{14}$.** The deep blue solution that was produced upon dissolving $Mo_2Cl_4(PEt_3)_4$ (0.35 g) in dichloromethane (40 mL) was treated with nitric oxide in the usual way for 1 h. The resulting brown-green solution was evaporated to ~5 mL. Thin-layer chromatography (TLC) using silica gel adsorbent showed the presence of more than one component in this reaction mixture. Attempts to precipitate a solid product either by the addition of such solvents as ethanol, ether, or hexane and cooling to 0 °C or by evaporation of the initial dichloromethane reaction solvent were unsuccessful, and a green oil was invariably obtained. Accordingly, it was necessary to resort to chromatography to isolate any crystalline reaction products.

A glass column (30 × 2 cm) was packed under a nitrogen atmosphere with 60–200 mesh silica gel and dichloromethane. The concentrated reaction solution (5 mL) was placed on top of the column and the elution process with dichloromethane was commenced. The first fraction that came off the column (50 mL) was colorless and was discarded. This was followed by a bright green eluent (130 mL) containing the molybdenum–nitrosyl complex. The dichloromethane solvent was evaporated under vacuum to afford a green oil which was redissolved in hexane. This solution was then evaporated at room temperature in a nitrogen atmosphere to afford soft, waxy green needles; yield 0.08 g. Attempts to "dry" these crystals under vacuum failed to change their nature. When warmed, they reverted to an oil and failed to sublime. Microanalytical data were always consistent with a complex containing a small amount of "lattice" hexane. Anal. Calcd for $C_{13.5}H_{33.5}Cl_2MoN_2O_2P_2$: C, 33.47; H, 6.91; Cl, 14.63. Found: C, 33.78; H, 6.90; Cl, 14.11.

**(iv) $Mo(NO)_2Cl_2(P\text{-}n\text{-}Bu_3)_2$.** The dark blue solution which was formed upon dissolving $Mo_2Cl_4(P\text{-}n\text{-}Bu_3)_2$ (0.4 g) in dichloromethane (40 mL) was reacted with nitric oxide for 2 h. The brown solution which resulted was evaporated to afford a dark brown oil which was found (by TLC) to contain more than one component.

A column was prepared as in (iii) by using silica gel and carbon tetrachloride. The oily reaction residue was dissolved in a small volume of carbon tetrachloride (~6 mL) and was then placed on the column. A yellow-green fraction was eluted with carbon tetrachloride and then evaporated in vacuo to afford a green oil. This oil was dried in vacuo for 12 h, by which time it had crystallized into a waxy solid which resembled closely the triethylphosphine complex $Mo(NO)_2Cl_2(PEt_3)_2$ in appearance; yield ~0.1 g. Anal. Calcd for $C_{24}H_{54}Cl_2MoN_2O_2P_2$: C, 45.65; H, 8.62; Cl, 11.23. Found: C, 45.44; H, 8.37; Cl, 11.08.

Other components of the original oily reaction mixture were eluted using toluene, a toluene–chloroform mixture, and chloroform, but our attempts to isolate solid characterizable products were unsuccessful and only unidentifiable tarry materials could be obtained. However, their infrared spectra did show the presence of coordinated NO.

**(v) $Mo(NO)_2Cl_2(dppm)$.** The action of nitric oxide on a dichloromethane solution (75 mL) of $Mo_2Cl_4(dppm)_2$ (0.60 g) effected a color change from blue-green to green-brown. After a reaction time of 1.5 h, the resulting reaction solution was concentrated to a small volume (10 mL) and then filtered into ice-cold pentane. The yellow solid which precipitated was filtered off, washed with pentane, and then dried; yield 0.5 g. Its infrared spectrum showed a broad NO stretching frequency at ~1600 $cm^{-1}$ which was accompanied by a shoulder, thus suggesting the presence of more than one component in this product.

A quantity of this yellow product (0.40 g) was dissolved in dichloromethane (10 mL) and then placed on a silica-gel column. The column was first eluted with dichloromethane and the resulting orange solution (~100 mL) was evaporated to a very small volume and then filtered into ice-cold pentane. The small quantity (~0.05 g) of the orange-brown solid which separated was collected and dried. The presence of one $\nu$(NO) band in its infrared spectrum at 1660 $cm^{-1}$, together with microanalytical data, supported its formulation as the mononitrosyl complex[11] $Mo(NO)Cl_3(dppm){\cdot}0.5C_5H_{12}$. Anal. Calcd for $C_{27.5}H_{28}Cl_3MoNOP_2$: C, 50.38; H, 4.27. Found: C, 50.30; H, 3.98.

The green band remaining on the column was eluted with chloroform–ethanol (50:1). The volume of the yellow-green fraction (~100 mL) was reduced under vacuum to ~8 mL. Filtration into ice-cold pentane afforded the yellow-green complex $Mo(NO)_2Cl_2(dppm)$ which was collected and washed with pentane prior to drying; yield 0.1 g. Anal. Calcd for $C_{25}H_{22}Cl_2MoN_2O_2P_2$: C, 48.94; H, 3.59; Cl, 11.56; mol wt 613. Found: C, 48.58; H, 3.77; Cl, 11.63; mol wt (acetone) 592.

Table I. Spectral Properties of Dinitrosyl Complexes of Molybdenum

| complex | medium[a] | electronic abs max (1200–400 nm) | IR spectra $\nu$(NO), cm$^{-1}$ | | binding energies,[b] eV | |
|---|---|---|---|---|---|---|
| | | | Nujol | $CH_2Cl_2$ | Mo $3d_{3/2,5/2}$ | N 1s |
| $Mo(NO)_2Br_2(PEtPh_2)_2$ | DR | 650 m, 460 vs | 1795, 1677 | 1797, 1685 | 233.1, 229.9 (1.2) | 401.6 |
| $Mo(NO)_2Cl_2(PEtPh_2)_2 \cdot 0.5CH_2Cl_2$ | DR | 645 m, 455 vs | 1785, 1693 | 1795, 1683 | 233.4, 230.3 (1.2) | 401.7 |
| $Mo(NO)_2Cl_2(PEt_3)_2 \cdot 0.25C_6H_{14}$ | DR | 640 w, 450 vs | 1775, 1660 | 1780, 1670 | 233.5, 230.6 (1.8) | |
| $Mo(NO)_2Cl_2(P\text{-}n\text{-}Bu_3)_2$ | DR | 645 m, 450 vs | 1760, 1645 | 1760, 1647 | 233.9, 230.6 (1.1) | 402.0 |
| $Mo(NO)_2Cl_2(dppm)$ | DR | 665 m, br, 455 vs | 1790, 1670[c] | 1790, 1677[c] | 233.5, 230.2 (1.8) | 400.9 |
| $Mo(NO)_2(NCS)_2(dppe)$ | DR | 625 sh?, 455 vs | 1787, 1675 | 1795, 1698 | 233.5, 230.8 (1.8) | 400.9, 397.7 |
| $Mo(NO)_2(NCS)_2(dppm)$ | DR | 450 sh | 1788, 1680 | 1795, 1693 | 233.5, 230.5 (1.6) | 401.1, 398.3 |
| $Mo(NO)_2Cl_2(PPh_3)_2$ | $CH_2Cl_2$ | 625 w, 450 vs | 1783, 1660[d] | 1790, 1670[e] | 233.4, 230.5[f] | 401.6 |

[a] DR = diffuse reflectance. [b] Full-width half-maximum values for the Mo $3d_{5/2}$ component are given in parentheses; binding energies are referenced to the carbon 1s binding energy of 285.0 eV for the phosphine ligands. [c] Literature data reported for a sample of $Mo(NO)_2Cl_2(dppm)$ prepared by a different procedure[16] gave $\nu$(NO) at 1780 and 1665 cm$^{-1}$ (in Nujol) and 1785 and 1670 cm$^{-1}$ (in $CH_2Cl_2$). [d] Data taken from ref 20. [e] Data taken from ref 14. [f] Data taken from ref 23.

**(vi) $Mo(NO)_2(NCS)_2(dppe)$.** Nitric oxide was passed through a yellow solution of $Mo_2(NCS)_4(dppe)_2$ (0.2 g) in dichloromethane (50 mL) for 1 h. The resulting brown solution was concentrated (~5 mL) and then filtered into ice-cold diethyl ether. The light brown powder which formed immediately was filtered off, washed with ethanol and pentane, and then dried in vacuo. The presence of a single component in this product was verified by TLC. The yield was 0.1 g. Anal. Calcd for $C_{28}H_{24}MoN_4O_2P_2S_2$: C, 50.15; H, 3.58; N, 8.36. Found: C, 50.63; H, 3.99; N, 8.06.

**(vii) $Mo(NO)_2(NCS)_2(dppm)$.** A procedure analogous to that described in (vi) was followed using $Mo_2(NCS)_4(dppm)_2$ (0.27 g) in dichloromethane (50 mL) and a reaction time of 1 h. The initial yellow color of the solution became brown and afforded a light brown product; yield 0.12 g. Anal. Calcd for $C_{27}H_{22}MoN_4O_2P_2S_2$: C, 49.41; H, 3.35; N, 8.53. Found: C, 50.32; H, 3.71; N, 7.73.

**B. Reactions of $Mo_2Cl_4(PEt_3)_4$ and $Mo_2(NCS)_4(dppe)_2$ with $NOPF_6$.** The behavior of metal-metal bonded dimers of molybdenum toward a reagent containing the nitrosonium ion, $NO^+$, such as $NOPF_6$, was briefly investigated. In contrast to the situation where gaseous nitric oxide was used, the reactions of complexes such as $Mo_2Cl_4(PEt_3)_4$ and $Mo_2(NCS)_4(dppe)_2$ were very complicated. The general reaction procedure which was employed involved the addition of an excess of solid $NOPF_6$ (~0.15 g) to a dichloromethane solution (15 mL) containing the molybdenum starting material (0.15 g). Next, the reaction mixture was stirred at room temperature under a nitrogen atmosphere. Several color changes were observed to take place during the first few minutes of reaction. After ~10 min, the reaction was stopped, but all attempts to recover solid products either by evaporating the solution to dryness or by adding organic solvents such as methanol, ether, or hexane were unsuccessful.

These reactions were repeated and an acetone or acetonitrile solution (5 mL) containing $NaBPh_4$ (0.2 g) was added to the reaction mixture and stirring continued for another 5 min. The resulting solid which formed was collected and washed with ether and then dried in vacuo. These products were highly contaminated with molybdenum–oxygen and phosphorus–oxygen species as evidenced by their infrared spectra. In the case of the reaction with $Mo_2(NCS)_4(dppe)_2$, a weak, broad band was observed in the region where the coordinated NO stretching frequency is expected. No further attempts were made to characterize these products.

**C. Attempted Reaction of $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$, $Mo_2Cl_4(dppm)_2$, $Mo_2(NSC)_4(PEt_3)_4$, and $Mo_2(NCS)_4(dppe)_2$ with Carbon Monoxide.** Carbon monoxide was passed through dichloromethane solutions of these complexes both at room temperature and under reflux conditions for several hours. In no instance was reaction observed to occur and the starting materials could be recovered unchanged.

**Physical Measurements.** These were recorded using the instrumentation described previously.[12,13]

## Results and Discussion

The most significant feature of the present study is the ease with which the Mo–Mo quadruple bond of the tertiary phosphine complexes $Mo_2X_4L_4$ and $Mo_2X_4(LL)_2$ is cleaved upon reaction with nitric oxide. The resulting complexes, together with details of their pertinent spectral data, are summarized in Table I.

Previous synthetic routes to such dinitrosyls of molybdenum have included (a) the reaction of triphenylphosphine and/or bis(diphenylphosphino)methane (dppm) with the nitrosyl halides $[Mo(NO)_2X_2]_n$, where X = Cl, Br, or I,[14–18] and the ethanol complex $Mo(NO)_2(EtOH)_2Cl_2$,[19] (b) the action of nitric oxide on $Mo(CO)_3(PPh_3)_2X_2$, where X = Cl or Br,[20] and (c) the reaction of nitrosyl bromide with the carbonyl derivative $Mo(CO)_4(PPh_3)_2$.[15] The complexes $Mo(NO)_2X_2(PPh_3)_2$ and $Mo(NO)_2X_2(dppm)_2$, where X = Cl, Br, or I, are the only phosphine derivatives which have been previously prepared by these methods.[21] Related procedures have been used to obtain tertiary arsine ($Ph_3As$ and $Ph_2AsCH_2AsPh_2$)[14–16,20] and phosphine oxide ($Ph_3PO$, $Ph_2EtPO$, and $Ph_2P(O)CH_2CH_2P(O)Ph_2$)[17,19] complexes of these types. The conversion of the dimers $Mo_2X_4L_4$, X = Cl or Br and L = $PEt_3$, P-*n*-$Bu_3$, or $PEtPh_2$, and $Mo_2X_4(LL)_2$, X = Cl or NCS and LL = dppm or dppe, to the monomers $Mo(NO)_2X_2L_2$ and $Mo(NO)_2X_2(LL)$ constitutes the first general synthetic route which is applicable to a wide range of phosphine ligands. Although we have restricted our attention to the complexes listed in Table I, there appears to be no reason that other such derivatives cannot be prepared by this method.

The rather low yields (approximately 25–30%) in which these dinitrosyl derivatives were isolated reflect their extremely high solubility in polar and nonpolar solvents. However, infrared spectral measurements on the reaction mixtures together with our isolation of both $Mo(NO)_2Cl_2(dppm)$ and $Mo(NO)Cl_3(dppm)$ in the case of the reaction between $Mo_2Cl_4(dppm)_2$ and nitric oxide reveal that the major reaction products are monomeric species.

The only difficulty experienced by us in the workup of the original reaction mixtures was in the case of the reactions between $Mo_2Cl_4(PR_3)_4$, where R = Et or *n*-Bu, and nitric oxide. The resulting complexes $Mo(NO)_2Cl_2(PR_3)_2$ were obtained in crystalline form with some difficulty. The waxy nature of these complexes together with their high solubility in a wide variety of polar and nonpolar solvents favored the formation of oils during the work-up procedures. In the case of $Mo(NO)_2Cl_2(PEt_3)_2$, crystallization was only effected by the formation of a hexane solvate of this complex. These observations are in accord with the results of an earlier study by Johnson,[15] who abandoned attempts to prepare the triethylphosphine complexes $Mo(NO)_2X_2(PEt_3)_2$ from $[Mo(NO)_2X_2]_n$, due to the "sticky non-crystalline" nature of the products.

**Electronic and Infrared Spectra.** To our knowledge, the electronic absorption spectra of phosphine derivatives of the types $Mo(NO)_2X_2L_2$ or $Mo(NO)_2X_2(LL)$ have not been reported previously. It is not out intention here to attempt to give detailed assignments of their electronic transitions but rather to report structure-related correlations. The transitions observed for the complexes prepared in the present study, together with data for $Mo(NO)_2Cl_2(PPh_3)_2$, which was prepared by a literature procedure,[14] are summarized in Table I. A single-crystal X-ray structure determination of the triphenylphosphine derivative showed that this complex has an octahedral geometry with a cis arrangement of bent NO groups.[22] It is apparent from an examination of the data in Table I that the complexes listed possess very similar electronic absorption spectra, with a very intense absorption at $\sim 450$ nm and a much weaker one between 620 and 670 nm. This evidence, together with the close similarity of their infrared spectra (Table I) which reveal two intense $\nu(\mathrm{NO})$ absorptions in the region 1650–1800 $\mathrm{cm}^{-1}$, is in accord with cis-octahedral arrangements of NO groups for all of the dinitrosyl complexes reported herein. In all instances, the lower energy $\nu(\mathrm{NO})$ mode is the broader and slightly more intense one of the two.

**X-ray Photoelectron Spectra (XPS).** We used this technique to assist us in fully characterizing the nitrosyl complexes isolated in this study. Our data are in excellent agreement with those reported[23] for $\mathrm{Mo(NO)_2Cl_2(PPh_3)_2}$ (Table I). Only one N 1s peak (located at 401–402 eV) was observed in the XPS of the chloride and bromide derivatives. However, the spectra of the thiocyanate complexes showed two N 1s binding energies, one at $\sim 401$ eV and the other at $\sim 398$ eV (Table I). This is consistent with our formulation of these compounds in which the lower energy peak (i.e., that at $\sim 398$ eV) is attributed to the nitrogen of the thiocyanate ligands.[24]

The Mo $3d_{3/2,5/2}$ binding energies which are presented in Table I are higher than those usually observed for authentic Mo(II) species such as $\mathrm{Mo_2X_4L_4}$ and other halide complexes which do not contain strong $\pi$-acceptor ligands.[10,25] Such complexes possess Mo $3d_{5/2}$ binding energies in the range 228.2–229.3 eV.[10,25] The effect of the $\pi$-acceptor nitrosyl ligands is to shift the Mo 3d peaks to higher energies relative to those of Mo(II) complexes.

**Comparisons with Related Reactions of Nitric Oxide and Carbon Monoxide with Other Compounds Containing Metal–Metal Multiple Bonds.** The molybdenum monomers $\mathrm{Mo(NO)_2X_2L_2}$ and $\mathrm{Mo_2(NO)_2X_2(LL)}$ which were prepared in this work constitute the first general series of dinitrosyl complexes of molybdenum, $\{\mathrm{Mo(NO)_2}\}^n$, which have been isolated by utilizing electronically unsaturated metal–metal bonded dimers as precursors. As mentioned earlier, the reaction of carbon monoxide with the rhenium species $\mathrm{Re_2X_4(PR_3)_4}$ affords the paramagnetic 17-electron compounds *trans*-$\mathrm{ReX_2(CO)_2(PR_3)_2}$.[2,3] Therefore, the disruption of the Mo–Mo multiple bond of the 16-electron $\mathrm{Mo_2X_4L_4}$ and $\mathrm{Mo_2X_4(LL)_2}$ dimers by nitric oxide to produce the stable dinitrosyl systems[26] is, by comparison to the rhenium(II) complexes, not unexpected. What is surprising, however, is the failure of the molybdenum dimers, which have the same molecular structure as their rhenium(II) analogues but a different electronic structure, to react with CO.[3] This difference in reactivity has been attributed to differences in the electronic structures of $\mathrm{Mo_2}^{4+}$ and $\mathrm{Re_2}^{4+}$ units which possess metal–metal quadruple and triple bonds, respectively.[3]

The behavior of these molybdenum(II) dimers toward NO and CO is quite different from the related reactions of the alkoxy derivatives of molybdenum(III), $\mathrm{Mo_2(OR)_6}$, which contain a Mo–Mo triple bond.[27,28] The latter complexes, which contain a 12-valence-shell electron configuration and are even more electronically unsaturated than $\mathrm{Mo_2X_4L_4}$ and $\mathrm{Mo_2X_4(LL)_2}$, react with NO to yield the diamagnetic 14-electron alkoxy-bridged dimers $\mathrm{[Mo(OR)_3NO]_2}$, in which the metal–metal bond is no longer present.[28] These differences reflect the greater tendency for electronically unsaturated Mo(II) species to approach the 18-valence-shell electronic configuration[26] than for Mo(III) species to do so.

The detailed mechanisms of the NO reactions which lead to the cleavage of the Mo–Mo quadruple bonds and the formation of $\mathrm{Mo(NO)_2X_2L_2}$ and $\mathrm{Mo(NO)_2X_2(LL)}$ have yet to be elucidated. However, the failure of the phosphine ligands to be oxidized to the appropriate phosphine oxides argues against the occurrence of Mo–P bond breaking,[29] since the release of free phosphine would lead to oxidation to phosphine oxide by the excess NO which is present.[17,30] Although such oxidations can occur even when the phosphine is bound to a metal,[30] the NO oxidation of free phosphine is much more facile.

In contrast to the interesting variety of reactions between NO and compounds containing metal–metal multiple bonds which are now just beginning to be discovered, very little information is available concerning the behavior of these same compounds toward the nitrosonium ion. We have shown that the reaction of $\mathrm{NOPF_6}$ with the rhenium dimers $\mathrm{Re_2X_4(PEt_3)_4}$ (X = Cl or Br) effects a one electron oxidation and affords the salts $\mathrm{[Re_2X_4(PEt_3)_4]PF_6}$ rather than nitrosyl compounds.[13] Recently, Kleinberg and his co-workers[31] investigated the reactions of nitrosyl chloride (NOCl) with $\mathrm{K_4Mo_2Cl_8}$ and $\mathrm{Mo_2(C_2H_3O_2)_4}$ in ethyl acetate. They reported that the only identifiable products were those in which the Mo–Mo bond of the starting complexes had been cleaved. After appropriate workup of the reaction mixtures, the compounds $\mathrm{K_2Mo(NO)Cl_5}$ and $\mathrm{Mo(NO)Cl_3{\cdot}2Ph_3PO}$ (upon the addition of triphenylphosphine oxide) were isolated when $\mathrm{K_4Mo_2Cl_8}$ was used as the starting material. The second of the above products was also formed in the acetate reaction.[31] However, these products were always contaminated with species containing molybdenum–oxygen bonds. Furthermore, it was noted[31] that extended reaction times resulted in marked decreases in the relative intensity of the NO stretching frequency and increases in the intensities of the infrared absorption bands attributed to Mo═O. These observations best explain the results we obtained when $\mathrm{NOPF_6}$ was reacted with $\mathrm{Mo_2Cl_4(PEt_3)_4}$ and $\mathrm{Mo_2(NCS)_4(dppe)_2}$ (see Experimental Section). It is possible that some type of nitrosyl complex was initially formed, but this was probably followed by the rapid loss of coordinated NO groups coupled with an increase in the amount of contaminants containing molybdenum–oxygen linkages. The occurrence of several color changes in the reaction mixture is not inconsistent with the above interpretation. Moreover, the infrared spectra of the materials which separated upon the addition of $\mathrm{NaBPh_4}$ show both $\nu(\mathrm{Mo{=}O})$ and $\nu(\mathrm{P{=}O})$ frequencies.

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**Registry No.** $\mathrm{Mo(NO)_2Br_2(PEtPh_2)_2}$, 69120-46-3; $\mathrm{Mo(NO)_2Cl_2(PEtPh_2)_2}$, 69120-47-4; $\mathrm{Mo(NO)_2Cl_2(PEt_3)_2}$, 69120-48-5; $\mathrm{Mo(NO)_2Cl_2(P\text{-}\mathit{n}\text{-}Bu_3)_2}$, 69120-49-6; $\mathrm{Mo(NO)_2Cl_2(dppm)}$, 69176-57-4; $\mathrm{Mo(NO)_2(NCS)_2(dppe)}$, 69120-50-9; $\mathrm{Mo(NO)_2(NCS)_2(dppm)}$, 69120-51-0; $\mathrm{Mo(NO)_2Cl_2(PPh_3)_2}$, 61950-44-5; $\mathrm{Mo(NO)Cl_3(dppm)}$, 69120-52-1; $\mathrm{Mo_2Br_4(PEtPh_2)_4}$, 69120-53-2; $\mathrm{Mo_2Cl_4(PEtPh_2)_4}$, 59752-92-0; $\mathrm{Mo_2Cl_4(PEt_3)_4}$, 59780-36-8; $\mathrm{Mo_2Cl_4(P\text{-}\mathit{n}\text{-}Bu_3)_4}$, 39306-31-5; $\mathrm{Mo_2Cl_4(dppm)_2}$, 69120-54-3; $\mathrm{Mo_2(NCS)_4(dppe)_2}$, 64784-51-6; $\mathrm{Mo_2(NCS)_4(dppm)_2}$, 64784-41-4.

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# Synthesis and Properties of Manganese Hydrides Having a Functional Silicon

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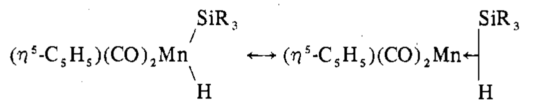
Complexes of the type $(\eta^5\text{-}CH_3C_5H_4)(CO)_2Mn(H)SiR_1R_2X$ where $R_1$ = phenyl, $R_2$ = 1-naphthyl, and X = hydrogen, chlorine, fluorine, or methoxy have been prepared, and their chemical behavior has been studied. The different types of reactions they undergo are the following: (i) deinsertion reactions with formation of $R_1R_2Si(H)X$, (ii) cleavage of the Mn-Si bond with water or methanol, (iii) substitution reactions at silicon without cleavage of the Mn-Si bond, (iv) formation of salts by abstraction of $H^+$, and (v) reaction with $LiAlH_4$, which leads first to reduction of the function X and then to formation of the anion $[(\eta^5\text{-}CH_3C_5H_4)(CO)_2MnSiR_1R_2H]^-$.

## Introduction

Recently we described the synthesis and the chemical behavior of optically active (−)-hydrido(1-naphthylphenylmethylsilyl)($\eta^5$-methylcyclopentadienyl)dicarbonylmanganese.[1] Cleavage reactions occur in three ways (see Scheme I).

The ease of deinsertion could be explained by taking into account the Si-H distance in the complex. This distance (1.76 Å) is shorter then the sum of the van der Waals radii (3.1 Å), showing a bonding interaction between both atoms.[2] This fact was represented by Graham and Hart-Davis as a resonance hybrid.[3]



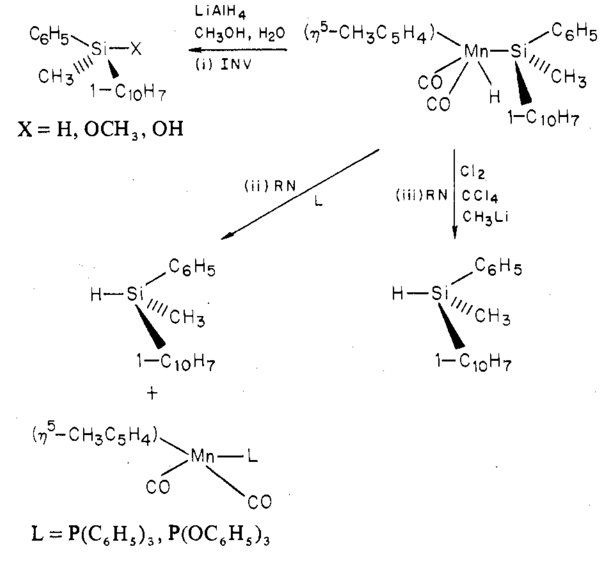
$$(\eta^5\text{-}C_5H_5)(CO)_2Mn\begin{matrix}\diagup SiR_3\\ \diagdown H\end{matrix} \longleftrightarrow (\eta^5\text{-}C_5H_5)(CO)_2Mn\leftarrow\begin{matrix}SiR_3\\ |\\ H\end{matrix}$$

Substitution at silicon modifies the chemical behavior of the complexes. For instance, the triphenylsilyl complex is inert toward triethylamine, but the trichlorosilyl analogue behaves as an acid and easily leads to the corresponding anion.[4]

$$(\eta^5\text{-}C_5H_5)(CO)_2Mn(H)SiCl_3 \xrightarrow{(C_2H_5)_3N} [(\eta^5\text{-}C_5H_5)(CO)_2MnSiCl_3]^-(C_2H_5)_3NH^+$$

In this paper we describe the preparation and the chemical properties of complexes having a monofunctional silicon atom.

Scheme I[a]



[a] RN = retention of configuration; INV = inversion of configuration.

## Experimental Section

All reactions were carried out under nitrogen, using a vacuum line, in Schlenk tubes. Photochemical reactions were performed in a Pyrex reaction vessel equipped with a water-cooled quartz finger. A 450 W UV lamp (Hanovia, high-pressure mercury) was placed inside the quartz finger.

Solvents were dried, distilled, and deoxygenated.

Melting points were taken under vacuum in a Dr. Tottoli's apparatus and are uncorrected. IR spectra were recorded in a Perkin-Elmer 257 spectrophotometer.

Satisfactory elemental analyses and mass spectra were obtained for all new compounds (Table V).

Starting material, $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$, was purchased from Strem Chemicals Inc. Literature methods were used for the synthesis of $(\eta^5\text{-}CH_3C_5H_4)(CO)_2Mn(H)Si(C_6H_5)_3$,[5] organosilicon compounds,[6] and $[(C_6H_5)_3P]_2NCl$.[7] All known compounds were compared with authentic samples.

**Silylmanganese Hydrides.** Hydrido(1-naphthylphenylhydrosilyl)($\eta^5$-methylcyclopentadienyl)dicarbonylmanganese, **1**, hydrido(1-naphthylphenylchlorosilyl)($\eta^5$-methylcyclopentadienyl)dicarbonylmanganese, **2**, hydrido(1-naphthylphenylfluorosilyl)($\eta^5$-methylcyclopentadienyl)dicarbonylmanganese, **3**, and hydrido(1-naphthylphenylmethoxysilyl)($\eta^5$-methylcyclopentadienyl)dicarbo-

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