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Contribution from the Department of Chemistry,
University of Nebraska, Lincoln, Nebraska 68588-0304

Synthesis, Characterization, and Reactions of Polymer-Bound Dinitrogen Complexes of Molybdenum[1]

T. Adrian George* and Bharat B. Kaul

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Studies of the reactions of acid with a bis(dinitrogen) complex of molybdenum anchored to a polymer support provide valuable information concerning the mechanism of nitrogen fixation. Two methods have been developed for attaching $\{Mo(N_2)_2\}$ to a microreticular resin, PS-diphos, in which $-P(Ph)CH_2CH_2PPh_2$ (diphos) is covalently bonded to a polystyrene–2% divinylbenzene copolymer, prepared by the reaction of $LiP(Ph)CH_2CH_2PPh_2$ with chloromethylated (16%) polystyrene. *trans*-$[Mo(N_2)_2$(PS-diphos)$(PPh_2Me)_2]$ (**2**) can be prepared either by (i) a phosphine-exchange between PS-diphos and *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ (**1**) or (ii) bubbling N_2 through a suspension of $[MoH_4$(PS-diphos)$(PPh_2Me)_2]$ in THF. The latter complex was prepared by reducing $MoCl_4(PPh_2Me)_2$ with $LiBHEt_3$ in THF in the presence of PS-diphos. Reaction of *trans*-$[Mo(N_2)_2$(PS-diphos)$(PPh_2Me)_2]$ with HBr in THF produced no ammonia whereas reaction of the nonanchored analogue produced significant amounts of ammonia. These data support a hypothesis that ammonia formation occurs as a result of the disproportionation of interacting intermediate hydrazido(2–) (NNH_2) complexes: no interaction occurred due to site isolation. A hydrazido(2–) complex of the anchored N_2 complex was prepared. Complex **2** reacted with HBr in CH_2Cl_2 to afford hydrazine but no ammonia, demonstrating that hydrazine is formed at a single metal center. Addition of HBr in THF to a 1:1 mixture of complexes **1** and **2** produced a 33% increase in yield of ammonia/mol of **1**. In an analogous experiment with **1** and **2** ($^{15}N_2$ labeled), the presence of $^{15}NH_3$ (identified as $^{14}N^{15}N$ and $^{15}N_2$ when the ammonia formed was oxidized by hypochlorite) indicated that the homogeneous and anchored complexes had interacted. *trans*-$[W(N_2)_2(PPh_2Me)_4]$ was also able to cause **2** to form ammonia in the presence of HBr in THF. The tungsten analogue of **2** was prepared by the phosphine-exchange method, but the loading was not as high.

Introduction

The mechanism of reduction of molecular nitrogen by the enzyme nitrogenase is a significant contemporary problem, the study of which is divided among many disciplines. Studies of the reactions of dinitrogen complexes of molybdenum and tungsten with acid that produce ammonia have provided a model against which comparisons with the natural system have been made.[2-7] A common dinitrogen-hydride intermediate that constantly appears in these model studies is the hydrazido(2–) ligand. Some years ago it was established that there is a significant difference in the behavior of the tungsten and molybdenum dinitrogen complexes.[8] Whereas tungsten was able to provide up to six electrons per tungsten during the reduction of N_2 to ammonia, it was shown later that molybdenum only provided up to three electrons in the analogous reaction (eqs 1 and 2; dpepp = $PhP(CH_2CH_2PPh_2)_2$).

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] \xrightarrow{8H^+} 2[NH_4]^+ + N_2 + \{W(VI)\} + 4PMe_2Ph \quad (1)$$

$$trans\text{-}[Mo(N_2)_2(dpepp)(PPh_3)] \xrightarrow[3Br^-]{4H^+} [NH_4]^+ + 1.5N_2 + MoBr_3(dpepp) + PPh_3 \quad (2)$$

An accumulation of data supports the suggestion that, during reduction of N_2 to ammonia in mono- and bis(dinitrogen) complexes of molybdenum the intermediate hydrazido(2–) complex undergoes a net, multistep disproportionation reaction as shown in eq 3 (X = Br, Cl; L = organophosphine).

$$[MoX(NNH_2)L_4]^+ + [MoX(NNH_2)L_4]^+ \xrightarrow[4X^-]{4H^+} 2[NH_4]^+ + N_2 + 2MoX_3L_3 + 2L \quad (3)$$

Thus one hydrazido(2–) complex loses N_2 and is a source of electrons for the other hydrazido(2–) complex, which is reduced to afford 2 mol of ammonia (eqs 4 and 5). The molybdenum-

$$\{Mo(IV)(NNH_2)\} \rightarrow \{Mo(III)\} + N_2 + 2H^+ + 3e \quad (4)$$

$$3e + \{Mo(IV)(NNH_2)\} \xrightarrow{6H^+} \{Mo(III)\} + 2[NH_4]^+ \quad (5)$$

containing product isolated in these reactions is MoX_3L_3. There is no irrefutable evidence that the hydrazido(2–) complex is both the oxidant and the reductant: one of the active species may be a diazenido (NNH) complex, for example.[9] In addition, one of the complexes loses a phosphine ligand before disproportionation occurs.[4] In order to carry out a systematic study of the electron-transfer behavior of unsubstituted hydrazido(2–) and related complexes, it is necessary to prevent the disproportionation reaction from occurring. For example, a THF or CH_2Cl_2 solution of a typical hydrazido(2–) complex of molybdenum produces small quantities of ammonia without adding acid. To prevent interaction between hydrazido(2–) complexes, efforts have been made to site-isolate complexes by anchoring them to a microreticular polystyrene polymer.

Dinitrogen complexes of transition metals have previously been attached to polymer supports. Collman et al.[10] bound Vaska's complex, *trans*-$[IrCl(CO)(PPh_3)_2]$, to triphenylphosphine-substituted 2% cross-linked polystyrene and demonstrated that an N_2 complex could be made by reacting the polymer-bound complex with *p*-nitrobenzyl azide. This was analogous to the same reaction carried out in solution. Brubaker, Grubbs, et al.[11] were able to

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(1) Reactions of Coordinated Dinitrogen. 26. Part 25: George, T. A.; Ma, L.; Shailh, S. N.; Tisdale, R. C.; Zubieta, J. *Inorg. Chem.*, in press.

(2) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852-1860. (b) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197-292.

(3) (a) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461-7467. (b) Hidai, M.; Mizobe, Y. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1989; Vol. 2, Chapter 2.

(4) (a) Baumann, J. A.; Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K.; Noddings, C. M. *Inorg. Chem.* **1985**, *24*, 3568-3578. (b) Bossard, G. E.; George, T. A.; Howell, D. B.; Lester, R. K. *Inorg. Chem.* **1983**, *22*, 1968-1970. (c) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6153-6154. (d) George, T. A. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; pp 405-441.

(5) (a) George, T. A.; Tisdale, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 5157-5159. (b) George, T. A.; Tisdale, R. C. *Inorg. Chem.* **1988**, *27*, 2909-2912. (c) George, T. A.; Tisdale, R. C. *Polyhedron* **1989**, *8*, 1756-1757.

(6) Lazarowych, N. J.; Morris, R. H.; Ressner, J. M. *Inorg. Chem.* **1986**, *25*, 3926-3932.

(7) Lowe, D. J.; Thorneley, R. N. F.; Smith, R. E. In *Metalloproteins, Part 1: Metal Proteins in Redox Roles*; Harrison, P. M., Ed.; Verlag Chemie: Weinheim, FRG, 1985; pp 207-249 and references cited therein.

(8) Anderson, S. N.; Fakley, M. E.; Richards, R. L.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1973-1980.

(9) Pickett, C. J. Personal correspondence.

(10) Collmann, J. P.; Hegedus, L. S.; Cooke, M. P.; Norton, J. R.; Dolcetti, G.; Marquardt, D. N. *J. Am. Chem. Soc.* **1972**, *94*, 1789-1790.

(11) (a) Bonds, W. D., Jr.; Brubaker, C. H., Jr.; Chandrasekaran, E. S.; Gibbons, C.; Grubbs, R. H.; Kroll, L. C. *J. Am. Chem. Soc.* **1975**, *97*, 2128-2132. (b) Lau, C.; Chang, B.; Grubbs, R. H.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1981**, *214*, 325-337.

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dramatically demonstrate the effectiveness of site-isolating a precatalyst to prevent deactivation of a catalyst by dimerization. Thus reduction of $(C_5H_5)_2TiCl_2$ attached to a 20% styrene–divinylbenzene copolymer generated an olefin hydrogenation catalyst that was 25–120 times more effective than the homogeneous analogue that was rapidly deactivated by the formation of bridged dimers. On the other hand, this same anchored catalyst would not reduce N_2, unlike the homogeneous system, because reduction required the presence of two neighboring Ti centers. More recently, Dubois[12] prepared a series of polymers containing the $\{Mo(N_2)_2\}$ unit by adding a solution of *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ to a polyacrylamide resin containing pendant mono-, di-, or tridentate phosphine ligands. Displacement of the monodentate ligands occurred rapidly. These polymers were attached to an electrode by evaporation of solvent. Attempts to study the formation of ammonia by electrochemical techniques were thwarted by loss of polymer from the electrode surface when acid was added. Along the same lines, Leigh and Pickett[13] attached $\{Mo(N_2)(dppe)_2\}$, where dppe = $Ph_2PCH_2CH_2PPh_2$, to a tin oxide electrode by coordination to an organonitrile that was anchored to the electrode surface. The molybdenum residue was reversibly oxidized, but no further chemistry was reported.

Since loss of a phosphine ligand occurs during conversion of the hydrazido(2–) complex to ammonia, attachment of $\{Mo(N_2)\}$ or $\{Mo(N_2)_2\}$ to a polymer must be through a multidentate ligand rather than a monodentate ligand. In this paper, we report two different methods of preparing a polymer-bound molybdenum–N_2 complex. Reactions of anchored complexes with acid provide strong evidence for the disproportionation mechanism. Some of these results have appeared in a preliminary communication.[14]

Experimental Section

General Procedures. All reactions and manipulations were carried out under dry oxygen-free N_2 or Ar or in vacuo by using standard inert-atmosphere techniques described previously.[4a] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The ^{31}P NMR spectra were obtained at room temperature in CD_2Cl_2 or C_6D_6 with a Varian VXR-200 spectrometer operating at 80.984 MHz. Chemical shifts are referenced to PPh_3 (–5.8 ppm vs 85% H_3PO_4 = 0.0 ppm). Phosphorus atom assignments: $CH_2(Ph)P_aCH_2CH_2P_b(Ph)_2$, P_xPh_2Me, P_xMe_2Ph. Infrared spectra were recorded on an Analect RFX-65 FTIR spectrometer.

Reagents and Materials. All solvents were rigorously dried by heating at reflux over an appropriate drying agent, followed by distillation under N_2. Solvents were saturated with N_2 immediately before use by bubbling N_2 through the solvent (≥0.5 h). Solvents used on the vacuum line were degassed through four or five freeze–pump–thaw cycles before use.

Chemicals were purchased from commercial sources and used without further purification except for anhydrous HBr, which was purified by a series of trap-to-trap distillations on the vacuum line and stored in a glass bulb. $^{15}N_2$ (98+%) was purchased from EG&G Mound Applied Technologies, Miamisburg, OH. Chloromethylated polystyrene–2% divinylbenzene copolymer beads (16% chloromethylated; 1.06 ± 0.05 mmol of Cl/g of resin) were purchased from Eastman Kodak Co., Rochester, NY.

Preparation of Compounds. The following compounds were prepared according to published procedures: $[MoCl_4(PPh_2Me)_2]$,[15] *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$,[16] *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$,[17] *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$,[18] *trans*-$[W(N_2)_2(dppe)(PPh_2Me)]$,[19] and $HP(Ph)CH_2CH_2PPh_2$.[20a] *trans*-$[W(N_2)_2(PPh_2Me)_4]$ was synthesized in high yield by modification of a published procedure.[21]

PS-P(Ph)CH$_2$CH$_2$PPh$_2$ (PS-diphos). In a 100-mL flask, 4.41 g (13.7 mmol) of $HP(Ph)CH_2CH_2PPh_2$, 5.6 mL of 2.5 M (14 mmol) of *n*-butyllithium in hexanes, and 30 mL of THF were combined. The red-orange solution of $LiP(Ph)CH_2CH_2PPh_2$ was transferred via a stainless steel cannula into a flask containing 5.18 g (5.58 mmol of Cl) of chloromethylated polystyrene–2% divinylbenzene, 40 mL of THF, and a magnetic stirbar. After stirring (48 h), unreacted $LiP(Ph)CH_2CH_2PPh_2$ was neutralized by addition of water (1.6 mL, 0.09 mmol). The resin was filtered off and washed with acetone (100 mL), water (200 mL), benzene (100 mL), methanol (200 mL), and acetone again (100 mL). The white resin was dried in vacuo (22 h). Yield: 7.06 g. Anal. Found: C, 86.57; H, 7.29; P, 5.33; Cl, 0.81 (by difference) (corresponds to 0.86 mmol of phosphine ligand/g of resin). ^{31}P NMR (swollen in C_6D_6): δ –13.36 (d, 1, J_{PP} = 23.5 Hz, P_a), –16.19 (broad s, 1, P_b).

***trans*-[Mo(N$_2$)$_2$(PS-diphos)(PPh$_2$Me)$_2$] (2).** To a suspension of PS-diphos (0.5 g, 0.4 mmol) in 20 mL THF was added a solution of *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ (0.5 g, 0.5 mmol) in 10 mL of THF. After the mixture was stirred for 48 h at room temperature, the bright orange polymer was filtered off, washed with THF until the filtrate was colorless, and dried in vacuo (24 h). Yield: 0.66 g. Anal. Calcd: Mo:P (atom:atom), 1.0:4.0; N, 3.04 (based on found Mo and P and assuming Mo:P:N = 1:4:4). Found: Mo, 4.48; P, 6.25; Mo:P, 1.0:4.2; N, 2.90 (N_2 gas measurement following oxidation by Br_2 in CH_2Cl_2) (corresponds to 0.48 mmol of complex/g of polymer). IR (KBr): ν(NN) 2022 (w), 1946 (vs) cm^{-1}. ^{31}P NMR (swollen in C_6D_6): δ 63 (b, P_{ab}), 21 (b, P_x).

***trans*-[Mo(^{15}N$_2$)$_2$(PS-diphos)(PPh$_2$Me)$_2$].** *trans*-$[Mo(N_2)_2$(PS-diphos)$(PPh_2Me)_2]$ (0.14 g) was suspended in 15 mL of THF, and the mixture was degassed through three freeze–pump–thaw cycles. The flask was pressurized (≈7 psi) with $^{15}N_2$ gas, and the mixture was stirred at room temperature for 24 h while being irradiated by four 100-W tungsten lamps. The orange resin was filtered off and dried in vacuo (24 h). Yield: 0.13 g. IR (KBr): ν(NN) 1950 (w), 1880 (vs) cm^{-1}.

[MoF(NNH$_2$)(PS-diphos)(PPh$_2$Me)$_2$]BF$_4$. *trans*-$[Mo(N_2)_2$(PS-diphos)$(PPh_2Me)_2]$ (0.15 g) was suspended in THF (15 mL), and the mixture was cooled to –78 °C. Aqueous HBF_4 (48%, 0.084 mL, 0.65 mmol) was added. The resultant mixture was allowed to warm slowly to room temperature and stirred for 20 h. The pale yellow polymer was filtered off, washed with THF (5 × 20 mL), and dried in vacuo (24 h). Yield: 0.115 g (76%). Anal. Calcd: Mo:P (atom:atom), 1.0:4.0. Found: Mo, 3.84; P, 4.85; Mo:P, 1.00:3.95. IR (KBr): ν(NH), 3333 (m), 3253 (s), 3163 (m) cm^{-1}. ^{31}P NMR (swollen in C_6D_6): δ 43 (b, P_{ab}), 8 (b, P_x).

[MoF(NNH$_2$)(dppe)(PPh$_2$Me)$_2$]BF$_4$. A solution of *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$ (0.2 g, 0.21 mmol) in THF (10 mL) was cooled to –78 °C and aqueous HBF_4 (48%, 0.11 mL, 0.84 mmol) added. The mixture was allowed to warm slowly to room temperature and stirred for 20 h. Hexane (30 mL) was added to precipitate a pale yellow oil. Solvent was decanted, and the yellow oil was washed with hexane (2 × 20 mL) and then evacuated for 3 h to give a semisolid product. This was triturated with 30 mL of hexane for 1 h. The yellow-gray solid was filtered off, washed with deoxygenated water (3 × 15 mL) and ether (3 × 20 mL), and dried in vacuo (24 h). Yield: 0.15 g (80%). Anal. Calcd for $C_{52}H_{52}BF_5N_2P_4Mo$: C, 60.6; H, 5.08; N, 2.21. Found: C, 60.24; H, 5.12; N, 2.40. IR (KBr): ν(NH) 3335 (m), 3253 (s), 3167 (m) cm^{-1}. ^{31}P NMR (CD_2Cl_2): δ 41.29 (complex dd, $J_{P_aP_x}$ = 160 Hz, J_{P_aF} = 32 Hz, P_a), 10.10 (complex dd, J_{P_xF} = 35 Hz, P_x).

Reaction of *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$] with PS-diphos. A solution of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ (0.48 g, 0.68 mmol) in THF (15 mL) was added to a suspension of PS-diphos (0.40 g, 0.34 mmol) in THF (10 mL). After the mixture was stirred for 48 h, the bright yellow polymer was filtered off, washed with THF until the filtrate was colorless, and dried in vacuo. The FTIR spectrum of the product displayed $\nu(N_2)$ at 2025 (w) and 1951 (ms) cm^{-1}, indicating the formation of a *trans*-bis(dinitrogen) complex. The ^{31}P NMR spectrum (swollen in C_6D_6) showed resonances due to uncomplexes phosphorus and very weak resonances due to coordinated phosphorus atoms. Increasing the reaction time to 96 h did not raise the loading of metal complex on the polymer.

Reaction of dppe with *cis*-[Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$]. A mixture of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ (0.2 g, 0.28 mmol) and dppe (0.113 g, 0.28 mmol) in benzene (10 mL) was stirred for 4 h to give an orange solution. After filtration, the filtrate was concentrated to ≈3 mL by vacuum distillation. Chilled methanol (20 mL) was added slowly and the mixture cooled to 0 °C for 2 h. The orange crystalline solid was filtered off, washed with methanol (2 × 10 mL), and dried in vacuo. Yield: 0.19 g (82%). Anal. Calcd for $C_{42}H_{46}N_4P_4Mo$: C, 60.87; H, 5.83; N, 6.76. Found: C, 60.93; H, 5.73; N, 6.54. IR (KBr): $\nu(N_2)$ 2018 (wm), 1953 (vs) cm^{-1}. ^{31}P

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(12) (a) DuBois, D. L.; Turner, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4989–4990. (b) DuBois, D. L. *Inorg. Chem.* **1984**, 2047–2052.

(13) Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1797–1800.

(14) Kaul, B. B.; Hayes, R. K.; George, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 2002–2003.

(15) Pennella, F. *Inorg. Synth.* **1974**, *15*, 43.

(16) George, T. A.; Noble, M. E. *Inorg. Chem.* **1978**, *17*, 1678–1679.

(17) George, T. A.; Hayes, R. K.; Mohammed, M. Y.; Pickett, C. J. *Inorg. Chem.* **1989**, *28*, 3269–3270.

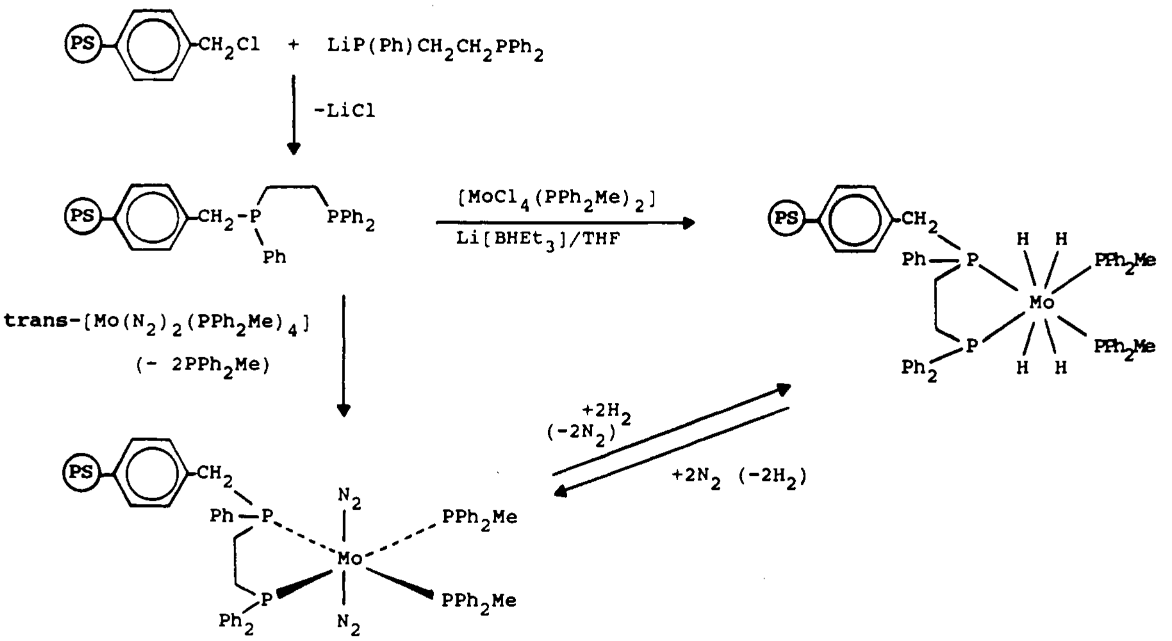
(18) George, T. A.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285–287.

(19) Lester, R. K. Ph.D. Dissertation, University of Nebraska, 1983.

(20) (a) Sanner, R. D.; Austin, R. G.; Wrighton, M. S.; Honnick, W. D.; Pittman, C. U., Jr. *Adv. Chem. Ser.* **1980**, *184*, 13–26. (b) Pittman, C. U., Jr.; Hirao, A. *J. Org. Chem.* **1978**, *43*, 640–646. (c) Pittman, C. U., Jr.; Lin, C.-C. *J. Org. Chem.* **1978**, *43*, 4928–4932.

(21) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2139–2142.

Scheme I



NMR (C_6D_6: AA′XX′): δ 66.0 (complex d, 1, $J_{P_aP_x}$ = 91 Hz, P_a), 5.17 (complex d, 1, P_x).

[Mo(H_4)(PS-diphos)(PPh_2Me)$_2$] (4). This reaction was carried out under dry prepurified Ar and with Ar saturated solvents. To PS-diphos (0.15 g, 0.13 mmol) suspended in THF (15 mL) was added a solution of [$MoCl_4$(PPh_2Me)$_2$] (0.085 g, 0.13 mmol) in THF (10 mL). After the reaction mixture was stirred for 10 min, $LiBHEt_3$ (2.6 mL, 2.6 mmol; 1.0 M in THF) was added. Immediately the color of the polymer darkened. After the mixture was stirred for 24 h at room temperature, the red-brown polymer was filtered off, washed with THF until the filtrate was colorless, and dried in vacuo. Yield: 0.175 g. Anal. Calcd: Mo:P, 1:4. Found: Mo, 4.27; P, 5.34; Mo:P, 1.00:3.95. IR (KBr): ν(MoH) 1725 cm^{-1}. ^{31}P NMR (swollen in C_6D_6): δ 86 (b, P_{ab}), 43 (b, P_x).

Attempts to synthesize [Mo(H_4)(dppe)(PPh_2Me)$_2$] by a variety of methods resulted in mixtures of [Mo(H_4)(dppe)(PPh_2Me)$_2$], [Mo(H_4)(dppe)$_2$], and [Mo(H_4)(PPh_2Me)$_4$] according to the ^{31}P NMR spectrum.

Conversion of [Mo(H_4)(PS-diphos)(PPh_2Me)$_2$] into *trans*-[Mo(N_2)$_2$(PS-diphos)(PPh_2Me)$_2$]. N_2 was bubbled through a suspension of [Mo(H_4)(PS-diphos)(PPh_2Me)$_2$] in THF (100 mL) for 12 h while it was irradiated with four 100-W tungsten lamps. The orange polymer was filtered off, washed with THF, and dried in vacuo. IR (KBr): ν(N_2) 2022 (w), 1946 (vs) cm^{-1}. The ^{31}P NMR spectrum (swollen in C_6D_6) was identical with that of **2**. Bubbling dry H_2 converted the *trans*-bis(dinitrogen) complex back to the tetrahydride complex. Two successive interconversions were satisfactorily carried out on the same sample without any sign of decomposition.

Reaction of [Mo($^{15}N_2$)$_2$(PS-diphos)(PPh_2Me)$_2$] with [Mo(N_2)$_2$(PPh_2Me)$_4$] and HBr. Ammonia Analysis and Oxidation to $^{28}N_2$, $^{29}N_2$, and $^{30}N_2$. In the drybox a 50-mL round-bottom flask with a stirbar was charged with the *trans*-[Mo($^{15}N_2$)$_2$(PS-diphos)(PPh_2Me)$_2$]. After the flask was evacuated to ≈10^{-5} Torr, excess HBr (≈15 mol) was condensed onto the solid at −196 °C, and the mixture was allowed to thaw slowly in the closed vessel. While the acid was thawing, the stirbar was used to agitate the solid to expose the complex to the thawing acid as effectively as possible. The freeze–thaw cycle was repeated five times. After all volatiles were removed, the flask was returned to the drybox, where an equimolar amount of *trans*-[Mo(N_2)$_2$(PPh_2Me)$_4$] was added to the sample of $^{15}N_2$-labeled anchored hydrazido(2−) complex. The reaction with excess HBr was repeated. After removal of the volatiles once again, excess HBr (≈20 mol) followed by THF (15 mL) was condensed onto the mixture of hydrazido(2−) complexes at −196 °C. The mixture was allowed to warm slowly to room temperature in the closed vessel and stired at room temperature for 48 h. THF was removed by vacuum distillation. Dichloromethane (15 mL) was added to the residue, followed by extraction with three portions of water (25 mL). The combined aqueous extracts were placed in a pear-shaped flask, and Ar was bubbled through the solution for 0.5 h. While bubbling with Ar was continued, the aqueous extract was cooled to −78 °C, and excess 3.5 mL (≈10 mol) NaOCl (5% chlorine) solution was added on top of the frozen mixture. The flask was then cooled to −196 °C and evacuated for 1 h. The closed flask was allowed to warm to room temperature and stirring maintained for 16 h. The mixture was again cooled to −196 °C, and evolved gases were transferred to a glass bulb by use of the Toepler pump. The evolved gases were analyzed by mass spectroscopy. Background: $^{28}N_2$, 99.3%; $^{29}N_2$, 0.7%; $^{30}N_2$, not determined. Sample: $^{28}N_2$, 97.3%; $^{29}N_2$, 2.6%; $^{30}N_2$, 0.1%.

The mass spectrometric data for the gas samples were obtained on a Kratos MS-50 mass spectrometer by the electron ionization technique. The ions of $^{28}N_2$, $^{29}N_2$, $^{30}N_2$, and $^{32}O_2$ were monitored at a resolution of 10000 by means of peak switching. Twenty 0.3-s sweeps of each mass were signal-averaged for each run. The values presented are the averages of five runs.

Results

A key requirement for reduction of N_2 in molybdenum–N_2 complexes is the presence of a labile ligand at the hydrazido(2−) stage in the reaction. Typically, this would be a monodentate organophosphine ligand, for example in [MoBr(NNH_2)(η^2-dpepp)(PMe_2Ph)$_2$]Br[5b] and [MoBr(NNH_2)(dpepp)(PPh_3)]Br,[4a,22] where dpepp = PhP($CH_2CH_2PPh_2$)$_2$. Therefore, attachment of the molybdenum–N_2 complex to the polymer should be through a bidentate ligand rather that either (i) a monodentate ligand, since that phosphine would dissociate and the complex would be free of the polymer, or (ii) a tridentate ligand like dpepp, since problems with isomers would arise.[22]

Preparation of the Phosphinated Polymer (Scheme I). Diphos, -P(Ph)$CH_2CH_2PPh_2$, was attached to a commercially available polymer by the reaction of LiP(Ph)$CH_2CH_2PPh_2$ with a chloromethylated polystyrene–2% divinylbenzene copolymer (Merrifield peptide resin) in which ca. 16% of the methyl groups were chlorinated. Previously, an analogous reaction had been employed to attach diphos directly to the aromatic ring of a polystyrene–2% divinylbenzene copolymer.[20] Elemental analysis of samples of PS-diphos from different preparations indicated that the phosphine loading was >85%. A ^{31}P NMR spectrum of the solvent-swollen polymer clearly showed a distinct resonance for each of the two different phosphorus atoms (see Figure 1).

Attachment of the Bis(dinitrogen) Complex to the Polymer (Scheme I). Two methods were developed, of which the first gave better results.

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(22) (a) George, T. A.; Koczon, L. M.; Tisdale, R. C.; Gebreyes, K.; Ma, L.; Shaikh, S.; Zubieta, J. *Polyhedron* **1990**, *9*, 545–551. (b) Gebreyes, K.; George, T. A.; Koczon, L. M.; Tisdale, R. C.; Zubieta, J. *Inorg. Chem.* **1986**, *25*, 405–407.

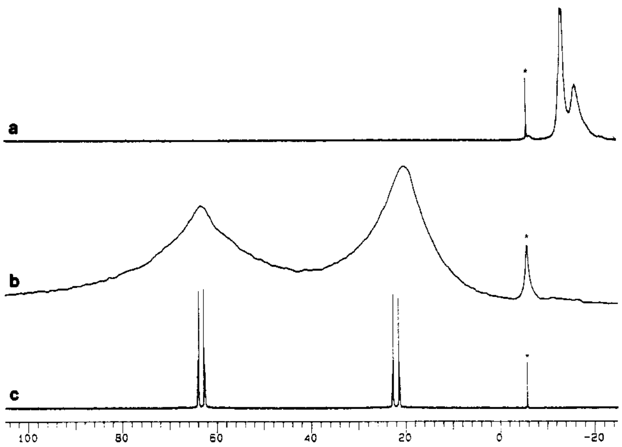

Figure 1. $^{31}P\{^1H\}$ NMR spectra (80.984 MHz, C_6D_6, 23 °C) of (a) PS-diphos, (b) *trans*-[$Mo(N_2)_2$(PS-diphos)$(PPh_2Me)_2$], and (c) *trans*-[$Mo(N_2)_2$(dppe)$(PPh_2Me)_2$]. * = PPh_3 internal reference.

(1) A phosphine-exchange method was employed that Dubois had successfully used to attach $\{Mo(N_2)_2\}$ to poly(acrylamide) resins.[12] Thus a sample of *trans*-[$Mo(N_2)_2(PPh_2Me)_4$] (**1**) IN THF solution was added to PS-diphos swollen in THF. After 48 h of stirring, the bright yellow resin was isolated by filtration and thoroughly washed. An intense absorption at 1946 cm^{-1} due to $\nu(N_2)$ was observed in the difference FTIR spectrum. Elemental analysis of samples of *trans*-[$Mo(N_2)_2$(PS-diphos)$(PPh_2Me)_2$] (**2**) gave a Mo:P of 1.0:4.2, indicating that almost all the diphos groups were chelated to molybdenum. Oxidation of samples of **2** with bromine in CH_2Cl_2 afforded ≥95% of the theoretical amount of N_2. These data suggested a loading of 0.48 mmol of complex/g of polymer. A ^{31}P NMR spectrum of the solvent-swollen complex clearly showed two broad resonances: one for coordinated PPh_2Me and the other for the unresolved phosphorus atoms of diphos (see Figure 1). The chemical shifts were very similar to those in *trans*-[$Mo(N_2)_2$(dppe)$(PPh_2Me)_2$] (**3**). No resonances were observed for uncomplexed diphos.

A similar reaction between PS-diphos and *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$] afforded *trans*-[$Mo(N_2)_2$(PS-diphos)$(PMe_2Ph)_2$] in low yield. An analogous reaction of PS-diphos with *trans*-[$W(N_2)_2(PPh_2Me)_4$] under varying conditions produced *trans*-[$W(N_2)_2$(PS-diphos)$(PPh_2Me)_2$] in low yield.

(2) It had been shown previously that coordinated N_2 and H_2 are often interchangeable specifically in the following reaction (eq 6).[23] Therefore if a molybdenum tetrahydride complex could

$$trans\text{-}[Mo(N_2)_2(dppe)_2] + 2H_2 \rightleftharpoons MoH_4(dppe)_2 + 2N_2 \quad (6)$$

be attached to the polymer, a metathesis reaction would generate an N_2 complex. No evidence of phosphine exchange occurred in reactions of PS-diphos and [$MoH_4(PPh_2Me)_4$] either at room temperature or upon heating or irradiation. However, it proved possible to synthesize [MoH_4(PS-diphos)$(PPh_2Me)_2$] (**4**) by reducing [$MoCl_4(PPh_2Me)_2$] with $LiBHEt_3$ in THF in the presence of PS-diphos.[24] Upon bubbling of N_2 through a suspension of **4** in THF, absorptions characteristic of **2** appeared in the FTIR spectrum. The tetrahydride **4** was regenerated by bubbling H_2 through a suspension of **2** in THF (Scheme I).

Reactions of 2 with Acids (See Table I). Reaction of **2** with excess tetrafluoroboric acid in THF afforded the hydrazido(2−) complex [$MoF(NNH_2)$(PS-diphos)$(PPh_2Me)_2$]BF_4, demonstrating that N_2 of the anchored complex is reactive toward protonation. In the FTIR spectrum, ν(NH) absorptions were identical (±4 cm^{-1}) with those in [$MoF(NNH_2)$(dppe)$(PPh_2Me)_2$]BF_4. A ^{31}P NMR spectrum of the solvent-swollen complex clearly showed two broad resonances, and the chemical shifts were very similar to those in [$MoF(NNH_2)$(dppe)$(PPh_2Me)_2$]BF_4. No resonances were observed for uncomplexed diphos. Reaction of **3** with excess HBr in THF produced 0.68 mol of ammonia and 1.49 mol of N_2/mol of Mo, which is typical for this type of molybdenum complex.[4a] In contrast, the reaction of **2** with excess HBr in THF for the same time period yielded *no ammonia*. This result is precisely what was predicted on the basis of the disproportionation mechanism that we had proposed. Dinitrogen, 1.25 mol/mol of Mo, was evolved.

In CH_2Cl_2, **3** reacted with HBr to produce both ammonia (0.41 mol) and hydrazine (0.42 mol). Hydrazine (0.24 mol) *but no ammonia* was produced when **2** was reacted with HBr in CH_2Cl_2. Similar results were obtained in toluene and between [$MoF(NNH_2)$(PS-diphos)$(PPh_2Me)_2$]BF_4 and HBr in CH_2Cl_2.

The Search for Electron Transfer. We believe site-isolation of the molybdenum complex stopped ammonia formation because intermolecular electron transfer was not possible. Addition of a suitable reducing agent should reactivate ammonia formation from the anchored complex. The most obvious choice of a reducing agent was a soluble molybdenum hydrazido(2−) complex, which itself gives ammonia, that could interact with a hydrazido(2−) complex attached to the polymer. Thus HBr and THF were condensed onto a 1:1 mixture of **1** and **2**, which was stirred for 48 h. The yield of ammonia was 1.01 mol/mol of **1** with a small amount of hydrazine (see Table I). A similar reaction of HBr with **1** in THF yielded 0.77 mol of ammonia/mol of **1** and a small amount of hydrazine. *Hence, there was a 30% increase in the amount of ammonia formed when **1** and **2** were together with acid.*

In order to demonstrate that ammonia was coming from **2**, the following labeling experiment was carried out (see Experimental Section). A mixture of hydrazido(2−) complexes was prepared by the reaction of HBr with $^{15}N_2$-labeled **2** (>90% $^{15}N_2$) and **1** in such a way that no N_2 exchange could occur. Following normal workup for ammonia analysis,[4a] the aqueous extract was treated with aqueous sodium hypochlorite, evolved N_2 formed by the oxidation of ammonia was collected by using a Toepler pump, and the ratio of isotopomers was determined by mass spectrometry. There was a 4-fold increase in dinitrogen-$^{14}N,^{15}N$ present compared with background, confirming the suggestion that some of the extra ammonia is derived from **2**. However, the mass spectral data gave no quantitative information about the amount of ammonia-^{15}N formed relative to ammonia-^{14}N, i.e. how much ammonia came from **2**. We are left to conclude that the increase in total ammonia yield is due to the interaction of intermediates derived from **1** and **2**. Support for this conclusion comes from the fact that, in experiments in which **1** is mixed with [$Mo(N_2)_2(dppe)_2$], [$Mo(N_2)_2(depe)_2$], or PS-diphos, no increase in the yield of ammonia above the **1**-only value was observed (see Table I).

The analogous tungsten complex *trans*-[$W(N_2)_2(PPh_2Me)_4$] (**5**) also interacted with **2**. Complex **5** reacted with HBr in THF to yield 0.45 mol of ammonia, 0.52 mol of hydrazine, and 1.26 mol of N_2/mol of **5**. In the presence of an equimolar amount of **2**, the yields changed to 0.85, 0.29, and 1.05 mol/mol of **5**, respectively.

Similar attempts were made to "activate" hydrazido(2−) complexes of molybdenum that do not produce ammonia. Thus mixtures of *trans*-[$Mo(N_2)_2(LL)_2$] (LL = dppe, $Et_2PCH_2CH_2PEt_2$) and **1** were reacted with HBr in THF. No change in ammonia yields over that of **1** alone was noted.

Discussion

Site-isolation of the $\{Mo(N_2)_2\}$ moiety on a microreticular polymer provides an opportunity to study the reactions of coordinated N_2 under conditions where no interaction between molybdenum complexes can occur. We attached $-P(Ph)CH_2CH_2PPh_2$ to a polystyrene polymer by using Merrifield's resin and applying known technology.[20] This bidentate ligand has previously been attached to a polystyrene resin by substitution directly at the para position[20,25] but never, as far as we could

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[23] (a) Archer, L. J.; George, T. A. *J. Organomet. Chem.* **1973**, *54*, C25–C26. (b) Archer, L. J.; George, T. A. *Inorg. Chem.* **1979**, *18*, 2079–2082.

[24] Crabtree, R. H.; Hlatky, G. G. *Inorg. Chem.* **1982**, *21*, 1273–1275.

Table I. Yields[a] of Nitrogen-Containing Products from Reactions of Bis(dinitrogen) and Hydrazido(2−) Complexes with HBr at 23 °C

expt no.	complexes	solvent (mol of HBr)	time, h	mol of product[b]			N_2 balance	
				NH_3	N_2H_4	N_2	mol	%
1	$[Mo(N_2)_2(PPh_2Me)_4]$	THF (20)	48	0.77	0.013	1.41	1.80	90
2	$[Mo(N_2)_2(PPh_2Me)_4]$ + $[Mo(N_2)_2(dppe)_2]$	THF (40)	46	0.76	trace			
3	$[Mo(N_2)_2(PPh_2Me)_4]$ + $[Mo(N_2)_2(depe)_2]$	THF (40)	48	0.77	trace			
4	$[Mo(N_2)_2(PPh_2Me)_4]$ + PS-diphos	THf (40)	48	0.71	trace			
5	$[Mo(N_2)_2$(PS-diphos)$(PPh_2Me)_2]$	THF (20)	48	0	trace	1.25		
		CH_2Cl_2 (20)	48	0	0.24	1.30	1.54	77
		toluene (20)	48	0	0.18			
		no solvent (15)	3			1.05		
6	$[Mo(N_2)_2(PPh_2Me)_4]$ + $[Mo(N_2)_2$(PS-diphos)$(PPh_2Me)_2]$	THF (40)	48	1.01	0.015	1.24	1.50	75
7	$[MoF(NNH_2)$(PS-diphos)$(PPh_2Me)_2]BF_4$	CH_2Cl_2 (20)	48	0	0.19			
8	$[Mo(N_2)_2(dppe)(PMePh_2)_2]$[c]	THF (20)	65	0.68	0	1.49	1.83	92
		CH_2Cl_2 (20)	48	0.41	0.42	1.40	2.00	100
9	$[W(N_2)_2(PPh_2Me)_4]$	THF (20)	46	0.45	0.52	1.26	2.00	100
10	$[W(N_2)_2(PPh_2Me)_4]$ + $[Mo(N_2)_2$(PS-diphos)$(PPh_2Me)_4]$	THF (40)	46	0.85	0.29	1.05	1.76	88

[a] Yields have an error of ±3%. [b] Per mole of Mo, except for experiments 2–4 and 6, which are based on moles of *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ only, and experiment 10, which is based on moles of *trans*-$[W(N_2)_2(PPh_2Me)_4]$ only. [c] Reference 4a.

ascertain, with a methylene spacer between the aromatic ring and the phosphorus atom. A major problem involved characterization of metal complexes on the polymer. FTIR spectroscopy proved particularly useful for providing evidence that an N_2 or hydrazido(2−) ligand was present, and ^{31}P NMR spectra of the solvent-swollen polymer were of value. Complex **1** reacted readily with PS-diphos to afford **2**. The intensity of $\nu(N_2)$ in the FTIR spectrum suggested high loading, which was confirmed by the P:Mo ratio determined from the elemental analysis and the N_2 analysis. *cis*-$[Mo(N_2)_2(Me_2Ph)_4]$ and *trans*-$[W(N_2)_2(PPh_2Me)_4]$ underwent phosphine exchange with PS-diphos to yield *trans*-$[Mo(N_2)_2$(PS-diphos)$(PMe_2Ph)_2]$ and the tungsten analogue of **2**, respectively, but the loading was low in both cases. Isomerization was also noted when *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ reacted with dppe to give *trans*-$[Mo(N_2)_2(dppe)(PMe_2Ph)_2]$. No exchange was observed between *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and PS-diphos.

Since the exchange method is limited by the lability of the phosphine ligands and increasing the temperature leads to loss of N_2, an alternative method of preparing N_2 complexes anchored to polystyrene was pursued. We chose to attach polyhydride complexes of the type that are known to react with N_2 to form N_2 complexes. This was done by reducing $[MoCl_4(PPh_2Me)_2]$ with $LiBHEt_3$ in the presence of PS-diphos. Replacement of H_2 by N_2 occurred readily.

To demonstrate that the reactivity of coordinated N_2 had not been affected by attachment of the complex to the polymer, **2** was reacted with aqueous HBF_4, which reacts with **3** to give a well-characterized hydrazido(2−) complex with distinctive ν(NH). Complex **2** was cleanly converted into $[MoF(NNH_2)$(PS-diphos)$(PPh_2Me)_2]BF_4$. This is the first example of the successful reaction of N_2 in a polymer-supported transition-metal complex. Further reaction with HBr in CH_2Cl_2 afforded hydrazine but no ammonia (see Table I). No attempt was made to characterize the hydrazido(2−) complex formed in the reaction of **2** and HBr, since the soluble analogue **3** reacts with HBr to give a mixture of $[MoBr(NNH_2)(dppe)(PPh_2Me)_2]Br$, $[MoBr_2(NNH_2)(dppe)(PPh_2Me)]$, and $[HPPh_2Me]Br$, from which we have been unable to obtain a single pure product.

The failure of **2** to produce ammonia upon reaction with HBr in THF clearly supports the hypothesis that at least two hydrazido(2−) or similar complexes must interact to produce ammonia. We believe that intermolecular electron transfer is a major component of the interaction. Ammonia formation occurred when a soluble hydrazido(2−) complex was added so that it could interact with the polymer-supported complex. Complexes **1** and $^{15}N_2$-labeled **2** were converted into their respective hydrazido(2−) complex in such a way that no N_2 exchange could occur between **1** and **2**. That some ammonia was derived from the anchored complex was shown by the formation of $^{15}NH_3$ and subsequent oxidation to dinitrogen-$^{14}N,^{15}N$.

Interestingly, even though **5** reacts with HBr in THF to yield both ammonia and hydrazine (100% N atom balance), a mixture of **2** and **5** reacted with HBr in THF and the yield of ammonia doubled (per mole of **5**) and hydrazine and N_2 yields decreased. Thus, a tungsten hydrazido(2−) (or related) complex is able to promote reaction of the anchored molybdenum complex.

In CH_2Cl_2, HBr reacted with **2** to produce hydrazine but no ammonia. We interpret this result to mean that hydrazine is being formed at a single metal center. The final molybdenum complex would be in the +4 oxidation state.[26]

trans-$[Mo(N_2)_2(LL)_2]$ (**6**) (LL = dppe, depe) react with HBr to form the hydrazido(2−) complex but no ammonia.[2] It has been argued that this is because there is no labile ligand. But can they behave as reducing agents in the presence of a system that does yield ammonia? To test this idea, mixtures of **1** and **6** were treated with HBr in THF. No change in ammonia yield was noted. This means that, for ammonia to be formed in the molybdenum complexes that have been studied, disproportionation must involve complexes that contain only three coordinated phosphorus atoms. Or, put another way, the precursor (to electron transfer) complex contains no more than three coordinated phosphorus atoms per molybdenum. None of these results exclude the coordination of a halide ion in place of the phosphine and the formation of a precursor complex with bridging halide ions.

Conclusion. Two conclusions can be drawn from this work. (i) The conversion to ammonia of the hydrazido(2−) or similar nitrogen hydride ligand in molybdenum complexes derived from complexes such as *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ entails disproportionation that involves interaction of two or more metal complexes. Disproportionation has been proposed previously as the pathway by which ammonia is formed from molybdenum hydrazido(2−) complexes,[2a,4a] and disproportionation is commonly observed in reactions of hydrides and oxides of nitrogen. In order to account for the stoichiometry of these reactions, electron transfer must be an important part of disproportionation. The success demonstrated in stimulating ammonia formation from the anchored hydrazido(2−) complex by adding both "homogeneous" molybdenum and tungsten hydrazido(2−) complexes suggests further experiments to probe the mechanism of electron transfer, namely studying reactions of one- and two-electron-reducing agents with anchored hydrazido(2−) complexes for evidence of further chemistry. Work along these lines is currently underway.

(ii) The four-electron conversion of coordinated N_2 into hydrazine can be accomplished at a single molybdenum center.

The failure to stimulate ammonia formation in complexes that normally form hydrazido(2−) complexes but not ammonia emphasizes the importance of having at least one labile ligand in both (or all) of the interacting complexes during disproportionation.

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(25) (a) Pittman, C. U., Jr. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, pp 553–611. (b) Hartley, F. R. *Supported Metal Complexes*; D. Reidel Publishing Co.: Boston, MA, 1985.

(26) George, T. A.; Howell, D. B. *Inorg. Chem.* **1984**, *23*, 1502–1503.

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Contribution from the Department of Chemistry,
Baker Laboratory, Cornell University, Ithaca, New York 14853

NMR Studies of Inversion and Dithiophosphate Methyl Group Exchange in Dialkoxybis(*O,O'*-dimethyl dithiophosphato)titanium(IV) Complexes. Evidence for a Bond-Rupture Mechanism[1]

Han-Mou Gau and Robert C. Fay*

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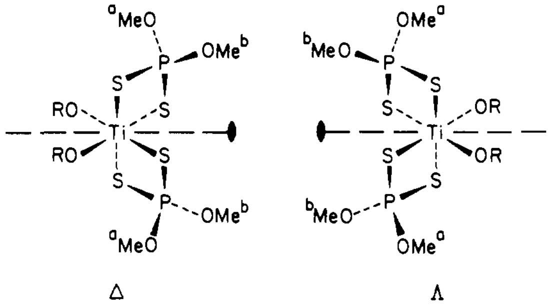
Dialkoxybis(*O,O'*-dimethyl dithiophosphato)titanium(IV) complexes, Ti(Me$_2$dtp)$_2$(OR)$_2$ (Me$_2$dtp = S$_2$P(OMe)$_2$; R = CH$_2$Ph, ^{i}Pr, CMe$_2$Et), have been prepared and characterized by chemical analysis and IR and ^{1}H NMR spectroscopy. Rates and activation parameters for inversion and dithiophosphate methyl group exchange in these cis-octahedral complexes have been determined by ^{1}H NMR spectroscopy (total line-shape analysis). Inversion, probed by the diastereotopic groups in the alkoxide ligands, and exchange of dtp methyl groups occur at the same rate by a common, intramolecular mechanism; $R_k = k_{inv}/k_{ex} = 1.0 \pm 0.2$. Activation parameters for the two processes are nearly identical. Permutational analysis indicates that the R_k values are consistent with the A_6 NMR averaging set. The R_k values rule out intramolecular twist mechanisms and all of the common bond-rupture mechanisms except rupture of a Ti–S bond trans to an alkoxide ligand to give a trigonal-bipyramidal intermediate that has the dangling ligand in an axial position. In accord with a bond-rupture mechanism, the rates increase with increasing steric bulk of the OR group. Kinetic results for the Ti(Me$_2$dtp)$_2$(OR)$_2$ complexes are contrasted with results for the analogous β-diketonate complexes, Ti(β-dik)$_2$(OR)$_2$, which rearrange via a twist mechanism. Also reported are related dichloro complexes, Ti(R$_2$dtp)$_2$Cl$_2$ (R = Me, Et, ^{i}Pr), and Ti(S$_2$PMe$_2$)$_2$(O^{i}Pr)$_2$.

Introduction

The mechanism of stereochemical rearrangements of metal chelate compounds has been an important problem in coordination chemistry since the days of Alfred Werner.[2] For intramolecular rearrangements of octahedral chelates, two classes of mechanisms have been considered: (1) metal–ligand bond rupture (chelate-ring opening) to give a five-coordinate intermediate[2] and (2) twisting mechanisms that effect rearrangement without rupture of any metal–ligand bonds.[3] Although much effort has been devoted to mechanistic studies of octahedral chelates,[4] in only a few cases has it proved possible to distinguish between bond-rupture and twisting mechanisms. The most thoroughly studied systems are cobalt(III) tris(β-diketonates),[5] which rearrange by a bond-rupture mechanism, and metal tris(α-substituted tropolonates)[6] and tris(N,N-disubstituted dithiocarbamates),[7] which undergo $\Delta \rightleftharpoons \Lambda$ inversion via the trigonal-twist mechanism.

A useful approach in mechanistic studies of metal chelate compounds is to compare the rates of two different processes.[5,8] For example, the relative rates of inversion and diketonate R group exchange in dialkoxybis(β-diketonato)titanium(IV) complexes, Ti(dik)$_2$(OR)$_2$ (OR = OCH$_2$Ph, OCH$_2$CHMe$_2$, OCHMe$_2$, OCMe$_2$Ph), and a dramatic decrease in these rates with increasing steric bulk of the alkoxide ligand strongly suggest that the Ti(dik)$_2$(OR)$_2$ complexes rearrange via a twist mechanism.[9] The closely related diolatobis(acetylacetonato)titanium(IV) complexes also rearrange by a twist mechanism.[10]

In this paper we report NMR studies of inversion and dithiophosphate (dtp) methyl group exchange in dialkoxybis(*O,O'*-dimethyl dithiophosphato)titanium(IV) complexes, Ti(Me$_2$dtp)$_2$(OR)$_2$ (OR = OCH$_2$Ph, OCHMe$_2$, OCMe$_2$Et). These complexes have a cis arrangement of alkoxide ligands (C_2 symmetry), and therefore they exist as chiral Δ and Λ enantiomers **1** that have



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inequivalent dtp methyl sites, a and b. The alkoxide ligands contain geminal H atoms or geminal methyl groups that serve as diastereotopic probes for measurement of the rates of $\Delta \rightleftharpoons \Lambda$ inversion (Figure 1). Comparison of the rates of inversion and dtp methyl group exchange indicates that the Ti(Me$_2$dtp)$_2$(OR)$_2$ complexes rearrange by a mechanism involving rupture of a Ti–S bond trans to an alkoxide ligand to give a trigonal-bipyramidal intermediate that has the dangling ligand in an axial position. By

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(1) Presented in part at the International Congress of Pacific Basin Societies, Honolulu, HI, Dec 1989. Abstracted from the Ph.D. thesis of H.-M.G., Cornell University, May 1987.

(2) Werner, A. *Chem. Ber.* **1912**, *45*, 3061.

(3) (a) Ray, P.; Dutt, N. K. *J. Indian Chem. Soc.* **1943**, *20*, 81. (b) Bailar, J. C., Jr. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165. (c) Springer, C. S., Jr.; Sievers, R. E. *Inorg. Chem.* **1967**, *6*, 852.

(4) (a) Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391. (b) Fortman, J. J.; Sievers, R. E. *Coord. Chem. Rev.* **1971**, *6*, 331. (c) Holm, R. H. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 9.

(5) (a) Gordon, J. G., II; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 5319. (b) Girgis, A. Y.; Fay, R. C. *Ibid.* **1970**, *92*, 7061.

(6) (a) Eaton, S. S.; Holm, R. H. *J. Am. Chem. Soc.* **1971**, *93*, 4913. (b) Eaton, S. S.; Hutchison, J. R.; Holm, R. H.; Muetterties, E. L. *Ibid.* **1972**, *94*, 6411. (c) Eaton, S. S.; Eaton, G. R. Holm, R. H.; Muetterties, E. L. *Ibid.* **1973**, *95*, 1116.

(7) (a) Duffy, D. J.; Pignolet, L. H. *Inorg. Chem.* **1972**, *11*, 2843. (b) Palazzatto, M. C.; Pignolet, L. H. *J. Chem. Soc., Chem. Commun.* **1972**, 6. (c) Palazzatto, M. C.; Duffy, D. J.; Edgar, B. L.; Que, L., Jr.; Pignolet, L. H. *J. Am. Chem. Soc.* **1973**, *95*, 4537. (d) Pignolet, L. H.; Duffy, D. J.; Que, L., Jr. *Ibid.* **1973**, *95*, 295. (e) Que, L., Jr.; Pignolet, L. H. *Inorg. Chem.* **1974**, *13*, 351.

(8) (a) Jurado, B.; Springer, C. S., Jr. *J. Chem. Soc., Chem. Commun.* **1971**, 85. (b) Pickering, M.; Jurado, B.; Springer, C. S., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 4503.

(9) (a) Fay, R. C.; Lindmark, A. F. *J. Am. Chem. Soc.* **1975**, *97*, 5928. (b) Fay, R. C.; Lindmark, A. F. *Ibid.* **1983**, *105*, 2118.

(10) (a) Baggett, N.; Poolton, D. S. P.; Jennings, W. B. *J. Chem. Soc., Chem. Commun.* **1975**, 239. (b) Baggett, N.; Poolton, D. S. P.; Jennings, W. B. *J. Chem. Soc., Dalton Trans.* **1979**, 1128.