J. Am. Chem. Soc. **1982**, *104*, 4367–4372

A New Approach to Nitrogen Fixation. Protonation of Dinitrogen Ligand by means of Hydridometal Carbonyls and the Synthesis of Alkoxide Hydrazido(2–) Complexes of Tungsten with Iron and Cobalt Carbonyl Complex Anions

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Received October 14, 1981

Abstract: Treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with an acidic hydridometal carbonyl, $HFeCo_3(CO)_{12}$, $H_2Fe(CO)_4$, or $HCo(CO)_4$, in methanol followed by KOH distillation formed ammonia and hydrazine in moderate yields. The influence of a hydrogen atmosphere upon improvement of the yields is significant. The formation of ammonia and hydrazine from *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ was negligibly small. Reactions of *trans*-$[W(N_2)_2(dpe)_2]$ (dpe = 1,2-bis(diphenylphosphino)ethane) with the hydride complexes in an alcohol gave alkoxide hydrazido(2–) complexes of the type *trans*-$[W(OR)(NNH_2)(dpe)_2]^+A^-$. The following combinations were used: $A = FeCo_3(CO)_{12}$, $R = CH_3$, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, *sec*-C_4H_9, c-C_6H_{11}, *n*-C_6H_{13}, and $CH_2C_6H_5$; $A = Co(CO)_4$, $R = CH_3$, C_2H_5; $A = Co_3(CO)_{10}$, $R = CH_3$. Alkoxide complexes $[Mo(OCH_3)_2(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ and $[Mo(OCH_3)(CO)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ were obtained from *trans*-$[Mo(N_2)_2(dpe)_2]$. The role of the hydridometal carbonyls and of the alcohols in the protonation reaction of the coordinated dinitrogen is discussed.

Since the report of the first dinitrogen complex in 1965,[1] the reactions of coordinated dinitrogen with various reagents such as Lewis acids,[2] organic halides,[3] acids,[4] and organolithium compounds[5] have been found.[6] Above all, catalytic reduction of molecular nitrogen under mild conditions via dinitrogen complexes is one of the most important goals in the chemistry of homogeneous catalysis. A more obvious approach to that goal has been the treatment of dinitrogen complexes with transition-metal hydrides or with hydrogen gas in the presence of a hydride as catalyst. Unfortunately, however, these reactions resulted in the displacement of the coordinated dinitrogen by hydride ligands in the case of transition-metal hydrides with tertiary phosphine ligands.[7,8] Although a number of hydridometal carbonyls were known, no reports concerning the reaction with dinitrogen complexes were available when the present study was commenced. The important discovery by Chatt and his co-workers in 1975,[9] that simple acids such as sulfuric and hydrochloric acids protonate the coordinated dinitrogen in tungsten and molybdenum dinitrogen complexes to form ammonia and hydrazine, and other subsequent studies[10] suggested to us that acidic hydridometal carbonyls would give similar results. As some hydridometal carbonyls can be prepared by the reaction of hydrogen gas with metal carbonyls,[11,12] we postulated that hydridometal carbonyls might catalyze the hydrogenation of the coordinated dinitrogen with hydrogen itself. Therefore we tried the reactions of acidic hydridometal carbonyls $H_2Fe(CO)_4$ and $HFeCo_3(CO)_{12}$ with *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = W or Mo) and actually obtained moderate yields of ammonia and hydrazine after base distillation of the reaction products.[13] Similar reactions have been studied independently by Hidai[14] and Yamamoto.[15] Attempts to clarify the reaction mechanism led to our isolation of novel alkoxide hydrazido(2–) complexes, $[W(OR)(NNH_2)(dpe)_2]^+A^-$ ($A = FeCo_3(CO)_{12}$ or $Co(CO)_4$) from *trans*-$[W(N_2)_2(dpe)_2]$.[16]

In this paper we describe (i) the extended series of protonation reactions to form ammonia and hydrazine by means of hydridometal carbonyls and (ii) the preparation of the alkoxide hydrazido(2–) complexes and time-dependent infrared spectra of the reaction mixtures. The scope and limitations of the use of hydridometal carbonyls as a means of nitrogen fixation are discussed.

Experimental Section

All manipulations were carried out under nitrogen atmosphere unless otherwise stated. The complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo[17] or W[10a]), *trans*-$[M(N_2)_2(dpe)_2]$ (M = Mo[4a,18,19] or W[4a,19]), $HMn(CO)_5$,[20] $H_2Fe(CO)_4$,[21] $HCo(CO)_4$ in hexane,[22] and $HFeCo_3(CO)_{12}$[23] were pre-

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(1) Allen, A. D.; Senoff, C. V. *J. Chem. Soc., Chem. Commun.* **1965**, 621.

(2) (a) Chatt, J.; Fay, R. C.; Richards, R. L. *J. Chem. Soc. A* **1971**, 702. (b) Chatt, J.; Crabtree, R. H.; Jeffery, E. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1973**, 1167. (c) Mercer, M.; Crabtree, R. H.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1973**, 808. (d) Robson, R. *Inorg. Chem.* **1974**, *13*, 475.

(3) (a) Ben-Shoshan, R.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1976**, *112*, C9. (b) Day, V. W.; George, T. A.; Iske, S. D. A., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 4127. (c) Bossard, G. E.; Busby, D. C.; Chang, M.; George, T. A.; Iske, S. D. A., Jr. *Ibid.* **1980**, *102*, 1001. (d) Chatt, J.; Head, R. A.; Hitchcock, P. B.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1977**, *133*, C1. (e) Bevan, P. C.; Chatt, J.; Leigh, G. J.; Leelamani, E. G. *Ibid.* **1977**, *139*, C59. (f) Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740.

(4) (a) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, *2074*. (b) Mariquez, J. M.; Sanner, R. D.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 3042. (c) Miura, Y.; Yamamoto, A. *Chem. Lett.* **1978**, 937.

(5) Sellmann, D.; Weiss, W. *J. Organomet. Chem.* **1978**, *160*, 183.

(6) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(7) Aresta, M.; Sacco, A. *Gazz. Chim. Ital.* **1972**, *102*, 755.

(8) Hidai, M.; Tominari, K.; Uchida, Y. *J. Am. Chem. Soc.* **1972**, *94*, 110.

(9) Chatt, J.; Pearman, A. J.; Richards, R. L. *Nature (London)* **1975**, *253*, 39.

(10) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852. (b) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1979**, *101*, 3405. (c) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *Ibid.* **1980**, *102*, 7461. (d) Baumann, J. A.; George, T. A. *Ibid.* **1980**, *102*, 6153.

(11) Schunn, R. A. "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 209.

(12) (a) Iwanaga, R. *Bull. Chem. Soc. Jpn.* **1962**, 774. (b) Ungnary, F. *J. Organomet. Chem.* **1972**, *36*, 363. (c) Albano, V. C.; Ceriotti, A.; Chini, P.; Ciani, G.; Martinengo, S.; Anker, W. M. *J. Chem. Soc., Chem. Commun.* **1975**, 859.

(13) Nishihara, H.; Mori, T.; Saito, T.; Sasaki, Y. *Chem. Lett.* **1980**, 667.

(14) Hidai, M.; Takahashi, T.; Yokotake, I.; Uchida, Y. *Chem. Lett.* **1980**, 645.

(15) Yamamoto, A., personal communication.

(16) Nishihara, H.; Saito, T.; Sasaki, Y. *Chem. Lett.* **1981**, 452.

(17) George, T. A.; Seibold, C. D. *Inorg. Chem.* **1973**, *12*, 2544.

(18) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639.

(19) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1980**, *20*, 119.

(20) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 198.

(21) Farmeay, K.; Kilner, M. *J. Chem. Soc. A* **1970**, 634.

(22) Orchin, M.; Rupilius, W. *Catal. Rev.* **1972**, *6*, 85.

(23) Chini, P.; Colli, L.; Perald, M. *Gazz. Chim. Ital.* **1960**, *90*, 1005.

0002-7863/82/1504-4367$01.25/0

pared by published methods. Infrared spectra were determined with a Hitachi IR spectrometer 260-30 and ^1H NMR spectra with a JEOL-JNM PS-100 spectrometer. All ^1H NMR spectra were recorded in CD_2Cl_2 without tetramethylsilane, and δ values were obtained by reference to the internal CH_2Cl_2 at δ 5.30. Elemental analyses were performed in the analytical laboratory of our department.

Quantitative Analysis of Ammonia and Hydrazine. The hydridometal carbonyl, dinitrogen complex, and solvent were brought together as follows.

$HMn(CO)_5$ and $H_2Fe(CO)_4$. A weighed sample of hydride cooled to −78 °C was added to a frozen suspension of a dinitrogen complex (50 mg) in methanol or tetrahydrofuran (10 mL) at −196 °C. For the reaction under hydrogen the frozen mixture was degassed under vacuum and hydrogen gas then introduced.

$HCo(CO)_4$. A hexane solution of $HCo(CO)_4$ cooled to −78 °C was added to a frozen suspension of a dinitrogen complex (50 mg) in methanol (10 mL) at −196 °C under carbon monoxide, and the frozen mixture was degassed under vacuum before introduction of hydrogen or nitrogen. The concentration of $HCo(CO)_4$ in hexane solution was measured by titration under an atmosphere of carbon monoxide.

$HFeCo_3(CO)_{12}$. A weighed sample of $HFeCo_3(CO)_{12}$, a dinitrogen complex (50 mg), and a solvent such as methanol, ethanol, 2-propanol, or ethylene glycol (10 mL) were mixed at room temperature. For the reaction under hydrogen the mixture was immediately frozen at −196 °C and degassed under vacuum before introducing the hydrogen gas.

After the mixture was stirred for the times given in Tables I–IV, volatile constituents were evaporated at temperatures below 0 °C into a trap containing 0.1 N H_2SO_4 (10 mL). The contents of the trap and the residue were separately treated with 40% aqueous KOH and the products distilled into 0.1 N H_2SO_4 (10 mL). Ammonia and hydrazine in each distillate were determined by colorimetric methods using indonaphthol[24] and *p*-(dimethylamino)benzaldehyde,[25] respectively, but only trace amounts were detected in the trap.

Preparation of $[W(OCH_3)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (1). The mixture of *trans*-$[W(N_2)_2(dpe)_2]$ (1.0 g, 1.0 mmol), $HFeCo_3(CO)_{12}$ (0.7 g, 1.2 mmol), methanol (10 mL), and toluene (15 mL) was stirred for 6 h at room temperature. After filtration, the dark brown residue was washed with methanol and toluene and recrystallized from dichloromethane–methanol to afford the black product **1**: yield 1.2 g (77%); ^1H NMR δ 2.56 (s, CH_3O), 2.5–3.1 (m, CH_2P; these two overlapping peaks give a combined intensity equal to 11 H), 3.36 (br s, NNH_2, 2 H), 6.8–7.6 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{65}H_{53}Co_3FeN_2O_{13}P_4W$: C, 48.48; H, 3.32; N, 1.74. Found: C, 48.43; H, 3.16; N, 1.65.

Preparation of $[W(OR)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (R = C_2H_5 (2), *n*-C_3H_7 (3), *i*-C_3H_7 (4), *n*-C_4H_9 (5), *sec*-C_4H_9 (6), c-C_6H_{11} (7), *n*-C_6H_{13} (8), $CH_2C_6H_5$ (9). These complexes were prepared by the same procedure as for **1**. Complex **5** was recrystallized from dichloromethane–ethanol, and all others were crystallized from dichloromethane–diethyl ether.

$[W(OC_2H_5)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (2): yield 76%; ^1H NMR δ 0.49 (t, CH_3C, 3 H, J_{HH} = 6.5 Hz), 2.65 (d, CH_2–O), 2.5–3.2 (m, CH_2P; the two overlapping, 10 H), 3.28 (br s, NNH_2, 2 H), 6.9–7.6 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{66}H_{55}Co_3FeN_2O_{13}P_4W$: C, 48.80; H, 3.41; N, 1.72. Found: C, 48.95; H, 3.34; N, 1.66.

$[W(O\text{-}n\text{-}C_3H_7)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (3): yield 59%; ^1H NMR δ 0.17 (t, CH_3C, 3 H, J_{HH} = 6.5 Hz), 0.5–1.1 (m, CH_2–C, 2 H), 2.38 (t, CH_2–O, J_{HH} = 6.5 Hz), 2.5–3.0 (m, CH_2P; the two overlapping, 10 H), 3.26 (br s, NNH_2, 2 H), 6.8–7.7 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{67}H_{57}Co_3FeN_2O_{13}P_4W$: C, 49.11; H, 3.51; N, 1.71. Found: C, 49.21; H, 3.35; N, 1.93.

$[W(O\text{-}i\text{-}C_3H_7)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (4): yield 62%; ^1H NMR δ 0.14 (d, CH_3-C, 6 H, J_{HH} = 6.0 Hz), 2.4–3.1 (br m, CH_2P and CH–O, 9 H), 3.17 (br s, NNH_2, 2 H), 6.8–7.8 (m, C_6H_5-P, 40 H). Anal. Calcd for $C_{67}H_{57}Co_3FeN_2O_{13}P_4W$: C, 49.11; H, 3.51; N, 1.71. Found: C, 49.11; H, 3.49; N, 1.73.

$[W(O\text{-}n\text{-}C_4H_9)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (5): yield 74%; ^1H NMR δ 0.4–1.0 (m, CH_2 and CH_3C, 7 H), 2.47 (t, CH_2–O, J_{HH} = 8.0 Hz), 2.5–3.1 (m, CH_2P; the two overlapping, 10 H), 3.31 (br s, NNH_2, 2 H), 6.8–7.6 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{68}H_{59}Co_3FeN_2O_{13}P_4W$: C, 49.42; H, 3.60; N, 1.70. Found: C, 49.49; H, 3.48; N, 1.75.

$[W(O\text{-}sec\text{-}C_4H_9)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (6): yield 37%; ^1H NMR δ −0.03 (t, $CH_3(CH_2)$, 3 H, J_{HH} = 7.5 Hz), 0.12 (d, $CH_3(CH)$, 3 H, J_{HH} = 6.0 Hz), 0.2–0.6 (m, CH_2, 2 H), 2.4–3.1 (br m, CH_2P and CH–O, 9 H), 3.15 (br s, NNH_2, 2 H), 6.8–7.7 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{68}H_{59}Co_3FeN_2O_{13}P_4W$: C, 49.42; H, 3.60; N, 1.70. Found: C, 49.45; H, 3.68; N, 1.74.

$[W(O\text{-}c\text{-}C_6H_{11})(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (7): yield 55%; ^1H NMR δ −0.1–1.4 (m, CH_2, 10 H), 2.2–3.1 (br m, CH_2P and CH–O, 9 H), 3.11 (br s, NNH_2, 2 H), 6.7–7.8 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{70}H_{61}Co_3FeN_2O_{13}P_4W$: C, 50.09; H, 3.66; N, 1.67. Found: C, 50.01; H, 3.43; N, 1.55.

$[W(O\text{-}n\text{-}C_6H_{13})(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (8): yield 42%; ^1H NMR δ 0.6–1.7 (m, CH_2 and CH_3C, 11 H), 2.3–3.2 (br m, CH_2P and CH_2–O, 10 H), 3.30 (br s, NNH_2, 2 H), 6.8–7.7 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{70}H_{63}Co_3FeN_2O_{13}P_4W$: C, 50.03; H, 3.78; N, 1.67. Found: C, 49.75; H, 3.68; N, 1.38.

$[W(OCH_2C_6H_5)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (9): yield 57%; ^1H NMR δ 2.4–3.0 (m, CH_2P, 8 H), 3.22 (br s, NNH_2, 2 H), 3.68 (s, CH_2–O, 2 H), 6.9–7.6 (m, C_6H_5P and C_6H_5C, 45 H). Anal. Calcd for $C_{71}H_{57}Co_3FeN_2O_{13}P_4W$: C, 50.56; H, 3.41; N, 1.66. Found: C, 50.91; H, 3.52; N, 1.62.

Preparation of $[W(OCH_3)(NNH_2)(dpe)_2]^+[Co(CO)_4]^-$ (10). A hexane solution of $HCo(CO)_4$ (5.8 mmol/40 mL) was added to the frozen mixture of *trans*-$[W(N_2)_2(dpe)_2]$ (1.0 g, 0.97 mmol) and methanol (10 mL) at −196 °C under carbon monoxide. The mixture was degassed under vacuum and nitrogen introduced. After the mixture was stirred for 20 h at −20 °C, the color of the suspension turned from orange to light yellow. After the solvent and excess $HCo(CO)_4$ were evaporated under vacuum below 0 °C, the residue was washed with methanol and hexane and recrystallized from dichloromethane–methanol to give the yellow product **10**: yield 0.6 g (51%); ^1H NMR δ 2.56 (s, CH_3O), 2.5–3.1 (m, CH_2P; the two overlapping, 11 H), 3.45 (br s, NNH_2, 2 H), 6.8–7.6 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{57}H_{53}CoN_2O_5P_4W$: C, 56.45; H, 4.40; N, 2.31. Found: C, 56.07; H, 4.26; N, 2.23.

Diethyl ether was added to the washing solution, from which dark green crystals separated after storing for 1 day. $[W(OCH_3)(NNH_2)(dpe)_2]^+[Co_3(CO)_{10}]^-$ (**12**): yield 0.1 g (7%); ^1H NMR δ 2.51 (s, CH_3O), 2.2–2.9 (br m, CH_2P; the two overlapping, 11 H), 3.22 (br s, NNH_2, 2 H), 6.7–7.7 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{63}H_{53}Co_3N_2O_{11}P_4W$: C, 50.49; H, 3.56; N, 1.87. Found: C, 50.22; H, 3.73; N, 1.80.

Preparation of $[W(OC_2H_5)(NNH_2)(dpe)_2]^+[Co(CO)_4]^-$ (11). A hexane solution of $HCo(CO)_4$ (8.9 mmol/60 mL) was added to the frozen mixture of *trans*-$[W(N_2)_2(dpe)_2]$ (1.3 g, 1.3 mmol), ethanol (15 mL), and toluene (15 mL) at −196 °C under carbon monoxide. The mixture was degassed under vacuum and nitrogen introduced. After the mixture was stirred for 44 h at −20 °C, the solvent and excess $HCo(CO)_4$ were evaporated under vacuum below 0 °C. The residue was washed with hexane and recrystallized from dichloromethane–toluene to give the yellow product **11**: yield 0.4 g (26%); ^1H NMR δ 0.48 (t, CH_3C, 3 H, J_{HH} = 6.5 Hz), 2.5–3.1 (m, CH_2P and CH_2O, 10 H), 3.33 (br s, NNH_2, 2 H), 6.7–7.7 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{58}H_{55}CoN_2O_5P_4W$: C, 56.79; H, 4.52; N, 2.28. Found: C, 56.59; H, 4.37; N, 2.04.

Preparation of $[W(OCH_3)(NNH_2)(dpe)_2]^+[B(C_6H_5)_4]^-$ (13). A solution of **1** (0.10 g, 0.062 mmol) in tetrahydrofuran (10 mL) containing $NaB(C_6H_5)_4$ (0.21 g, 0.61 mmol) was stirred for 20 min. The solution was filtered, and after addition of diethyl ether (30 mL) it was left standing for 1 day. The light yellow crystals which separated were washed with diethyl ether (20 mL × 2) and recrystallized from dichloromethane–diethyl ether: yield 0.064 g (77%); ^1H NMR δ 2.2–3.0 (br m, CH_2P and CH_3O, 11 H), 3.41 (br s, NNH_2, 2 H), 6.5–8.2 (m, C_6H_5P and C_6H_5B, 60 H). Anal. Calcd for $C_{77}H_{73}BN_2OP_4W$: C, 67.95; H, 5.41; N, 2.06. Found: C, 67.89; H, 5.36; N, 2.00.

Reaction of *trans*-$[Mo(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$ and Methanol. A suspension of *trans*-$[Mo(N_2)_2(dpe)_2]$ (1.01 g, 1.06 mmol) and $HFeCo_3(CO)_{12}$ (0.61 g, 1.07 mmol) in toluene–methanol (20 mL/10 mL) was stirred at room temperature for 36 h. After the precipitate formed was filtered off and washed with methanol (20 mL × 2), toluene (20 mL) was added to it. By filtration it was separated into two constituents, the toluene-insoluble and toluene-soluble constituents. The toluene-insoluble constituent was crystallized from dichloromethane–methanol and then washed with methanol and hexane to give the black product $[Mo(OCH_3)_2(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (**14**): yield 0.235 g (15.4%); IR (KBr disk) 2810 (ν(CH) of OCH_3); 1049 (ν(OC of OCH_3); 2068, 1980, 1927, 1859, 1810 (ν(CO)) cm^{-1}. Anal. Calcd for $C_{66}H_{54}Co_3FeMoO_{14}P_4$: C, 52.03; H, 3.57. Found: C, 52.33; H, 3.47.

Evaporation of toluene from the solution containing the toluene-soluble constituent gave a black oil. This oil was again dissolved in dichloromethane (20 mL), to which hexane (60 mL) was added to give black crystals. Recrystallization from dichloromethane–hexane gave the product $[Mo(OCH_3)(CO)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (**15**); IR (KBr disk) 2810 (ν(CH) of OCH_3); 1126 (ν(OC) of OCH_3); 2068, 1993, 1965, 1925, 1883, 1860 (sh), 1813 (ν(CO)) cm^{-1}; ^1H NMR δ 2.01 (s, CH_3O, 3 H), 2.72 (m, CH_2P, 8 H), 7.34 (m, C_6H_5P, 40 H). Anal. Calcd for $C_{66}H_{51}Co_3FeMoO_{14}P_4$: C, 52.13; H, 3.38. Found: C, 52.26; H, 3.25.

Attempted Preparation of Tungsten Hydrazido(2−) Complexes with PMe_2Ph Ligands. *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (0.49 g, 0.62 mmol) was

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(24) Morita, Y.; Kogure, Y. *Nippon Kagaku Zasshi* **1963**, *84*, 816.

(25) Watt, G. W.; Chrisp, G. P. *Anal. Chem.* **1952**, *24*, 2006.

Table I. Reaction of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] with $HFeCo_3(CO)_{12}$[a]

entry	mol ratio, Fe/W	atm[c]	solvent[d]	time, h	yield[b] NH$_3$	yield[b] N$_2$H$_4$
1	6.5	in vacuo	MeOH	20	0.05	0.02
2	12.4	N_2	MeOH	20	0.05	0.05
3	6.5	H_2	MeOH	1	0.03	t[h]
4	6.0	H_2	MeOH	4	0.03	0.01
5	6.4	H_2	MeOH	20	0.09	0.01
6	5.7	H_2 (0.8)	MeOH	20	0.09	0.01
7	6.3	H_2 (2)	MeOH	20	0.09	0.02
8	6.0	H_2 (3)	MeOH	20	0.19	0.03
9	5.9	H_2 (4)	MeOH	20	0.04	0.02
10	5.5	H_2 (5)	MeOH	20	0.06	0.01
11	7.5	H_2 (10)	MeOH	20	0.03	0.02
12	6.1	N_2 (9), H_2 (3)	MeOH	20	0.13	0.02
13	0.9	H_2	MeOH	20	0	t[h]
14	1.8	H_2	MeOH	20	t[h]	t[h]
15	3.0	H_2	MeOH	20	0.06	0.01
16	18.1	H_2	MeOH	20	0.32	0.01
17	6.5	H_2	MeOH[e]	20	0.01	0
18[f]	6.0	H_2 (3)	MeOH	20	0.08	0.03
19	6.0	H_2	EtOH	20	0.01	0.04
20	6.1	H_2	*i*-PrOH	20	0.01	t[h]
21	5.7	H_2	EG[g]	20	0.01	t[h]

[a] Reaction carried out at 20 °C. [b] mol/W atom. [c] 0.3 atm unless otherwise stated in parentheses. [d] 10 mL. [e] 100 mL. [f] $RhCl(PPh_3)_3$ (1.0 mol/W atom) added. [g] Ethylene glycol. [h] t = trace (less than 0.005 mol/W atom).

Table II. Reaction of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] with $H_2Fe(CO)_4$

entry	mol ratio, Fe/W	atm[b]	solvent[c]	temp, °C	time, h	yield[a] NH$_3$	yield[a] N$_2$H$_4$
22	30	N_2	MeOH	−10	20	0.05	0.01
23	30	N_2	MeOH	−10	65	0.01	0.03
24	30	H_2	MeOH	−10	0.5	0	0.03
25	30	H_2	MeOH	−10	1	0.10	0.17
26	30	H_2	MeOH	−10	2	0.01	0.06
27	30	H_2	MeOH	−10	4	0.23	0.01
28	30	H_2	MeOH	−10	20	0.19	0.01
29	30	H_2	MeOH	−20	45	0.20	0.01
30	30	H_2	MeOH	−10	138	0.28	0.03
31	30	H_2 (40)	MeOH	−10	20	0.07	0.02
32	1	H_2	MeOH	−10	20	t[e]	0.01
33	2	H_2	MeOH	−10	20	t[e]	0.01
34	3	H_2	MeOH	−10	20	0.25	0.04
35	4	H_2	MeOH	−10	20	0.01	t[e]
36	5	H_2	MeOH	−10	20	0.06	0.02
37	6	H_2	MeOH	−10	20	0.17	0.02
38	15	H_2	MeOH	−10	20	0.18	0.01
39[d]	30	H_2	MeOH	−10	20	0.22	0.05
40	30	N_2	THF	−10	20	0.01	0.01
41	30	H_2	THF	−10	20	0.03	0.01
42	30	H_2	THF	−10	20	0.03	0.01

[a] mol/W atom. [b] 0.3 atm unless otherwise stated in parentheses. [c] 10 mL. [d] $MgSO_4$ added. [e] t = trace (less than 0.005 mol/W atom).

Table III. Reaction of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] with $HCo(CO)_4$[a]

entry	mol ratio, Co/W	atm[c]	yield[b] NH$_3$	yield[b] N$_2$H$_4$
43	25	in vacuo	0.09	0.01
44	25	N_2	0.06	0.06
45	25	CO	0.02	0.01
46	27	H_2	0.16	0.02
47	25	H_2 (5)	0.05	0.01
48	25	N_2 (30), H_2 (10)	0.02	t[d]

[a] Reaction carried out in methanol (10 mL)–hexane (12 mL) for 20 h at −20 °C. [b] mol/W atom. [c] 0.3 atm unless otherwise stated in parentheses. [d] t = trace (less than 0.005 mol/W atom).

Table IV. Other Reactions[a]

entry	complex	hydride[c]	atm[d]	temp, °C	yield[b] NH$_3$	yield[b] N$_2$H$_4$
49	$W(N_2)_2(PMe_2Ph)_4$	none	N_2	−20	t[g]	t[g]
50	$W(N_2)_2(PMe_2Ph)_4$	none	N_2 (1)	20	0.01	0.01
51	$W(N_2)_2(PMe_2Ph)_4$	none	H_2	20	t	t
52	$W(N_2)_2(PMe_2Ph)_4$	H_2SO_4	N_2 (1)	20	1.84[f]	0.03[f]
53	$W(N_2)_2(PMe_2Ph)_4$	Mn (9.2)	H_2	−10	0.01	0
54	$W(N_2)_2(dpe)_2$	$FeCo_3$ (5.9)	H_2	20	t[g]	0
55	$W(N_2)_2(dpe)_2$	Fe (30)	H_2	−10	0	0
56	$Mo(N_2)_2(PMe_2Ph)_4$	$FeCo_3$ (13.8)	H_2	20	0.02	0
57	$Mo(N_2)_2(PMe_2Ph)_4$	Fe (30)	H_2	−10	0.01	0
58	$Mo(N_2)_2(PEt_2Ph)_4$	Fe (30)	N_2	−10	0.01	0.01
59[e]	$Mo(N_2)_2(PEt_2Ph)_4$	Fe (30)	H_2	−10	0.01	t[g]

[a] Reaction carried out in methanol (10 mL) for 20 h. [b] mol/M atom (M = W or Mo). [c] Mn = $HMn(CO)_5$, Fe = $H_2Fe(CO)_4$, and $FeCo_3$ = $HFeCo_3(CO)_{12}$; mol/M atom (M = W or Mo) stated in parentheses. [d] 0.3 atm unless otherwise stated in parentheses. [e] Tetrahydrofuran (10 mL) used instead of methanol. [f] NH_3, 1.98, and N_2H_4, 0.03 (by Chatt[10a]). [g] t = trace (less than 0.005 mol/M atom (M = Mo or W)).

treated with $HFeCo_3(CO)_{12}$ (0.72 g, 1.26 mmol) in methanol (8 mL) at 0 °C for 4 h. The green product which precipitated was separated and washed with hexane and then extracted with dichloromethane. The extract was chromatographed on a silica gel column (Wako Gel, 100 mesh) with a mixed solvent of dichloromethane and hexane (1:4) as an eluant. $HFeCo_3(CO)_{11}(PMe_2Ph)$ (0.043 g) was isolated from a red-purple band. Anal. Calcd for $C_{19}H_{12}Co_3FeO_{11}P$: C, 33.56; H, 1.78. Found: C, 33.44; H, 1.69. $HFeCo_3(CO)_{10}(PMe_2Ph)_2$ (0.29 g) was isolated from a purple band. Anal. Calcd for $C_{26}H_{23}Co_3FeO_{10}P_2$: C, 39.53; H, 2.93. Found: C, 39.48; H, 3.07. A green band remained, the main part of which was probably $HFeCo_3(CO)_9(PMe_2Ph)_3$ judging from the comparison of its infrared spectrum with that of an authentic sample prepared by the reaction of $HFeCo_3(CO)_{12}$ and PMe_2Ph in methanol. It did not prove possible to isolate any pure tungsten-containing compound.

Measurement of Infrared Spectra at Intervals during the Course of Formation of 1. *trans*-[$W(N_2)_2(dpe)_2$] (20 mg) in suspension in methanol containing $HFeCo_3(CO)_{12}$ (15 mg) was stirred at 0 °C under nitrogen. The progress of the reaction was followed by withdrawing samples of the product at intervals for running infrared spectra (see Figure 2).

Results and Discussion

Formation of Ammonia and Hydrazine from Tungsten and Molybdenum Dinitrogen Complexes by Means of Hydridometal Carbonyls. Tables I–IV show the results of quantitative analysis of ammonia and hydrazine obtained by the base distillation of the reaction products of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] with $HFeCo_3(CO)_{12}$ (Table I), $H_2Fe(CO)_4$ (Table II), or $HCo(CO)_4$ (Table III) and of other reactants (Table IV). Our principal interest in these results has been to establish whether acidic hydridometal carbonyls merely play the role of simpler acids or display some specific hydrogenation activity.

Information[26] on the quantitative aspects of acidity of hydridometal carbonyls has been scarce until some recent systematic studies.[27] A few hydride complexes show strong acidity. Hieber et al.[28] have shown that $HCo(CO)_4$ in methanol is as strong as hydrochloric or nitric acids and that $H_2Fe(CO)_4$ in methanol is stronger than acetic acid. $HFeCo_3(CO)_{12}$ in THF–H_2O[23] has been reported to be as acidic as hydrochloric acid, but $HMn(CO)_5$ is almost neutral in water.[26,27] The results of the reactions of these hydridometal carbonyls with *cis*-[$W(N_2)_2(PMe_2Ph)_4$] indicate that almost no ammonia and hydrazine formed in the absence of the hydrides (no. 49–51) or in the presence of $HMn(CO)_5$ (no. 53) but that considerable amounts of ammonia (maximum 0.32 mol/W, no. 16) and hydrazine (maximum 0.17 mol, no. 25) formed in the presence of the acidic reactants $HFeCo_3(CO)_{12}$,

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(26) Schunn, R. A. "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 238.

(27) Walker, H. W.; Kresge, C. T.; Ford, P. C.; Pearson, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 7428.

(28) Hieber, W.; Hübel, W. *Z. Elektrochem.* **1953**, *57*, 235.

$H_2Fe(CO)_4$, or $HCo(CO)_4$. The results indicate that in the protonation of the coordinated dinitrogen the acidity of hydridometal carbonyls is most important; that is to say, hydridometal carbonyls participate in the reaction as strong acids. However, the lower yields compared with those from reactions using simpler acids[10a] (e.g., 1.84 mol/W, sulfuric acid) are indicative of the existence of unfavorable side reactions.

One of the reasons for the inferior protonation activity of the hydridometal carbonyls toward coordinated dinitrogen seems to be the displacement of N_2 or PMe_2Ph ligands in *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ by CO in the carbonyl complexes. Attempts to prepare methoxide hydrazido(2–) complexes by the treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with $HCo(CO)_4$ or $HFeCo_3(CO)_{12}$ failed, and $HFeCo_3(CO)_{12-n}(PMe_2Ph)_n$ ($n = 1, 2$) was found to be formed in the latter case. When two N_2 ligands in the tungsten complex are substituted by CO, protonation of N_2 is naturally not to be expected. Even if only one N_2 or a small number of PMe_2Ph ligands are displaced by CO to form *cis*-$[W(N_2)(CO)(PMe_2Ph)_4]$ or *cis*-$[W(N_2)_2(CO)_n(PMe_2Ph)_{4-n}]$, respectively, the reactivity of the coordinated dinitrogen toward an acid will decrease due to the greater back-donation of electrons to CO ligands.

The yield of ammonia is higher in the reactions in methanol than in THF as the comparison of runs no. 28 and 41 in Table II shows. This result is probably due to the protonating activity of alcohols rather than to their solvent role. Methanol and ethanol are sufficiently acidic to protonate coordinated dinitrogen under irradiation or at reflux temperatures.[10a] It has been postulated that electron flow from oxo ligands onto tungsten is a requisite condition for reduction of the coordinated dinitrogen beyond the NNH_2 stage and that alkoxide ligands can play this role.[10a] In the protonation reactions of the coordinated dinitrogen by simpler acids HX, X^- coordinates to the central metal, whereas a metal carbonyl anion does not coordinate to the metal and a vacant site remains available for an alkoxide ligand. The isolation of $[W(OR)(NNH_2)(dpe)_2]^+A^-$ ($A = FeCo_3(CO)_{12}$ or $Co(CO)_4$) (vide infra) together with the formation of ammonia and hydrazine in the reactions of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with a hydridometal carbonyl in methanol lends support to the assumption that alkoxide complex formation is a very important step in the protonation reaction of the coordinated dinitrogen by a hydridometal carbonyl in an alcohol. By analogy, intermediate alkoxide complexes are also likely to form from the PMe_2Ph complex, and in fact formation of a common species $[W(OMe)_2(NNH_2)(PMe_2Ph)_3]$ in dilute methanol solutions of HX has been reported.[29] In the protonation of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with simpler acids, ammonium salts were formed,[10a] which indicated that the protonation had proceeded to the NH_3 stage. However, we have not been able to detect analogous ammonium salts, $(NH_4)^+A^-$ ($A = FeCo_3(CO)_{12}$, $HFe(CO)_4$ or $Co(CO)_4$), in the reaction mixtures, and at present it is not certain to what stage the protonation has proceeded before KOH distillation.

Because we had considered it probable that H_2 gas might be involved in the reduction of the coordinated dinitrogen, comparative experiments were made under hydrogen or nitrogen or under vacuum. The results confirm the significant influence of hydrogen upon the yields of reduction products. Comparisons of no. 2 vs. no. 16 in Table I, no. 22 vs. no. 28 in Table II, and no. 44 vs. no. 46 in Table III indicate a promotive effect of hydrogen. However, at hydrogen pressure above 4 atm, the formation of ammonia and hydrazine tended to decrease (no. 5–11, Table I). This may be a consequence of increasing hydrogen pressure causing substitution of the coordinated dinitrogen in *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ by hydrogen.

Promotive effect due to hydrogen is probably caused either by stabilization of some tungsten hydride intermediate which is converted into nitrogen hydride or by the interaction of hydrogen with the carbonyl complex anion to result in the hydrogenation of the hydrazido(2–) ligand. We consider the latter possibility is more likely because promotive effect due to hydrogen seems absent in the reaction of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) with sulfuric acid in methanol,[10a] although some hydride intermediates are formed in the reaction of tungsten dinitrogen complexes with halogen acids.[4a,10c,30] We are now seeking further evidence for the interaction of H_2 with the carbonyl complex anion.

The yields of ammonia and hydrazine from *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ are much higher than those from *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ as the comparisons of runs no. 16 vs. no. 56 and no. 28 vs. no. 57 indicate. This is explicable through the stronger reducing power of tungsten than molybdenum. It is reported that the protonation proceeds as far as the NH_3 stage in the case of tungsten but just to the N_2H_2 stage in the molybdenum complex from which ammonia forms only after base distillation.[10a] Recently Baumann and George have determined the fate of molybdenum in the reaction of $[Mo(N_2)_2(triphos)(PPh_3)]$ with HBr to form ammonia by isolating $MoBr_3(triphos)$ in >90% yield.[10d] Molybdenum is oxidized to Mo(III) in contrast with the tungsten in $[W(N_2)_2(PMe_2Ph)_4]$ which is probably oxidized as far as W(VI),[10a] which explains the lower yields of ammonia per metal for molybdenum. Failure to find evidence of formation of $[Mo(OCH_3)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (vide infra) suggests that *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ is hardly protonated even to the NNH_2 stage, in contrast with the tungsten dinitrogen complexes in their reaction with hydridometal carbonyls.

It may be noted that *trans*-$[W(N_2)_2(dpe)_2]$ gives only negligible amounts of ammonia and hydrazine (Table IV). The result is probably due to the inertness of the dpe ligand toward displacement by alkoxide.

In summary the evidence indicates that the reactions of tungsten and molybdenum dinitrogen complexes with hydridometal carbonyls show features in common with the reactions in which simpler acids are used. However, the yields of ammonia and hydrazine are lower because of rather facile ligand displacement reaction caused by the carbonyl ligands in the hydrides. As metal carbonyl complex anions do not coordinate to tungsten or molybdenum, the role of alcohols as protonation agents is emphasized by the ready formation of alkoxide complexes. Alcohol stabilizes the hydrazido(2–) complex by coordinating to the metal as alkoxide in exchange with an outer-sphere carbonyl complex anion which in turn regenerates the hydridometal carbonyl with the proton from the alcohol. The alkoxide ligand is likely to assist the further protonation of the hydrazido(2–) moiety by donating some negative charge to the metal. It is noteworthy that a hydrogen atmosphere promotes the protonation of the coordinated dinitrogen.

Synthesis of Alkoxide Hydrazido(2–) Complexes of Tungsten with Carbonyl Complex Anions. We attempted to isolate intermediate complexes from the reaction mixtures of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and an acidic hydridometal carbonyl to elucidate the stages of the protonation of the coordinated dinitrogen and to understand the reason for the upper limit of the yields of ammonia and hydrazine (vide supra). However, the isolation of such complexes was unsuccessful due to the displacement reactions by CO ligands (vide infra). Therefore, *trans*-$[W(N_2)_2(dpe)_2]$, which did not form ammonia nor hydrazine but was considered to give more stable complexes,[4a] was treated with hydridometal carbonyls in alcohols.

Using, for example, the reaction of *trans*-$[W(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$ in methanol, we have isolated novel tungsten hydrazido(2–) complex coordinated by a methoxide and two dpe ligands and with a counterion $[FeCo_3(CO)_{12}]^-$ (eq 1). As the

$$\begin{aligned} &trans\text{-}[W(N_2)_2(dpe)_2] + HFeCo_3(CO)_{12} + CH_3OH \rightarrow \\ &\quad \underset{\mathbf{1}}{trans\text{-}[W(OCH_3)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-} + N_2 \quad (1) \end{aligned}$$

solubility of the dinitrogen complex in methanol is low, the reaction was carried out by using the compound in suspension. The product was obtained as a dark brown solid, soluble in dichloromethane at room temperature, slightly soluble in methanol, toluene, or diethyl ether, but insoluble in hexane. The solid is air-stable but

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[29] Henderson, R. A. *J. Organomet. Chem.* **1981**, *208*, C51.

[30] Chatt, J.; Kan, C. T.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2032.

Table V. Spectroscopic Data of Alkoxide Hydrazido(2-) Complexes $[W(OR)(NNH_2)(dpe)_2]^+A^-$

			infrared,[a] cm^{-1}				
complex	R	A	ν(NH) vw	ν(OC) m	ν(CO)	other(s)	^1H NMR,[b] δ(NNH_2)
1	CH_3	$FeCo_3(CO)_{12}$	3352 3264	1144 -1126	2052 w, 1990 vs, 1960 sh, 1924 s, 1856 w, 1806 s	2798 w	3.36
2	C_2H_5	$FeCo_3(CO)_{12}$	3338 3282	1073	2069 w, 2000 vs, 1970 sh, 1927 s, 1860 w, 1810 s	1378 w, 918 w	3.28
3	n-C_3H_7	$FeCo_3(CO)_{12}$	3361 3270	1084	2070 w, 1996 vs, 1969 sh, 1925 s, 1859 w, 1816 s	1384 w	3.26
4	i-C_3H_7	$FeCo_3(CO)_{12}$	3362 3269	1127	2070 w, 1995 vs, 1964 sh, 1933 s, 1861 w, 1818 s	1379 w, 1366 w, 1337 w, 990 m, 850 w	3.17
5	n-C_4H_9	$FeCo_3(CO)_{12}$	3349 3275	1084	2059 w, 1999 vs, 1972 sh, 1933 s, 1853 w, 1819 s	1382 w	3.31
6	*sec*-C_4H_9	$FeCo_3(CO)_{12}$	3340 3261	1110 br	2068 w, 1998 vs, 1961 sh, 1925 s, 1858 w, 1815 s	1368 w, 1336 w, 1036 w, 928 w	3.15
7	c-C_6H_{11}	$FeCo_3(CO)_{12}$	3345 3264	1080	2070 w, 1996 vs, 1969 sh, 1931 s, 1861 w, 1816 s	2929 m, 1364 w, 1348 w, 989 m, 895 w, 850 w, 799 w, 653 m	3.11
8	n-C_6H_{13}	$FeCo_3(CO)_{12}$	3340 3261	1088	2070 w, 1997 vs, 1966 sh, 1929 s, 1858 w, 1816 s	1381 w	3.30
9	$CH_2C_6H_5$	$FeCo_3(CO)_{12}$	3345 3259	1071 br	2070 w, 1997 vs, 1966 sh, 1931 s, 1861 w, 1806 s	1454 w, 1366 w, 1210 w, 919 w	3.22
10	CH_3	$Co(CO)_4$	3346 3260	1119 sh	1886 vs	2798 w	3.45
11	C_2H_5	$Co(CO)_4$	3362 3268	1065	1886 vs	1375 w, 912 w	3.33
12	CH_3	$Co_3(CO)_{10}$	3374 3264	1120	2046 w, 1975 vs, 1954 sh, 1886 m, 1771 w, 1731 m	2791 w	3.22
13	CH_3	$B(C_6H_5)_4$	3336 3240	1121 br		3056 m, 2799 w, 1582 m, 848 w, 739 w, 616 m	3.41

[a] KBr disk; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [b] The spectra were measured in CD_2Cl_2 without tetramethylsilane, and δ values were estimated with reference to the internal CH_2Cl_2 at δ 5.30. Other ^1H NMR data are shown in the Experimental Section.

sensitive to atmospheric oxidation in solution.

The infrared spectrum shows weak absorptions assignable to ν(NH) at 3352 and 3264 cm^{-1}. These bands shift to 2500 and 2388 cm^{-1} on treatment with D_2O. The ^1H NMR spectrum of the complex shows a signal at δ 3.36 (2 H) due to the N_2H_2 group, which disappears upon addition of D_2O. These spectral properties are similar to those of $[WCl(NNH_2)(dpe)_2][B(C_6H_5)_4]$ (ν(NH) 3340, 3240 cm^{-1}; δ(NH) 3.02),[4a] so that it is very likely that N_2H_2 is again coordinated to tungsten as the hydrazido(2-) ligand, NNH_2. The infrared absorptions due to the methoxide group are observed at 2798 cm^{-1} (ν(CH)) and at 1144-1126 cm^{-1} (ν(OC)). The ^1H NMR spectrum of the complex indicates a signal at δ 2.56, due to methoxide, which overlaps that from the CH_2 of dpe. The infrared absorptions 1990 and 1806 cm^{-1} are assignable to ν(CO) of terminal and bridging carbonyl groups, respectively, of $[FeCo_3(CO)_{12}]^-$. The anionic nature of $[FeCo_3(CO)_{12}]^-$ is reflected in its bridging carbonyl stretching vibration which is shifted from the 1888-cm^{-1} band of $HFeCo_3(CO)_{12}$. Such shifts to lower wavenumbers are also observed in the infrared absorptions of $[N(C_2H_5)_4]^+[FeCo_3(CO)_{12}]^-$ (1829 cm^{-1})[23] and $K^+[FeCo_3(CO)_{12}]^-$ (1774 cm^{-1}). Complex **1** undergoes $[FeCo_3(CO)_{12}]^-$ exchange with tetraphenylborate ion in solution at room temperature to give the light yellow complex, $[W(OCH_3)(NNH_2)(dpe)_2]^+[B(C_6H_5)_4]^-$ (**13**). The mutual trans positions of NNH_2 and OCH_3 groups as well as a tetrahedral structure for $FeCo_3(CO)_{12}$ have been shown by a single-crystal X-ray structure analysis of the complex **1** (Figure 1).[31]

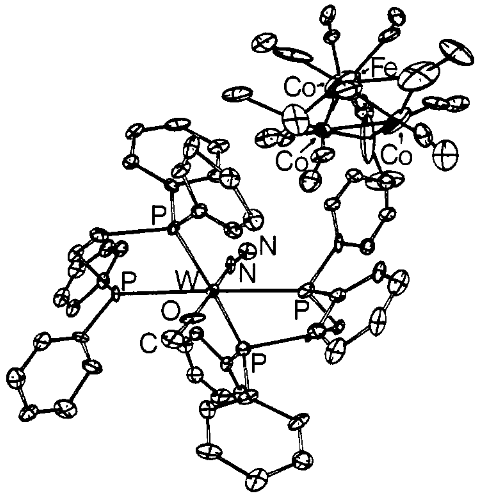

Figure 1. View of the $[W(OCH_3)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ molecule, drawn by ORTEP.

It has been established that the reactions of *trans*-$[M(N_2)_2(dpe)_2]$ with acids HX (M = Mo and W; X = Cl and Br) afford hydrazido(2-) complexes $[MX_2(NNH_2)(dpe)_2]$,[4a] and compounds of the type $[MX(NNH_2)(dpe)_2]^+A^-$ (A = BF_4, PF_6, ClO_4, $B(C_6H_5)_4$) containing the corresponding cation have been synthesized.[4a] The complexes obtained in the present study seem to be the first examples of alkoxide hydrazido(2-) complexes of tungsten with dpe ligands. In addition, other alkoxide hydrazido(2-) complexes with $[FeCo_3(CO)_{12}]^-$ (**2**-**9**) have been prepared from ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, cyclohexanol, 1-hexanol, and benzyl alcohol.

Hydridotetracarbonylcobalt gives alkoxide hydrazido(2-) complexes **10** and **11** which contain $[Co(CO)_4]^-$. As $HCo(CO)_4$ is unstable, the reaction was carried out at -20 °C under nitrogen atmosphere. They are air-sensitive even in solid states, and their color turns from yellow to green in air. A byproduct [W-

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(31) Crystal data are as follows: mol wt 1590.37, triclinic space group $P1$, a = 10.721 (1) Å, b = 14.403 (2) Å, c = 10.650 (1) Å, α = 96.61 (1)°, β = 96.80 (1)°, γ = 84.01 (1)°, U = 1615.2 (3) $Å^3$, Z = 1, D(calcd) = 1.62, D(measd) = 1.62 Mg m^{-3}, μ(Mo Kα) = 1.87 mm^{-1}, and R = 0.083 for 5248 reflections. Because of the disorder, precise bond distances and bond angles have not been obtained. Some of the tentative values are given: W-P(average) = 2.52 (1) Å, W-N = 2.00 (2) Å, W-O = 1.76 (2) Å, N-N = 1.25 (3) Å, O-C(methyl) = 1.51 (3) Å, Co-*Co*(average) = 2.37 (1) Å, Fe-Co(average) = 2.41 (1) Å; O-W-N = 176.0°, W-N-N = 174.7°, W-O-C(methyl) = 171.2°. Cf. (a) Huie, B. T.; Knobler, C. B.; Kaesz, H. D. *J. Chem. Soc., Chem. Commun.* **1975**, 684. (b) Teller, R. G.; Wilson, R. D.; McMullan, R. K.; Koetzle, T. F.; Bau, R. *J. Am. Chem. Soc.* **1978**, *100*, 3071.

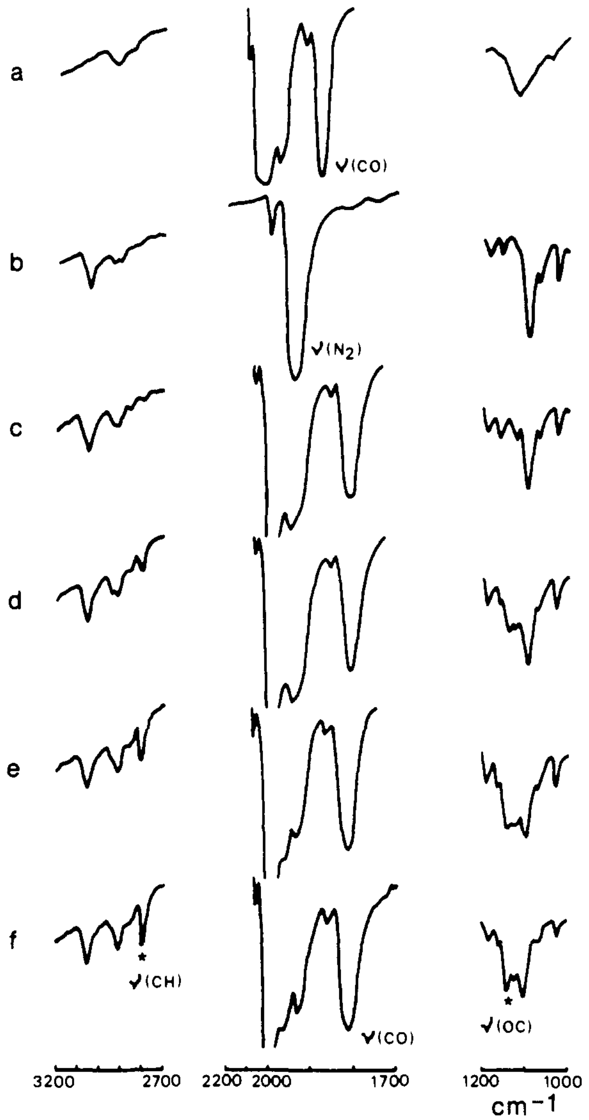

Figure 2. Infrared spectra of methanol-free samples from the reaction of *trans*-$[W(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$: a, $HFeCo_3(CO)_{12}$; b, *trans*-$[W(N_2)_2(dpe)_2]$; c, reaction mixture treated for 50 min; d, after 3 h; e, after 6 h; f, $[W(OCH_3)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (asterisk denotes bands due to the OCH_3 group).

$(OCH_3)(NNH_2)(dpe)_2]^+[Co_3(CO)_{10}]^-$ (**12**) was also obtained in 7% yield.

Complexes **2**–**12** show ν(NH) at 3374–3259 cm^{-1} and singlet peaks of the NNH_2 groups at δ 3.11–3.45. The infrared absorptions of the alkoxide groups in **1**–**12** show ν(OC) at 1144–1065 cm^{-1}. The chemical shifts of the protons of the alkoxide groups shift to higher field than those of the corresponding free alcohol. For example, the OCH_3 protons shift ca. 0.9 ppm, and those in the OCH_2CH_3 group shift more than 1 ppm. The $[FeCo_3(CO)_{12}]^-$ in **2**–**9** are discrete anions showing terminal and bridging carbonyl stretching frequencies at 2000–1996 and 1819–1806 cm^{-1}, respectively. The ν(CO) in **10** and **11** lies at 1886 cm^{-1} near ν(CO) in solid salts of $[Co(CO)_4]^-$.[32] The ν(CO) in **12** (1975 and 1886 cm^{-1}) are near the wavenumbers for $Li^+[Co_3(CO)_{10}]^-$ (2000 and 1865 cm^{-1}).[33]

Attempts to synthesize $[Mo(OCH_3)(NNH_2)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ by the reaction of *trans*-$[Mo(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$ in methanol resulted in loss of the coordinated dinitrogen and formation of a mixture of several complexes, from which $[Mo(OCH_3)_2(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (**14**) and $[Mo(OCH_3)(CO)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$ (**15**) were isolated as crystalline compounds and were characterized. Also the attempts to isolate a PMe_2Ph analogue, $[W(OCH_3)(NNH_2)(PMe_2Ph)_4]^+[FeCo_3(CO)_{12}]^-$, were unsuccessful, and we isolated only $HFeCo_3(CO)_{12-n}(PMe_2Ph)_n$ ($n = 1, 2$) as pure compounds.

The Mechanism of Formation of NNH_2 Complexes. The infrared spectra of solid samples which were prepared by evaporating methanol from the reaction mixtures of *trans*-$[W(N_2)_2(dpe)_2]$ and $HFeCo_3(CO)_{12}$ in methanol at 0 °C showed the shift of bridging carbonyl ν(CO) in $HFeCo_3(CO)_{12}$ (1888 cm^{-1}) to 1806 cm^{-1} corresponding to an anionic $[FeCo_3(CO)_{12}]^-$ group (Figure 2). The shift is almost complete within 50 min (c). However, the bands assignable to ν(CH) of the OCH_3 group (2798 cm^{-1}) after 50 min were negligibly weak. The intensity became much stronger in the samples (d, e) which were prepared by using reaction times of 3–6 h.

We presently correlate the results with the following mechanism. The first step is rapid protonation of *trans*-$[W(N_2)_2(dpe)_2]$ with a $HFeCo_3(CO)_{12}$ to form $[W(N_2H)(dpe)_2]^+[FeCo_3(CO)_{12}]^-$[34] concomitant with displacement of a N_2. Coordination of CH_3O^- to tungsten occurs rapidly after the relatively slow protonation of the N_2H moiety by the second $HFeCo_3(CO)_{12}$. Henderson has also proposed that HX (X = Cl, Br, or HSO_4) adds two protons to the coordinated dinitrogen in *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = W or Mo) in an alcohol solvent.[29] Since we have not obtained any hydrazido(2–) complex in the reaction of *trans*-$[W(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$ in benzene,[34] the equilibrium in the second protonation by the acid is presumably predominantly shifted to the $W-N_2H$ and the formation of the $W-NNH_2$ complex is assisted by the coordination of an alkoxide ligand to tungsten.

Registry No. 1, 77662-78-3; **2**, 77662-79-4; **3**, 77662-81-8; **4**, 82026-59-3; **5**, 82026-61-7; **6**, 82026-63-9; **7**, 82026-65-1; **8**, 82026-67-3; **9**, 82026-69-5; **10**, 77662-74-9; **11**, 77662-76-1; **12**, 77662-77-2; **13**, 82078-94-2; **14**, 82043-94-5; **15**, 82026-71-9; $HFeCo_3(Co)_{11}(PMe_2Ph)$, 82026-72-0; $HFeCo_3(Co)_{10}(PMe_2Ph)_2$, 82026-73-1; $HFeCo_3(CO)_9(PMe_2Ph)_3$, 78492-19-0; *trans*-$[W(N_2)_2(dpe)_2]$, 28915-54-0; *trans*-$[Mo(N_2)_2(dpe)_2]$, 25145-64-6; *cis*-$[W(N_2)_2(PMe_2Ph)_4]$, 28915-53-9; *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$, 32457-67-3; *cis*-$[Mo(N_2)_2(PEt_2Ph)_4]$, 82078-95-3; $HFeCo_3(CO)_{12}$, 21750-96-9; $HCo(CO)_4$, 16842-03-8; $H_2Fe(CO)_4$, 12002-28-7; $HMn(CO)_5$, 16972-33-1.

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(32) Edgell, W. F.; Huff, J.; Thomas, J.; Lehman, H.; Angell, C.; Asato, G. *J. Am. Chem. Soc.* **1960**, *82*, 1254.

(33) Fachinetti, G. *J. Chem. Soc., Chem. Commun.* **1979**, 396.

(34) Treatment of *trans*-$[W(N_2)_2(dpe)_2]$ (0.3 mmol) with $HFeCo_3(CO)_{12}$ (0.4 mmol) in benzene (20 mL) at room temperature for 16 h and subsequent crystallization from dichloromethane–toluene afforded black crystals (0.3 g) whose elemental analysis data agreed with the formula $[W(N_2H)(dpe)_2]^+[FeCo_3(CO)_{12}]^-\cdot{}^1/_2CH_2Cl_2$ (Calcd for $C_{64.5}H_{50}ClCo_3FeN_2O_{12}P_4W$: C, 47.79; H, 3.11; N, 1.73. Found: C, 47.99; H, 2.88; N, 1.69.) Full characterization of the complex is now in progress.