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Synthesis and Reactivity of Tungsten− and Molybdenum−Dinitrogen Complexes Bearing Ferrocenyldiphosphines toward Protonolysis

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Novel tungsten− and molybdenum−dinitrogen complexes bearing 1,1′-bis(diethylphosphino)ferrocenes as auxiliary ligands have been prepared and characterized crystallographically. Reactions of these complexes with an excess amount of sulfuric acid in methanol at room temperature yield ammonia in good yields. This result is in sharp contrast to the previous result that protonolysis of tungsten− and molybdenum−dinitrogen complexes bearing conventional diphosphines such as 1,2-bis(diphenylphosphino)ethane does not produce ammonia. Reactions of the dinitrogen complexes with 2 equiv of trifluoromethanesulfonic acid give the corresponding hydrazido complexes as intermediates. Molecular structures of these hydrazido complexes have been determined by X-ray analysis.

Introduction

Development of dinitrogen fixation systems under ambient reaction conditions is one of the most important subjects in chemistry. Toward this end, the preparation and reactivity of transition metal dinitrogen complexes have been intensively investigated for the last several decades.[1,2] The first transition metal−dinitrogen complex, $[Ru(N_2)(NH_3)_5]X_2$ (X = Br, I, BF_4, PF_6), was reported by Allen and Senoff in 1965.[3] As to the group 6 metal−dinitrogen complex, *trans*-$[Mo(N_2)_2(dppe)_2]$ (dppe = 1,1′-bis(diphenylphosphino)ethane) was reported by Hidai and his co-workers in 1969.[4] In 1975 Chatt and his co-workers found the formation of ammonia by protonolysis of tungsten− and molybdenum−dinitrogen complexes $[M(N_2)_2(PR_3)_4]$ (M = W, Mo).[5] We have so far disclosed that reactions of the tungsten−dinitrogen complexes with ruthenium−dihydrogen complexes at 55 °C give ammonia in good yields based on the W atom.[6] We believe that this methodology provides a promising pathway to produce ammonia from dinitrogen and dihydrogen under mild reaction conditions. More recently, the use of multimetallic centers to activate molecular dinitrogen provided a significant advance for the development of effective transformation of coordinated dinitrogen molecules.[7,8]

Ferrocene and its derivatives are widely used as structural units for the construction of unusual compounds and components in material sciences.[9] Moreover, ferrocene-based ligands are of

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(1) For recent reviews, see: (a) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115. (b) Gambarotta, S. *J. Organomet. Chem.* **1995**, *500*, 117. (c) Fryzuk, M. D.; Johnson, S. A *Coord. Chem. Rev.* **2000**, *200−202*, 379. (d) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385. (e) Gambarotta, S.; Scott, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5298. (f) Hidai, M.; Mizobe, Y *Can. J. Chem.* **2005**, *83*, 358. (g) Himmel, H.-J.; Reiher, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6264.

(2) For recent examples of mononuclear complexes, see: (a) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76. (b) Curley, J. J.; Sceats, E. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2006**, *128*, 14036. (c) Smythe, N. C.; Schrock, R. R.; Muller, P.; Weare, W. W. *Inorg. Chem.* **2006**, *45*, 9197. (d) Bart, S. C.; Chłopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901. (e) Scott, J.; Vidyaratne, I.; Korobkov, I.; Gambarotta, S.; Budzelaar, P. H. M. *Inorg. Chem.* **2008**, *47*, 896.

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

(4) Hidai, M.; Tominari, K.; Uchida, Y.; Misono, A. *Chem. Commun.* **1969**, 1392.

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

(6) (a) Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 506. (b) Nishibayashi, Y.; Takemoto, S.; Iwai, S.; Hidai, M. *Inorg. Chem.* **2000**, *39*, 5946.

(7) For recent examples of homometallic complexes, see: (a) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527. (b) Evans, W. J.; Lee, D. S.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2006**, *128*, 14176. (c) Hirotsu, M.; Fontaine, P. P.; Zavalij, P. Y.; Sita, L. R. *J. Am. Chem. Soc.* **2007**, *129*, 12690. (d) Bart, S. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 7212. (e) Akagi, F.; Matsuo, T.; Kawaguchi, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 8778. (f) Knobloch, D. J.; Toomey, H. E.; Chirik, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 4248. (g) Morello, L.; Ferreira, M. J.; Patrick, B. O.; Fryzuk, M. D. *Inorg. Chem.* **2008**, *47*, 1319.

(8) For heterometallic complexes, see: (a) Mizobe, Y.; Yokobayashi, Y.; Oshita, H.; Takahashi, T.; Hidai, M. *Organometallics* **1994**, *13*, 3764. (b) O'Donoghue, M. B.; Zanetti, N. C.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 2753. (c) Mindiola, D. J.; Meyer, K.; Cherry, J.-P. F.; Baker, T. A.; Cummins, C. C. *Organometallics* **2000**, *19*, 1622. (d) Ishino, H.; Nagano, T.; Kuwata, S.; Yokobayashi, Y.; Ishii, Y.; Hidai, M.; Mizobe, Y. *Organometallics* **2001**, *20*, 188. (e) Mori, H.; Seino, H.; Hidai, M.; Mizobe, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5431.

(9) (a) Hudson, R. D. A. *J. Organomet. Chem.* **2001**, *637−639*, 47. (b) Nishihara, H. *Adv. Inorg. Chem.* **2002**, *53*, 41. (c) Nakamura, E. *Pure Appl. Chem.* **2003**, *75*, 427. (d) van Staveren, D. R.; Metzler-Nolte, N. *Chem. Rev.* **2004**, *104*, 5931. (e) Nakamura, E. *J. Organomet. Chem.* **2004**, *689*, 4630. (f) J. Inorg. Organomet. Polym. Mater. **2005**, *15*,No. 1 (the special issue celebrating the 50th anniversary of polyferrocenes). (g) Fouda, M. F. R.; Abd-Elzaher, M. M.; Abdelsamaia, R. A.; Labib, A. A. *Appl. Organomet. Chem.* **2007**, *21*, 613. (h) Gao, Y.; Shreeve, J. M. *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 19. (i) Seiwert, B.; Karst, U. *Anal. Bioanal. Chem.* **2008**, *390*, 181.

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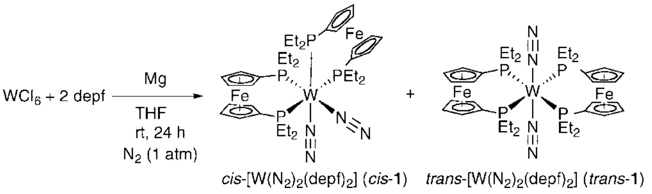
Scheme 1



increasing importance for transition-metal-catalyzed organic syntheses including asymmetric transformations based on the planar chirality of ferrocene derivatives.[10,11] For instance, 1,1′-bis(diphenylphosphino)ferrocene (dppf) became a commonly used ligand because of relatively large bite angles, capacity of dative bond formation with electron-deficient metal centers, and chemical robustness of the ferrocene skeleton.[11] As an extension of our continuing study,[12] we have now envisaged the preparation of tungsten− and molybdenum−dinitrogen complexes bearing ferrocenyldiphosphines as auxiliary ligands. Herein, we report the synthesis and characterization of tungsten− and molybdenum−dinitrogen complexes bearing 1,1′-bis(diethylphosphino)ferrocene (depf) such as [M(N$_2$)$_2$(depf)$_2$] together with their stoichiometric reactivity toward protonolysis.

Results and Discussion

Treatment of WCl$_6$ with 2 equiv of depf in the presence of an excess amount of magnesium in tetrahydrofuran (THF) under a dinitrogen atmosphere at room temperature for 24 h gave a mixture of *cis*- and *trans*-[W(N$_2$)$_2$(depf)$_2$] (**1**) in the ratio of 6: 1 (Scheme 1). The major isomer (*cis*-**1**) was isolated in 19% yield by recrystallization. The IR spectrum of *cis*-**1** exhibited two strong ν_{NN} bands at 1972 and 1906 cm^{-1}, consistent with the *cis* arrangement of two dinitrogen ligands. These ν_{NN} frequencies of *cis*-**1** are lower than those of *cis*-[W(N$_2$)$_2$(PR$_3$)$_4$] complexes as shown in Table 1. This result indicates that the depf ligand has a highly electron-donating nature as a result of strong π-back-donation from the tungsten center to the dinitrogen ligands. In the ^{31}P{^{1}H} NMR spectrum of *cis*-**1**, two triplet peaks were observed at −5.1 and −1.9 ppm corresponding to phosphorus atoms *cis* and *trans* to dinitrogen ligands or vice versa. The molecular structure of *cis*-**1** was unambiguously clarified by X-ray crystallography, an ORTEP drawing of *cis*-**1** being shown in Figure 1. Selected bond lengths and angles of *cis*-**1** are listed in Table 2. Around the octahedrally coordinated tungsten center, two dinitrogen ligands occupied *cis* positions each other. The W−N(1) and N(1)−N(2) distances of 1.994(3) and 1.121(5) Å are not unusual. The bite angle of the diphosphine ligand (P1−W−P2 89.05(3)°) is smaller than that observed for [W(CO)$_4$(dppf)][14] (95.24(5)°) and [W(CO)$_3$(NCMe)(dppf)][15] (98.05(6)°), but similar to [W(CO)$_3$(η^2-C$_{60}$)(dppf)][14] (88.63(4)°), suggesting steric congestion around the tungsten center of *cis*-**1**. The W−Fe distance of 4.61 Å precludes the direct bonding interaction between the tungsten and iron atoms.[16,17] Separately, we confirmed that no intercon-

Table 1. IR and Electrochemical Data of Tungsten− and Molybdenum−Dinitrogen Complexes

complex[a]	ν_{NN}/cm^{-1} [b]	$E_{1/2}$/V[c]	ref
cis-W(N$_2$)$_2$(depf)$_2$ (*cis*-**1**)	1972, 1906	−0.88qr	this work
cis-W(N$_2$)$_2$(PMe$_3$)$_4$	1980, 1920[d]		13a
cis-W(N$_2$)$_2$(PPhMe$_2$)$_4$	1991, 1913	−0.83qr	13b
cis-W(N$_2$)$_2$(dppm)$_2$	2000, 1935[e]		13c
trans-W(N$_2$)$_2$(depf)$_2$ (*trans*-**1**)	1883	−0.95	this work
trans-W(N$_2$)$_2$(depe)$_2$	1904	−0.96	13d, 13e
trans-W(N$_2$)$_2$(dchpe)$_2$	1880[e]	−1.02	13e
trans-W(N$_2$)$_2$(PPhMe$_2$)$_4$	1898	−0.83	13b
trans-W(N$_2$)$_2$(dppe)$_2$	1943	−0.68	13d, 13e
trans-W(N$_2$)$_2$(PPh$_2$Me)$_4$	1910[e]	−0.71[f]	13f
trans-Mo(N$_2$)$_2$(depf)$_2$ (*trans*-**2**)	1907	−0.97	this work
trans-Mo(N$_2$)$_2$(depe)$_2$	1928	−0.97	13e, 13g
trans-Mo(N$_2$)$_2$(dppe)$_2$	1976[e]	−0.70	13e
trans-Mo(N$_2$)$_2$(PPh$_2$Me)$_4$	1922	−0.71	13h, 13i

[a] dppm = 1,1′-bis(diphenylphosphino)methane. depe = 1,1′-bis(diethylphosphino)ethane. dchpe = 1,1′-bis(dicyclohexylphosphino)ethane. [b] KBr pellet. [c] Relative to ferrocene−ferrocenium couple in THF. qr = quasi-reversible. [d] *n*-Hexane solution. [e] Nujol mull. [f] This work.

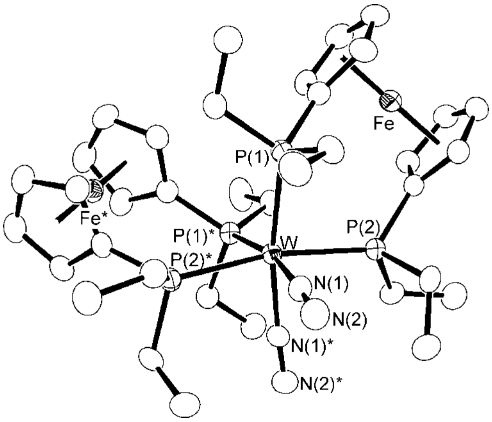


Figure 1. ORTEP view of *cis*-**1** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

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(10) (a) Colacot, T. J. *Chem. Rev.* **2003**, *103*, 3101. (b) Barbaro, P.; Bianchini, C.; Giambastiani, G.; Parisel, S. L. *Coord. Chem. Rev.* **2004**, *248*, 2131. (c) Gómez Arrayás, R.; Adrio, J.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 7674. (d) Fihri, A.; Meunier, P.; Hierso, J.-C. *Coord. Chem. Rev.* **2007**, *251*, 2017.

(11) *Ferrocenes. Homogenous Catalysis, Organic Synthesis, Material Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995.

(12) (a) Nishibayashi, Y.; Uemura, S. *Synlett* **1995**, 79. (b) Nishibayashi, Y.; Segawa, K.; Ohe, K.; Uemura, S. *Organometallics* **1995**, *14*, 5486. (c) Nishibayashi, Y.; Segawa, K.; Takada, H.; Ohe, K.; Uemura, S. *Chem. Commun.* **1996**, 847. (d) Nishibayashi, Y.; Takei, I.; Hidai, M. *Organometallics* **1997**, *16*, 3091. (e) Nishibayashi, Y.; Singh, J. D.; Arikawa, Y.; Uemura, S.; Hidai, M. *J. Organomet. Chem.* **1997**, *531*, 13. (f) Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1998**, *17*, 3420. (g) Takemoto, S.; Kuwata, S.; Nishibayashi, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 6428. (h) Takei, I.; Nishibayashi, Y.; Arikawa, Y.; Uemura, S.; Hidai, M. *Organometallics* **1999**, *18*, 2271. (i) Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1999**, *18*, 2291. (j) Takemoto, S.; Kuwata, S.; Nishibayashi, Y.; Hidai, M. *Organometallics* **2000**, *19*, 3249. (k) Chung, K.-G.; Miyake, Y.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2725. (l) Takei, I.; Nishibayashi, Y.; Ishii, Y.; Mizobe, Y.; Uemura, S.; Hidai, M. *Chem. Commun.* **2001**, 2360. (m) Iwata, T.; Miyake, Y.; Nishibayashi, Y.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1548. (n) Nishibayashi, Y.; Yamauchi, A.; Onodera, G.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 5875. (o) Onodera, G.; Nishibayashi, Y.; Uemura, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3819. (p) Shimada, Y.; Miyake, Y.; Matsuzawa, H.; Nishibayashi, Y. *Chem. Asian J.* **2007**, *2*, 393.

(13) (a) Carmona, E.; Galindo, A.; Poveda, M. L.; Rogers, R. D. *Inorg. Chem.* **1985**, *24*, 4033. (b) George, T. A.; DeBord, J. R. D.; Kaul, B. B.; Pickett, C. J.; Rose, D. J. *Inorg. Chem.* **1992**, *31*, 1295. (c) Dadkhah, H.; Dilworth, J. R.; Fairman, K.; Kan, C. T.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1523. (d) Nordwig, B. L.; Ohlsen, D. J.; Beyer, K. D.; Brummer, J. G. *Inorg. Chem.* **2006**, *45*, 858. (e) Hussain, W.; Leigh, G. J.; Mohd.-Ali, H.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1703. (f) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2139. (g) Filippou, A. C.; Schnakenburg, G.; Philippopoulos, A. I.; Weidemann, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 5979. (h) George, T. A.; Noble, M. E. *Inorg. Chem.* **1978**, *17*, 1678. (i) Lazarowych, N. J.; Morris, R. H.; Ressner, J. M. *Inorg. Chem.* **1986**, *25*, 3926.

(14) Song, L.-C.; Liu, J.-T.; Hu, Q.-M.; Wang, G.-F.; Zanello, P.; Fontani, M. *Organometallics* **2000**, *19*, 5342.

(15) Hsu, S. C. N.; Yeh, W.-Y.; Chiang, M. Y. *J. Organomet. Chem.* **1995**, *492*, 121.

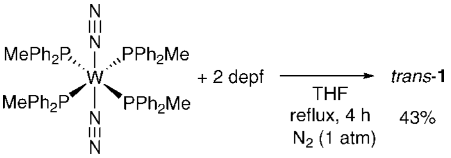
(16) Bandoli, G.; Dolmella, A. *Coord. Chem. Rev.* **2000**, *209*, 161.

Table 2. Selected Interatomic Distances and Bond Angles for *cis*-1[a]

	Distances (Å)		
W−P(1)	2.5129(10)	W−P(2)	2.4655(10)
W−N(1)	1.994(3)	N(1)−N(2)	1.121(5)
W···Fe	4.6101(6)		
	Angles (deg)		
P(1)−W−P(2)	89.05(3)	P(1)−W−P(1)*	103.45(3)
P(1)−W−P(2)*	98.42(3)	P(2)−W−P(2)*	167.96(3)
P(1)−W−N(1)	86.73(10)	P(1)−W−N(1)*	168.40(12)
P(2)−W−N(1)	87.14(10)	P(2)−W−N(1)*	83.90(10)
N(1)−W−N(1)*	83.74(14)	W−N1−N2	174.2(4)

[a] Asterisks denote atoms related by the symmetry operation $-x$, y, $-z+1/2$.

Scheme 2



version between *cis*-**1** and *trans*-**1** was observed at room temperature for several days. Unfortunately, when dppf was used in place of depf, the formation of the corresponding tungsten−dinitrogen complex was not observed at all.

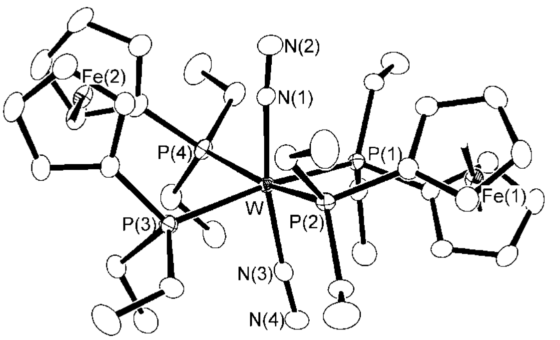
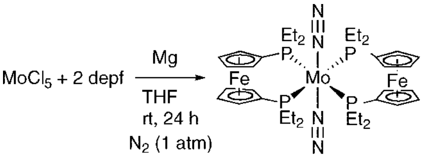


Figure 2. ORTEP view of *trans*-**1** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Selected Interatomic Distances and Bond Angles for *trans*-1

	Distances (Å)		
W−P(1)	2.4858(6)	W−P(2)	2.4856(9)
W−P(3)	2.4789(6)	W−P(4)	2.4667(8)
W−N(1)	1.993(2)	W−N(3)	1.999(2)
N(1)−N(2)	1.136(3)	N(3)−N(4)	1.139(3)
W···Fe(1)	4.5269(4)	W···Fe(2)	4.4301(4)
	Angles (deg)		
P(1)−W−P(2)	95.72(2)	P(3)−W−P(4)	84.99(2)
P(1)−W−P(3)	169.53(2)	P(1)−W−P(4)	91.11(2)
P(2)−W−P(3)	90.32(2)	P(2)−W−P(4)	165.48(2)
P(1)−W−N(1)	88.61(6)	P(1)−W−N(3)	85.57(6)
P(2)−W−N(1)	82.59(8)	P(2)−W−N(3)	88.98(9)
P(3)−W−N(1)	100.67(6)	P(3)−W−N(3)	85.99(6)
P(4)−W−N(1)	84.79(8)	P(4)−W−N(3)	104.34(9)
N(1)−W−N(3)	169.24(11)	W−N(1)−N(2)	174.9(2)
W−N(3)−N(4)	174.0(2)		

Scheme 3



trans-**2**
13%

Heating of *trans*-[W(N_2)$_2$(PPh_2Me)$_4$][18] with 2 equiv of depf in THF at reflux temperature for 4 h gave *trans*-**1** in 43% isolated yield (Scheme 2). No formation of *cis*-**1** was observed after the reaction. The IR spectrum of *trans*-**1** exhibited a ν_{NN} band at 1883 cm^{-1}, which is one of the most red-shifted values among the reported tungsten−dinitrogen complexes such as *trans*-[W(N_2)$_2$(PR_3)$_4$], as shown in Table 1. A cyclic voltammogram of *trans*-**1** showed a reversible one-electron oxidation wave at −0.95 V (versus the ferrocene−ferrocenium redox couple), corresponding to the W(0/I) redox couple. This value is similar to those of *trans*-[W(N_2)$_2$(depe)$_2$] (depe = 1,1′-bis(diethylphosphino)ethane) and *trans*-[W(N_2)$_2$(dchpe)$_2$] (dchpe = 1,1′-bis(dicyclohexylphosphino)ethane) (Table 1). These results indicate that the electron donation from each depf ligand proved to be as strong as two trialkylphosphine ligands. As a result, the strong π-back-donation ability of **1** is expected to make the ligating dinitrogen molecules highly reactive. In the ^{31}P{^{1}H} NMR spectrum of *trans*-**1**, a singlet peak was observed at −7.2 ppm (s with ^{183}W satellite, $^1J_{P-W}$ = 316 Hz). The molecular structure of *trans*-**1** was unambiguously clarified by X-ray crystallography, an ORTEP drawing of *trans*-**1** being shown in Figure 2. Selected bond lengths and angles of *trans*-**1** are listed in Table 3. Similar to *cis*-**1**, there is no bonding interaction between tungsten and iron centers (W−Fe: 4.43 and 4.52 Å).[13,14] The bite angles of two depf ligands in *trans*-**1** differ significantly (P(1)−W−P(2) 85.11(3)°, P(3)−W−P(4) 95.81(3)°), which corresponds to a synperiplanar and staggered conformation of the ferrocene units, the rotation angles of ferrocene units being 9.9° and 47.3°, respectively.[19] The distortion of the N(1)−W−N(3) angle in *trans*-**1** is probably due to the steric repulsion of the coordinated ligands. The other bond distances and angles are almost the same as those of *cis*-**1**.

The molybdenum−dinitrogen complex *trans*-[Mo(N_2)$_2$(depf)$_2$] (*trans*-**2**) was prepared by a similar procedure to that of *cis*-**1**. Treatment of $MoCl_5$ with 2 equiv of depf in the presence of an excess amount of magnesium in THF under an atmosphere of dinitrogen at room temperature for 24 h gave *trans*-**2** in 13% yield (Scheme 3). The IR spectrum of *trans*-**2** exhibited one ν_{NN} band at 1907 cm^{-1} consistent with the *trans* conformation. No *cis* isomer was observed at all probably due to the so-far-known fast *cis*−*trans* isomerization of molybdenum analogues.[20] The molecular structure of *trans*-**2** was unambiguously clarified by X-ray crystallography, an ORTEP drawing of *trans*-**2** being shown in Figure 3. Selected bond lengths and angles of *trans*-**2** are listed in Table 4. The crystals of *trans*-**2** were isomorphous to those of *trans*-**1**, and the structural parameters of *trans*-**2** are also the same as those of *trans*-**1**.

Next, we examined the reactivity of the tungsten− and molybdenum−dinitrogen complexes **1** and **2** toward protonolysis

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(17) (a) Seyferth, D.; Hames, B. W.; Rucker, T. G. *Organometallics* **1983**, *2*, 472. (b) Akabori, S.; Kumagai, T.; Shirahige, T.; Sato, S.; Kawazoe, K.; Tamura, C.; Sato, M. *Organometallics* **1987**, *6*, 526. (c) Sato, M.; Sekino, M.; Katada, M.; Akabori, S. *J. Organomet. Chem.* **1989**, *377*, 327. (d) Sato, M.; Suzuki, K.; Asano, H.; Sekino, M.; Kawata, Y.; Habata, Y.; Akabori, S. *J. Organomet. Chem.* **1994**, *470*, 263. (e) Hembre, R. T.; McQueen, J. S.; Day, V. W. *J. Am. Chem. Soc.* **1996**, *118*, 798. (f) Arnold, J.; Shafir, A. *J. Am. Chem. Soc.* **2001**, *123*, 9212. (g) Metallinos, C.; Tremblay, D.; Barrett, F. B.; Taylor, N. J. *J. Organomet. Chem.* **2006**, *691*, 2044. (h) Carver, C. T.; Monreal, M. J.; Diaconescu, P. L. *Organometallics* **2008**, *27*, 363.

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

(19) Löwendahl, J.-M.; Håkansson, M. *Organometallics* **1995**, *14*, 4736.

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

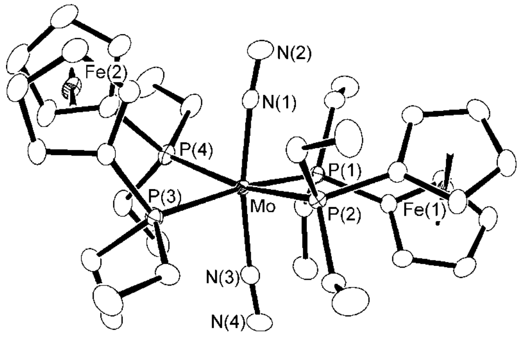
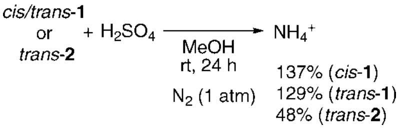


Figure 3. ORTEP view of *trans*-**2** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 4. Selected Interatomic Distances and Bond Angles for *trans*-2

	Distances (Å)		
Mo−P(1)	2.4991(4)	Mo−P(2)	2.4971(6)
Mo−P(3)	2.4945(4)	Mo−P(4)	2.4801(6)
Mo−N(1)	2.0097(16)	Mo−N(3)	2.0211(15)
N(1)−N(2)	1.124(2)	N(3)−N(4)	1.122(2)
Mo···Fe(1)	4.5366(3)	Mo···Fe(2)	4.4391(2)
	Angles (deg)		
P(1)−Mo−P(2)	95.563(18)	P(3)−Mo−P(4)	84.883(17)
P(1)−Mo−P(3)	169.675(19)	P(1)−Mo−P(4)	91.208(17)
P(2)−Mo−P(3)	90.417(17)	P(2)−Mo−P(4)	165.647(17)
P(1)−Mo−N(1)	88.56(4)	P(1)−Mo−N(3)	85.82(4)
P(2)−Mo−N(1)	82.78(5)	P(2)−Mo−N(3)	88.86(6)
P(3)−Mo−N(1)	100.56(4)	P(3)−Mo−N(3)	85.90(4)
P(4)−Mo−N(1)	84.76(5)	P(4)−Mo−N(3)	104.28(6)
N(1)−Mo−N(3)	169.43(7)	Mo−N(1)−N(2)	174.32(16)
Mo−N(3)−N(4)	173.8(2)		

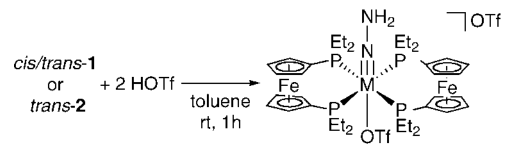
Scheme 4



because it is well-known that the stoichiometric reactions of tungsten− and molybdenum−dinitrogen complexes bearing at least one monodentate phosphine with a Brønsted acid gave ammonia and/or hydrazine.[5,21]

Treatment of *cis*- and *trans*-**1** with an excess amount of sulfuric acid in methanol at room temperature for 24 h produced ammonia in 137% and 129% yields based on the W atom, respectively (Scheme 4). In both cases, no formation of hydrazine was observed. On the other hand, the reaction of *trans*-**2** with sulfuric acid under the same reaction conditions gave ammonia in 48% yield based on the Mo atom. These results are apparently different from the previous results that protonolysis of tungsten− and molybdenum−dinitrogen complexes bearing conventional diphosphines such as 1,2-bis(diphenylphosohino)ethane does not produce ammonia.[22]

Scheme 5



3 (M = W)
4 (M = Mo)

To obtain more information on the reaction pathway for the formation of ammonia, we investigated reactions of **1** and **2** with 2 equiv of trifluoromethanesulfonic acid (HOTf) in toluene at room temperature for 1 h. As a result, the corresponding hydrazido complexes *trans*-[M(NNH$_2$)(OTf)(depf)$_2$]OTf (**3**; M = W, **4**; M = Mo) were obtained in 58% and 41% isolated yields, respectively (Scheme 5). Molecular structures of **3** and **4** were unambiguously clarified by X-ray crystallography, ORTEP drawings of **3** and **4** being shown in Figures 4 and 5. Selected bond lengths and angles of **3** and **4** are listed in Tables 5 and 6. In both cases, a hydrogen bond was observed between

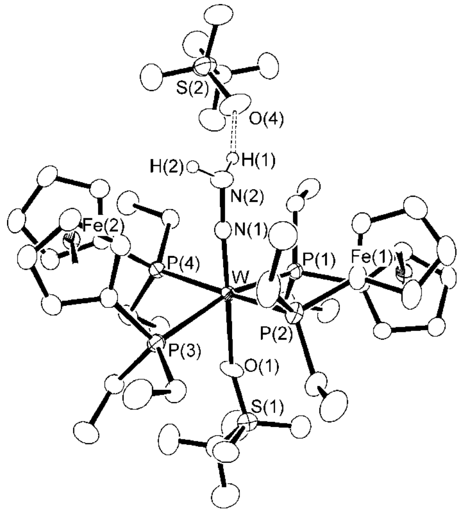


Figure 4. ORTEP view of **3** with 50% thermal ellipsoids. Hydrogen atoms except for the hydrazido ligand are omitted for clarity.

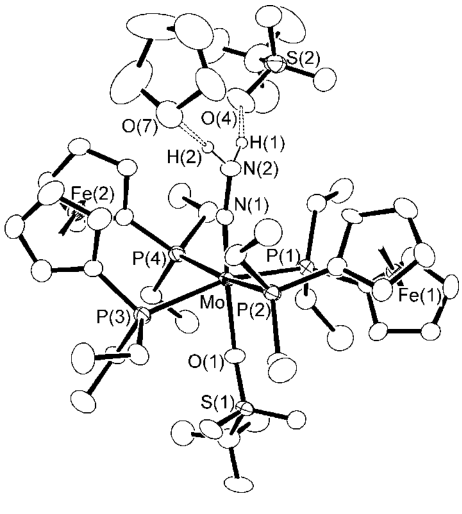


Figure 5. ORTEP view of $\mathbf{4}\cdot\mathrm{THF}\cdot0.5\mathrm{C_6H_{14}}$ with 50% thermal ellipsoids. Hydrogen atoms except for the hydrazido ligand and *n*-hexane solvate are omitted for clarity.

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(21) (a) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074. (b) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852. (c) Hidai, M.; Mizobe, Y.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1978**, 1187. (d) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1979**, *101*, 3405. (e) Anderson, S. N.; Fakley, M. E.; Richards, R. L.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1973. (f) Anderson, S. N.; Richards, R. L.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1986**, 245.

(22) (a) Heath, G. A.; Mason, R.; Thomas, K. M. *J. Am. Chem. Soc.* **1974**, *96*, 259. (b) Hidai, M.; Kodama, T.; Sato, M.; Hirakawa, M.; Uchida, Y. *Inorg. Chem.* **1976**, *15*, 2694. (c) Chatt, J.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 121. (d) Nishihara, H.; Mori, Y.; Nakano, K.; Saito, T.; Sasaki, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4367. (e) Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 917. (f) Bakar, M. A.; Hughes, D. L.; Hussain, W.; Leigh, G. J.; Macdonald, C. J.; Mohd.-Ali, H. *J. Chem. Soc., Dalton Trans.* **1988**, 2545. (g) Barclay, J. E.; Hills, A.; Hughes, D. L.; Leigh, G. J.; Macdonald, C. J.; Bakar, M. A.; Mohd.-Ali, H. *J. Chem. Soc., Dalton Trans.* **1990**, 2503.

Table 5. Selected Interatomic Distances and Bond Angles for 3

Distances (Å)			
W–P(1)	2.5459(8)	W–P(2)	2.5397(8)
W–P(3)	2.5948(8)	W–P(4)	2.5492(8)
W–N(1)	1.748(2)	W–O(1)	2.2195(18)
N(1)–N(2)	1.350(3)	N(2)–H(1)	0.99(4)
N(2)–H(2)	0.94(4)	O(4)···H(1)	1.93(4)
W···Fe(1)	4.5709(4)	W···Fe(2)	4.3407(4)
Angles (deg)			
P(1)–W–P(2)	94.24(2)	P(3)–W–P(4)	86.98(2)
P(1)–W–P(3)	164.07(2)	P(1)–W–P(4)	92.35(2)
P(2)–W–P(3)	88.11(2)	P(2)–W–P(4)	171.58(2)
P(1)–W–N(1)	94.26(8)	P(1)–W–O(1)	82.90(6)
P(2)–W–N(1)	87.58(8)	P(2)–W–O(1)	97.05(6)
P(3)–W–N(1)	101.58(8)	P(3)–W–O(1)	81.18(6)
P(4)–W–N(1)	86.71(8)	P(4)–W–O(1)	88.96(6)
N(1)–W–O(1)	174.72(10)	W–N(1)–N(2)	177.1(2)

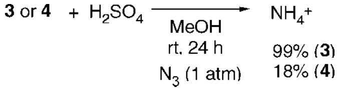
Table 6. Selected Interatomic Distances and Bond Angles for $4 \cdot THF \cdot 0.5C_6H_{14}$

Distances (Å)			
Mo–P(1)	2.5459(11)	Mo–P(2)	2.5664(9)
Mo–P(3)	2.5921(11)	Mo–P(4)	2.5999(9)
Mo–N(1)	1.730(2)	Mo–O(1)	2.237(2)
N(1)–N(2)	1.345(4)		
N(2)–H(1)	1.00(4)	N(2)–H(2)	0.94(4)
O(4)···H(1)	1.85(3)	O(7)···H(2)	1.95(4)
Mo···Fe(1)	4.5929(6)	Mo···Fe(2)	4.4150(6)
Angles (deg)			
P(1)–Mo–P(2)	93.85(3)	P(3)–Mo–P(4)	85.49(3)
P(1)–Mo–P(3)	163.76(3)	P(1)–Mo–P(4)	91.44(3)
P(2)–Mo–P(3)	91.75(3)	P(2)–Mo–P(4)	169.86(3)
P(1)–Mo–N(1)	92.70(12)	P(1)–Mo–O(1)	82.28(8)
P(2)–Mo–N(1)	84.02(9)	P(2)–Mo–O(1)	97.02(7)
P(3)–Mo–N(1)	103.05(12)	P(3)–Mo–O(1)	81.91(8)
P(4)–Mo–N(1)	87.10(9)	P(4)–Mo–O(1)	92.26(7)
N(1)–Mo–O(1)	174.93(14)	Mo–N(1)–N(2)	171.1(3)

one of the oxygen atoms of the triflate anion and one of the terminal hydrogen atoms of the hydrazido ligand. There was no structural evidence for the electronic interaction between the tungsten or molybdenum and iron atoms in the hydrazido complexes.

We confirmed the formation of ammonia from reactions of hydrazido complexes with an excess amount of sulfuric acid in methanol at room temperature for 24 h (Scheme 6). These results indicate that the formation of ammonia proceeds via hydrazido complexes as key intermediates. We could not detect any structurally defined complexes after the protonation of these hydrazido complexes with sulfuric acid, only free depf ligand being observed by $^{31}P\{^1H\}$ NMR.

Scheme 6



Since the first discovery of the formation of ammonia from the coordinated dinitrogen molecules on molybdenum and tungsten atoms, many efforts have been made including a mechanistic study on the reaction pathway.[5,18,21–25] As a result, it is generally known that molybdenum– and tungsten–dinitrogen complexes bearing monodentate phosphines as auxiliary ligands, $[M(N_2)_2(PR_3)_4]$ (M = Mo, W), produce ammonia and/or hydrazine by treatment with Brønsted acid such as sulfuric acid in methanol.[5,21] Interestingly, no formation of ammonia was observed when molybdenum– and tungsten–dinitrogen complexes bearing chelating diphosphines as auxiliary ligands, $[M(N_2)_2L_2]$ (M = Mo, W, L = dppe, depe), were employed; only the formation of the corresponding hydrazido complexes was observed.[22] Our observation is the first example of the formation of ammonia from molybdenum– and tungsten–dinitrogen complexes bearing two chelating diphosphines via the corresponding hydrazido complexes as intermediates. At present, we have not yet clarified the exact role of depf in these dinitrogen complexes, but it may be possible that the electron transfer process from ferrocene units to the tungsten or molybdenum center assists the reduction of the dinitrogen molecule into ammonia because George and his co-worker previously indicated the critical role of the ferrocene moiety on the formation of ammonia and/or hydrazine from other types of molybdenum monodinitrogen complexes, $[Mo(N_2)\{PhP(C_2H_4PPh_2)_2\}L]$ (L = dppf, dppe, dppm, 2 PPh_3).[26]

In summary, we have newly designed and prepared novel tungsten– and molybdenum–dinitrogen complexes bearing 1,1′-bis(diethylphosphino)ferrocenes. Protonation of these complexes with an excess amount of sulfuric acid in methanol produced ammonia in good yields. This result is in sharp contrast to the previous findings that protonolysis of tungsten– and molybdenum–dinitrogen complexes bearing conventional diphosphines such as 1,2-bis(diphenylphosohino)ethane does not produce ammonia. Stoichiometric reactions of the dinitrogen complexes with 2 equiv of trifluoromethanesulfonic acid yielded the corresponding hydrazido complexes as reactive intermediates. Molecular structures of newly prepared complexes were confirmed by X-ray analysis.

Experimental Section

General Method. ^1H NMR (270 MHz) and $^{31}P\{^1H\}$ NMR (109 MHz) spectra were measured on a JEOL Excalibur 270 spectrometer, and ^{31}P chemical shifts were quoted relative to an external standard of 85% H_3PO_4. IR spectra were recorded on a JASCO FT/IR 4100 Fourier transform infrared spectrophotometer. Elemental analyses were performed at Microanalytical Center of The University of Tokyo. Cyclic voltammograms were recorded on an ALS/Chi model 610C electrochemical analyzer with platinum working electrode in THF containing 0.1 M $^nBu_4NBF_4$ as a supporting electrolyte. The potentials are quoted relative to the ferrocene/ferrocenium couple. All manipulations were performed under a dry nitrogen atmosphere. Solvents were dried over appropriate reagents and distilled prior to use. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled from calcium hydride. The complex *trans*-$[W(N_2)_2(PPh_2Me)_4] \cdot 1.5THF$ was prepared by the literature method[18] and recrystallized from THF–^iPrOH. Other reagents were purchased and used as received.

Preparation of 1,1′-Bis(diethylphosphino)ferrocene (depf).[27] A mixture of ferrocene (9.30 g, 50.0 mmol), TMEDA (15.0 mL, 99.4 mmol), and ^nBuLi (1.55 M, 80.0 mL, 124 mmol) in *n*-hexane

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(23) (a) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766. (b) Hidai, M.; Takahashi, T.; Yokotake, I.; Uchida, Y. *Chem. Lett.* **1980**, 645. (c) Hanson, I. R.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 390. (d) Galindo, A.; Hills, A.; Hughes, D. L.; Richards, R. L.; Hughes, M.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1990**, 283. (e) George, T. A.; Kaul, B. B.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 1706.

(24) (a) Lehnert, N.; Tuczek, F. *Inorg. Chem.* **1999**, *38*, 1671. (b) Horn, K. H.; Lehnert, N.; Tuczek, F. *Inorg. Chem.* **2003**, *42*, 1076.

(25) As a related reaction system, Schrock and his co-workers discovered the catalytic formation of ammonia by using a molybdenum–dinitrogen complex: Schrock, R. R. Acc. Chem. Res. **2005**, *38*, 955, and references therein.

(26) George, T. A.; Tisdale, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 5157.

(27) Gusev, O. V.; Peganova, T. A.; Kalsin, A. M.; Vologdin, N. V.; Petrovskii, P. V.; Lyssenko, K. A.; Tsvetkov, A. V.; Beletskaya, I. P. *Organometallics* **2006**, *25*, 2750.

Table 7. Summary of Crystallographic Data

	cis-**1**·2.5THF	*trans*-**1**	*trans*-**2**	**3**	**4**·THF·0.5C_6H_{14}
formula	$C_{46}H_{76}N_4Fe_2O_{2.5}P_4W$	$C_{36}H_{56}N_4Fe_2P_4W$	$C_{36}H_{56}N_4Fe_2MoP_4$	$C_{38}H_{58}N_2F_6Fe_2O_6P_4S_2W$	$C_{45}H_{73}N_2F_6Fe_2MoO_7P_4S_2$
fw	1144.57	964.30	876.39	1236.44	1263.72
cryst size/mm	0.25 × 0.20 × 0.20	0.30 × 0.30 × 0.25	0.50 × 0.30 × 0.20	0.25 × 0.25 × 0.20	0.50 × 0.50 × 0.07
color, habit	orange-yellow block	orange-red prism	orange-red prism	orange plate	orange plate
cryst syst	*monoclinic*	*triclinic*	*triclinic*	*monoclinic*	*triclinic*
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a/Å	16.7672(9)	10.3251(5)	10.3341(3)	16.9906(5)	10.8177(5)
b/Å	13.9265(6)	12.9548(7)	12.9756(4)	14.3654(3)	11.2497(5)
c/Å	21.5321(10)	16.0045(8)	16.0505(4)	19.4780(5)	23.4127(9)
α/deg	90	68.5308(15)	68.4688(18)	90	77.5875(14)
β/deg	116.4261(9)	75.0976(15)	75.0902(17)	105.0220(6)	78.6013(15)
γ/deg	90	75.3906(16)	75.3883(8)	90	84.5651(16)
V/Å^3	4502.6(4)	1895.23(17)	1904.58(9)	4591.7(2)	2723.69(20)
Z	4	2	2	4	2
d_c/g cm^{-3}	1.688	1.690	1.528	1.788	1.541
μ(Mo Kα)/mm^{-1}	3.374	3.986	1.274	3.426	1.014
no. of data collected	21 335	18 639	17 543	42 091	25 891
no. of unique data (R_{int})	5159 (0.056)	8599 (0.032)	8462 (0.024)	10 471 (0.041)	12 301 (0.047)
no. of params refined	286	480	480	608	686
$R1^a$ ($F^2 > 2\sigma$)	0.036	0.024	0.026	0.025	0.053
$wR2^b$ (all data)	0.088	0.063	0.090	0.056	0.162
goodness of fit indicator^c	1.03	1.01	1.02	1.00	1.00
residual electron density/e Å^{-3}	+1.66 to −0.81	+1.45 to −1.15	+0.50 to −0.67	+1.57 to −1.09	+1.46 to −1.13

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $[\sum w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$.

(80 mL) was stirred at room temperature overnight. The orange precipitates were separated from the supernatant by decantation and were washed with *n*-hexane (50 mL). After removal of the washings, the precipitates were suspended into hexane (80 mL). To the suspension was added PEt_2Cl (12.8 g, 103 mmol), and the mixture was stirred at room temperature for 1 day. The reaction mixture was filtered with a Celite pad, and the filtrate was concentrated *in vacuo*. The orange, oily residue was subjected to silica gel column chromatography. Elution with *n*-hexane−benzene (1:1) afforded depf (12.2 g, 67%) as an orange oil, which solidified below 0 °C. ^{1}H NMR (C_6D_6): δ 4.19−4.17 (m, 4H, C_5H_4), 4.17−4.14 (m, 4H, C_5H_4), 1.65−1.43 (m, 8H, CH_2), 1.05 (dt, $^3J_{PH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, 12H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −27.1 (s).

Synthesis of *cis*-[W(N$_2$)$_2$(depf)$_2$] (*cis*-1). To a mixture of magnesium turnings (303 mg, 12.5 mmol) and depf (420 mg, 1.16 mmol) in THF (15 mL) was added WCl_6 (221 mg, 0.557 mmol). The suspension was stirred under dinitrogen atmosphere at room temperature for 24 h. After concentration in vacuo, the residue was extracted with benzene. Removal of benzene and washing with *n*-hexane afforded a yellow powder. Recrystallization from THF−*n*-hexane gave dark yellow blocks of *cis*-**1**·2.5THF (121 mg, 19%). ^{1}H NMR (C_6D_6): δ 4.35 (br, 2H, C_5H_4), 4.30 (br, 2H, C_5H_4), 4.16 (br, 2H, C_5H_4), 4.13 (br, 2H, C_5H_4), 4.03 (br, 2H, C_5H_4), 4.00 (br, 2H, C_5H_4), 3.93 (br, 4H, C_5H_4), 3.00−2.75 (m, 4H, CH_2), 2.58−2.24 (m, 8H, CH_2), 2.15−1.97 (m, 4H, CH_2), 1.63−1.39 (m, 12H, CH_3), 0.93−0.70 (m, 12H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −5.1 (t with ^{183}W satellite, $^3J_{PP}$ = 9 Hz, $^1J_{PW}$ = 322 Hz), −1.9 (t with ^{183}W satellite, $^3J_{PP}$ = 9 Hz, $^1J_{PW}$ = 316 Hz). IR (KBr): ν_{NN} 1972, 1906 cm^{-1}. Anal. Calcd for $C_{46}H_{76}N_4Fe_2O_{2.5}P_4W$ (**1**·2.5THF): C, 48.27; H, 6.69; N, 4.90. Found: C, 48.29; H, 6.67; N, 4.86.

Synthesis of *trans*-[W(N$_2$)$_2$(depf)$_2$] (*trans*-1). A mixture of *trans*-[W(N$_2$)$_2$(PPh$_2$Me)$_4$]·1.5THF (217 mg, 0.189 mmol) and depf (173 mg, 0.478 mmol) in THF (10 mL) was heated at reflux for 4 h. The solution was concentrated under reduced pressure. The dark red oil was extracted with 30 mL of *n*-hexane. The extract was concentrated and recrystallized from THF−*n*-hexane, giving orange-red prisms of *trans*-**1** (86 mg, 0.089 mmol) in 43% yield. ^{1}H NMR (C_6D_6): δ 4.47−4.44 (m, 8H, C_5H_4), 4.12−4.09 (m, 8H, C_5H_4), 2.53−2.25 (m, 16H, CH_2), 1.24−1.06 (m, 24H, CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ −7.2 (s with ^{183}W satellite, $^1J_{P-W}$ = 316 Hz). IR (KBr): ν_{NN} 1883 cm^{-1}. Anal. Calcd for $C_{36}H_{56}N_4Fe_2P_4W$: C, 44.84; H, 5.85; N, 5.81. Found: C, 44.99; H, 5.78; N, 5.80.

Synthesis of *trans*-[Mo(N$_2$)$_2$(depf)$_2$] (*trans*-2). To a mixture of magnesium turnings (159 mg, 6.54 mmol) and depf (213 mg, 0.588 mmol) in THF (8 mL) was added $MoCl_5$ (70 mg, 0.256 mmol). The mixture was stirred under dinitrogen atmosphere at room temperature for 24 h. After concentration in vacuo, the residue was extracted with benzene. Removal of benzene and recrystallization from *n*-hexane at −30 °C afforded orange-red prisms of *trans*-**2** (28 mg, 13%). ^{1}H NMR (C_6D_6): δ 4.48−4.44 (m, 8H, C_5H_4), 4.13−4.10 (m, 8H, C_5H_4), 2.39−2.13 (m, 16H, CH_2), 1.23−1.10 (m, 24H, CH_3). ^{31}P NMR (C_6D_6): δ 19.6 (s). IR (KBr): ν_{NN} 1907 cm^{-1}. Anal. Calcd for $C_{36}H_{56}N_4Fe_2MoP_4$: C, 49.34; H, 6.44; N, 6.39. Found: C, 49.23; H, 6.33; N, 6.23.

Synthesis of [W(NNH$_2$)(OTf)(depf)$_2$]OTf (3). To a toluene (10 mL) solution of *trans*-**1** (97 mg, 0.10 mmol) was added trifluoromethanesulfonic acid (HOTf) (31 mg, 0.20 mmol). The resulting dark yellow solution was concentrated to dryness. Recrystallization from THF−ether−*n*-hexane (10:10:1) afforded pale orange plates (53.5 mg, 42%). X-ray analysis and elemental analysis indicated that the crystals were composed of **3** and **3**·THF·0.5C_6H_{14} in a ratio of 3:1.[28] ^{1}H NMR (C_6D_6): δ 7.94 (br, 2H, NNH_2), 4.56 (br, 4H, C_5H_4), 4.35 (br, 4H, C_5H_4), 4.30 (br, 4H, C_5H_4), 4.03 (br, 4H, C_5H_4), 2.61−2.40 (m, 4H, CH_2), 2.35−2.23 (m, 12H, CH_2), 1.06−0.86 (m, 24H, CH_3). ^{31}P NMR (C_6D_6): δ 1.5 (s with ^{183}W satellite, $^1J_{P-W}$ = 286 Hz). IR (KBr): ν_{NH} 3295 cm^{-1}. Anal. Calcd for $C_{39.75}H_{61.75}N_2F_6Fe_2O_{6.25}P_4S_2W$ (3:1 mixture of **3** and **3**·THF·0.5C_6H_{14}): C, 37.73; H, 4.92; N, 2.21. Found: C, 37.65; H, 4.84; N, 2.21.

Synthesis of 3 from *cis*-1. The complex *cis*-**1** (49 mg, 0.046 mmol) was treated with HOTf (14 mg, 0.089 mmol) in THF (5 mL). After 1 h, the solution was concentrated and the residue was recrystallized from THF−-*n*-hexane to give **3** in 58% yield (34 mg).

Synthesis of [Mo(NNH$_2$)(OTf)(depf)$_2$]OTf (4). *trans*-**2** (86.2 mg, 0.0984 mmol) was treated with HOTf (30.4 mg, 0.0.203 mmol) in toluene (12 mL). After 1 h, the solution was concentrated and the residue was washed with *n*-hexane. Recrystallization from THF−ether containing a small amount of *n*-hexane gave orange platelet crystals of **4**·THF·0.5C_6H_{14} (51.4 mg, 41%). ^{1}H NMR

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(28) Crystal data of **3**·THF·0.5C_6H_{14} are given in the Supporting Information.

(C_6D_6): δ 9.56 (br, 2H, NNH_2), 4.63 (br, 4H, C_5H_4), 4.41 (br, 4H, C_5H_4), 4.36 (br, 4H, C_5H_4), 4.06 (br, 4H, C_5H_4), 2.53−2.12 (m, 16H, CH_2), 1.07−0.89 (m, 24H, CH_3). ^{31}P NMR (C_6D_6): δ 17.7 (s). IR (KBr): ν_{NH} 3268 cm^{-1}. Anal. Calcd for $C_{45}H_{73}N_2F_6Fe_2MoO_7P_4S_2$ (**4**·THF·$0.5C_6H_{14}$): C, 42.77; H, 5.82; N, 2.22. Found: C, 42.68; H, 5.88; N, 2.16.

Protonolysis of Complexes 1−4. To a methanol (5 mL) suspension of a complex (ca. 40 μmol) was added H_2SO_4 (0.05 mL). After 24 h stirring at room temperature, ammonia was base distilled and quantified by the indophenol method.[29] Hydrazine was also analyzed by *p*-(dimethylamino)benzaldehyde reagent.[30]

X-ray Crystallography. Crystallographic data are summarized in Table 7. The paraffin-coated crystals were placed on a nylon loop and mounted on a Rigaku RAXIS RAPID imagining plate system. Data were collected at −100 °C under a cold nitrogen stream using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Data were corrected for absorption, Lorentz, and polarization effects. Structures were solved by the direct methods[31] and expanded using Fourier techniques.[32] Badly disordered THF molecules cocrystallizing with *cis*-**1** could not be located successfully, but the treatment of the five highest peaks as carbon atoms gave better results. A disordered methyl group in **3** was refined isotropically. Anisotropic thermal parameters were introduced for the other non-hydrogen atoms. Hydrogen atoms of hydrazido ligands in complex **3** and **4** were located from a difference Fourier map and were refined isotropically. All other hydrogen atoms were generated at calculated positions (d_{C-H} = 0.97 Å) and treated as riding atoms with isotropic thermal factors. Full-matrix least-squares refinement on F^2 was carried out until the maximum parameter-shift/esd converged to less than 0.001.[33] All calculations were performed using the Crystal Structure software package.[34] Crystallographic data are given in a CIF file.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Chaney, A. L.; Marbach, E. P. *Clinical Chem.* **1962**, *8*, 130.

(30) Watt, G. W.; Chrisp, J. D *Anal. Chem.* **1952**, *24*, 2006.

(31) SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. C.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(32) DIRDIF99: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-99 program system; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1999.

(33) Carruthers, J. R.; Rollett, J. S.; Betteridge, P. W.; Kinna, D.; Pearce, L.; Larsen, A.; Gabe, E. *CRYSTALS* Issue 11; Chemical Crystallography Laboratory: Oxford, U.K., 1999.

(34) *Crystal Structure 3.8*, Crystal Structure Analysis Package; Rigaku and Rigaku Americas, 2000−2007.