Syntheses, Structures, and Reactivities of **Heterobimetallic Bridging Dinitrogen Complexes Containing Group 6 and Group 4 or 5 Transition Metals¹**

Hiroshige Ishino, Tatsuya Nagano, Shigeki Kuwata, Youhei Yokobayashi, Youichi Ishii,* and Masanobu Hidai*,†

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Ťokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Yasushi Mizobe

Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8558, Japan

Received August 8, 2000

A series of heterobimetallic dinitrogen complexes containing group 6 and group 4 or 5 transition metals were synthesized by the reaction of the tungsten or molybdenum dinitrogen complexes cis- $[W(N_2)_2(PMe_2Ph)_4]$ (1) and trans- $[M(N_2)_2(dppe)_2]$ (2) (M = W, Mo) with group 4 or group 5 compounds such as $[CpTiCl_3]$, $[Cp_2M'Cl_2]$ (M' = Ti, Zr, Hf), or $[Cp'M'Cl_4]$ (Cp' = Cp, Cp^{*}; M' = Nb, Ta). Crystallographic studies of the complexes thus obtained including $[WCl(PMe_2Ph)_4(\mu-N_2)TiCpCl_2]$ and $[WCl(PMe_2Ph)_4(\mu-N_2)NbCpCl_3]$ revealed that the M-N-N-M' core is essentially linear, and the N-N bond is regarded to have the formal bond order of 2. Several μ -N₂ complexes with methyl ligands at the group 4 or 5 metal center were also obtained through the reaction of dinitrogen complexes $\mathbf{1}$ and $\mathbf{2a}$ (M = W) with the methyl complexes [Cp₂ZrMeCl], [TaMe₃Cl₂], and [NbMe₂Cl₃]. The reaction of the complex $[WCl(dppe)_2(\mu-N_2)TiCpCl_2]$ with Li₂S₅ afforded the η^2 -pentasulfido complex $[WCl(dppe)_2(\mu-N_2)TiCpCl_2]$ N₂)TiCpS₅], where the η^2 -S₅ ligand forms a six-membered chelate ring with the chair conformation. Protonation of the μ -N₂ complexes having PMe₂Ph ligands gave NH₃ in moderate yield, concurrent with the formation of a small amount of NH₂NH₂.

Introduction

Activation and chemical transformation of molecular dinitrogen at metal centers under mild conditions have been the subject of current attention.²⁻⁷ In particular, recent advances in the studies on the active site of nitrogenase⁸ have aroused intense interest in properties and reactivities of dinitrogen bound at multinuclear transition metal centers, and intriguing reactivities of multinuclear μ -N₂ complexes have been found which include the N–N fission.^{9–12} However, most of the μ -N₂

- (4) Bazhenova, T. A.; Silov, A. E. Coord. Chem. Rev. 1995, 95, 69-145
- 145.
 (5) Hidai, M.; Mizobe, Y. In *Molybdenum Enzymes, Cofactors and Model Systems*; Stiefel, E. I., Coucouvanis, D., Newton, W. E., Eds.; American Chemical Society: Washington, DC, 1993; pp 346–362.
 (6) Leigh, G. J. *Acc. Chem. Res.* **1992**, *25*, 177–181.
 (7) Hidai, M.; Mizobe, Y. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1989; Vol. 2, pp 53–114.
- 114.
- (8) Howard, J. B.; Rees, D. C. Chem. Rev. 1996, 96, 2965-2982.
- (9) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N.; Rizzoli,
 (9) Caselli, A.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N.; Rizzoli,
 (10) Clentsmith, G. K. B.; Bates, V. M. E.; Hitchcock, P. B.; Cloke,
 G. N. J. Am. Chem. Soc. 1999, 121, 10444–10445.

complexes investigated so far are homobimetallic compounds, and the chemistry of heterobimetallic dinitrogen complexes still remains to be explored. In fact, the structurally characterized μ -N₂ complexes containing two different transition metals have been very limited in number.11,13-19

In the course of our continuous study on reactivities of the molybdenum and tungsten dinitrogen complexes such as cis-[W(N₂)₂(PMe₂Ph)₄] (1) and trans-[M(N₂)₂- $(dppe)_2$] $(dppe = Ph_2PCH_2CH_2PPh_2)$ (**2a**, M = W; **2b**, M = Mo), we have previously found that the coordinated dinitrogen in this type of tungsten complexes is attacked by Lewis acids including not only group 13 metal (B,²⁰

- (12) Berno, P.; Gambarotta, S. Angew. Chem., Int. Ed. Engl. 1995, 34, 822-824.
- (13) Mindiola, D. J.; Meyer, K.; Cherry, J.-P. F.; Baker, T. A.; Cummins, C. C. *Organometallics* **2000**, *19*, 1622–1624.
- (14) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R.; Reiff, W. M. Inorg. Chem. **1999**, *38*, 243–252.
- (15) O'Donoghue, M. B.; Zanetti, N. C.; Davis, W. M.; Schrock, R.
 R. J. Am. Chem. Soc. 1997, 119, 2753–2754.
- K. J. Am. Chem. Soc. 1997, 113, 2135-2134.
 (16) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale,
 M. G. J. Am. Chem. Soc. 1990, 112, 4338-4345.
 (17) Cradwick, P. D.; Chatt, J.; Crabtree, R. H.; Richards, R. L. J. Chem. Soc., Chem. Commun. 1975, 351-352.
- (18) Mercer, M. J. Chem. Soc., Dalton Trans. 1974, 1637–1640.
 (19) Mercer, M.; Crabtree, R. H.; Richards, R. L. J. Chem. Soc., Chem. Commum. 1973, 808–809.
 (20) Ishino, H.; Ishii, Y.; Hidai, M. Chem. Lett. 1998, 677–678.

[†] Present address: Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan. E-mail: hidai@mail.rs.noda. sut.ac.jp.

⁽¹⁾ Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 70. Part 69: Nishibayashi, Y.; Takemoto, S.; Iwai, (2) Hidai, M. *Inorg. Chem.*, in press.
(2) Hidai, M.; Mizobe, Y. *Chem. Rev.* 1995, *95*, 1115–1133.
(3) Gambarotta, S. *J. Organomet. Chem.* 1995, *500*, 117–126.

⁽¹¹⁾ Peters, J. C.; Cherry, J.-P. F.; Thomas, J. C.; Baraldo, L.; Mindiola, D. J.; Davis, W. M.; Cummins, C. C. J. Am. Chem. Soc. 1999, 121, 10053-10067.

Al,²¹ Ga²²) compounds but also group 4 metal (Ti, Zr, Hf) complexes²³ to afford the μ -N₂ complexes. Treatment of **1** with [Cp₂TiCl₂] (Cp = η^{5} -C₅H₅) or [Cp₂MCl₂]/NaI (M = Zr, Hf) affords the heterobimetallic bridging dinitrogen complexes [WX(PMe₂Ph)₄(μ -N₂)MCp₂Cl] (**3a**, M = Ti, X = Cl; **3b**, M = Zr, X = I; **3c**, M = Hf, X = I) in good yield. We have now extended this study to the reactions of complexes **1** and **2** with other group 4 and 5 transition metal complexes. Here we describe synthesis, characterization, and some reactivities of a series of heterobimetallic dinitrogen complexes in which the μ -N₂ ligand bridges group 6 and group 4 or 5 metal centers.

Results and Discussion

Synthesis of Group 4–Group 6 Heterobimetallic Bridging Dinitrogen Complexes. In the previous communication,²³ we reported that [Cp₂TiCl₂] shows moderate reactivity toward complex 1 at 50 °C to give the heterobimetallic bridging dinitrogen complex 3a in good yield. $[Cp_2MCl_2]$ (M = Zr, Hf) also reacts with 1 in the presence of NaI to form analogous μ -N₂ complexes **3b** and **3c**. The crystallographically determined molecular structure of $[WI(PMe_2Ph)_3(py)(\mu-N_2)ZrCp_2Cl]$ (3b', py = pyridine) derived from **3b** and pyridine revealed the linear W(μ -N₂)Zr core with the formal (N₂)^{2–} ligand. To expand the scope of this synthetic method for heterobimetallic μ -N₂ complexes, we turned our attention to the mono-Cp complex [CpTiCl₃], which is expected to have higher reactivity toward dinitrogen complexes owing to its strong Lewis acidic nature. When complex **1** was allowed to react with an equimolar amount of [CpTiCl₃] in benzene at room temperature, rapid reaction took place to form the heterodinuclear μ -N₂ complex [WCl(PMe₂Ph)₄(μ -N₂)TiCpCl₂] (4), which was isolated in good yield after recrystallization (eq 1). The IR spectrum of 4 showed a medium absorption at



1408 cm⁻¹ characteristic of the ν (NN) band, suggesting that the N–N bond has a double bond character, and **4** may be viewed as the formal (N₂)²⁻-bridged W(II)–Ti-(IV) complex. It is to be noted that the ν (NN) value of complex **4** is considerably lower than that (1468 cm⁻¹) of complex **3a**.²³ Substitution of the 15e⁻ fragment TiCp₂Cl in **3a** with the 11e⁻ fragment TiCpCl₂ causes stronger π -donation from the N₂ ligand to the titanium atom, which is reflected in the lower ν (NN) value. The ¹H NMR and ³¹P NMR spectra showed a broad Me



Figure 1. Molecular structures of **4** (A) and $9a \cdot 3CH_2Cl_2$ (B). Solvating CH_2Cl_2 molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

singlet at δ 1.63 and a singlet with ¹⁸³W satellites (J_{WP} = 277 Hz) at δ –24.5, respectively, indicating the trans configuration of the chloride and μ -N₂ ligands around the tungsten center. Attempted reactions of **1** with [Cp*TiCl₃] (Cp* = η^5 -C₅Me₅), [CpZrCl₃], [Cp*ZrCl₃], or [Cp*HfCl₃] failed to give any isolable heterobimetallic μ -N₂ complexes.

The molecular structure of complex **4** was unambiguously determined by X-ray diffraction study (Figure 1). Selected bond distances and angles are collected in Table 1, and an ORTEP drawing is given in Figure 1. In accordance with the spectral data, complex **4** has an octahedral configuration around the tungsten center with the mutually trans μ -N₂ and chloride ligands, and the titanium center adopts a typical three-legged piano

⁽²¹⁾ Takahashi, T.; Kodama, T.; Watakabe, A.; Uchida, Y.; Hidai, M. J. Am. Chem. Soc. **1983**, *105*, 1680–1681.

⁽²²⁾ Takagahara, K.; Ishino, H.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1998**, 897–898.

⁽²³⁾ Mizobe, Y.; Yokobayashi, Y.; Oshita, H.; Takahashi, T.; Hidai, M. Organometallics **1994**, *13*, 3764–3766.

Table 1. Selected Bond Distances and Angles in 4 and 9a·3CH₂Cl₂

	4 (X = $Cl(3)$)	$9\mathbf{a} \cdot 3CH_2Cl_2 \ (X = N(3))$
	Distances (Å)	
W(1) - N(1)	1.782(5)	1.85(1)
N(1) - N(2)	1.270(8)	1.21(2)
Ti(1) - N(2)	1.792(5)	1.82(1)
W(1)-P(1)	2.525(6)	2.483(4)
W(1)-P(2)	2.523(5)	2.489(5)
W(1)-P(3)	2.513(6)	2.533(4)
W(1)-P(4)	2.509(5)	2.516(5)
Ti(1)-Cl(1)	2.313(3)	2.299(6)
Ti(1)-Cl(2)	2.317(3)	2.307(6)
	Angles (deg)	
W(1) - N(1) - N(2)	166(1)	178(1)
X - W(1) - N(1)	176.8(5)	178.4(6)
Ti(1) - N(2) - N(1)	168.8(8)	179(1)
P(1)-W(1)-N(1)	97.7(5)	88.4(4)
P(2)-W(1)-N(1)	86.4(5)	87.2(4)
P(3)-W(1)-N(1)	94.4(5)	97.4(4)
P(4)-W(1)-N(1)	88.9(5)	100.7(4)

stool structure. The W-N-N-Ti array in 4 is almost linear, and this type of linear structure is ubiquitous in dinuclear μ -N₂ complexes.^{2,24} The core structure is closely related to that of the previously reported W-Zr complex **3b**'.²³ The Ti-N distance at 1.792(5) Å is shorter than that found in the Mo–Ti μ -N₂ complex $[(Ph^{t}BuN)_{3}Ti(\mu - N_{2})Mo\{N^{t}Bu(3, 5 - Me_{2}C_{6}H_{3})\}_{3}]$ (1.880(3) Å)¹¹ but is in the range of Ti–N double bond distances found in titanium amido complexes such as $[TiCl_2\{\eta^5:$ η^{1} -C₅H₄(CH₂)₃NⁱPr}] (1.867(2)^Å),²⁵ [Cp*Ti(NMe₂)(CH₂-Ph)₂] (1.887(2) Å),²⁶ and [CpTiCl₂(NPPh₃)] (1.78(1) Å).²⁷ The W-N distance at 1.782(5) Å also indicates a multiple-bonding character as found in complex 3b'. The N–N bond distance of 1.270(8) Å is slightly longer than those of the above-mentioned Mo-Ti complex (1.229(4) Å) and **3b'** (1.24(2) Å), and the N₂ fragment in **4** may be viewed as a formal $(N_2)^{2-}$ ligand which acts as a fourelectron donor to each of the tungsten and titanium centers.

Although the dinitrogen complexes with dppe ligands **2** are unreactive toward $[Cp_2TiCl_2]$, they react smoothly with $[CpTiCl_3]$. Thus, when the tungsten complex 2a was treated with an equimolar amount of [CpTiCl₃] at room temperature, $[WCl(dppe)_2(\mu-N_2)TiCpCl_2]$ (5a), the dppe analogue of 4, was isolated in good yield. The spectral data of **5a** including the IR absorption at 1412 cm^{-1} attributable to the ν (NN) vibration are consistent with the formulation. The ¹H NMR signal of the Cp ligand appeared in the high-field region (δ 5.70) compared with those of **3a** (δ 6.30) and **4** (δ 6.44), which is accounted for by the shielding effect of a phenyl group of the dppe ligands located nearby (vide infra). The molybdenum dinitrogen complex 2b similarly reacted with [CpTiCl₃] to give the analogous Mo-Ti complex $[MoCl(dppe)_2(\mu-N_2)TiCpCl_2]$ (5b).

Complex $[Cp_2Ti(OTf)_2]$ (OTf = OSO₂CF₃) was also effective for the synthesis of μ -N₂ W-Ti complexes from either **1** or **2a**, and $[W(OTf)(PMe_2Ph)_4(\mu$ -N₂)TiCp₂(OTf)] (**6a**) or $[W(OTf)(dppe)_2(\mu$ -N₂)TiCp₂(OTf)] (**6b**) was obtained, respectively. The low electroconductivity of **6a** and **6b** (6.6 S cm² mol⁻¹ for **6a** and 6.9 S cm² mol⁻¹ for **6b** in CH₂Cl₂) implies that they are essentially nonelectrolytes with coordinated OTf ligands. It should be noted that treatment of chloro complexes such as **3a** or **5a** with AgOTf failed to give the corresponding OTf derivatives.

The anionic dinitrogen complex *trans*-[NBu₄][W(NCS)-(N₂)(dppe)₂] (**7**) readily derived from complex **2a** shows higher reactivities toward electorophiles than **2a**, which is substantiated in the reactions with fluoroarene complexes.^{28,29} As expected, complex **7** smoothly reacted with [Cp₂MCl₂] (M = Ti, Zr, Hf) and [Cp'TiCl₃] (Cp' = Cp, Cp*) at room temperature to give [W(NCS)(dppe)₂-(μ -N₂)MCp₂Cl] (**8a**, M = Ti; **8b**, M = Zr; **8c**, M = Hf) and [W(NCS)(dppe)₂(μ -N₂)TiCp'Cl₂] (**9a**, Cp' = Cp; **9b**, Cp' = Cp*), respectively (eq 2). The IR spectra of **8a**-c



showed strong absorptions at 2049–2056 cm⁻¹ and medium absorptions at 1545–1559 cm⁻¹ attributable to the ν (NCS) and ν (NN) bands, respectively, while the ν -(NN) values for **9a** (1441 cm⁻¹) and **9b** (1433 cm⁻¹) were considerably lower (vide supra). The ¹H NMR and ³¹P NMR spectra also agreed well with the formulation.

The molecular structure of $9a \cdot 3CH_2Cl_2$ was confirmed crystallographically. As shown in Figure 1, the structure around the dinuclear core of 9a is closely related to that of **4** except that the W(1)-N(1) and Ti(1)-N(2) bonds in **9a** are slightly elongated, while the N(1)-N(2) bond distance is shorter than that in **4**. The CpTi moiety is situated in the vicinity of one of the dppe phenyl rings

 ⁽²⁴⁾ Henderson, R. A. Transition Met. Chem. 1990, 15, 330–336.
 (25) Sinnema, P.-J.; Veen, L.; Spek, A. L.; Veldman, N.; Teuben, J. H. Organometallics 1997, 16, 4245–4247.

⁽²⁶⁾ Sinnema, P.-J.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2000**, *598*, 179–181.

⁽²⁷⁾ Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. J. Chem. Soc., Dalton Trans. 1986, 377–383.

⁽²⁸⁾ Ishii, Y.; Kawaguchi, M.; Ishino, Y.; Aoki, T.; Hidai, M. Organometallics 1994, 13, 5062-5071.

⁽²⁹⁾ Ishii, Y.; Ishino, Y.; Aoki, T.; Hidai, M. J. Am. Chem. Soc. 1992, 114, 5429–5430.

 Table 2. Selected Bond Distances and Angles in 10a·CH₂Cl₂·Et₂O and 10d·2MeCN

	$10a \cdot CH_2Cl_2 \cdot Et_2O$ (M = Nb)	10d •2MeCN (M = Ta)
	Distances (Å)	
W(1) - N(1)	1.785(7)	1.783(7)
N(1) - N(2)	1.254(9)	1.275(9)
M(1) - N(2)	1.852(7)	1.857(8)
M(1) - Cl(1)	2.492(3)	2.462(3)
M(1) - Cl(2)	2.434(3)	2.446(3)
M(1)-Cl(3)	2.481(3)	2.449(3)
	Angles (deg)	
W(1)-N(1)-N(2)	176.0(6)	173.5(6)
Cl(4) - W(1) - N(1)	176.4(2)	173.5(6)
M(1) - N(2) - N(1)	179.1(6)	174.2(7)

(C(21)–C(26)). Such conformation is required to accommodate the bulky CpTi group and explains the observation that the Cp protons of the μ -N₂ complexes with dppe ligands resonate in a higher field region (δ 5.6–5.9) than those of the PMe₂Ph analogues (δ 6.1–6.5). In contrast with the above reactions, [Cp*ZrCl₃] did not react with complex 7, and [CpZrCl₃] or [Cp*HfCl₃] gave the W(I) dinitrogen complex *trans*-[W(NCS)(dppe)₂(N₂)]³⁰ as the only characterized product.

Synthesis of Group 5–Group 6 Heterobimetallic Bridging Dinitrogen Complexes. Synthesis of a series of W–Nb and W–Ta μ -N₂ complexes was also examined to compare the reactivities of the group 4–group 6 and group 5–group 6 heterobimetallic μ -N₂ complexes. When complex 1 was allowed to react with [Cp'MCl₄] (M = Nb, Ta; Cp' = Cp, Cp*) in benzene at room temperature, the μ -N₂ complexes [WCl(PMe₂Ph)₄-(μ -N₂)MCp'Cl₃] (10a, M = Nb, Cp' = Cp; 10b, M = Nb, Cp' = Cp*; 10c, M = Ta, Cp' = Cp; 10d, M = Ta, Cp' = Cp*) were formed in high yield (eq 3). The ¹H NMR



spectra of **10a**–**d** showed a broad singlet assignable to the PMe protons, and the ³¹P{¹H} NMR spectra exhibited a singlet with ¹⁸³W satellites. In the IR spectra, medium absorptions attributable to the ν (NN) band were observed at 1385–1435 cm⁻¹, where the ν (NN) values of the W–Nb complexes **10a** and **10b** are lower than those of the W–Ta analogues **10c** and **10d** by ca. 40 cm⁻¹.

The molecular structures of complex **10a**·CH₂Cl₂·Et₂O and **10d**·2MeCN were unambiguously determined by X-ray diffraction study. Selected bond distances and angles are listed in Table 2, and their ORTEP drawings



Figure 2. Molecular structures of $10a \cdot CH_2Cl_2 \cdot Et_2O$ (A) and $10d \cdot 2MeCN$ (B). Solvating ether and MeCN molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

are depicted in Figure 2. In agreement with the spectral data, the tungsten centers in **10a** and **10d** have an octahedral configuration with the mutually trans μ -N₂ and chloro ligands, and the niobium and tantalum centers take a square pyramidal geometry with the Cp' ligand at the apex. The W–N–N–Nb and W–N–N–Ta arrays are almost linear, as observed in **3b'**, **4**, and **9a**·3CH₂Cl₂. The N–N bond distances (1.254(9) Å for **10a**·CH₂Cl₂·Et₂O and 1.275(9) Å for **10d**·2MeCN) are

⁽³⁰⁾ Chatt, J.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 121–127.



Figure 3. Molecular structure of $11a \cdot \text{Et}_2\text{O}$. Solvating ether molecule and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (deg): W(1)-N(1), 1.806(8); N(1)-N(2), 1.25(1); Nb(1)-N(2), 1.868(9); 2.467-(4); W(1)-N(1)-N(2), 171.1(8); Nb(1)-N(2)-N(1), 175.0-(8).

close to that of **4** and correspond to the bond order of 2. Thus, the oxidation state of the diamagnetic metal centers in these complexes may be assigned to be W(II)– M(V) (M = Nb, Ta). Crystallographically characterized heterobimetallic dinitrogen complexes containing group 5 metals have not been known until very recently. The Mo–V and Mo–Nb complexes [{[(Me₃SiNCH₂CH₂)₃N]-Mo(μ -N₂)}₂VCl(THF)] (N–N, 1.217(7) and 1.221(7) Å)¹⁴ and [{(3,5-Me₂C₆H₃)^tBuN}₃Mo(μ -N₂)Nb{NⁱPr(C₆H₃Me₂-3,5)}₃] (N–N, 1.235(10) Å)¹³ have been considered as formal (N₂)^{2–} complexes, and their N–N distances are compared well with those found for **10a** and **10d**.

Complexes **2a** and **7** also gave analogous μ -N₂ complexes [WCl(dppe)₂(μ -N₂)MCpCl₃] (**11a**, M = Nb; **11b**, M = Ta) and [W(NCS)(dppe)₂(μ -N₂)MCpCl₃] (**12a**, M = Nb; **12b**, M = Ta) in good yield on reactions with [CpMCl₄] (M = Nb, Ta). However, they failed to react with [Cp*MCl₄] probably due to steric reasons. The molecular structure of **11a**·Et₂O established by crystal-lographic study is given in Figure 3. The structure around the dinuclear core is closely related to that of **10a**.

Reactions of the Heterobimetallic Dinitrogen Complexes with Unsaturated Compounds. Metal– nitrogen multiple bonds have been known to undergo interesting reactions with unsaturated compounds including the [2+2] cycloaddition to form a metallacycle.^{31–33} Aiming at developing new coupling reactions of the μ -N₂ ligand and organic unsaturated compounds, reactions of complexes **4**, **5a**, **6a**, **10a**, **10d**, **11a**, and **11b** with various alkenes, alkynes, CO, and isocyanides were examined. Unfortunately, however, most of the attempted reactions yielded a complex mixture of uncharacterized products. Only in the reaction of **10d** with ^tBuNC (5 equiv) at 50 °C did substitution of one PMe₂-Ph ligand on the tungsten atom take place to form [WCl (PMe₂Ph)₃(^tBuNC)(μ -N₂)TaCp*Cl₃] (**13**) in moderate yield. Complex **13** showed a ν (CN) absorption at 2112 cm⁻¹ as well as a ν (NN) absorption at 1458 cm⁻¹, and the ¹H and ³¹P{¹H} NMR data suggest the *mer* arrangement of the PMe₂Ph ligands. It should also be mentioned that complex **10d** did not undergo ligand substitution with pyridine or 2,2'-bipyridine, although one of the PMe₂Ph ligands in the W–Zr complex **3b** was readily displaced by pyridine to give **3b**'.

Synthesis of Bridging Dinitrogen Complexes with Alkyl Ligands. Attempts to introduce methyl ligands to the dinuclear cores of the μ -N₂ complexes 4, 5a, 6a, 9a, 10a, 10c, 11a, or 11b by reactions with MeLi or MeMgBr resulted in the reduction of the tungsten center to give the parent dinitrogen complexes 1 and 2a as the only characterizable product. Use of other alkylmetals such as Me₂Zn and Me₄Sn was not successful either. However, several μ -N₂ complexes with alkyl ligands were obtained through the reaction of the dinitrogen complexes 1, 2, and 7 with [Cp₂ZrMeCl], [Me₃TaCl₂], or [Me₂NbCl₃].

Although the reaction of **1** with [Cp₂ZrMeCl] did not proceed in the absence of NaI, addition of excess NaI effectively promoted the reaction to give the μ -N₂ complex [WI(PMe₂Ph)₄(μ -N₂)ZrCp₂Me] (**14a**). The IR spectrum of **14a** showed a medium ν (NN) band at 1541 cm⁻¹, and the Me signal in its ¹H NMR appeared as a singlet at δ 0.37. In contrast with the reaction of **1**, the anionic dinitrogen complex **7** reacted with [Cp₂ZrMeCl] in the absence of NaI to form [W(NCS)(dppe)₂(μ -N₂)ZrCp₂-Me] (**14b**). This complex exhibited a singlet at δ –0.02 in the ¹H NMR spectrum attributable to the Zr–Me group. The molecular structure of **14b** confirmed by crystallographic study is shown in Figure 4. The Zr(1)– C(1) distance at 2.342(8) Å is not unusual, and other metrical features are similar to those observed in **3b**'.

On the other hand, treatment of 1 and 2 with [Me₃-TaCl₂] afforded [WCl(PMe₂Ph)₄(μ -N₂)TaMe₃Cl] (15a) and $[MCl(dppe)_2(\mu-N_2)TaMe_3Cl]$ (15b, M = W; 15c, M = Mo), respectively, in moderate yield. In the 1 H NMR spectra, the Me signals of these complexes were observed as a singlet at δ 0.45, 0.23, and 0.13, respectively, and the spectrum of 15b showed essentially no temperature dependence over the range 20 to -60 °C. A structure having a trigonal bipyramidal tantalum center with the chloro and μ -N₂ ligands at the apical positions is consistent with the spectral data, but we must await further investigation to clarify the detailed structure of 15. Similarly, complexes 2 reacted with [Me₂NbCl₃] to produce $[MCl(dppe)_2(\mu-N_2)NbMe_2Cl_2]$ (16a, M = W; 16b, M = Mo). Complexes **14–16** are thermally stable up to 70 °C, and migration of the Me group from the metal to the μ -N₂ ligand has not been observed so far.

Reaction of the Heterobimetallic Dinitrogen Complexes with Li_2S_5 . In relevalence to the active site of nitrogenase, great interest has been focused on multimetallic dinitrogen complexes having sulfur-based ligands, although examples of such complexes are still

⁽³¹⁾ Blake, R. E.; Antonelli, D. M.; Henling, L. M.; Schaefer, W. P.; Hardcastle, K. I.; Bercaw, J. E. *Organometallics* **1998**, *17*, 718–725. (32) Fairfax, D.; Stein, M.; Livinghouse, T.; Jensen, M. *Organometallics* **1997**, *16*, 1523–1525.

⁽³³⁾ Walsh, P. J.; Hollander, F. J.; Bergman, R. G. Organometallics 1993, 12, 3705–3723.



Figure 4. Molecular structure of **14b**. Hydrogen atoms except for the $Zr-CH_3$ hydrogens are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (deg): W(1)-N(1), 1.850(5); N(1)-N(2), 1.223(7); Zr(1)-N(2), 2.042(6); Zr(1)-C(1), 2.342(8); W(1)-N(1)-N(2), 173.6(5); Zr(1)-N(2)-N(1), 174.6(5); C(1)-Zr(2)-N(2), 98.4(3).

limited.^{34–36} Having a series of heterobimetallic μ -N₂ complexes in hand, we next investigated their reactions with sulfur ligands. When complex **5a** was treated with Li₂S₅ in THF at room temperature, the μ -N₂ complex with the pentasulfido ligand [WCl(dppe)₂(μ -N₂)TiCpS₅] (**17**) was isolated in good yield (eq 4). However, at-



tempted reactions of **4**, **10a**, or **11a** with Li₂S₅ and of **5a** with Li₂S, Li₂S₂, or [NH₄]₂[WS₄] led to uncharacterized mixtures. The ¹H and ³¹P NMR spectra of **17** were comparable to those of **5a**, and the IR spectrum of **17** showed a medium ν (NN) absorption at 1406 cm⁻¹, which is slightly lower than that of **5a**. These spectral data indicate that the core structure of **5a** was maintained during the reaction with Li₂S₅.

Table 3. Selected Bond Distances and Angles in17.1.5Et₂O

	17 1.4	JLL20	
$ \begin{array}{l} W(1)-N(1)\\ Ti(1)-N(2)\\ Ti(1)-S(5)\\ S(2)-S(3)\\ S(4)-S(5) \end{array} $	Distan 1.799(8) 1.827(9) 2.374(4) 2.033(6) 2.053(5)	$\begin{array}{c} \mbox{nces (Å)} \\ N(1)-N(2) \\ Ti(1)-S(1) \\ S(1)-S(2) \\ S(3)-S(4) \end{array}$	1.247(9) 2.406(4) 2.055(5) 2.050(6)
$\begin{array}{l} W(1)-N(1)-N(2)\\ Ti(1)-N(2)-N(1)\\ S(5)-Ti(1)-N(2)\\ Ti(1)-S(5)-S(4)\\ S(2)-S(3)-S(4) \end{array}$	Angle 176.5(7) 172.6(7) 98.2(3) 100.4(2) 106.5(2)	$ s (deg) \\ Cl(1)-W(1)-N(1) \\ S(1)-Ti(1)-N(2) \\ Ti(1)-S(1)-S(2) \\ S(1)-S(2)-S(3) \\ S(3)-S(4)-S(5) $	177.1(3) 97.1(3) 102.1(2) 105.8(2) 105.1(2)
	S4 S5 S5 P1 P1	S2 S1 T11 P3 P4 W1 C11	

Figure 5. Molecular structures of $17.1.5Et_2O$. Solvating ether molecules and hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

The molecular structure of complex **17**·1.5Et₂O was confirmed by an X-ray diffraction study. Selected bond distances and angles are summarized in Table 3, and an ORTEP drawing is given in Figure 5. In agreement with the spectral data, complex **17** has a linear W–N– N–Ti core with the N–N bond distance at 1.247(9) Å. The η^2 -pentasulfido ligand is bonded to the Ti atom to form a six-membered ring with the chair conformation, and the CpTiS₅ fragment takes the structure that minimizes the steric congestion with the dppe ligands on the tungsten atom. The distances of the Ti–S (2.406-(4), 2.374(4) Å) and S–S (2.033(6)–2.055(5) Å) bonds are comparable with those found in other titanium polysulfido complexes including [Cp₂TiS₅].^{37,38} Investigation into the reactivity of **17** is now in progress.

Protonation of Heterobimetallic Dinitrogen Complexes with H_2SO_4. The protonation of coordinated dinitrogen to form NH_3 or NH_2NH_2 requires the concomitant transfer of six or four electrons, respectively, from the metal center. Therefore, as far as mononuclear

⁽³⁴⁾ O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. J. Am. Chem. Soc. **1990**, *112*, 4331–4338.

⁽³⁵⁾ Henderson, R. A.; Morgan, S. H. *J. Chem. Soc., Dalton Trans.* **1990**, 1107–1109.

⁽³⁶⁾ Schrock, R. R.; Wesolek, M.; Liu, A. H.; Wallace, K. C.; Dewan, J. C. *Inorg. Chem.* **1988**, *27*, 2050–2054.

⁽³⁷⁾ Müller, E. G.; Petersen, J. L.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91–112.

⁽³⁸⁾ Epstein, E. F.; Bernal, I. J. Organomet. Chem. **1971**, 26, 229–245.

Table 4. Protonation of Bridging Dinitrogen Ligands Forming Ammonia and/or Hydrazine^a

complex	yield of NH ₃ (%) ^a	yield of NH ₂ NH ₂ (%) ^a
3a ^b	43	8
$\mathbf{3b}^{b}$	17	16
4	36	2
10a	44	6
10b	34	2
10c	29	9
10d	41	0
15a	23	10

^a Based on total nitrogen in the N₂ complex. Reaction conditions: heterobimetalic dinitrogen complex (0.050-0.100 mmol); H₂SO₄ (10 equiv); MeOH (3 mL); room temperature; 3 h; under Ar. ^b See ref 23.

dinitrogen complexes are concerned, such conversion is expected to occur effectively only with complexes of highly electron-rich metal centers such as complex 1, where all the electrons are provided from the single metal. On the other hand, the conversion of coordinated dinitrogen to nitrogen hydrides on multimetallic complexes is presumed to require less electrons per one metal atom, and more diversified metals are expected to effect such reactions. In fact, it has been demonstrated that various types of multinuclear dinitrogen complexes yield NH₃ and NH₂NH₂ on protonolysis under mild conditions.²

To gain information about the chemical properties of dinitrogen activated by the group 4 or 5-group 6 metal pairs, we have investigated the protonation reactions with H₂SO_{4.} Representative results are summarized in Table 4 together with the values for **3a** and **3b** reported previously.²³ As observed with **3a** and **3b**, the heterobimetallic μ -N₂ complexes with PMe₂Ph ligands, **4**, **10a**-**d**, and **15a**, gave NH₃ in 23–44% yield, while NH₂- NH_2 was formed in lower yield (0–10%). Essentially no N₂ gas evolution was observed. Unfortunately, we could not characterize the metal products, and the fate of nitrogen is not fully understood. On the other hand, complexes having dppe ligands (5a, 5b, 8b, 8c, 11a, and 11b) gave much lower yields of NH₃ (0-6%) and NH₂- NH_2 (0–1%), and considerable amounts of the starting complexes were recovered. It should be pointed out that NH₂NH₂ is most commonly observed as the major nitrogen hydride product in the protonation of homobimetallic μ -N₂ complexes.² In addition, protonolysis of heterodinuclear μ -N₂ complexes has not been studied extensively. It has been reported that treatment of the W-Ta complex [Cp*WMe₃(µ-N₂)TaCp*Me₂] with HOTf gives the mononuclear tungsten hydrazido(1-) complex $[Cp*Me_3W(\eta^2-NHNH_2)][OTf]$ and $[Cp*TaMe_2(OTf)_2]$,³⁹ while the hydrolysis of the Re-Cr complex [ReCl(PMe₂- $Ph_{4}(\mu-N_{2})CrCl_{3}(THF)_{2}$] results in the formation of $[ReCl(N_2)(PMe_2Ph)_4]$.⁴⁰ In contrast, the reaction of the Mo-W µ-N₂ complex [Cp*MoMe₃(µ-N₂)WCp*Me₃] with HCl affords NH₃ in 16% yield based on the total nitrogen.¹⁶ In the protonation reactions of the heterobimetallic μ -N₂ complexes derived from **1**, the group 4 or 5 fragment seems to have minor effects on the NH₃/ NH₂NH₂ selectivity, although the mechanism of the protonation and N-N bond cleavage at the dinuclear cores is still unclear.

Finally, reduction of the μ -N₂ complexes **4**, **5a**, **10a**, and 10b with sodium or magnesium was also examined, since the conversion of μ -N₂ complexes to the corresponding nitrides in the presence 9,10,11,13 or absence 41-43of alkali metals has recently been established. However the only characterized products were the parent dinitrogen complexes 1 and 2a.

Concluding Remarks

We have succeeded in the systematic synthesis of a series of heterobimetallic dinitrogen complexes containing group 6 and group 4 or 5 transition metals. The synthetic method established in this study provides an important approach to the chemistry of dinitrogen activated by two different metal centers, which still remains much less developed in comparison with the chemistry of homodinuclear dinitrogen complexes. The spectroscopic and structural properties of the μ -N₂ complexes newly prepared were examined in detail, revealing that the μ -N₂ moiety is best regarded as a formal $(N_2)^{2-}$ ligand. Protonation of the coordinated dinitrogen in these complexes gave rise to the formation of ammonia and hydrazine, whereas migration of a Me group from the group 4 or 5 metal center to the dinitrogen ligand has not been observed. The lability of the chloro ligands on the titanium atom in 5a also enabled us to obtain the sulfur-rich bridging dinitrogen complex **17**, which is a rare example of μ -N₂ complexes with sulfur donor ligands and is interesting in relevalence to the metal-sulfur multinuclear structure in the active site of nitrogenase. Further study on the chemical transformation of the μ -N₂ ligand in the group 6–group 4 or 5 heterodinuclear complexes is under way.

Experimental Section

General Procedure. All reactions were carried out under a dry nitrogen atmosphere unless otherwise noted. Solvents were dried by usual methods and distilled before use. Li₂S₅⁴⁴ and complexes 1,45 2a,45 2b,46 7,30 [Cp2ZrMeCl],47 [Cp*NbCl4],48 [CpTaCl₄],⁴⁹ [Me₃TaCl₂],⁵⁰ and [Me₂NbCl₃]⁵¹ were prepared according to the literature methods. Other reagents were commercially obtained and used without further purification.

¹H and ³¹P{¹H} NMR spectra were recorded on a JEOL JNM-EX-270 (1H, 270 MHz; 31P, 109 MHz) or JEOL JNM-LA-400 (1H, 400 MHz; 31P, 162 MHz) spectrometer. IR spectra were recorded on a Shimadzu FTIR-8100M spectrophotometer. Quantitative GLC analyses were carried out on a Shimadzu GC-8A instrument equipped with a thermal conductivity

(42) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. J. Am. Chem. Soc. 1996, 118, 8623-8638.

- (44) Shaver, A.; Mccall, J. M.; Marmolejo, G. Inorg. Synth. 1990, 27. 59-65.
- (45) Chatt, J.; Heath, G. A.; Richards, R. L. J. Chem. Soc., Dalton Trans. 1974, 2074-2082.
- (46) Dilworth, J. R.; Richards, R. L.; Chen, G. J.-J.; MacDonald, J. W. Inorg. Synth. 1980, 20, 119–127.
 (47) Jordan, R. F. J. Organomet. Chem. 1985, 294, 321–326.

- (49) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. J. Chem. Soc., Dalton Trans. 1980, 1156-1160.
- (50) Schrock, R. R.; Sharp, P. R. J. Am. Chem. Soc. 1978, 100, 2389-2399
- (51) Fowles, G. W. A.; Rice, D. A.; Winkins, J. D. J. Chem. Soc., Dalton Trans. 1972, 2313-2318.

⁽³⁹⁾ Glassman, T. E.; Liu, A. H.; Schrock, R. R. Inorg. Chem. 1991, 30, 4723-4732.

⁽⁴⁰⁾ Chatt, J.; Fay, R. C.; Richards, R. L. J. Chem. Soc., A 1971, 702.

⁽⁴¹⁾ Cummins, C. C. Chem. Commun. 1998, 1777-1786.

⁽⁴³⁾ Laplaza, C. E.; Johnson, A. R.; Cummins, C. C. J. Am. Chem. Soc. 1996, 118, 709-710

⁽⁴⁸⁾ Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. J. Am. Chem. Soc. 1988, 110, 5008-5017.

detector using a Molecular Sieve 13X column. Elemental analyses were performed with a Perkin-Elmer 2400 series II CHN analyzer.

Preparation of [WCl(PMe₂Ph)₄(\mu-N₂)TiCp₂Cl] (3a). Complex **1** (500.0 mg, 0.631 mmol) and [Cp₂TiCl₂] (157.0 mg, 0.631 mmol) were dissolved in benzene (12.5 mL) at room temperature, and the mixture was stirred for 17 h at 50 °C. Then the solution was concentrated to ca. 6 mL under vacuum at room temperature. Layering the benzene solution with hexane afforded **3a** as a black solid, which was collected, washed with hexane, and dried in vacuo (466.0 mg, 73% yield): ¹H NMR (C₆D₆) δ 1.57 (s, 24H, PMe), 6.30 (s, 10H, Cp), 6.98–7.54 (m, 20H, Ph); IR (KBr) 1468 (m) cm⁻¹. Anal. Calcd for C₄₂H₅₄-Cl₂N₂P₄TiW: C, 49.78; H, 5.37; N, 2.76. Found: C, 49.40; H, 5.61; N, 2.53.

Preparation of [WI(PMe₂Ph)₄(μ-N₂)ZrCp₂Cl]·0.5C₆H₆ (3b·0.5C₆H₆), [WI(PMe₂Ph)₃(py)(μ-N₂)ZrCp₂Cl]·0.5py (3b'· 0.5py), and [WI(PMe₂Ph)₄(μ-N₂)HfCp₂Cl]·C₆H₆ (3c·C₆H₆). Complex 1 (200.0 mg, 0.252 mmol), [Cp₂ZrCl₂] (73.8 mg, 0.252 mmol), and NaI (550.0 mg, 3.70 mmol) were dissolved in benzene (5 mL) at room temperature, and the mixture was stirred for 16 h at 50 °C under dark. Then the solution was cooled to room temperature and filtered. Layering the filtered solution with hexane afforded **3b**·0.5C₆H₆ as a dark red solid, which was collected, washed with hexane, and dried in vacuo (192.0 mg, 64% yield): ¹H NMR (C₆D₆) δ 1.71 (s, 24H, PMe), 6.33 (s, 10H, Cp), 6.98–7.48 (m, 20H, Ph); IR (KBr) 1518 (m) cm⁻¹. Anal. Calcd for C₄₅H₅₇ClIN₂P₄WZr: C, 45.52; H, 4.84; N, 2.36. Found: C, 45.59; H, 4.89; N, 2.22.

The pyridine complex [WI(PMe₂Ph)₃(py)(μ -N₂)ZrCp₂Cl]-0.5py (**3b**'·0.5py) was obtained in 44% yield by dissolving complex **3b**·0.5C₆H₆ in pyridine followed by addition of hexane to the pyridine solution and further recrystallization of the solid deposited from toluene–pyridine/hexane. ¹H NMR (C₄D₈O): δ 1.50 (t, 6H, J = 2.7 Hz, trans PMe), 1.59 (t, 6H, J= 2.7 Hz, trans PMe), 1.90 (d, 6H, J = 6.0 Hz, unique PMe), 6.24 (s, 10H, Cp), 6.82–7.41 (m, 15H, Ph). This complex is somewhat unstable in solution, and signals of the pyridine ligand were obscured by overlapping with those of decomposition products. IR (KBr): 1541 (m) cm⁻¹. Anal. Calcd for C_{41.5}H_{50.5}ClIN_{3.5}P₃WZr: C, 44.16; H, 4.51; N, 4.34. Found: C, 44.62; H, 4.56; N, 4.30.

Complex **3c**·C₆H₆ was prepared from **1**, [Cp₂HfCl₂], and NaI as a brown solid in 60% yield by a procedure similar to that described for complex **3b**·0.5C₆H₆. ¹H NMR (C₆D₆): δ 1.77 (s, 24H, PMe), 6.29 (s, 10H, Cp), 6.99–7.70 (m, 20H, Ph); IR (KBr) 1545 (m) cm⁻¹. Anal. Calcd for C₄₈H₆₆ClHfIN₂P₄W: C, 43.89; H, 4.60; N, 2.13. Found: C, 43.85; H, 4.63; N, 2.08.

Preparation of [WCl(PMe₂Ph)₄(μ-N₂)TiCpCl₂] (4). Complex 1 (225.2 mg, 0.284 mmol) and [CpTiCl₃] (62.2 mg, 0.284 mmol) were dissolved in benzene (5 mL) at room temperature. With rapid evolution of nitrogen gas, the color of the solution immediately changed from orange to dark green. The mixture was stirred for a further 8 h, and the solvent was evaporated under vacuum to give a dark green solid. The residual solid was dissolved in CH₂Cl₂, and the solution was filtered. Layering the CH₂Cl₂ solution with ether afforded black crystals of **4**, which were collected, washed with ether, and dried in vacuo (196.0 mg, 70% yield): ¹H NMR (CDCl₃) δ 1.63 (s, 24H, PMe), 6.44 (s, 5H, Cp), 7.27–7.46 (m, 20H, Ph); ³¹P{¹H} NMR (CDCl₃) δ –24.5 (s with ¹⁸³W satellites, *J*_{WP} = 277 Hz); IR (KBr) 1408 (m) cm⁻¹. Anal. Calcd for C₃₇H₄₉Cl₃N₂P₄TiW: C, 45.17; H, 5.02; N, 2.85. Found: C, 45.50; H, 5.29; N, 2.70.

Preparation of [WCl(dppe)₂(μ -N₂)**TiCpCl**₂]·**CH**₂**Cl**₂·**Et**₂**O (5a·CH**₂**Cl**₂·**Et**₂**O) and [MoCl(dppe)**₂(μ -N₂)**TiCpCl**₂] (**5b)**. Complex **2a** (198.0 mg, 0.191 mmol) and [CpTiCl₃] (41.9 mg, 0.191 mmol) were dissolved in THF (5 mL) at room temperature. With rapid evolution of nitrogen gas, the color of the solution changed from orange to dark green. The mixture was stirred for a further 8 h, and the solvent was evaporated to give a dark green solid. The residual solid was dissolved in

CH₂Cl₂, and the solution was filtered. Layering the CH₂Cl₂ solution with ether afforded black crystals of **5a**·CH₂Cl₂·Et₂O, which were collected, washed with ether, and dried in vacuo (166.2 mg, 63% yield): ¹H NMR (CDCl₃) δ 2.46, 2.89 (br, 4H each, CH₂ of dppe), 5.70 (s, 5H, Cp), 6.66–7.67 (m, 40H, Ph); ³¹P{¹H} NMR (CDCl₃) δ 36.0 (s with ¹⁸³W satellites, $J_{WP} = 284$ Hz); IR (KBr) 1412 (m) cm⁻¹. Anal. Calcd for C₆₂H₆₅Cl₅N₂OP₄-TiW: C, 53.69; H, 4.72; N, 2.02. Found: C, 53.49; H, 4.60; N, 2.19.

Complex **5b** was prepared from **2b** and [CpTiCl₃] as black crystals in 78% yield by a procedure similar to that described for complex **5a**·CH₂Cl₂·Et₂O: ¹H NMR (CDCl₃) δ 2.31, 2.66 (br, 4H each, CH₂ of dppe), 5.73 (s, 5H, Cp), 6.78–7.77 (m, 40H, Ph); ³¹P{¹H} NMR (CDCl₃) δ 52.9 (s); IR (KBr) 1416 (m) cm⁻¹. Anal. Calcd for C₅₇H₅₃Cl₃MoN₂P₄Ti: C, 60.05; H, 4.69; N, 2.46. Found: C, 60.13; H, 5.06; N, 2.22.

Preparation of [W(OTf)(PMe₂Ph)₄(μ-N₂)**TiCp**₂(**OTf)]** (**6a).** Complex **1** (120.1 mg, 0.152 mmol) and [Cp₂Ti(OTf)₂] (72.2 mg, 0.152 mmol) were dissolved in benzene (3 mL) at room temperature. With rapid evolution of nitrogen gas, the color of the solution immediately changed from orange to black. The mixture was stirred for further 30 min and filtered. Addition of hexane to the filtrate afforded **6a** as a brown solid (181.3 mg, 96% yield): ¹H NMR (C₆D₆) δ 1.51 (s, 24H, PMe), 6.21 (s, 10H, Cp), 6.98–7.23 (m, 20H, Ph); ³¹P{¹H} NMR (C₆D₆) δ –25.4 (s with ¹⁸³W satellites, *J*_{WP} = 290 Hz); IR (KBr) 1555 (m) cm⁻¹. Anal. Calcd for C₄₄H₅₄F₆N₂O₆P₄S₂TiW: C, 42.60; H, 4.39; N, 2.26. Found: C, 42.90; H, 4.59; N, 2.23.

Preparation of [W(OTf)(dppe)₂(μ-N₂)**TiCp**₂(**OTf)] (6b).** Complex **2a** (172.0 mg, 0.166 mmol) and [Cp₂Ti(OTf)₂] (79.0 mg, 0.166 mmol) were dissolved in benzene (3 mL) at room temperature. With rapid evolution of nitrogen gas, the color of the solution changed from orange to black, and a black solid began to precipitate. The suspension was stirred for further 30 min, and the solvent was evaporated under vacuum to give a black solid. The residual solid was dissolved in THF, and the solution was filtered. Layering the THF solution with hexane afforded **6b** as a brown solid (151.6 mg, 88% yield): ¹H NMR (C₄D₈O) δ 2.60, 3.10 (br, 4H each, CH₂ of dppe), 5.91 (s, 10H, Cp), 6.68–7.52 (m, 40H, Ph); ³¹P{¹H} NMR (C₄D₈O) δ 41.4 (s with ¹⁸³W satellites, $J_{WP} = 297$ Hz); IR (KBr) 1545 (m) cm⁻¹. Anal. Calcd for C₆₄H₅₈F₆N₂O₆P₄S₂TiW: C, 51.77; H, 3.94; N, 1.89. Found: C, 52.03; H, 4.33; N, 2.12.

Preparation of [W(NCS)(dppe)₂(µ-N₂)TiCp₂Cl]·CH₂Cl₂ $(8a \cdot CH_2Cl_2)$, $[W(NCS)(dppe)_2(\mu - N_2)ZrCp_2Cl] \cdot CH_2Cl_2$ $(8b \cdot CH_2Cl_2)$ CH₂Cl₂), and [W(NCS)(dppe)₂(µ-N₂)HfCp₂Cl]·0.5CH₂Cl₂ (8c.0.5CH2Cl2). Complex 7 (110.4 mg, 0.084 mmol) and [Cp2-TiCl₂] (21.0 mg, 0.084 mmol) were dissolved in benzene (3 mL), and the mixture was stirred for 10 h at room temperature. During this period, the color of the solution gradually changed from black to dark red. Then the reaction mixture was evaporated under vacuum to give a black solid. The residual solid was dissolved in CH₂Cl₂, and the solution was filtered. Layering the CH₂Cl₂ solution with hexane afforded black crystals of 8a·CH₂Cl₂, which were collected, washed with hexane, and dried in vacuo (71.0 mg, 62% yield): ¹H NMR (CDCl₃) δ 2.54, 2.95 (br, 4H each, CH₂ of dppe), 5.65 (s, 10H, Cp), 6.44–7.55 (m, 40H, Ph); ${}^{31}P{}^{1}H$ NMR (CDCl₃) δ 37.9 (s with ¹⁸³W satellites, $J_{WP} = 288$ Hz); IR (KBr) 2049 (s), 1545 (m) cm $^{-1}\!.$ Anal. Calcd for $C_{64}H_{60}Cl_3N_3P_4STiW\!\!:$ C, 56.31; H, 4.43; N, 3.08. Found: C, 56.01; H, 4.54; N, 2.75.

The zirconium analogue **8b**·CH₂Cl₂ was prepared from **7** and $[Cp_2ZrCl_2]$ by a procedure similar to that described for complex **8a**·CH₂Cl₂ and isolated as black crystals in 65% yield: ¹H NMR (CDCl₃) δ 2.41, 2.77 (br, 4H each, CH₂ of dppe), 5.85 (s, 10H, Cp), 6.49–7.66 (m, 40H, Ph); ³¹P{¹H} NMR (CDCl₃) δ 44.6 (s with ¹⁸³W satellites, $J_{WP} = 292$ Hz); IR (KBr) 2056 (s), 1549 (m) cm⁻¹. Anal. Calcd for C₆₄H₆₀Cl₃N₃P₄SWZr: C, 54.57; H, 4.29; N, 2.98. Found: C, 54.17; H, 4.51; N, 2.92.

The hafnium analogue $8c \cdot 0.5 CH_2 Cl_2$ was prepared similarly from 7 and $[Cp_2HfCl_2]$ and isolated as black crystals in 66%

yield: ¹H NMR (CDCl₃) δ 2.17, 2.56 (br, 4H each, CH₂ of dppe), 5.60 (s, 10H, Cp), 6.66–7.50 (m, 40H, Ph); ³¹P{¹H} NMR (CDCl₃) δ 47.2 (s with ¹⁸³W satellites, $J_{WP} = 286$ Hz); IR (KBr) 2056 (s), 1559 (m) cm⁻¹. Anal. Calcd for C_{63.5}H₅₉Cl₂HfN₃P₄-SW: C, 52.48; H, 4.09; N, 2.89. Found: C, 52.44; H, 4.36; N, 2.55.

Preparation of [W(NCS)(dppe)₂(μ-N₂)**TiCpCl**₂]·3CH₂Cl₂ (9a·3CH₂Cl₂) and [W(NCS)(dppe)₂(μ-N₂)**TiCp*Cl**₂] (9b). Complex 7 (109.7 mg, 0.084 mmol) and [CpTiCl₃] (18.4 mg, 0.084 mmol) were dissolved in benzene (3 mL), and the mixture was stirred for 17 h at room temperature. The resulting reaction mixture was evaporated under vacuum to give a green solid. The residual solid was dissolved in CH₂Cl₂, and the solution was filtered. Layering the CH₂Cl₂ solution with ether afforded dark green crystals of 9a·3CH₂Cl₂, which were collected, washed with ether, and dried in vacuo (68.0 mg, 54% yield): ¹H NMR (CDCl₃) δ 2.49, 2.81 (br, 4H each, CH₂ of dppe), 5.80 (s, 5H, Cp), 6.55–7.63 (m, 40H, Ph); ³¹P{¹H} NMR (CDCl₃) δ 38.2 (s with ¹⁸³W satellites, *J*_{WP} = 284 Hz); IR (KBr) 2041 (s), 1441 (m) cm⁻¹. Anal. Calcd for C₆₁H₅₉Cl₈N₃P₄STiW: C, 48.67; H, 3.95; N, 2.79. Found: C, 49.02; H, 3.77; N, 2.88.

Complex **9b** was prepared from **7** and [Cp*TiCl₃] as dark green crystals in 64% yield by a similar procedure except that **9b** was isolated by recrystallization from ClCH₂CH₂Cl/hexane: ¹H NMR (C₆D₆) δ 1.90 (s, 15H, Cp*), 2.19, 2.58 (br, 4H each, CH₂ of dppe), 6.63–7.88 (m, 40H, Ph); ³¹P{¹H} NMR (C₆D₆) δ 44.3 (s with ¹⁸³W satellites, $J_{WP} = 286$ Hz); IR (KBr) 2041 (s), 1433 (m) cm⁻¹. Anal. Calcd for C₆₃H₆₃Cl₂N₃P₄STiW: C, 57.29; H, 4.81; N, 3.18. Found: C, 57.19; H, 4.79; N, 3.16.

Preparation of [WCl(PMe₂Ph)₄(µ-N₂)NbCpCl₃]·CH₂Cl₂· Et₂O (10a·CH₂Cl₂·Et₂O), [WCl(PMe₂Ph)₄(μ -N₂)NbCp*Cl₃]· C_7H_8 (10b· C_7H_8), [WCl (PMe₂Ph)₄(μ -N₂)TaCpCl₃]·CH₂Cl₂ $(10c \cdot CH_2Cl_2)$, and $[WCl(PMe_2Ph)_4(\mu - N_2)TaCp^*Cl_3]$ (10d). Complex 1 (4.20 g, 5.30 mmol) and [CpNbCl₄] (1.59 g, 5.30 mmol) were dissolved in benzene (20 mL) at room temperature. With rapid evolution of nitrogen gas, the color of the solution changed from orange to black. The mixture was stirred for a further 30 min and evaporated under vacuum to give a black oil. The residual oil was dissolved in CH₂Cl₂, and the solution was filtered. Layering the CH₂Cl₂ solution with ether afforded black crystals of 10a·CH₂Cl₂·Et₂O, which were collected, washed with ether, and dried in vacuo (5.48 g, 85% yield): ¹H NMR (CDCl₃) δ 1.61 (s, 24H, PMe), 6.37 (s, 5H, Cp), 7.12-7.48 (m, 20H, Ph); ${}^{31}P{}^{1}H$ NMR (CDCl₃) δ -27.7 (s with ${}^{183}W$ satellites, $J_{WP} = 273$ Hz); IR (KBr) 1395 (m) cm⁻¹. Anal. Calcd for C42H61Cl6N2NbOP4W: C, 41.24; H, 5.03; N, 2.29. Found: C, 40.99; H, 4.84; N, 2.09.

Complex **10b**·C₇H₈ was obtained in 98% yield as a dark green powder by the reaction of **1** with [Cp*NbCl₄] and recrystallization from toluene/hexane: ¹H NMR (C₆D₆) δ 1.56 (s, 24H, PMe), 2.26 (s, 15H, Cp*), 6.97–7.57 (m, 20H, Ph); ³¹P-{¹H} NMR (C₆D₆) δ –27.3 (s with ¹⁸³W satellites, *J*_{WP} = 275 Hz); IR (KBr) 1385 (m) cm⁻¹. Anal. Calcd for C₄₉H₆₇Cl₄N₂-NbP₄W: C, 47.98; H, 5.51; N, 2.28. Found: C, 47.89; H, 5.65; N, 2.04.

Complex $10c \cdot CH_2Cl_2$ was obtained in 74% yield as a dark red powder by the reaction of 1 with [CpTaCl_4] followed by recrystallization from CH_2Cl_2/hexane: 1H NMR (CDCl_3) δ 1.65 (s, 24H, PMe), 6.41 (s, 5H, Cp), 7.31–7.46 (m, 20H, Ph); $^{31}P-\{^1H\}$ NMR (CDCl_3) δ –24.6 (s with ^{183}W satellites, $J_{WP}=275$ Hz); IR (KBr) 1435 (m) cm $^{-1}$. Anal. Calcd for $C_{38}H_{51}Cl_6N_2P_4$ -TaW: C, 36.89; H, 4.15; N, 2.26. Found: C, 37.08; H, 4.27; N, 2.29.

Complex **10d** was obtained in 95% yield as a dark red powder by the reaction of **1** with [Cp*TaCl₄] followed by recrystallization from toluene/hexane: ¹H NMR (C₆D₆) δ 1.57 (s, 24H, PMe), 2.38 (s, 15H, Cp*), 6.98–7.42 (m, 20H, Ph); ³¹P-{¹H} NMR (C₆D₆) δ –24.9 (s with ¹⁸³W satellites, $J_{WP} = 277$ Hz); IR (KBr) 1426 (m) cm⁻¹. Anal. Calcd for C₄₂H₅₉Cl₄N₂P₄-TaW: C, 41.27; H, 4.86; N, 2.29. Found: C, 41.65; H, 5.09; N, 2.21. Dark red crystals of **10d**·2MeCN suitable for the crystal-

lographic study were obtained by recrystallization of $10d\ \mbox{from }CH_2Cl_2\mbox{-MeCN/ether}.$

Preparation of [WCl(dppe)₂(µ-N₂)NbCpCl₃]·Et₂O (11a· Et₂O) and [WCl(dppe)₂(µ-N₂)TaCpCl₃] (11b). Complex 2a (164.6 mg, 0.159 mmol) and [CpNbCl₄] (47.6 mg, 0.159 mmol) were dissolved in THF (5 mL) at room temperature. With rapid evolution of nitrogen gas, the color of the solution immediately changed from orange to black. The mixture was stirred for a further 1 h, and the solvent was evaporated under vacuum to give a dark green solid. The residual solid was dissolved in CH₂Cl₂, and the solution was filtered. Slow diffusion of ether into the filtrate deposited black crystals of 11a·Et₂O (164.8 mg, 75% yield): ¹H NMR (CDCl₃) δ 2.68, 2.90 (br, 4H each, CH₂ of dppe), 5.86 (s, 5H, Cp), 6.67–7.66 (m, 40H, Ph); ³¹P-{¹H} NMR (CDCl₃) δ 34.1 (s with ¹⁸³W satellites, $J_{WP} = 275$ Hz); IR (KBr) 1383 (m) cm⁻¹. Anal. Calcd for C₆₁H₆₃Cl₄N₂-NbOP₄W: C, 52.99; H, 4.59; N, 2.03. Found: C, 52.88; H, 4.22; N, 2.32.

Complex **11b** was prepared similarly from **2a** and [CpTaCl₄] as a brown powder in 46% yield: ¹H NMR (CDCl₃) δ 2.61, 2.87 (br, 4H each, CH₂ of dppe), 5.86 (s, 5H, Cp), 6.68–7.69 (m, 40H, Ph); ³¹P{¹H} NMR (CDCl₃) δ 36.9 (s with ¹⁸³W satellites, $J_{WP} = 281$ Hz); IR (KBr) 1419 (m) cm⁻¹. Anal. Calcd for C₅₇H₅₃-Cl₄N₂P₄TaW: C, 49.02; H, 3.83; N, 2.01. Found: C, 49.03; H, 4.02; N, 1.64.

Preparation of [W(NCS)(dppe)₂(μ-N₂)NbCpCl₃]·THF (**12a**·THF) and [W(NCS)(dppe)₂(μ-N₂)TaCpCl₃] (12b). Complex 7 (186.1 mg, 0.142 mmol) and [CpNbCl₄] (42.6 mg, 0.142 mmol) were dissolved in THF (3 mL), and the mixture was stirred for 1 h at room temperature. The resulting solution was filtered, and layering the THF solution with hexane afforded black crystals of **12a**·THF (179.0 mg, 90% yield): ¹H NMR (CD₂Cl₂) δ 2.64, 2.83 (br, 4H each, CH₂ of dppe), 5.84 (s, 5H, Cp), 6.55–7.60 (m, 40H, Ph); ³¹P{¹H} NMR (CD₂Cl₂) δ 35.5 (s with ¹⁸³W satellites, $J_{WP} = 277$ Hz); IR (KBr) 2029 (s), 1395 (m) cm⁻¹. Anal. Calcd for C₆₂H₆₁Cl₃N₃NbOP₄SW: C, 53.07; H, 4.38; N, 2.99. Found: C, 52.89; H, 4.24; N, 3.28.

Complex **12b** was prepared in 98% yield as a dark red powder by the reaction of **7** with [CpTaCl₄] followed by recrystallization from toluene/hexane: ¹H NMR (CD₂Cl₂) δ 2.55, 2.89 (br, 4H each, CH₂ of dppe), 5.96 (s, 5H, Cp), 6.60–7.61 (m, 40H, Ph); ³¹P{¹H} NMR (CD₂Cl₂) δ 37.4 (s with ¹⁸³W satellites, $J_{WP} = 281$ Hz); IR (KBr) 2037 (s), 1420 (m) cm⁻¹. Anal. Calcd for C₅₈H₅₃Cl₃N₃P₄STaW: C, 49.09; H, 3.76; N, 2.96. Found: C, 49.02; H, 3.89; N, 2.67.

Preparation of [WCl(PMe₂Ph)₃('BuNC)(μ-N₂)TaCp*Cl₃] (13). Complex 9d (177.0 mg, 0.145 mmol) and 'BuNC (70.1 mg, 0.236 mmol) were dissolved in ClCH₂CH₂Cl (3 mL), and the mixture was stirred for 10 h at 50 °C. The resulting solution was evaporated under vacuum, and the residual dark red solid was dissolved in toluene. Slow diffusion of hexane into the filtrated toluene solution deposited a red powder of 12 (44.0 mg, 26% yield): ¹H NMR (C₆D₆) δ 0.95 (s, 9H, 'Bu), 1.29 (d, 6H, *J* = 7.8 Hz, unique PMe), 1.78 (t, 6H, *J* = 3.7 Hz, trans PMe), 1.80 (t, 6H, *J* = 3.9 Hz, trans PMe), 2.30 (s, 15H, Cp*), 6.97–7.67 (m, 15H, Ph); ³¹P{¹H} NMR (C₆D₆) δ –20.3 (d with ¹⁸³W satellites, *J*_{WP} = 260 Hz); IR (KBr) 2112 (m), 1458 (m) cm⁻¹. Anal. Calcd for C₃₉H₅₇Cl₄N₃P₃TaW: C, 40.12; H, 4.92; N, 3.60. Found: C, 40.34; H, 5.17; N, 3.98.

Preparation of [WI(PMe₂Ph)₄(μ-N₂)ZrCp₂Me] (14a). Complex **1** (182.1 mg, 0.230 mmol), [Cp₂ZrMeCl] (62.5 mg, 0.230 mmol), and NaI (418 mg, 2.79 mmol) were dissolved in toluene (5 mL), and the mixture was stirred for 20 h at 50 °C. The resulting reaction mixture was filtered, and the solvent was evaporated under vacuum to give a black solid. Recrystallization from CH₂Cl₂/hexane afforded **14a** as a brown powder, which was collected, washed with hexane, and dried in vacuo (128.6 mg, 31% yield): ¹H NMR (C₆D₆) δ 0.37 (s, 3H, ZrMe), 1.67 (s, 24H, PMe), 6.11 (s, 10H, Cp), 6.79–7.58 (m, 20H, Ph); ³¹P{¹H} NMR (C₆D₆) δ -31.8 (s with ¹⁸³W satellites,

 $J_{\rm WP} = 290$ Hz); IR (KBr) 1541 (m) cm⁻¹. Anal. Calcd for C₄₃H₅₇-IN₂P₄WZr: C, 45.79; H, 5.09; N, 2.48. Found: C, 45.42; H, 5.33; N, 2.72.

Preparation of [W(NCS)(dppe)₂(µ-N₂)ZrCp₂Me] (14b). Complex 7 (225.0 mg, 0.172 mmol) and [Cp₂ZrMeCl] (46.9 mg, 0.172 mmol) were dissolved in benzene (5 mL), and the mixture was stirred for 1 h at room temperature. Then the reaction mixture was evaporated under vacuum, and the residual black solid was extracted with THF. Layering the THF solution with hexane afforded black crystals of 14b (196.7 mg, 88% yield): ¹H NMR (CDCl₃) δ -0.02 (s, 3H, ZrMe), 2.32, 2.68 (br, 4H each, CH2 of dppe), 5.66 (s, 10H, Cp), 6.48-7.66 (m, 40H, Ph); ³¹P-{¹H} NMR (CDCl₃) δ 45.8 (s with ¹⁸³W satellites, $J_{WP} = 297$ Hz); IR (KBr) 2060 (s), 1557 (m) cm⁻¹. Anal. Calcd for $C_{64}H_{61}N_3P_4SWZr;\ C,\ 58.98;\ H,\ 4.72;\ N,\ 3.22.\ Found:\ C,\ 58.82;$ H, 4.63; N, 3.12.

Preparation of $[WCl(PMe_2Ph)_4(\mu-N_2)TaMe_3Cl]$ (15a), $[WCl(dppe)_2(\mu-N_2)TaMe_3Cl]$ (15b), and $[MoCl(dppe)_2(\mu-N_2)TaMe_3Cl]$ N2)TaMe3Cl] (15c). Complex 1 (187.0 mg, 0.236 mmol) and [Me₃TaCl₂] (70.1 mg, 0.236 mmol) were dissolved in toluene (3 mL) at room temperature. With rapid evolution of nitrogen gas, the color of the solution changed from orange to black. The mixture was stirred for a further 30 min and filtered. Layering the filtrate with hexane afforded **15a** as a brown powder, which was collected, washed with hexane, and dried in vacuo (165.7 mg, 66% yield): ¹H NMR (C₄D₈O) δ 0.45 (s, 9H, TaMe), 1.68 (s, 24H, PMe), 6.94-7.44 (m, 20H, Ph); ³¹P-{¹H} NMR (C₄D₈O) δ -19.9 (s with ¹⁸³W satellites, $J_{WP} = 278$ Hz); IR (KBr) 1480 (m) cm⁻¹. Anal. Calcd for C₃₅H₅₃Cl₂N₂P₄-TaW: C, 39.61; H, 5.03; N, 2.64. Found: C, 40.00; H, 4.84; N,

Complex 15b was prepared similarly from 2a and [Me₃-TaCl₂] in 55% yield: ¹H NMR (C₄D₈O) δ 0.23 (s, 9H, TaMe), 2.41, 2.99 (br, 4H each, CH₂ of dppe), 6.73–7.75 (m, 40H, Ph); $^{31}P{^{1}H} NMR (C_4D_8O) \delta 42.0$ (s with ^{183}W satellites, $J_{WP} = 290$ Hz); IR (KBr) 1470 (m) cm⁻¹. Anal. Calcd for $C_{55}H_{57}Cl_2N_2P_4$ -TaW: C, 50.60; H, 4.40; N, 2.15. Found: C, 50.55; H, 4.02; N, 1.99.

Complex 15c was prepared in 59% yield as a black powder by the reaction of with 2b with [Me₃TaCl₂] and recrystallization from CH₂Cl₂/hexane: ¹H NMR (C₄D₈O) δ 0.13 (s, 9H, TaMe), 2.46, 2.92 (br, 4H each, CH₂ of dppe), 6.73-7.74 (m, 40H, Ph); ${}^{31}P{}^{1}H$ NMR (C₄D₈O) δ 55.5 (s); IR (KBr) 1483 (m) cm⁻¹. Anal. Calcd for C₅₅H₅₇Cl₂MoN₂P₄Ta: C, 54.25; H, 4.72; N, 2.30. Found: C, 53.99; H, 4.42; N, 1.93.

Preparation of [WCl(dppe)₂(µ-N₂)NbMe₂Cl₂] (16a· CH2Cl2) and [MoCl(dppe)2(µ-N2)NbMe2Cl2] (16b). Complex 2a (360.8 mg, 0.348 mmol) and [Me₂NbCl₃] (79.8 mg, 0.348 mmol) were dissolved in benzene (3 mL) at room temperature. With rapid evolution of nitrogen gas, the color of the solution changed from orange to black. The mixture was stirred for a further 30 min, and the solvent was evaporated under vacuum to give a black solid. The residual solid was dissolved in CH₂-Cl₂, and the solution was filtered. Layering the CH₂Cl₂ solution with hexane afforded black crystals of 16a·CH₂Cl₂ (222.2 mg, 48% yield): ¹H NMR (C₆D₆) δ 1.25 (s, 6H, NbMe), 2.28, 2.61 (br, 4H each, CH₂ of dppe), 6.79–7.75 (m, 40H, Ph); ³¹P{¹H} NMR (C₆D₆) δ 35.1 (s with ¹⁸³W satellites, $J_{WP} = 281$ Hz); IR (KBr) 1406 (m) cm⁻¹. Anal. Calcd for $C_{55}H_{56}Cl_5N_2NbP_4W$: C, 49.93; H, 4.27; N, 2.12. Found: C, 50.27; H, 4.17; N, 1.73.

Complex 16b was prepared from 2b and [Me₂NbCl₃] as a black powder in 74% yield by a similar procedure except that 16b was isolated by recrystallization from benzene/hexane: ¹H NMR (CDCl₃) & 0.65 (s, 6H, NbMe), 2.44, 2.80 (br, 4H each, CH2 of dppe), 6.71-7.55 (m, 40H, Ph); ³¹P{¹H} NMR (CDCl₃) δ 51.5 (s); IR (KBr) 1408 (m) cm⁻¹. Anal. Calcd for C₅₄H₅₄Cl₃-MoN₂NbP₄: C, 56.39; H, 4.73; N, 2.44. Found: C, 56.50; H, 4.58; N, 2.04.

Preparation of [WCl(dppe)₂(µ-N₂)TiCpS₅]·0.5Et₂O (17· 0.5Et₂O). To a dark yellow solution of Li₂S₅ prepared from S₈ (0.046 mmol) and LiBEt₃H (0.147 mmol) in THF (5 mL) was added 5a·CH₂Cl₂·Et₂O (90.4 mg, 0.065 mmol), and the resultant black solution was stirred for 24 h at room temperature. A brown solid precipitated during this period was filtered off, washed with a small amount of EtOH, and dried in vacuo. Recrystallization of this precipitate from CHCl₃/ether deposited black crystals, which were collected, washed with ether, and dried in vacuo to give 17.0.5Et₂O (58.5 mg, 66% yield): ¹H NMR (CDCl₃) δ 2.50, 2.90 (br, 4H each, CH₂ of dppe), 5.61 (s, 5H, Cp), 6.60–7.60 (m, 40H, Ph); ${}^{31}P{}^{1}H{}$ NMR (\hat{CDCl}_{3}) δ 42.0 (s with ¹⁸³W satellites, $J_{WP} = 290$ Hz); IR (KBr) 1406 (m) cm⁻¹. Anal. Calcd for C₅₉H₅₈ClN₂O_{0.5}P₄S₅TiW: C, 52.32; H, 4.32; N, 2.07. Found: C, 52.20; H, 4.63; N, 2.08. X-ray diffraction study of the crystalline sample clearly indicated that it contains 1.5 molecules of ether per one molecule of 17, but the crystals gave off a part of the ether molecules on drying under vacuum to give a sample with the empirical formula of 17.0.5 Et₂O.

Reaction of the Heterobimetallic Dinitrogen Complexes with H₂SO₄. In a typical run, concentrated H₂SO₄ (10 equiv) was added to a suspension of 10d (95.8 mg, 0.078 mmol) in MeOH (3 mL) under argon, and the mixture was stirred at room temperature for 3 h. The gaseous phase was analyzed by GLC, which showed that essentially no dinitrogen gas was evolved. Then the solution was dried up, and the amounts of ammonia and hydrazine included in the residue were determined as described previously.52

Crystallography. Single crystals of 4, 9a·3CH₂Cl₂, 10a·CH₂-Cl₂·Et₂O, **10d**·2MeCN, **11a**·Et₂O, **14b**, and **17**·1.5Et₂O suitable for X-ray analyses were sealed in Pyrex glass capillaries under an argon atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC-7R four-circle automated diffractometer with Mo K α (λ = 0.71069 Å) radiation and a graphite monochromator at 21 °C using the ω -2 θ scan technique. Empirical absorption correction based on ψ scans and Lorentz-polarization correction were applied. For compounds 9a·3CH₂Cl₂, 10a·CH₂Cl₂·Et₂O, 10d·2MeCN, 11a·Et₂O, and 14b, decay (17.57, 3.35, 17.33, 6.14, and 9.62%, respectively) was observed during the data collection, and a correction for decay was applied in each case. Details of the X-ray diffraction study are summarized in Tables 5 and 6. The structure solution and refinements were performed by using the teXsan program package.53 The positions of the nonhydrogen atoms were determined by direct methods (SIR 9254 for 9a·3CH₂Cl₂) or by Patterson methods (DIRDIF PATTY⁵⁵ for the others) and expanded using Fourier techniques. The CH₂Cl₂ molecules in 9a·3CH₂Cl₂, the CH₂Cl₂ and ether molecules in $10a \cdot CH_2Cl_2 \cdot Et_2O$, and the MeCN molecules in $10d \cdot$ 2MeCN showed signs of disorder and could not be refined satisfactorily. The non-hydrogen atoms of these solvent molecules were found from the difference Fourier maps and included in the refinement with fixed isotropic parameters. One of the ether molecules in $17.1.5Et_2O$ was found to be located on the center of symmetry. The carbon and oxygen atoms of this ether molecule were included in the refinement as fixed atoms, where the disordered methylene carbon atoms were considered to have the occupancies of 50%. Isotropic thermal parameters were used for the carbon and oxygen atoms of the ether molecule in 11a-Et₂O. All other nonhydrogen atoms were refined by full-matrix least-squares techniques with anisotropic thermal parameters, and the hydrogen atoms except for those of the solvent molecules in

⁽⁵²⁾ Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. J. Am. Chem. Soc. 1980, 102, 7461–7475.

⁽⁵³⁾ teXsan: Crystal Structure Analysis Package; Molecular Struc-

⁽⁵⁴⁾ Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.;
Giacovazzo, C.; Guagliardi, A.; Polidori, G. J. Appl. Crystallogr. 1994, 27. 435.

⁽⁵⁵⁾ PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

Table 5. Crystallographic Data for 4, 9a·3CH₂Cl₂, 10a·CH₂Cl₂·Et₂O, and 10d·2MeCN

	4	$9a \cdot 3CH_2Cl_2$	$10a \cdot CH_2Cl_2 \cdot Et_2O$	10d·2MeCN
formula	C ₃₇ H ₄₉ Cl ₃ N ₂ P ₄ TiW	C ₆₁ H ₅₉ Cl ₈ N ₃ P ₄ STiW	C42H61Cl6N2NbOP4W	$C_{46}H_{65}Cl_4N_4P_4TaW$
fw	983.81	1505.49	1223.33	1304.55
space group	Сс	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	15.563(2)	12.290(2)	10.753(5)	11.917(2)
b. Å	16.800(1)	13.700(3)	22.320(6)	12.769(3)
c. Å	15.932(2)	20.359(4)	21.467(6)	18.984(3)
α , deg		98.86(2)		87.14(1)
β , deg	92.36(1)	106.33(1)	99.39(4)	89.32(1)
γ , deg		93.63(2)		66.33(1)
V. Å ³	4162.1(8)	3229(1)	5083(3)	2642.4(8)
Ź	4	2	4	2
$d_{\rm calc}$, g cm ⁻³	1.570	1.548	1.598	1.640
μ_{calc} , cm ⁻¹	33.31	24.08	29.63	46.01
R^a	0.027	0.068	0.050	0.040
R_{w}^{b}	0.032	0.070	0.061	0.041
••				

^a $R = \sum ||F_0| - |F_c|| / \sum |F_0|$. ^b $R_w = [\sum w(F_0| - |F_c|)^2 / \sum wF_0^2]^{1/2}, w = 1/\sigma^2(F_0)$.

	11a ·Et ₂ O	14b	17 •1.5Et ₂ O
formula	C ₆₁ H ₆₃ Cl ₄ N ₂ NbOP ₄ W	C ₆₄ H ₆₁ N ₃ P ₄ SWZr	C ₆₃ H ₆₈ ClN ₂ O _{1.5} P ₄ S ₅ TiW
fw	1382.65	1303.23	1428.64
space group	$P2_1/n$	$P2_1/a$	$P2_1/n$
a, Å	19.539(4)	17.815(4)	13.531(2)
b, Å	14.883(2)	17.584(4)	18.472(4)
c. Å	20.185(4)	18.606(4)	25.416(2)
$\hat{\beta}$. deg	90.31(2)	95.57(2)	98.477(8)
V. Å ³	5869(1)	5800(2)	6283(1)
Ź	4	4	4
$d_{\rm calc}$, g cm ⁻³	1.564	1.492	1.510
$\mu_{\rm calc}, {\rm cm}^{-1}$	24.89	23.52	23.12
R^a	0.044	0.037	0.049
R_w^b	0.047	0.036	0.038

 ${}^{a} R = \sum ||F_{\rm o}| - |F_{\rm c}|| / \sum |F_{\rm o}|. \ {}^{b} R_{\rm w} = [\sum w(|F_{\rm o}| - |F_{\rm c}|)^2 / \sum wF_{\rm o}^2]^{1/2}, \ w = 1/\sigma^2(F_{\rm o}).$

10a·CH₂Cl₂·Et₂O and the disordered ether molecule in **17**· 1.5Et₂O were included in the refinements with fixed isotropic parameters.

Acknowledgment. This work was supported by a Grant-in-Aid for Specially Promoted Research (09102004) from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Tables of atom coordinates, anisotropic thermal parameters, and bond distances and angles for **4**, $9a \cdot 3CH_2Cl_2$, $10a \cdot CH_2Cl_2 \cdot Et_2O$, $10d \cdot 2MeCN$, $11a \cdot Et_2O$, 14b, and $17 \cdot 1.5Et_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000684J