

Preparation and Protonation of Tungsten- and Molybdenum-Dinitrogen Complexes Bearing Bis(dialkylphosphinobenzene)chromiums as Auxiliary Ligands

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Tungsten- and molybdenum-dinitrogen complexes bearing bis(dialkylphosphinobenzene)chromiums have been prepared and characterized by X-ray crystallography. Reactions of these dinitrogen complexes with an excess amount of sulfuric acid in methanol at room temperature give ammonia in good yields. Stoichiometric reactions of some dinitrogen complexes with 2 equiv of trifluoromethanesulfonic acid afford the corresponding hydrazido complexes, which may be considered to be one of the reactive intermediates.

Introduction

Metallocene- and bis(arene)metal-based ligands are widely used in organometallic chemistry and material sciences due to their unique electronic and structural properties.¹ For example, 1,1'-bis(diphenylphosphino)ferrocene (dppf) is well known to work as a common diphosphine ligand for a variety of transition metal complexes in organic synthesis because of a relatively large bite angle, capacity of dative bond formation with electron-deficient metal centers, and chemical robustness of the ferrocene skeleton.² Recently, we have reported the preparation of tungsten- and molybdenum-dinitrogen complexes bearing ferrocenyl- or ruthenocenyl-diphosphines as auxiliary ligands $[M(N_2)_2(L)_2]$ (M = W, Mo; L = ferrocenylor ruthenocenyl-diphosphines; depf = 1, 1'-bis(diethylphosphino)ferrocene, depr=1,1'-bis(diethylphosphino)ruthenocene, dmpr = 1,1'-bis(dimethylphosphino)ruthenocene).³ Reactions of these dinitrogen complexes with an excess amount of sulfuric acid afforded ammonia in good yields. Although the detailed reaction mechanism is not yet clear, we believe that the metallocene moiety in these complexes plays an important role in the facile conversion of the coordinated dinitrogen into ammonia. This result is in sharp contrast to the

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Results and Discussion

Bis(dialkylphosphinobenzene)chromiums were prepared by a similar procedure to that for bis(diphenylphosphinobenzene)chromium.^{5a} Dilithiation of bis(benzene)chromium with *n*-butyllithium-TMEDA in cyclohexane at reflux temperature afforded a powder of bis(dilithiobenzene)chromium, which was treated with Et₂PCl to give *b*is(diethylphosphinobenzene)chromium (bepc) in 41% yield (Scheme 1). Similarly,

Scheme 1



*b*is(dimethylphosphinobenzene)*c*hromium^{5c,5g} (bmpc) was prepared in 58% yield using Me₂PCl in place of Et₂PCl.

The reaction of *trans*- $[W(N_2)_2(PPh_2Me)_4]$ with 2 equiv of bmpc at 60 °C for 48 h gave *trans*- $[W(N_2)_2(bmpc)_2]$ (1) as a major product (Scheme 2). Recrystallization from THF-



hexane afforded orange-red prisms of 1 in 29% yield. The IR spectra of 1 exhibited one absorption band of $v_{\rm NN}$ at 1885 cm⁻¹. indicating trans arrangement of two dinitrogen ligands. The IR spectral data of 1 also displayed the strong electron-donating property of bmpc. In the ${}^{31}P{}^{1}H$ NMR spectrum, the four phosphorus atoms were observed equivalently at -19.8 ppm with a tungsten satellite (${}^{1}J_{PW} = 316$ Hz). The molecular structure of 1 was unequivocally determined by X-ray crystallography. An ORTEP drawing and selected bond distances and angles of 1 are shown in Figure 1. Two dinitrogen ligands are oriented trans to each other. The bite angles of the bmpc ligand in 1 are 93.60(4)° and 93.47(4)°. The W-Cr distances of 4.7679(7) and 4.7472(7) Å indicate no bonding interaction between chromium and tungsten atoms. A cyclic voltammogram of 1 showed two reversible one-electron oxidation waves corresponding to two Cr(0/I) redox couples at -1.19 and -1.12 V, respectively. This result indicates the presence of a weak electronic interaction between two chromium centers in 1. An oxidation wave of the



Figure 1. ORTEP view of 1 with 50% thermal ellipsoids. Selected interatomic distances (Å) and bond angles (deg): W-P(1) 2.4607(11), W-P(2) 2.4727(12), W-P(3) 2.4759(11), W-P(4) 2.4754(13), W-N(1) 1.990(4), W-N(3) 2.000(4), N(1)-N(2) 1.138(6), N(3)-N(4) 1.140(6), $W\cdots Cr(1)$ 4.7679(7), $W\cdots Cr(2)$ 4.7473(7), P(1)-W-P(2) 93.60(4), P(1)-W-P(3) 175.42(4), P(1)-W-P(4) 87.36(4), P(2)-W-P(3) 85.78(4), P(2)-W-P(4) 177.23(4), P(3)-W-P(4) 93.47(4), N(1)-W-N(3) 178.83(15), W-N(1)-N(2) 178.7(3), W-N(3)-N(4) 178.8(3).

W(0/I) redox couple in 1 was observed at -0.49 V. When we compared this value with those of the W(0/I) redox couple in other dinitrogen complexes as shown in Table 1, complex 1 was revealed to show significant anodic shift of the potential.

The reaction of *trans*-[W(N₂)₂(PPh₂Me)₄] with 1 equiv of bmpc at 60 °C for a short reaction time such as 2 h gave *trans*-[W(N₂)₂(bmpc)(PPh₂Me)₂] (2) in 86% isolated yield (Scheme 2). The IR spectrum of 2 showed one strong ν_{NN} absorption band at 1892 cm⁻¹, indicating a *trans* conformation of two dinitrogen ligands. In the ³¹P{¹H} NMR spectrum, two doublet signals along with the tungsten-183 satellites were observed at -19.1 and -6.0 ppm, which were assigned to phsophorous atoms of bmpc and PPh₂Me ligands, respectively. A cyclic voltammogram of 2 showed two reversible one-electron oxidation waves at -1.16 and -0.53 V corresponding to Cr(0/I) and W(0/I) redox couples, respectively. Separately, we confirmed that complex 2 was easily converted to 1 in 47% yield when a solution of 2 with bmpc was heated at 60 °C for 48 h.

On the other hand, the reaction of *trans*- $[W(N_2)_2$ - $(PPh_2Me_4)_4$ with 2 equiv of bepc proceeded sluggishly. A mixture of trans- $[W(N_2)_2(bepc)_2]$ (3) and trans- $[W(N_2)_2 (bepc)(PPh_2Me)_2$ (4) was formed when the reaction was carried out at 60 °C for 48 h (Scheme 3). Fortunately, both complexes are isolated in 41% and 17% yields, respectively. The IR, NMR, and analytical data of 3 and 4 supported the molecular structures of 3 and 4 (see Experimental Section for details). The molecular structure of 4 was unequivocally determined by X-ray crystallography. An ORTEP drawing and selected bond distances and angles of 4 are shown in Figure 2. The bite angle of the bepc ligand in **4** is $96.43(4)^{\circ}$. The W–Cr distance of 4.7622(7) Å in 4 indicated no bonding interaction between chromium and tungsten atoms. A cyclic voltammogram of 4 showed two reversible one-electron oxidation waves at -1.17 and -0.54 V corresponding to



Table 1. IR and Electrochemical	Data of Tungsten-	and Molybdenum-	-Dinitrogen Complexes
	0	r v	

		E	$E_{1/2}/\mathrm{V}^{\ c}$	
complex ^{<i>a</i>}	$\nu_{ m NN}/{ m cm}^{-1}{}^{b}$	Cr(0/I)	W(0/I) or Mo(0/I)	ref
$trans-W(N_2)_2(bmpc)_2(1)$	1885	-1.19, -1.12	-0.49	this work
$trans-W(N_2)_2(bmpc)(PPh_2Me)_2$ (2)	1892	-1.16	-0.53	this work
$trans-W(N_2)_2(bepc)_2$ (3)	1880	e	_e	this work
$trans-W(N_2)_2(bepc)(PPh_2Me)_2$ (4)	1895	-1.17	-0.54	this work
$trans-W(N_2)_2(depf)_2$	1883		-0.95	3a
$trans-W(N_2)_2(depr)_2$	1879		-0.97	3b
$trans-W(N_2)_2(depe)_2$	1895		-0.96	8a, 8b
$trans-W(N_2)_2(dppe)_2$	1943		-0.68	8a, 8b
$trans-W(N_2)_2(dchpe)_2$	1880^{d}		-1.02	8b
$trans-W(N_2)_2(depr)(PPh_2Me)_2$	1895		-0.83	3b
$trans-W(N_2)_2(dmpr)(PPh_2Me)_2$	1899		-0.80	3b
$trans-W(N_2)_2(dppe)(PPh_2Me)_2$	1920^{d}			8c
$trans-W(N_2)_2(PPhMe_2)_4$	1898		-0.83	8d
$trans-W(N_2)_2(PPh_2Me)_4$	1899		-0.71	3a, 8c
$trans-Mo(N_2)_2(bmpc)_2$ (5)	1923	-1.18, -1.10	-0.49	this work
$trans-Mo(N_2)_2(bmpc)(PPh_2Me)_2$ (6)	1918	-1.17	-0.56	this work
$trans-Mo(N_2)_2(bepc)_2(7)$	1906	e	_ ^e	this work
$trans-Mo(N_2)_2(bepc)(PPh_2Me)_2$ (8)	1919	-1.18	-0.57	this work
$trans-Mo(N_2)_2(depf)_2$	1907		-0.97	3a
$trans-Mo(N_2)_2(depe)_2$	1928		-0.97	8b, 8e
$trans-Mo(N_2)_2(dppe)_2$	1975		-0.70	8b
$trans-Mo(N_2)_2(dmpr)(PPh_2Me)_2$	1923		-0.80	3b
$trans-Mo(N_2)_2(dppe)(PPh_2Me)_2$	1943 ^d			8c
$trans-Mo(N_2)_2(PPh_2Me)_4$	1922		-0.71	8f, 8g
bmpc		-1.14		this work
bepc		-1.12		this work

 a dppe = 1,1'-bis(diphenylphosphino)ethane. depe = 1,1'-bis(diethylphosphino)ethane. dchpe = 1,1'-bis(dicyclohexylphosphino)ethane. b Asymmetric NN stretching bands in KBr pellet. c Relative to ferrocene—ferrocenium couple in THF. d Nujol mull. e A cyclic voltammogram could not be carried out due to the low solubility in THF.

Cr(0/I) and W(0/I) redox couples, respectively. The properties of **4** are almost the same as those of **2**. Unfortunately, the cyclic voltammogram of **3** could not be carried out due to the low solubility of **3** in THF.

Analogous molybdenum-dinitrogen complexes were obtained by a similar procedure. The reaction of trans-[Mo(N₂)₂-(PPh₂Me₄)₄] with 2 equiv of bmpc at room temperature for 48 h gave trans-[Mo(N₂)₂(bmpc)₂] (5) in 56% isolated yield (Scheme 4). The IR, NMR, and analytical data supported the molecular structure of 5 (see Experimental Section for details). The molecular structure of 5 was unequivocally determined by X-ray crystallography. An ORTEP drawing and selected bond distances and angles of 5 are shown in Figure 3. The electrochemical behavior of 5 was also quite similar to that of 1. In fact, a cyclic voltammogram of 5 showed three reversible oneelectron oxidation waves at -1.18, -1.10, and -0.49 V corresponding to two Cr(0/I) redox couples and one Mo(0/I)redox couple, respectively (Table 1). When the reaction of *trans*- $[Mo(N_2)_2(PPh_2Me_4)_4]$ with 1 equiv of bmpc was carried out at room temperature for 6 h, trans-[Mo(N₂)₂(bmpc)- $(PPh_2Me_4)_2$ (6) was isolated in 37% yield (Scheme 4). The spectroscopic and analytical data were consistent with the molecular structure of 6 (see Experimental Section for details).

Similarly, *trans*-[Mo(N₂)₂(bepc)₂] (7) and *trans*-[Mo(N₂)₂-(bepc)(PPh₂Me)₂] (8) were obtained in 25% and 35% yields, respectively (Scheme 5). The IR, NMR, and analytical data supported the molecular structures of 7 and 8 (see Experimental Section for details). The molecular structure of 8 was unequivocally determined by X-ray crystallography. An ORTEP drawing and selected bond distances and angles of 8 are shown in Figure 4.

Next, we investigated the reactivity of these tungsten- and molybdenum-dinitrogen complexes toward protonolysis. Protonation of dinitrogen complexes with an excess amount

Scheme 4



of sulfuric acid in methanol at room temperature for 24 h produced ammonia in good to high yields. Typical results are shown in Table 2. The yield of ammonia was based on the tungsten or molybdenum atom. In any case, no hydrazine was detected at all as a product. Similar to the previous results, the protonation of dinitrogen complexes⁹ bearing two monodentate phosphines as auxiliary ligands such as **2**,

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Figure 2. ORTEP view of 4 with 50% thermal ellipsoids. Selected interatomic distances (Å) and bond angles (deg): W-P(1) 2.5066(13), W-P(2) 2.5171(13), W-P(3) 2.4638(13), W-P(4) 2.4728(13), W-N(1) 2.005(4), W-N(3) 2.009(3), N(1)-N(2) 1.123(5), N(3)-N(4) 1.142(5), $W \cdots Cr$ 4.7622(7), P(1)-W-P(2) 96.43(4), P(1)-W-P(3) 166.98(4), P(1)-W-P(4) 88.92(4), P(2)-W-P(3) 91.44(4), P(2)-W-P(4) 168.34(4), P(3)-W-P(4) 85.30(4), N(1)-W-N(3) 177.84(16), W-N(1)-N(2) 179.6(4), W-N(3)-N(4) 179.4(3).

4, 6, and 8 gave ammonia in good to high yields (Table 2, runs 2, 4, 6, and 8). Interestingly, the protonation of dinitrogen complexes bearing two bis(dialkylphosphinobenzene)chromiums (bmpc and bepc) as auxiliary ligands such as 1, 3, 5, and 7 gave also ammonia in similar yields (Table 2, runs 1, 3, 5, and 7). This result is in sharp contrast to those from molybdenum- and tungsten-dinitrogen complexes bearing chelating diphosphines as auxiliary ligands [M(N₂)₂L₂] (M = Mo, W; L = dppe, depe), where ammonia was not produced by protonation and only the formation of the corresponding hydrazido complexes was observed.⁴ On the other hand, the result described in this paper was similar to those of protonation of tungsten- and molybdenum-dinitrogen complexes bearing ferrocenyl- and ruthenocenyl-diphosphines such as *trans*- $[M(N_2)_2L_2]$ (M = W, Mo; L = depf, depr) with sulfuric acid, where ammonia was obtained in good to high yields.³ At present, we have not yet clarified the exact role of these chelating metallocenes and bis-(dialkylphosphinobenzene)chromiums in the conversion of the coordinated dinitrogen into ammonia.



Figure 3. ORTEP view of 5 with 50% thermal ellipsoids. Selected interatomic distances (Å) and bond angles (deg): Mo-P-(1) 2.4782(6), Mo-P(2) 2.4831(6), Mo-N(1) 2.0401(17), N(1)-N(2) 1.101(2), Mo···Cr 4.7693(2), P(1)-Mo-P(2) 93.892(19), P(1)-Mo-P(1)* 85.80(2), P(1)-Mo-P(2)* 177.895(16), P(2)-Mo-P(2)* 86.49(2), Mo-N(1)-N(2) 179.71(18). Asterisks denote atoms related by the symmetry operation -x, +y, 1/2-z.



Figure 4. ORTEP view of 8 with 50% thermal ellipsoids. Selected interatomic distances (Å) and bond angles (deg): Mo-P(1) 2.5273(16), Mo-P(2) 2.5397(14), Mo-P(3) 2.4836(17), Mo-P(4) 2.4911(14), Mo-N(1) 2.010(4), Mo-N(3) 2.012(4), N(1)-N(2) 1.135(7), N(3)-N(4) 1.125(6), Mo\cdots Cr 4.7784(9), P(1)-Mo-P(2) 96.22(5), P(1)-Mo-P(3) 167.50(5), P(1)-Mo-P(4) 89.06(5), P(2)-Mo-P(3) 91.31(5), P(2)-Mo-P(4) 168.63(4), P(3)-Mo-P(4) 85.35(5), N(1)-Mo-N(3) 177.76(16), Mo-N(1)-N(2) 178.1(4), Mo-N(3)-N(4) 179.3(4).





Table	2.	Protonation	of T	ſungsten	· and	Moly	bdenu	m-Dinit	rogen
				Complex	xes. ^a				

$[M(N_2)_2L_4]$	excess H_2SO_4	ки I - Н	
	MeOH rt, 24 h	-	NH4
	rt, 24 h		

run	$[M(N_2)_2L_4]$	yield of NH_4^+ (%)
1	trans- $[W(N_2)_2(bmpc)_2](1)$	51
2	$trans-[W(N_2)_2(bmpc)(PPh_2Me)_2]$ (2)	124
3	$trans-[W(N_2)_2(bepc)_2]$ (3)	148
4	$trans-[W(N_2)_2(bepc)(PPh_2Me)_2]$ (4)	152
5	$trans-[Mo(N_2)_2(bmpc)_2]$ (5)	64
6	$trans-[Mo(N_2)_2(bmpc)(PPh_2Me)_2](6)$	33
7	$trans-[Mo(N_2)_2(bepc)_2]$ (7)	16
8	trans- $[Mo(N_2)_2(bepc)(PPh_2Me)_2](8)$	41

^{*a*} All reactions were carried out by treatment of dinitrogen complex (0.035 mmol) with an excess amount of sulfuric acid (0.05 mL) in methanol (5 mL) at room temperature for 24 h. ^{*b*} The yield of $\rm NH_4^+$ was determined by the indophenol method (see Experimental Section for details). The yield of $\rm NH_4^+$ was based on the W or Mo atom.

Hoping to obtain any information on the reaction pathway for ammonia, we tried to isolate some reactive intermediates. The reaction of 1 with 2 equiv of trifluoromethanesulfonic acid at room temperature for 10 min gave the corresponding tungsten hydrazido complex [W(NNH₂)-(OTf)(bmpc)₂]OTf (9) in 41% isolated yield (Scheme 6). Unfortunately, we could not obtain any detailed information from 9 by NMR because of its low solubility, but its molecular structure was unequivocally determined by X-ray crystallography. An ORTEP drawing and selected bond distances and angles of 9 are shown in Figure 5. The W-N and N–N bond lengths of 1.737(4) and 1.345(8) Å in 9 were similar to those of the previously reported tungsten hydrazido complexes.^{4,9} The W-Cr distances of 4.7445(12) and 4.7799(13) Å indicated no bonding interaction between chromium and tungsten atoms. A hydrogen bond was observed between one of the oxygen atoms of the triflate anion and one of the terminal hydrogen atoms of the hydrazido ligand. Similarly, the corresponding molybdenum hydrazido complex [Mo(NNH₂)(OTf)(bmpc)₂]OTf (10) was obtained in 44% yield from the reaction of 5 with 2 equiv of trifluoromethanesulfonic acid under the same reaction conditions (Scheme 6). Separately, we carried out the protonolysis of the isolated hydrazido complexes (9 and 10) and found the formation of ammonia in 68% and 55% yields, respectively. These results indicate that the ammonia formation might proceed via hydrazido complexes as key intermediates. However, we could not detect any structurally defined complexes after the protonation of dinitrogen and hydrazido complexes with an excess amount of sulfuric acid.

In summary, we have prepared and characterized tungsten- and molybdenum-dinitrogen complexes bearing bis-(dialkylphosphinobenzene)chromiums as auxiliary ligands.



Figure 5. ORTEP view of 9 with 50% thermal ellipsoids. Selected interatomic distances (Å) and bond angles (deg): W-P(1) 2.5281(15), W-P(2) 2.5598(19), W-P(3) 2.5350(15), W-P(4) 2.5665(18), W-N(1) 1.736(4), W-O(1) 2.209(3), N-(1)-N(2) 1.346(8), N(2)-H(1) 0.98(10), $H(1)\cdots O(4) 2.06(11)$, $W\cdots Cr(1) 4.7442(11)$, $W\cdots Cr(2) 4.7800(12)$, $Cr(1)\cdots Cr(2)$ 9.5236(16).

Protonation of these complexes with an excess amount of sulfuric acid in methanol produced ammonia in good to high yields. This result is in sharp contrast to the previous finding that protonolysis of tungsten- and molybdenumdinitrogen complexes bearing conventional diphosphines such as 1,2-bis(diphenylphosohino)ethane does not produce ammonia. We believe that the sandwich structure of bis(benzene)chromium plays an important role for the facile conversion of the coordinated dinitrogen into ammonia, although its exact role has not yet been clarified. Stoichiometric reactions of the dinitrogen complexes with 2 equiv of trifluoromethanesulfonic acid yielded the corresponding hydrazido complexes, which may be considered to be one of the reactive intermediates.

Experimental Section

General Method. ¹H NMR (270 MHz), ¹³C{¹H} (67.8 MHz), and ³¹P{¹H} NMR (109 MHz) spectra were measured on a JEOL Excalibur 270 spectrometer, and ³¹P chemical shifts were quoted relative to an external standard of 85% H₃PO₄. IR spectra were recorded on a JASCO FT/IR 4100 Fourier transform infrared spectrophotometer. Elemental analyses were performed on an Exeter Analytical CE-440 elemental analyzer. Cyclic voltammograms were recorded on an ALS/Chi model 610C electrochemical analyzer with platinum working electrode in THF containing 0.1 M "Bu₄NBF₄ as a supporting electrolyte. The potentials were 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. Complexes trans-[W(N₂)₂(PPh₂Me)₄]·1.5THF,^{8c} trans-[Mo(N₂)₂(PPh₂Me)₄],¹⁰ and bmpc^{5g} were prepared by the literature methods. Chlorodialkylphosphines ($R_2PCl; R =$ Me, Et) were prepared by the reaction of Et₂NPCl₂ with

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alkylmagnesium bromide in ether followed by treatment with 2 equiv of HCl in diethyl ether.¹¹ Other reagents were purchased and used as received.

Preparation of bepc. To a mixture of bis(benzene)chromium (1.00 g, 4.80 mmol) and TMEDA (2.0 mL, 13.3 mmol) in cyclohexane (30 mL) was added "BuLi (1.58 M in hexane, 8.0 mL, 12.6 mmol). The reaction mixture was heated at reflux for 2 h. After cooling, the supernatant was removed by decantation. The residue was washed with n-hexane (20 mL x 2) and dried in vacuo. The solid was suspended in cold diethyl ether (30 mL, -30 °C), and Et₂PCl (1.41 g, 11.3 mmol) was slowly added to the suspension. The mixture was stirred at room temperature overnight. Volatiles were removed under vacuum. The orange-brown residue was extracted with toluene (20 mL). The extract was passed through an alumina pad. The eluent was concentrated to dryness, giving a crude product. Recrystallization from *n*-hexane at -35 °C afforded a dark yellow microcrystalline solid of bepc in 41% yield (763 mg). 1 H NMR (C₆D₆): δ 4.53 (br t, $J_{HH} = 5$ Hz, 4H), 4.42–4.31 (m, 6H), 1.59 (dq, $J_{HP} = 3$ Hz, $J_{HH} = 7$ Hz, 8H), 1.05 (dt, $J_{HP} = 15$ Hz, $J_{HH} = 7$ Hz, 12H). ³¹P{¹H} NMR (C₆D₆): δ –12.7 (s). Anal. Calcd for C₂₀H₃₀CrP₂: C, 62.49; H, 7.87. Found: C, 62.29; H, 7.73.

Preparation of *trans*-[W(N₂)₂(bmpc)₂] (1). A toluene (15 mL) solution of *trans*-[W(N₂)₂(PPh₂Me)₄]·1.5THF (143 mg, 0.137 mmol) and bmpc (100 mg, 0.305 mmol) was heated at 60 °C for 48 h. The solution was concentrated under reduced pressure, giving a dark orange oil. After washing with *n*-hexane, the solid residue was crystallized from THF–*n*-hexane at -35 °C, affording orange-red crystals of **1** (36 mg, 29%). ¹H NMR (C₆D₆): δ 4.69 (br d, J_{HH} = 5 Hz, 8H), 4.35 (br t, J_{HH} = 5 Hz, 4H), 4.27 (br t, J_{HH} = 5 Hz, 8H), 1.85 (br s, 24H). ³¹P{¹H} NMR (C₆D₆): δ -19.8 (s with ¹⁸³W satellite, J_{P-W} = 316 Hz). IR (KBr): ν_{NN} 1968vw, 1885vs cm⁻¹. Anal. Calcd for C₃₂H₄₄N₄Cr₂P₄W: C, 42.87; H, 4.95; N, 6.25. Found: C, 43.18; H, 5.06; N, 6.41.

Preparation of *trans*-[W(N₂)₂(bmpc)(PPh₂Me)₂] (2). A toluene (15 mL) solution of *trans*-[W(N₂)₂(PPh₂Me)₄]·1.5THF (300 mg, 0.261 mmol) and bmpc (100 mg, 0.305 mmol) was heated at 60 °C for 2 h. The solution was concentrated under reduced pressure, giving a dark orange oil. To the residue was added diethyl ether (5 mL), and the mixture was cooled at -35 °C overnight, precipitating an orange-red crystalline solid of **2**·Et₂O (234 mg, 86%). ¹H NMR (C₆D₆): δ 7.61 (t, *J*_{HH} = 8 Hz, 8H), 7.13-6.96 (m, 12H), 4.59 (t, *J*_{HH} = 5 Hz, 4H), 4.26 (d, *J*_{HH} = 5 Hz, 2H), 4.18 (t, *J*_{HH} = 5 Hz, 4H), 2.03 (d, *J*_{HP} = 5 Hz, 6H), 1.36 (d, *J*_{HP} = 6 Hz, 12H). ³¹P{¹H} NMR (C₆D₆): δ -6.0 (d with ¹⁸³W satellite, *J*_{PP} = 108 Hz, *J*_{PW} = 311 Hz), -19.1 (d with ¹⁸³W satellite, *J*_{PP} = 108 Hz, *J*_{PW} = 322 Hz). IR (KBr): 1964w, 1892vs cm⁻¹. Anal. Calcd for C₄₆H₅₈N₄CrOP₄W (**2**·Et₂O): C, 52.80; H, 5.59; N, 5.13. Found: C, 52.99; H, 5.61; N, 5.37.

Conversion of 2 to 1. A toluene (15 mL) solution of $2 \cdot \text{Et}_2\text{O}$ (506 mg, 0.485 mmol) and bmpc (199 mg, 0.606 mmol) was heated at 60 °C for 48 h. The solution was concentrated under reduced pressure, giving a dark orange oil. After washing with *n*-hexane, the solid residue was crystallized from THF–*n*-hexane at -35 °C, affording orange-red crystals of 1 (205 mg, 47%).

Preparation of *trans*-[W(N₂)₂(bepc)₂] (3) and *trans*-[W(N₂)₂-(bepc)₂(PPh₂Me)₂] (4). A THF (15 mL) solution of *trans*-[W(N₂)₂(PPh₂Me)₄]·1.5THF (345 mg, 0.300 mmol) and bepc (250 mg, 0.650 mmol) was heated at 60 °C for 48 h. As the reaction proceeded, orange-red precipitates were formed. The precipitates were dried *in vacuo* after decantation and washing with a small amount of THF to give an orange-red powder of **3** (125 mg, 41%). Crystals of **4**·0.5THF were obtained from the supernatant of the reaction mixture by recrystallizing from THF-*n*-hexane (55 mg, 17%).

Data for 3. ¹H NMR (C_6D_6): δ 4.72 (d, $J_{HH} = 5$ Hz, 8H), 4.43 (t, $J_{HH} = 5$ Hz, 4H), 4.30 (t, $J_{HH} = 5$ Hz, 8H), 2.70–2.54

(m, 8H), 2.52–2.33 (m, 8H), 1.33–1.18 (m, 24H). ${}^{31}P{}^{1}H{}$ NMR (C₆D₆): δ –6.6 (s with ${}^{183}W$ satellite, J_{PW} = 310 Hz). IR (KBr): ν_{NN} 1975vw, 1880vs cm⁻¹. Anal. Calcd for C₄₀H₆₀N₄Cr₂P₄W: C, 47.63; H, 6.00; N, 5.55. Found: C, 47.40; H, 5.80; N, 5.43.

Data for 4. ¹H NMR (C₆D₆): δ 7.67 (br t, $J_{HH} = 7$ Hz, 8H), 7.13–6.98 (m, 12H), 4.68 (t, $J_{HH} = 5$ Hz, 4H), 4.36 (dt, $J_{HH} =$ 2 and 5 Hz, 2H), 4.22 (t, $J_{HH} = 5$ Hz, 4H), 2.23–2.13 (m, 4H), 2.10 (d, $J_{HP} = 5$ Hz, 6H), 1.65 (br s, 4H), 1.02–0.86 (m, 12H). ³¹P{¹H} NMR (C₆D₆): δ –3.5 (dt with ¹⁸³W satellite, $J_{PP} = 111$ and 3 Hz, $J_{PW} = 313$ Hz), -19.1 (br d, $J_{PP} = 111$ Hz). IR (KBr): ν_{NN} 1966w, 1895vs cm⁻¹. Anal. Calcd for C₄₈H₆₀CrN₄O_{0.5}P₄W (**4**·0.5THF): C, 54.35; H, 5.70; N, 5.28. Found: C, 54.57; H, 5.90; N, 4.95.

Preparation of *trans-*[Mo(N₂)₂(bmpc)₂] (5). A toluene (20 mL) solution of *trans-*[Mo(N₂)₂(PPh₂Me)₄] (466 mg, 0.489 mmol) and bmpc (327 mg, 0.996 mmol) was stirred at room temperature for 48 h. After concentration of the reaction mixture, the residue was washed with diethyl ether (15 mL) and extracted with toluene (15 mL). The toluene extract was dried under vacuum, and the residue was dissolved in 5 mL of THF and layered with 10 mL of *n*-hexane. Standing at -35 °C overnight afforded an orange-yellow crystalline solid of 5 (220 mg, 56%). ¹H NMR (C₆D₆): δ 4.69 (br d, $J_{HH} = 5$ Hz, 8H), 4.39–4.25 (m, 12H), 1.75 (br s, 24H). ³¹P{¹H} NMR (C₆D₆): δ 8.3 (s). IR (KBr): ν_{NN} 1996w, 1923vs cm⁻¹. Anal. Calcd for C₃₂H₄₄-N₄Cr₂MoP₄: C, 47.54; H, 5.49; N, 6.93. Found: C, 47.54; H, 5.59; N, 6.70.

Preparation of *trans*-[Mo(N₂)₂(bmpc)(PPh₂Me)₂] (6). A toluene (20 mL) solution of *trans*-[Mo(N₂)₂(PPh₂Me)₄] (191 mg, 0.200 mmol) and bmpc (69 mg, 0.210 mmol) was stirred at room temperature for 6 h. After concentration of the reaction mixture, the residue was treated with diethyl ether (10 mL), affording an orange-red crystalline solid. The solid was washed with *n*-hexane (10 mL) and dried under vacuum to give **6**·0.5Et₂O (68 mg, 37%). ¹H NMR (C₆D₆): δ 7.62 (m, 8H), 7.10–6.98 (m, 12H), 4.40–4.35 (m, 4H), 4.24–4.18 (m, 6H), 1.89 (br d, *J*_{HP} = 2 Hz, 6H), 1.33 (br d, *J*_{HP} = 5 Hz, 12H). ³¹P{¹H} NMR (C₆D₆): δ 21.9 (d, *J*_{PP} = 93 Hz), 9.9 (d, *J*_{PP} = 93 Hz). IR (KBr): ν_{NN} 1994w, 1918vs cm⁻¹. Anal. Calcd for C₄₄H₅₃N₄CrMoO_{0.5}P₄: C, 57.58; H, 5.82; N, 6.10. Found: C, 57.36; H, 5.85; N, 5.84.

Preparation of *trans*-[Mo(N₂)₂(bepc)₂] (7) and *trans*-[Mo(N₂)₂-(bepc)₂(PPh₂Me)₂] (8). A THF (10 mL) solution of *trans*-[Mo(N₂)₂(PPh₂Me)₄] (192 mg, 0.202 mmol) and bepc (158 mg, 0.411 mmol) was stirred at room temperature for 48 h. As the reaction proceeded, orange-brown precipitates were formed. The precipitates were dried *in vacuo* after decantation and washing with a small amount of THF to give pure 7 (47 mg, 25%). On the other hand, an orange crystalline solid of 8.0.5THF was obtained from the supernatant after recrystallizing from THF–*n*-hexane (66 mg, 34%).

Data for 7. ¹H NMR (C₆D₆): δ 4.73 (d, $J_{HH} = 5$ Hz, 8H), 4.43 (t, $J_{HH} = 5$ Hz, 4H), 4.32 (t, $J_{HH} = 5$ Hz, 8H), 2.57–2.2.43 (m, 8H), 2.38–2.23 (m, 8H), 1.32–1.20 (m, 24H). ³¹P{¹H} NMR (C₆D₆): δ 23.5 (s). IR (KBr): ν_{NN} 1989w, 1906vs cm⁻¹. Anal. Calcd for C₄₀H₆₀N₄Cr₂MoP₄: C, 52.18; H, 6.57; N, 6.08. Found: 51.47; H, 6.60; N, 5.55.

Data for 8. ¹H NMR (C₆D₆): δ 7.67 (br t, $J_{HH} = 7$ Hz, 8H), 7.12–6.96 (m, 12H), 4.69 (t, $J_{HH} = 5$ Hz, 4H), 4.35 (dt, $J_{HH} = 2$ and 5 Hz, 2H), 4.24 (t, J = 5 Hz, 4H), 2.10–1.93 (m, 4H), 1.96 (d, $J_{HP} = 5$ Hz, 6H), 1.52 (br s, 4H), 1.05–0.92 (m, 12H). ³¹P{¹H} NMR (C₆D₆): δ 24.1 (d, $J_{PP} = 91$ Hz), 20.1 (d, $J_{PP} = 91$ Hz). IR (KBr): ν_{NN} 1994w, 1919vs cm⁻¹. Anal. Calcd for C₄₈H₆₀CrN₄MoO_{0.5}P₄ (**8**·0.5THF): C, 59.26; H, 6.22; N, 5.76. Found: C, 58.39; H, 6.01; N, 5.43.

Preparation of [W(NNH₂)(OTf)(bmpc)₂]OTf (9). To a benzene (4 mL) solution of **1** (89 mg, 99 μ mol) was added HOTf (32 mg, 211 μ mol) in benzene (1 mL). The solution was stirred at room temperature for 10 min to form dark yellow precipitates.

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Table 3. Summary	of	Crystallogr	aphic Data

	1	4 •0.5THF	5.2THF	8.0.5THF	9.2THF
formula	$C_{32}H_{44}N_4Cr_2P_4W$	C ₄₈ H ₆₀ N ₄ CrO _{0.5} P ₄ W	C40H60N4Cr2MoO2P4	C48H60N4CrMoO0.5P4	$C_{42}H_{62}N_2Cr_2F_6O_8P_4S_2W$
fw	896.46	1060.77	952.77	972.86	1312.81
cryst size/mm	$0.40 \times 0.30 \times 0.20$	$0.12 \times 0.10 \times 0.08$	$0.55 \times 0.50 \times 0.05$	$0.50 \times 0.25 \times 0.10$	$0.50 \times 0.20 \times 0.03$
color, habit	orange-red prism	orange prism	orange-yellow plate	orange plate	dark yellow plate
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	<i>Pbcn</i> (No. 60)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
$a/{ m \AA}$	14.7803(7)	11.0977(3)	14.5417(3)	11.0795(5)	16.7101(9)
b/\dot{A}	12.6823(6)	19.5256(6)	10.0118(3)	19.6088(7)	10.0276(4)
c/Å	18.9408(8)	21.2340(5)	28.9647(6)	21.2952(9)	31.4981(14)
β/deg	105.9520(19)	97.8723(7)	90	97.9919(15)	103.4649(19)
$V/Å^3$	3413.7(3)	4557.8(2)	4216.91(18)	4581.6(3)	5132.8(4)
Z	4	4	4	4	4
$d_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.744	1.546	1.501	1.410	1.699
μ (Mo K α)/mm ⁻¹	4.208	2.943	0.990	0.690	2.932
no. of data collected	$31096(2\theta < 55^\circ)$	$42313(2\theta < 55^\circ)$	$38509(2\theta < 55^\circ)$	$36678~(2\theta < 50^\circ)$	$44149(2\theta < 55^\circ)$
no. of unique data (R_{int})	7839 (0.073)	10349 (0.119)	4787 (0.057)	8390 (0.086)	1116 (0.076)
no. of params refined	432	581	270	581	587
$R_1^a (F^2 > 2\sigma)$	0.036	0.044	0.027	0.050	0.049
wR_2^b (all data)	0.050	0.057	0.064	0.098	0.106
goodness of fit indicator ^c	1.01	1.01	1.01	1.03	1.01
residual electron density/e $Å^{-3}$	+1.79 to -1.76	+2.33 to -1.99	+0.72 to -0.55	+1.65 to -1.88	+2.87 to -1.99

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{o}| / \sum |F_{o}| \cdot {}^{b}wR_{2} = \left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o})^{2}\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{o}^{2})^{2} / (N_{obs} - N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{o}^{2})^{2} / (N_{obs} - N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{o}^{2})^{2} / (N_{obs} - N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{o}^{2})^{2} / (N_{obs} - N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{o}^{2} + N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{o}^{2})^{2} / (N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F_{o}^{2} - F_{o}^{2} + N_{obs})\right]^{1/2} \cdot {}^{c}\left[\sum w(F$

The volatile materials were removed under vacuum. The residue was extracted with THF (10 mL) and recrystallized from THF–*n*-hexane to afford dark yellow rectangular crystals of **9**·2THF. Drying under vacuum resulted in the partial loss of a solvent molecule to give a yellow powder of **9**·THF (51 mg, 41%). Detailed information was not obtained by NMR because of the low solubility of **9**. IR (KBr): $\nu_{\rm NH}$ 3262 cm⁻¹. Anal. Calcd for C₃₈H₅₄N₂Cr₂F₆O₇P₄S₂W (**9**·THF): C, 36.79; H, 4.39; N, 2.26. Found: C, 36.98; H, 4.14; N, 2.23.

Preparation of [Mo(NNH₂)(OTf)(bmpc)₂]OTf (10). To a benzene (4 mL) solution of **5** (42 mg, 52 μ mol) was added HOTf (17 mg, 113 μ mol) in benzene (1 mL). The solution was stirred at room temperature for 10 min to form dark yellow precipitates. The volatile materials were removed under vacuum. The residue was extracted with THF (6 mL) and recrystallized by adding *n*-hexane (6 mL) to afford a dark yellow crystalline solid. Drying under vacuum gave a yellow solid of **10** · 1.5THF (27 mg, 44%). Detailed information was not obtained by NMR because of the low solubility of **10**. IR (KBr): $\nu_{\rm NH}$ 3243 cm⁻¹. Anal. Calcd for C₄₀H₅₈N₂Cr₂F₆MoO_{7.5}P₄S₂ (**10** · 1.5THF): C, 40.41; H, 4.92; N, 2.36. Found: C, 40.16; H, 4.66; N, 2.26.

Protonation of Dinitrogen Complexes. To a dinitrogen complex (35 μ mol) suspended in methanol (5 mL) was added concentrated sulfuric acid (0.05 mL). The mixture was stirred at room temperature for 24 h. To the resulting green solution was added aqueous KOH (30 wt %, 10 mL). After stirring for 10 min, the mixture was distilled under reduced pressure. Volatiles were passed through aqueous sulfuric acid (0.5 M, 10 mL), where ammonia was trapped as ammonium sulfate. The collected ammonia was quantified by the indophenol method.¹² No hydrazine was detected by *p*-(dimethylamino)benzaldehyde reagent.¹³

X-ray Crystallography. Crystallographic data are summarized in Table 3. 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-monochrometed Mo K α radiation (λ = 0.71069 Å). Data were corrected for absorption, Lorentz, and polarization effects. Structures were solved by the direct methods (SIR97)¹⁴ and expanded using Fourier techniques.¹⁵ Anisotropic thermal parameters were introduced for non-hydrogen atoms. A hydrogen atom (H1) of 9 was located from a difference Fourier map and was refined isotropically. The 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 maximum parameter-shift/esd converged to less than 0.001.16 All calculations were performed using the Crystal Structure software package.¹⁷ 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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