A Study of High Oxidation State Complexes of the Type $[W(\eta^5\text{-}C_5Me_5)Me_2X]_2(\mu\text{-}N_2)$, Including X-ray Structures of $[W(\eta^5\text{-}C_5Me_5)Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ and $[W(\eta^5\text{-}C_5Me_5)Me_2(S\text{-}2,4,6\text{-}C_6H_2Me_3)]_2(\mu\text{-}N_2)$

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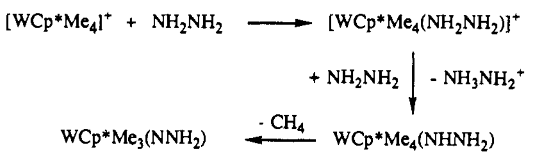
Abstract: A high yield route (80–90%) to the bridging dinitrogen complex $[WCp^*Me_3]_2(\mu\text{-}N_2)$ (**1**) consists of the reduction of $WCp^*Me_3(OTf)$ by sodium amalgam in the presence of dinitrogen. **1** reacts with HOTf (2 or excess (6) equiv) to give $[WCp^*Me_2(OTf)]_2(\mu\text{-}N_2)$ or $[WCp^*Me(OTf)_2]_2(\mu\text{-}N_2)$, respectively, with C_6F_5COOH, C_6F_5OH, or C_6F_5SH to give complexes of the form $[WCp^*Me_2(X)]_2(\mu\text{-}N_2)$ ($X = OC_6F_5$, etc.), and with tetrabromocatechol to give $[WCp^*Me(O_2C_6Br_4)]_2(\mu\text{-}N_2)$. $[WCp^*Me_2(OTf)]_2(\mu\text{-}N_2)$ reacts with NaSR ($R = 2,4,6\text{-}C_6H_2Me_3$ or $2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3$) to give complexes of the form $[WCp^*Me_2(SR)]_2(\mu\text{-}N_2)$, and $[WCp^*Me(OTf)_2]_2(\mu\text{-}N_2)$ reacts with perfluoropinacolate (PFP) to give $[WCp^*Me(PFP)]_2(\mu\text{-}N_2)$. X-ray structures of $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ and $[WCp^*Me_2(S\text{-}2,4,6\text{-}C_6H_2Me_3)]_2(\mu\text{-}N_2)$ show that the complexes have structures that are similar to that of **1**, except the N–N bond lengths are shorter. Crystal data for $[WCp^*Me_2(S\text{-}2,4,6\text{-}C_6H_2Me_3)]_2(\mu\text{-}N_2)$ are $a = 24.916$ (7) Å, $c = 8.700$ (5) Å, $V = 4677$ (5) Å^3, space group = $P3_221$ (no. 154), $Z = 3$, $M_r = 1028.80$, $\rho = 1.10$ g/cm^3, $\mu = 38.49$ cm^{-1}. Final $R_1 = 0.050$ and $R_2 = 0.067$. Crystal data for $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ are $a = 9.081$ (3) Å, $b = 12.390$ (2) Å, $c = 8.660$ (2) Å, $\alpha = 95.74$ (1)°, $\beta = 90.54$ (2)°, $\gamma = 71.54$ (2)°, $V = 919.4$ (4) Å^3, space group = $P\bar{1}$ (no. 2), $Z = 1$, $M_r = 1092.42$, $\rho = 1.973$ g/cm^3, $\mu = 64.69$ cm^{-1}. Final $R_1 = 0.057$ and $R_2 = 0.077$. ^{15}N NMR data are reported for all complexes.

The Fe–Mo cofactor of the enzyme nitrogenase is a polyheteronuclear cluster that contains an approximate 1/6/9 ratio of Mo:Fe:S in which molybdenum is separated by less than 3 Å from 2–3 iron atoms and is in a relatively high resting oxidation state (probably 4+).[1] Genetic evidence implicates FeMo-co as the site of binding and reduction of dinitrogen.[1e] Recent discoveries suggest that molybdenum is not required for reduction of dinitrogen; nitrogenases are also known that contain vanadium[2] or tungsten.[3]

The vast majority of isolable molecular nitrogen complexes, either monometallic complexes in which dinitrogen binds "end-on" or bimetallic μ-N_2 complexes, contain an "electron-rich" metal in a relatively low oxidation state.[4] The traditional explanation is that backbonding to molecular nitrogen thereby is maximized. The best known examples of low oxidation state bis-dinitrogen complexes are of the type *cis*- and *trans*-$M(N_2)_2L_4$ (M = Mo or W; L = phosphine) and $M(N_2)_2L_2$ (L = bidentate phosphine).[4-6] These complexes contain dinitrogen ligands with N–N bond orders of ~3 and bond distances only slightly longer than that in unbound N_2 (1.0976 Å). The nitrogen ligand in these complexes can be protonated with relative ease by strong acids to yield either hydrazido(2–) species[5] (M=N—NH_2) or less than stoichiometric amounts of ammonia and hydrazine depending on the complex and reaction conditions.[6]

Scheme I



$$WCp^*Me_3(NNH_2) + [WCp^*Me_4]^+ \xrightarrow{\text{base}} [WCp^*Me_3]_2(\mu\text{-}N_2) + CH_4 \quad (1)$$

The best known, well-characterized, relatively high oxidation state dinitrogen complexes are d^2 titanium(II) or zirconium(II) complexes of the type $[MCp^*_2(N_2)]_2(\mu\text{-}N_2)$ ($Cp^* = \eta^5\text{-}C_5Me_5$).[7] Complexes such as $(PMe_2Ph)_4ClRe(N_2)MoCl_4(OMe)$ also are known in which W or Mo in a relatively high oxidation state and Re in a relatively low oxidation state are bound to dinitrogen.[4a,e] More recently discovered high oxidation state μ-dinitrogen complexes of niobium(III) or tantalum(III) contain a dinitrogen ligand that apparently is in a highly reduced state, as evidenced by the relatively long N–N bond (~1.30 Å).[8,9a,b] It can be argued that two d electrons from each metal have been donated to dinitrogen to produce a "hydrazido(4–)" ligand, oxidizing the two metal centers to d^0. The ability of niobium and tantalum to form

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bimetallic complexes that contain a hydrazido(4–) ligand, while titanium and zirconium do not, could be traced to the tendency for niobium and tantalum to form (formally double or triple) multiple bonds to carbon, nitrogen, or oxygen, while group 4 metals in general do not as commonly.[10] If so, then molybdenum(IV) and tungsten(IV), metals for which multiple metal–ligand bonds are even more common,[10] also should form complexes of the type M=N—N=M in which M could be said to be M(VI).

In this paper we present the synthesis and some chemistry of an authentic tungsten hydrazido(4–) complex, $[WCp^*Me_3]_2(\mu\text{-}N_2)$, along with the preparation and structures of several closely related derivatives that contain metal–oxygen or metal–sulfur bonds. Analogous molybdenum and molybdenum/tungsten complexes are reported in the following paper.[11] We believe that some understanding of the chemistry of dinitrogen complexes of tungsten in a high oxidation state, even though such complexes contain nonbiomimetic ligands, ultimately should help us understand how dinitrogen is reduced by molybdenum or tungsten nitrogenases. A portion of these results has been reported in a preliminary communication.[12]

Results and Discussion

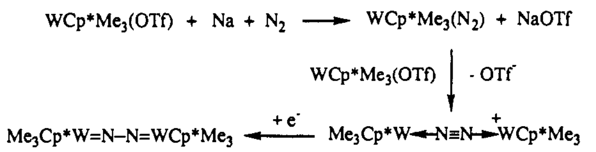
Preparation of $[WCp^*Me_3]_2(\mu\text{-}N_2)$. $[WCp^*Me_3]_2(\mu\text{-}N_2)$ (**1**) was first prepared by treating $[WCp^*Me_4]^+$ with hydrazine.[12] Scheme I shows the likely mechanism for the first half of the reaction. $[WCp^*Me_4(NH_2NH_2)]^+$, $WCp^*Me_4(NHNH_2)$, and $WCp^*Me_3(NNH_2)$ all have been isolated and characterized.[13a] $[WCp^*Me_4(NH_2NH_2)]^+$ originally was prepared by protonating $WCp^*Me_4(NHNH_2)$,[13a] although we have found recently that it can be prepared by carefully adding 1 equiv of hydrazine to $[WCp^*Me_4]^+$.[13b] $WCp^*Me_4(NHNH_2)$ is known to decompose to $WCp^*Me_3(NNH_2)$, while $[WCp^*Me_4(NH_2NH_2)]^+$ is deprotonated readily with triethylamine to give $WCp^*Me_4(NHNH_2)$. The synthesis probably is completed in an analogous set of reactions involving the hydrazido(2–) ligand in $WCp^*Me_3(NNH_2)$(eq 1). In fact, a better yield of **1** is realized if the synthesis is carried out in just this manner. $WCp^*Me_4(NHNH_2)$ has been structurally characterized;[13a] the structure of $[WCp^*Me_4(NH_2NH_2)]^+$ is believed to be very similar. $WCp^*Me_3(NNH_2)$ is believed to be a tetragonal pyramid having a linear hydrazido(2–) ligand. Many complexes that contain a linear hydrazido(2–) ligand are known.[4,5,6,14]

Related hydrazine-based routes to **1** employ different bases to remove protons from hydrazine. For example, the relatively basic methylene ligand in $WCp^*Me_3(CH_2)$, which can be generated at low temperature by deprotonating $[WCp^*Me_4]^+$ with triethylamine,[15] accepts a proton from $WCp^*Me_3(NNH_2)$ to give an intermediate that loses methane (eq 2). Side reactions,

$$WCp^*Me_3(NNH_2) + WCp^*Me_3(CH_2) \rightarrow WCp^*Me_3(NNH)WCp^*Me_4 \rightarrow CH_4 + \mathbf{1} \quad (2)$$

probably those that lead to decomposition of $WCp^*Me_3(CH_2)$ at temperatures necessary for it to react with hydrazine, limit the yield to only ~60%. If 1 equiv of hydrazine is added to 2 equiv of $WCp^*Me_3(CH_2)$, then the yield of **1** is reduced further to ~35%. If 1 equiv of hydrazine is added to 2 equiv of WCp^*Me_5, then the yield of **1** returns to ~60%, possibly because WCp^*Me_5 is significantly more stable than $WCp^*Me_3(CH_2)$.

Scheme II



It would be most desirable to prepare **1** directly from dinitrogen. Initial attempts involved reduction of "WCp^*Me_3Cl" under dinitrogen with sodium amalgam. "WCp^*Me_3Cl" was prepared by the reaction between 6 equiv of WCp^*Me_4 and $[WCp^*Cl_4]_2$ in dichloromethane, but it does not appear to be a single compound analogous to square-pyramidal WCp^*Me_4.[15] This may in part explain why yields of **1** prepared by reducing WCp^*Me_3Cl under dinitrogen were low (~5%).[12] In the process of attempting to react HCl selectively with WCp^*Me_4 to give "WCp^*Me_3Cl", we discovered that triflic acid reacted smoothly with WCp^*Me_4 to give yellow crystalline $WCp^*Me_3(OTf)$ (eq 3). $WCp^*Me_3(OTf)$ *can* be reduced smoothly and reproducibly under dinitrogen to give **1** in 85–90% yield (eq 4). We still have little knowledge of the details of this remarkable reaction. It seems most plausible

$$WCp^*Me_4 + HOTf \rightarrow WCp^*Me_3(OTf) + CH_4 \quad (3)$$

$$2WCp^*Me_3(OTf) + 2Na/Hg + N_2 \xrightarrow{\text{ether}} \mathbf{1}\ (>90\%) + 2NaOTf \quad (4)$$

that the first step is reduction of $WCp^*Me_3(OTf)$ to $[WCp^*Me_3(OTf)]^-$, followed by loss of triflate and formation of a dinitrogen complex, e.g., $WCp^*Me_3(N_2)$ (mode of N_2 bonding unspecified). As shown in Scheme II, an end-on bound dinitrogen ligand may be basic enough to displace triflate from $WCp^*Me_3(OTf)$ to give a dimer that accepts another electron to give **1**. Reduction of $WCp^*Me_3(OTf)$ does not appear to be successful with use of other reducing agents (this aspect is still under investigation), so sodium may play a more intimate role than implied in the mechanism shown in Scheme II. If dinitrogen is omitted from the system, then a complex mixture of products is formed, some of which are dimeric methylidyne complexes.[15] **1**-$^{15}N_2$ can be prepared readily by reducing $WCp^*Me_3(OTf)$ under $^{15}N_2$.

$[WCp^*Me_3]_2(\mu\text{-}N_2)$ (**1**) is a red, crystalline, virtually air-stable compound that can be chromatographed on silica (40 Å) employing pentane as the solvent. **1** also may be purified by chromatography on an alumina column (7% H_2O), also with pentane as the eluant. It appears to be relatively stable to water (in THF) and even to KOH in aqueous THF. It reacts with acids, as outlined in the following section. Proton and carbon NMR spectra are straightforward; the proton NMR spectrum (in C_6D_6) exhibits a 2:1 pattern of singlet resonances for the methyl groups on the metal at 1.0 and 0.66 ppm, respectively.

Preparation of Dinitrogen Complexes Related to 1. Addition of excess gaseous HCl to **1** in ether, toluene, or dichloromethane yields red, crystalline **2a** (eq 5, X = Cl). Analogous reactions

$$[WCp^*Me_3]_2(\mu\text{-}N_2) + 2HX \rightarrow 2CH_4 + [WCp^*Me_2(X)]_2(\mu\text{-}N_2) \quad (5)$$

$$X = Cl\ (\mathbf{2a}),\ OTf\ (\mathbf{2b}),\ O_2CC_6F_5\ (\mathbf{2c}),\ OC_6F_5\ (\mathbf{2d}),\ SC_6F_5\ (\mathbf{2e})$$

between **1** and other relatively strong acids yield **2b–e** smoothly. **1** does not react readily with phenol or benzoic acid. It reacts with HBF_4 in diethyl ether, but the initial and final products appear to be unstable and so far have not been characterized. However, by carrying out the same reaction in the presence of 50 equiv of acetonitrile $\{[WCp^*Me_2(CH_3CN)]_2(\mu\text{-}N_2)\}^{2+}(BF_4^-)_2$ is obtained. Since the X-ray structure of **2d** (see below) shows that the OC_6F_5 ligand is located trans to the dinitrogen ligand, we assume at this stage that the structures of related derivatives are similar, except that of **2c** where the benzoate ligand is likely to bind in a bidentate fashion to create a symmetric pseudooctahedral metal environment. Proton and carbon NMR spectra of all species are straightforward and do not change significantly upon cooling samples down to –80 °C.

We can only speculate on the mechanism of reaction between **1** and strong acids. A strong possibility is initial protonation of the bridging dinitrogen ligand followed by proton transfer to a

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Table I. Crystal Data for $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ (**2d**) and $[WCp^*Me_2(S\text{-}2,4,6\text{-}C_6H_2Me_3)]_2(\mu\text{-}N_2)$ (**2f**)

empirical formula	$W_2C_{36}H_{42}N_2O_2F_{10}$	$W_2C_{42}H_{64}S_2N_2$
formula weight	1092.42	1028.80
crystal system	triclinic	trigonal
a	9.081 (3) Å	24.916 (7) Å
b	12.390 (2) Å	
c	8.660 (2) Å	8.700 (5) Å
α	95.74 (1)°	
β	90.54 (2)°	
γ	71.54 (2)°	
V	919.4 (4) Å^3	4677 (5) Å^3
space group	$P\bar{1}$ (no. 2)	$P3_221$ (no. 154)
Z	1	3
ρ (calcd)	1.973 g/cm^3	1.10 g/cm^3
μ	64.69 cm^{-1}	38.49 cm^{-1}
final R_1, R_2	0.057, 0.077	0.050, 0.067

cis methyl group, attack on the metal by the counter anion, and rearrangement to give the species in which X is trans to μ-N_2. An attractive alternative is coordination of X in HX to the metal followed by direct transfer of a proton from X to a methyl group.

If **1** is exposed to an excess (6 equiv) of triflic acid in dichloromethane, then what we propose to be insoluble $[WCp^*Me(OTf)_2]_2(\mu\text{-}N_2)$(**3a**) precipitates from solution over a period of 12 h. A soluble species (**3b**) can be obtained by recrystallizing **3a** from acetonitrile. On the basis of proton NMR spectra **3b** appears to have the stoichiometry $\{[WCp^*Me(CH_3CN)_2]_2(\mu\text{-}N_2)\}^{4+}(OTf^-)_4$. However, ^{15}N NMR studies (see later) suggest that the dinitrogen ligand is radically different from what it is in related complexes and that the acetonitrile may not be behaving as a simple donor ligand. This proposal is discussed further later.

Other derivatives that appear to be analogous to **2a–e** can be prepared as shown in eq 6 (M = Na or Li, SMes = S-2,4,6-$C_6H_2Me_3$, TIPT = S-2,4,6-C_6H_2-i-Pr_3). **2g** also can be prepared from **2a** as shown in eq 7, and **2d** also has been prepared by the method shown in eq 6.

$$[WCp^*Me_2(OTf)]_2(\mu\text{-}N_2) + 2MSR \rightarrow [WCp^*Me_2(SR)]_2(\mu\text{-}N_2) + 2MOTf \quad (6)$$

$$SR = SMes\ (\mathbf{2f}),\ TIPT\ (\mathbf{2g});\ M = Li\ or\ Na$$

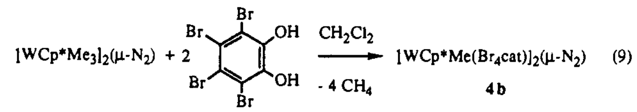
$$[WCp^*Me_2Cl]_2(\mu\text{-}N_2) + 2LiTIPT \rightarrow [WCp^*Me_2(TIPT)]_2(\mu\text{-}N_2) + 2LiCl \quad (7)$$

It is interesting to note that **2f** and **2g** cannot be prepared by adding RSH to **1**. The reduced acidity of ordinary thiols (the pK_a of HSMes is 7.40) relative to C_6F_5OH (pK_a = 5.86)[16] or C_6F_5SH must in part be the reason, although steric problems may also slow down or prevent reactions involving TIPTH or HSMes. Proton NMR spectra of both **2f** and **2g** are temperature dependent and are discussed in detail in a later section.

It is possible to prepare derivatives in which two of the three methyl groups in **1** are replaced by oxygen ligands, as shown in eq 8 and 9. Although **4b** is formed in high yield and is well-characterized, it is a mixture of inseparable isomers arising from the two possible relative geometries at each end of the molecule, as judged by NMR studies to be described later. The room temperature ^1H NMR spectrum of **4a** indicates that only one isomer is present.

$$[WCp^*Me(OTf)_2]_2(\mu\text{-}N_2) + 2\ Li_2PFP \xrightarrow{ether} [WCp^*Me(PFP)]_2(\mu\text{-}N_2) + 4\ LiOTf \quad (8)$$

4a (PFP = $OC(CF_3)_2C(CF_3)_2O$)



X-ray Studies. X-ray studies on both $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ and $[WCp^*Me_2(SMes)]_2(\mu\text{-}N_2)$ were carried out. Crystal data are shown in Table I. Important bond distances and angles can be found in Tables II and III. A drawing of $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ is shown in Figure 1, and a drawing of $[WCp^*Me_2(SMes)]_2(\mu\text{-}N_2)$ is shown in Figure 2.

Table II. Important Bond Distances (Å) and Angles (deg) in $[Cp^*WMe_2(OC_6F_5)]_2(\mu\text{-}N_2)$

W(1)–N(1)	1.775 (9)	N(1)–W(1)–C(1)	88.9 (5)
W(1)–C(1)	2.13 (1)	N(1)–W(1)–C(2)	86.6 (5)
W(1)–C(2)	2.11 (2)	O(1)–W(1)–C(2)	75.6 (6)
W(1)–O(1)	2.079 (8)	N(1)–W(1)–O(1)	134.9 (4)
O(1)–C(21)	1.32 (1)	C(2)–W(1)–C(1)	135.7 (6)
N(1)–N(1)*	1.26 (2)	W(1)–N(1)–N(1)*	169.0 (1)
O(1)–W(1)–C(1)	76.9 (5)	W(1)–O(1)–C(21)	142.0 (8)

Table III. Important Bond Distances (Å) and Angles (deg) in $[Cp^*WMe_2(SMes)]_2(\mu\text{-}N_2)$

W(1)–N(1)	1.774 (8)	N(1)–W(1)–C(1)	85.8 (5)
W(1)–C(1)	2.20 (1)	N(1)–W(1)–C(2)	89.7 (5)
W(1)–C(2)	2.21 (1)	N(1)–W(1)–S(1)	118.1 (3)
N(1)–N(1)*	1.27 (2)	C(1)–W(1)–C(2)	143.4 (5)
W(1)–S(1)	2.453 (4)	W(1)–S(1)–C(21)	117.5 (5)
S(1)–C(21)	1.78 (1)	W(1)–N(1)–N(1)*	172.0 (1)

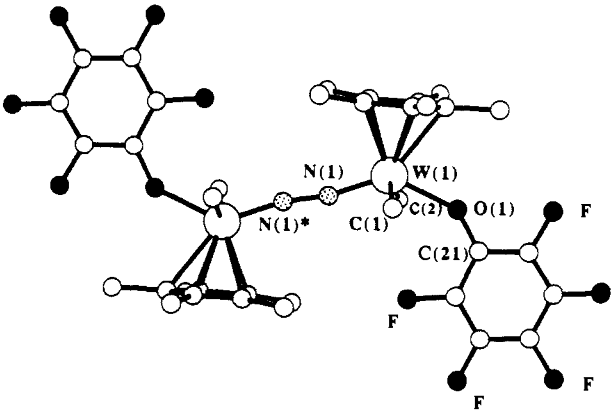


Figure 1. A view of the structure of $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ (**2d**).

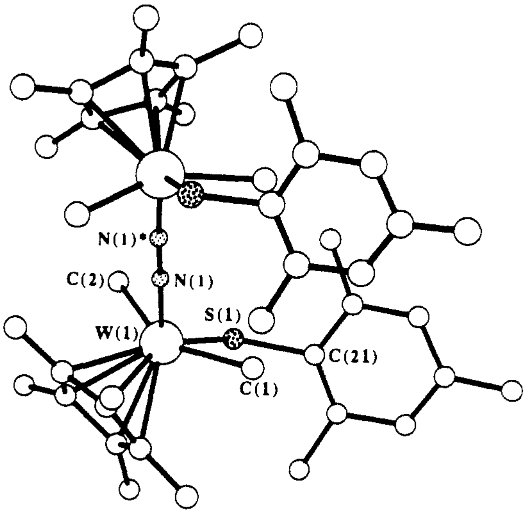


Figure 2. A view of the structure of $[WCp^*Me_2(S\text{-}2,4,6\text{-}C_6H_2Me_3)]_2(\mu\text{-}N_2)$ (**2f**).

The geometry around the metal in $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ is close to a pseudotetragonal pyramid (four-legged piano stool), as is shown most clearly in the nearly identical values for N(1)–W(1)–O(1) (135.0 (4)°) and C(2)–W(1)–C(1) (135.7 (6)°). The smaller O–W–C angles (~76°) compared to the N–W–C angles (86–89°) probably can be ascribed to steric repulsion between the two ends of the molecule or to a repulsion between the methyl groups and the nitrogen atom in the short multiple metal–nitrogen bond. The bond lengths in the Cp* ligand and the W–C(ring) distances and angles are all normal. Note that the two Cp* ligands are arranged in a transoid fashion across the W_2N_2 system.

Table IV. ^{15}N NMR Data for Dinitrogen Complexes of the Hydrazido(4−) Type

complex	δ^a (ppm)
$[WCp^*Me_3]_2(\mu\text{-}N_2)$ (**1**)	428.7^b
$[WCp^*Me_2(OTf)]_2(\mu\text{-}N_2)$ (**2b**)	403.3
$[WCp^*Me_2(O_2CC_6F_5)]_2(\mu\text{-}N_2)$ (**2c**)	411.8
$[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ (**2d**)	421.3
$[WCp^*Me_2(SC_6F_5)]_2(\mu\text{-}N_2)$ (**2e**)	405.5
$[WCp^*Me_2(SMes)]_2(\mu\text{-}N_2)$ (**2f**)	411.3^c
$[WCp^*Me_2(TIPT)]_2(\mu\text{-}N_2)$ (**2g**)	413.0
"$\{[WCp^*Me(CH_3CN)_2]_2(\mu\text{-}N_2)\}^{4+}(OTf^-)_4$" (**3b**)	246.3
$[WCp^*Me(Br_4cat)]_2(\mu\text{-}N_2)$ (**4b**)	451.0, 451.8
$[Ta(CHCMe_3)(PMe_3)_2Cl]_2(\mu\text{-}N_2)^d$	414.0
$[TaCl(C_2H_4)(PMe_3)_3]_2(\mu\text{-}N_2)^d$	374.0
$\{[WCp^*Me_2(CH_3CN)]_2(\mu\text{-}N_2)\}^{2+}(BF_4^-)_2$	392.4

^{a}Quoted with respect to liquid ammonia (0 ppm). Spectra are referenced to an external reference of $C_6H_5{}^{15}NH_2$ (56.5 ppm downfield of liquid ammonia). Solvent is CD_2Cl_2. $^b J_{NW}$ = 125 Hz, $^2J_{NW}$ = 104 Hz. $^c J_{NW}$ = 68.6 Hz. ^{d}See ref 8a.

The molecule has a crystallographically imposed 2-fold axis that passes through the N–N bond. The W–O bond length is somewhat longer and the W–O–C bond angle somewhat smaller than is typically observed for ordinary alkoxides in high oxidation state tungsten complexes, where π bonding is often thought to be significant. One would expect π bonding from a perfluorophenoxide ligand to be reduced from what it would be in an ordinary phenoxide ligand, but π bonding in the metal–nitrogen multiple bond trans to the phenoxide ligand should also lead to a decrease in π bonding between oxygen and tungsten.

The short W–N bond, large W–N–N angle, and long N–N bond are all typical of known "hydrazido(4−)" complexes,[8,9,11] including $[WCp^*Me_3]_2(\mu\text{-}N_2)$.[9c]

The basic structure of $[WCp^*Me_2(SMes)]_2(\mu\text{-}N_2)$ differs from that of $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ in two ways; the core geometry around each metal is approximately halfway between a square pyramid and a trigonal bipyramid,[17] and the two ends of the molecule are now twisted only ~120° with respect to one another (Figure 2). Distortion of the core geometry toward trigonal bipyramidal (with the methyl ligands in axial positions) is most evident in the relatively large C(1)–W–C(2) angle (143.4 (5)°) and relatively small S–W–N angle (118.1 (3)°) compared to analogous angles in $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$. In part this distortion arises from orientation of the thiolate ligand so that the S–C bond is more or less lined up with one of the W–C bonds, i.e., the "equatorial" thiolate is oriented toward one of the "axial" methyl ligands. There is ample evidence that thiolate ligands, especially relatively bulky ones, prefer to bind in equatorial positions in trigonal bipyramids and to be oriented toward one of the axial ligands. For example, three bulky thiolate ligands always bind "two up, one down" in equatorial positions in trigonal bipyramids.[18] In $[WCp^*Me_2(SMes)]_2(\mu\text{-}N_2)$ the orientation could be determined by π bonding between what amounts to an sp^3 hybrid on sulfur and a ~d_{xy} orbital whose lobes are directed between the sulfur and carbon ligands. The nature of bonding of hydrazido(1−) ligands in related tungsten Cp* complexes[13a] was explained in similar terms. The practical consequence is that each end of the molecule becomes unsymmetric, and two isomers could be formed depending on the relative orientation of the thiolate ligand at each end. If the molecule is twisted so that the Cp* ligands are transoid with respect to one another (as in $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$), then the thiolate ligands may be cisoid, as found in this crystal of **2f**, or transoid. A specific orientation and fluxionality of the thiolate ligand can be observed in proton NMR spectra, as discussed below.

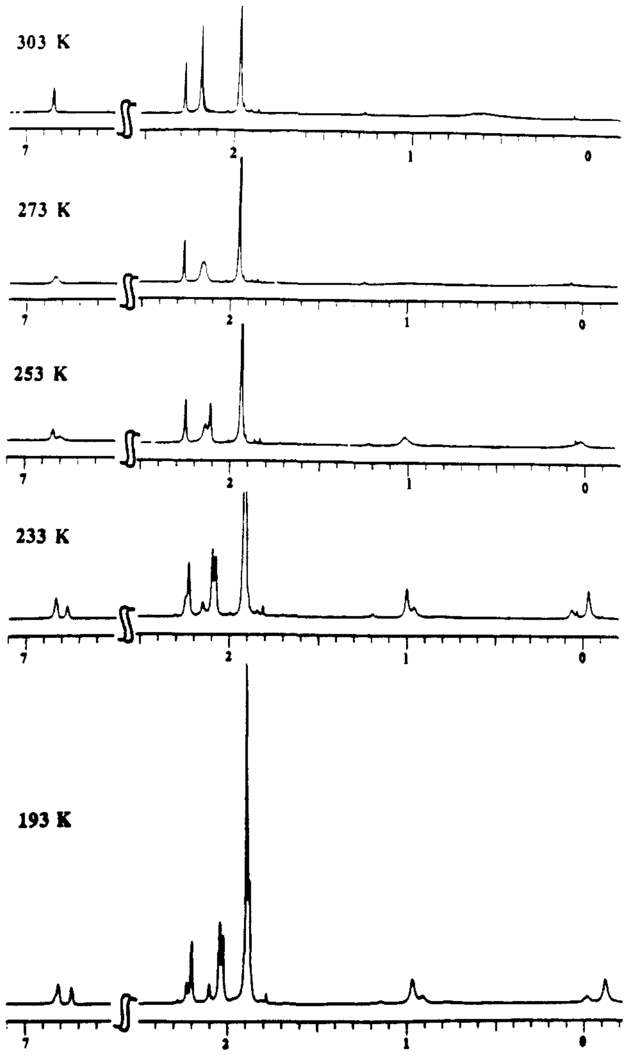


Figure 3. Variable temperature NMR spectra of $[WCp^*Me_2(S\text{-}2,4,6\text{-}C_6H_2Me_3)]_2(\mu\text{-}N_2)$ (**2f**).

NMR Studies. The proton and carbon NMR spectra of **2a–e** are relatively unremarkable. However, the proton NMR spectra of **2f** and **2g** are temperature dependent. The more complex of the two situations is **2g**, so we will discuss the spectra of **2f** only and assume that the two cases are analogous. At 343 K the proton NMR spectrum of **2f** in toluene-d_8 shows a set of resonances characteristic of a symmetric molecule, analogous to spectra of the symmetric molecules **2a–e**. As the sample is cooled in CD_2Cl_2 (Figure 3), two sets of mesityl, Cp*, methyl, and meta resonances appear in a ratio of ~2:1. The greatest change is found in the average methyl resonance at ~0.6 ppm; it collapses to a 2:1 set of resonances at 0.94 ppm and a 2:1 set of resonances at −0.06 ppm. We assign the resonances with the same intensity to "axial" methyl groups, one that is relatively near a phenyl ring, and one that is not. If the thiolate ligands are either "cisoid" (as found in **2f** above) or "transoid", then two isomers can form, each containing two types of methyl groups. A fluxional process that consists of a "wiper-like" motion of the thiolate ligands from an orientation along one W–Me bond to an orientation along the other would equilibrate the two types of methyl groups and the two isomers. In contrast, there is no ^{1}H NMR evidence at −80 °C for a single orientation of the pentafluorothiolate ligand along one

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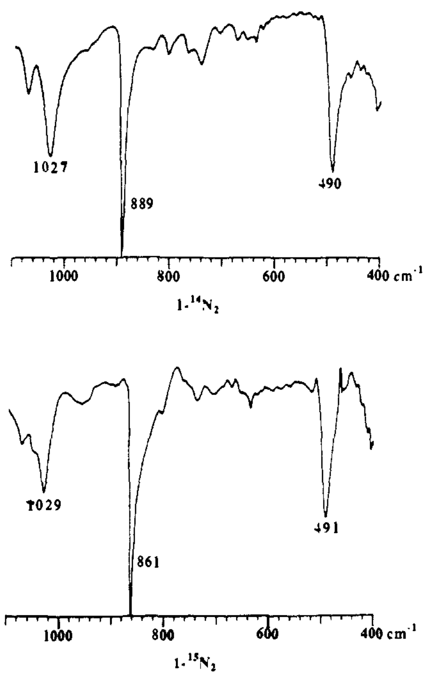

Figure 4. IR spectra of **1** and **1**-$^{15}N_2$ as films on KBr (by evaporation of solvent).

of the W–Me bonds in **2e**. The pentafluorothiolate ligand is almost certainly a significantly poorer π bonding ligand than the mesitylthiolate ligand in **2f**, and therefore if one orientation is preferred, the barrier to the ligand flipping to the other orientation is relatively small.

^{15}N chemical shifts are shown in Table IV. All spectra are referenced to an external standard of $C_6H_5{}^{15}NH_2$ (56.5 ppm downfield of liquid ammonia).[19] In the parent compound **1** it was possible in a concentrated sample to observe the one- and two-bond coupling of ^{15}N to tungsten. Values of 125 and 104 Hz, respectively, suggest a significant degree of delocalization throughout the WNNW system. The chemical shift for N_2 in **3b** (246.3 ppm) stands out as an anomaly. The chemical shift of the μ-N_2 ligand in $\{[WCpMe_2(CH_3CN)]_2(\mu\text{-}N_2)\}^{2+}(BF_4^-)_2$ is 392.4 ppm, so one would not expect the chemical shift in **3b** to differ so significantly. Therefore we suspect that this species does not contain two simple η^1-acetonitrile ligands per metal. An attempted X-ray study on suitable crystals grown over several weeks from acetonitrile suggested that they were actually $[WCp^*Me(CH_3CN)_4]^{3+}$, although disorder prevented a complete solution. This result could be explained if the μ-N_2 ligand in **3b** were more like neutral dinitrogen than hydrazido(4–) and therefore susceptible to displacement by acetonitrile. In view of these findings **3b** almost certainly will have to be reformulated in due course.

Infrared and Electrochemical Studies. The 1100–400-cm^{-1} region of the IR spectra or **1** ($^{14}N_2$ and $^{15}N_2$ labeled) as films on KBr are shown in Figure 4. The spectrum of **1** consists of three major medium strength peaks, only one of which (at 889 cm^{-1}) shifts upon ^{15}N labeling (to 861 cm^{-1}). In the spectra of **2d** and **2g** analogous peaks shift upon ^{15}N labeling, from 901 to 870 cm^{-1} in **2d**, and from 873 to 850 cm^{-1} in **2g**. In **4b** there is no peak between 850 and 900 cm^{-1} and the IR spectra are complicated by aryl peaks in the region below 850 cm^{-1}. Nevertheless, a peak at 834 cm^{-1} appears to shift to 809 cm^{-1} upon ^{15}N labeling. Consequently we tentatively assign the 834-cm^{-1} peak in **4b** as being analogous to those found in spectra of **1**, **2d**, and **2g**. It should be noted that similar IR bands were observed for hydrazido(4–) complexes of tantalum.[8a] In the case of $[Ta(CH\text{-}t\text{-}Bu)(PMe_3)_2Cl]_2(\mu\text{-}N_2)$ a peak at 847 cm^{-1} shifts to 820 cm^{-1}. The exact nature of the mode responsible for these absorptions was not proposed. On the basis of two peaks being observed in the IR spectrum of $[Cp^*Me_3Mo](\mu\text{-}N_2)[WCp^*Me_3]$[11] and the observation of a similar peak in $WCp^*Me_3(NNH_2)$ and related complexes,[13b] we now believe that the mode is basically a M=N stretch. Although there has been some controversy surrounding the assignment of $\nu(MN)$ in organoimido complexes,[10] there is now considerable evidence that in the absence of mixing with other modes $\nu(MN)$ will be found in the 800–1000-cm^{-1} region, consistent with the conclusion we are coming to with respect to μ-N_2 complexes of the hydrazido(4–) type.

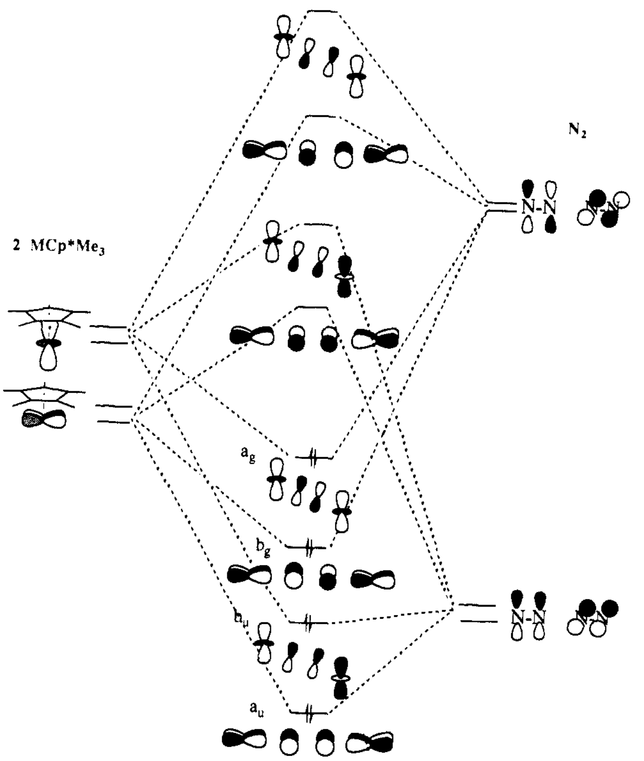

Figure 5. A molecular orbital diagram for π bonding in the W_2N_2 complexes.

Cyclic voltammograms (CV) of these complexes show no reversible oxidation or reduction waves in the region −2 to +1.5 V. Irreversible waves can be observed in some cases, however. In general it appears that these complexes are relatively easy to oxidize (>0.40 V) but quite difficult to reduce (<−1.30 V). (All electrochemical studies were done in methylene chloride versus Ag/AgCl using tetrabutylammonium tetrafluoroborate as the electrolyte.) $[Cp^*WMe_2(SC_6F_5)]_2(\mu\text{-}N_2)$ shows an irreversible oxidation wave at +1.0 V and an irreversible reduction wave at −1.65 V. A reduction wave at +0.1 V due to the reduction of the oxidation product is also observed. $[Cp^*WMe_2(SMes)]_2(\mu\text{-}N_2)$ shows two small irreversible oxidation waves at +0.55 and +0.80 V; no reduction waves are seen. $[Cp^*WMe_2(OC_6F_5)]_2(\mu\text{-}N_2)$ has two oxidation waves at +0.65 and +1.05 V and a very small reduction wave at −1.6 V. The CV of $[Cp^*WMe(O_2C_6Br_4)]_2(\mu\text{-}N_2)$ also has two oxidation waves at +0.40 and +0.85 V, while the reduction wave is at −1.3 V. The fact that the electrochemistry under these conditions is not clean is unfortunate. The data are included here only for the sake of completeness.

Bonding in $[WCp^*Me_2X]_2(\mu\text{-}N_2)$ Complexes. The σ bonding molecular orbitals for the W_2N_2 system are constructed straightforwardly and are filled. Molecular orbitals for the π-system in $[WCp^*Me_3]_2(\mu\text{-}N_2)$ are shown in Figure 5. The two metal-based orbitals available for π bonding are the d_{z^2} and d_{xy} orbitals.[20] The d_{xy} orbital lies between the metal–ligand bonds and so is the lower of the two in energy. The nitrogen-based π orbitals are the two orthogonal bonding and two orthogonal an-

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tibonding orbitals. Two electrons from each metal (WCp^*X_3 is formally d^2) and four electrons from the N–N fragment are available for π-interactions.

One π bonding orbital on N_2 can combine with the symmetric combination of d_{xy} orbitals to give the a_u MO, while the orthogonal π bonding orbital on N_2 can combine with the antisymmetric combination of d_{z^2} orbitals to give the b_u MO. The two orthogonal π-antibonding orbitals on N_2 can combine with the antisymmetric combination of d_{xy} orbitals to give a b_g MO and the symmetric combination of d_{z^2} orbitals to give an a_g MO. The relative energies of the b_u and b_g MO's is uncertain, but that is not crucial since neither is the HOMO. The a_u and b_u orbitals have bonding N–N character and are principally nitrogen-based, while the b_g and a_g orbitals are probably primarily metal-based and are N–N antibonding. When the eight π electrons fill up these four orbitals, the a_g becomes the HOMO. It is important to note that the LUMO is probably N–N bonding and M–N antibonding in character. Therefore promotion of an electron from the HOMO to the LUMO would result in a stronger N–N bond and weaker M–N bonds. Oxidation would yield stronger M–N bonding and weaker N–N bonding, while reduction would yield the opposite.

Substitution of the methyl group trans to the N–N moiety by a thiolate or phenoxide ligand appears to result in a shorter N–N bond distance, although as we said earlier the bond length differences are of marginal significance statistically because of the inherent inaccuracy in determining the N–N bond length when the nitrogen atoms are located between two tungsten atoms. Let us assume that such differences are significant and look for an explanation. One explanation that involves the σ bonding system is that the more polarizable X ligand (S or O vs C) forms a stronger σ bond to the metal, thus lengthening the trans (W–N) bond (1.775 and 1.776 Å versus 1.742 Å in the methyl case) and resulting in a shorter (N–N) distance. Another explanation involves the π bonding system. A filled p orbital on oxygen or sulfur should interact principally with the LUMO. Addition of electron density to this MO should result in longer W–N bonds and a shorter N–N bond. We find the explanation involving the π bonding system more attractive, even though neither the thiolate nor the pentafluorophenoxide is a strong π bonding ligand, since metal–nitrogen π bonding is of such overwhelming importance in reducing the nitrogen–nitrogen bond order. In the recent past we have attempted to create four-coordinate d^2 tungsten or molybdenum complexes that would bind and reduce dinitrogen, but in the cases where such complexes have been prepared they have turned out to contain either strong σ donating and moderately strong π bonding ligands (thiolates[21]) or relatively powerful π bonding ligands (2,6-dialkylphenoxides[22]). The fact that we have not been able to prepare $[WCp^*Me_2X]_2(\mu\text{-}N_2)$ complexes in which X is a relatively good π bonding ligand (e.g., an ordinary alkoxide) could be used as evidence that such species are indeed destabilized toward loss of dinitrogen. Future studies will be aimed toward a further elucidation of the importance of π bonding in relatively high oxidation state molecular nitrogen complexes.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres HE43-2 drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride was distilled from calcium hydride under nitrogen. Deuterated NMR solvents were passed through a column of activated alumina and stored over 4 Å molecular sieves. NMR data are listed in parts per million relative to Me_4Si for ^1H and ^{13}C and relative to $CFCl_3$ for ^{19}F. Coupling constants are quoted in Hertz. ^{15}N labeled compounds were all prepared in a manner analogous to that used to prepare ^{14}N compounds.

Long T_1 values were expected in ^{15}N NMR studies, since no protons are attached.[19] Spectra were obtained at 50.653 MHz in order to increase the contribution of the chemical shift anisotropy (CSA) term to the rate of relaxation $(T_1^{CSA})^{-1}$. Optimum pulse widths were calculated by using an estimated T_1 of 100 and delay time of 2 s. Since data could be acquired at high frequency it was not necessary to add relaxation agents. In several cases attempts to acquire spectra at lower frequency failed. Data can be found in Table IV.

Electrochemical data was obtained by using a Princeton Applied Research Model 173 Potentiostat/Galvanostat and Model 175 Universal Programmer, in conjunction with a Houston Instruments RE-0089 X-Y Recorder. Cyclic voltammograms were obtained in the drybox at approximately 25 °C in either dichloromethane (distilled twice from calcium hydride) containing ~0.1 M $[N(n\text{-}Bu)_4][PF_6]$ as supporting electrolyte. $E^{1/2}$ values are referenced to Ag/Ag^+ and uncorrected for junction potentials.

Preparation of Complexes. $WCp^*Me_3(OTf)$. Triflic acid (1.50 g, 10 mmol) in 20 mL of diethyl ether was added to a stirred solution of WCp^*Me_4 (3.79 g, 10 mmol) in diethyl ether (20 mL). Gas evolved, and an orange solid began to precipitate. The reaction mixture was stirred at room temperature for 30 min and then cooled to –40 °C. The orange solid was filtered off, washed with cold pentane, and dried in vacuo: yield of $WCp^*Me_3(OTf)$ 4.28 g (83%). The product may be recrystallized from diethyl ether at –40 °C: ^1H NMR (C_6D_6) δ 38 (v br, C_5Me_5); EPR (C_6D_6) $g = 1.985$ $\Delta\nu_{1/2} = 40$ G. Anal. Calcd for $WC_{14}H_{24}F_3O_3S$: C, 32.76; H, 4.71. Found: C, 32.81; H 4.79.

$[WCp^*Me_3]_2(\mu\text{-}N_2)$ (1). (a) From $WCp^*Me_3(NNH_2)$ and $[WCp^*Me_4]^+PF_6^-$. $WCp^*Me_3(NNH_2)$(0.2 g, 0.51 mmol) and $[WCp^*Me_4]^+PF_6^-$ (1 equiv) were stirred together in 15 mL of ether for 12 h. The mixture was filtered, and the ether was removed in vacuo to give a 57% yield of **1**. The crude product was recrystallized from pentane at –30 °C: ^1H NMR (C_6D_6) δ 1.63 (s, 5, C_5Me_5), 1.0 (s, 2, WMe), 0.66 (s, 1, WMe). Anal. Calcd for $WC_{13}H_{24}N$: C, 41.29; H, 6.40; N, 3.70. Found: C, 41.09; H, 6.41; N, 3.81.

(b) From "WCp^*Me_3Cl". WCp^*Me_4 (0.42 g, 1.1 mmol) and WCp^*Cl_4 (0.17 g, 0.37 mmol) were stirred together in dichloromethane for 12 h. The solvent was removed in vacuo to give a red solid. This solid was extracted with THF, and the solution was filtered. The solution was placed in a glass pressure vessel, and 0.41% Na/Hg (8.3 g, 1.48 mmol) was added. The solution was pressurized to 40 psi with N_2 and stirred for 12 h. The solvent was removed in vacuo, and the solid residue was extracted with pentane and filtered. The mixture was filtered, and the solvent was removed from the filtrate to yield 0.3 g of a red solid. Recrystallization from cold pentane gave 0.05 g of **1** (5%).

(c) From $WCp^*Me_3(CH_2)$ and $WCp^*Me_3(NNH_2)$. $WCp^*Me_3(NNH_2)$[13a] (0.276 g) was dissolved in 10 mL of dichloromethane at –78 °C. The resulting solution was added to a solution of $WCp^*Me_3(CH_2)$ prepared in situ from $[WCp^*Me_4]^+PF_6^-$ (0.367 g, 0.7 mmol) and triethylamine (0.15 mL, ca. 1 mmol) in dichloromethane (10 mL) at –78 °C.[15] The reaction mixture was allowed to warm to room temperature (~30 min) and was stirred for an additional 30 min. The solvent was removed in vacuo leaving a red solid which was recrystallized from pentane to give **1** (0.297 g, 56%).

(d) From WCp^*Me_5. $[WCp^*Me_4]^+PF_6^-$ (1.75 g, 3.34 mmol) in ether (25 mL) was treated with MeLi (~7 mL of a 0.48 M solution in ether) to form a red solution of WCp^*Me_5.[15] Hydrazine (1.5 mL, 46 mmol) was added, and a pale precipitate formed (presumed to be $LiPF_6$). The reaction mixture was protected from light, stirred for 45 h at room temperature, and filtered through a plug of alumina and Celite. The solvent was removed from the filtrate in vacuo to give a red-brown residue that was extracted with a 1:1 mixture of pentane and ether. The extract was filtered, and the solvent was removed in vacuo to yield **1** (0.895 g, 71%).

(e) From $WCp^*Me_3(OTf)$. A solution of $WCp^*Me_3(OTf)$ (1.03 g, 2 mmol) was cooled to –40 °C in 50 mL of ether. At this temperature most of the $WCp^*Me_3(OTf)$ crystallized out of solution. Na/Hg (0.5%) (9.5 g, ~2 mmol of sodium) was added to the cold, stirred mixture. The mixture was stirred for 2 h and allowed to warm up to room temperature. The reaction mixture was filtered, and the solvent was removed in vacuo. The resulting red solid was extracted with toluene, the solution was filtered, and the toluene was removed from the filtrate in vacuo to yield **1** (0.64 g, 84%). Yields can be as high as 90%.

$[WCp^*Me_3]_2(\mu\text{-}^{15}N_2)$. A solution of $WCp^*Me_3(OTf)$ (1.03 g, 2 mmol) in 50 mL of ether was placed in a three-necked flask in the drybox. Na/Hg (0.5%) (9.5 g, ca. 2 mmol sodium) was placed in a side-arm attached to the flask. The apparatus was brought out of the box and placed on a high vacuum line. All $^{14}N_2$ gas was removed from

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the WCp*Me$_3$(OTf) solution by freeze–pump thawing the reaction flask at least 4 times. $^{15}N_2$ gas (99.4% ^{15}N) was then allowed into the reaction vessel. Na/Hg was added to the stirred mixture. See Table IV for ^{15}N NMR data.

[WCp*Me$_2$Cl]$_2$(μ-N$_2$) (2a). [WCp*Me$_3$]$_2$(μ-N$_2$) (0.290 g, 0.38 mmol) in 10 mL of ether was treated with ~4 mL of ether that had been saturated with HCl. An orange precipitate formed immediately. The reaction mixture was stirred at −78 °C for 20 min and then allowed to warm as volatiles were removed in vacuo. The solid orange residue was washed with pentane and dried in vacuo; yield 0.2 g (66%). The solid was recrystallized from a mixture of chloroform and pentane to yield orange-brown plates: ^{1}H NMR (CDCl$_3$) δ 2.00 (s,15,C$_5$Me$_5$), 1.03 (s,6,WMe); ^{13}C{^{1}H} (CDCl$_3$) δ 113.6 (*C*$_5$Me$_5$) 38.4 (WMe), 10.6 (C$_5$*Me*$_5$). Anal. Calcd for $WC_{12}H_{21}ClN$: C, 36.16; H, 5.31; N, 3.51. Found: C, 35.80; H, 5.33; N, 3.49.

[WCp*Me$_2$(OTf)]$_2$(μ-N$_2$) (2b). An ether (5 mL) solution of [WCp*Me$_3$]$_2$(μ-N$_2$) (0.171 g, 0.23 mmol) was cooled to −40 °C, and triflic acid (0.070 g, 2.1 equiv) in 5 mL of cold ether was added. As the reaction mixture was warmed to room temperature, an orange-brown precipitate formed. After 30 min the reaction mixture was cooled to −40 °C. The solid precipitate was filtered off, washed with ether, and dried in vacuo: yield 0.186 g (78%). The crude product was recrystallized from a minimum amount of dichloromethane: ^{1}H NMR (CDCl$_3$) δ 2.10 (s, 30, C$_5$Me$_5$), 1.15 (s, 12, WMe); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 117.2 (*C*$_5$Me$_5$), 42.6 (WMe), 11.1 (C$_5$*Me*$_5$); ^{19}F NMR (CDCl$_3$) δ −78.4. Anal. Calcd for $WC_{13}H_{21}F_3NO_3S$: C, 30.48; H, 4.13; N, 2.73. Found: C, 30.55; H, 4.34; N, 2.82.

[WCp*Me(OTf)$_2$]$_2$(μ-N$_2$) (3a). A suspension of triflic acid (0.693 g, 4.62 mmol) in 10 mL of dichloromethane was added to a solution of **1** (0.582 g, 0.77 mmol) in 10 mL of dichloromethane. Gas evolved and a copper-colored precipitate formed slowly. The reaction mixture was stirred for 12 h, and 20 mL of ether was added. The reaction mixture was filtered, and the solid product was washed with ether and was dried in vacuo: yield 0.772 g (78%). Anal. Calcd for $WC_{13}H_{18}F_6NO_6S_2$: C, 24.16; H, 2.81; N, 2.17. Found: C, 24.14; H, 2.97; N, 2.88. The complex is too insoluble in noncoordinating solvents to be spectroscopically characterized.

{[WCp*Me(CH$_3$CN)$_2$]$_2$(μ-N$_2$)}$^{4+}$(OTf$^-$)$_4$ (3b). Acetonitrile (0.5 mL) was added to a suspension of [WCp*Me(OTf)$_2$]$_2$(μ-N$_2$) (0.129 g, 0.1 mmol) in 5 mL of dichloromethane to give a homogeneous orange-red solution. Ether was layered on top of the solution, and the two layers were allowed to diffuse together as the mixture was cooled to −40 °C. Red crystals formed. The crystals were redissolved in a mixture of dichloromethane (3 mL) and acetonitrile (0.25 mL). The solution was cooled to −40 °C, and red crystals formed, were filtered off, washed with ether, and dried in vacuo: yield 0.121 g (83%): ^{1}H NMR (CD$_3$CN) δ 2.86 (d, 12, bound CH$_3$CN), 1.90 (s, 30, C$_5$Me$_5$), 1.27 (s, 6, WMe). The resonance at 2.86 ppm gradually decreased in intensity over a period of weeks at room temperature as a resonance for free acetonitrile at 1.97 ppm grew in as coordinated acetonitrile slowly exchanged with deuterated acetonitrile solvent: ^{1}H NMR (CD$_2$Cl$_2$) δ 2.99 (s, 12, CH$_3$CN), 1.96 (s, 30, C$_5$Me$_5$), 1.37 (s, 6, WMe); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 138.7 (CH$_3$*C*N), 107.0 (*C*$_5$Me$_5$), 50.8 (WMe), 10.5 (C$_5$*M*e$_5$), 5.3 (*C*H$_3$CN).

[WCp*Me$_2$(O$_2$CC$_6$F$_5$)]$_2$(μ-N$_2$) (2c). A suspension of pentafluorobenzoic acid (0.127 g, 0.6 mmol) in 5 mL of pentane was stirred, while a solution of **1** (0.227 g, 0.3 mmol) in 15 mL of pentane was added. A precipitate formed slowly. After 16 h the solid precipitate was washed with pentane until the washings were almost colorless. The remaining yellow solid was dried in vacuo: yield 0.12 g (35%). The solid can be recrystallized from a mixture of dichloromethane and pentane: ^{1}H NMR (C$_6$D$_6$) δ 1.78 (s, 30, C$_5$Me$_5$), 1.29 (s, 12, WMe); ^{19}F NMR (C$_6$D$_6$) δ −142.2 (m, C$_6$F$_5$COO), −155.7 (m, C$_6$F$_5$COO), −162.9 (m, C$_6$F$_5$COO); ^{13}C NMR (CD$_2$Cl$_2$) δ 291.5 (s, C$_6$F$_5$*C*OO), 159.1 (s, C$_{ipso}$), 144.4 (d, *C*$_6$F$_5$COO), 141.4 (d, *C*$_6$F$_5$COO), 137.8 (d, *C*$_6$F$_5$COO), 115.6 (s, *C*$_5$Me$_5$), 34.8 (q, WMe), 11.0 (q, C$_5$*Me*$_5$). Anal. Calcd for $WC_{19}H_{21}F_5NO_2$: C, 39.74; H, 3.69; N, 2.44. Found: C, 39.56; H, 3.86; N, 2.52.

[WCp*Me$_2$(OC$_6$F$_5$)]$_2$(μ-N$_2$) (2d). (a) From [WCp*Me$_3$]$_2$(μ-N$_2$). A solution of **1** (0.087 g, 0.115 mmol) in 6 mL of dichloromethane was stirred, while a solution of C$_6$F$_5$OH (0.085 g, 4 equiv) in 4 mL of dichloromethane was added. The reaction mixture was stirred for 12 h. The solvent was then removed in vacuo, and the red solid was washed with ether: yield 0.06 g (50%). The product can be recrystallized from a mixture of dichloromethane and pentane: ^{1}H NMR (CD$_2$Cl$_2$) δ 2.07 (s, 15, C$_5$Me$_5$), 0.71 (s, 6, WMe); ^{19}F NMR (CD$_2$Cl$_2$) δ −162.80 (dd, 2, F$_0$), −168.89 (t, 2, F$_m$), −178.11 (tt, 1, F$_p$). Anal. Calcd for $WC_{18}H_{21}F_5NO$: C, 39.58; H, 3.87; N, 2.56. Found: C, 39.33; H, 3.96; N, 2.61.

(b) From [WCp*Me$_2$(OTf)]$_2$(μ-N$_2$). A suspension of [WCp*Me$_2$(OTf)]$_2$(μ-N$_2$) (0.03 g, 0.03 mmol) was stirred in 4 mL of diethyl ether as an ether solution of NaOC$_6$F$_5$ (0.013 g, 2.1 equiv) was added. The resulting solution was stirred for 3 h, NaOTf was filtered off, and ether was removed from the filtrate in vacuo to give a red powder. The red powder was recrystallized from a minimum amount of CH$_2$Cl$_2$ layered with pentane.

[WCp*Me$_2$(TIPT)]$_2$(μ-N$_2$) (2g). (a) From [WCp*Me$_2$(OTf)]$_2$(μ-N$_2$). A suspension of [WCp*Me$_2$(OTf)]$_2$(μ-N$_2$) (0.149 g, 0.146 mmol) was stirred in 5 mL of diethyl ether as an ether solution of LiTIPT (0.074 g, 2.1 equiv) was added. The resulting solution was stirred for 30 min, LiOTf was filtered off, and ether was removed from the filtrate in vacuo to give a red powder, yield 87%: ^{1}H NMR (C$_6$D$_6$) δ 7.20 (s, 4, H$_m$), 3.50 (br, 4, C*H*Me$_2$), 2.75 (br, 2, C*H*Me$_2$), 1.74 (s, 30, Cp*), 1.42 (br, 6, WMe), 0.70 (br, 6, WMe); ^{1}H NMR (CD$_2$Cl$_2$) δ 6.91 (s, 4, H$_m$), 3.40 (br, 2, C*H*Me$_2$), 3.05 (br, 4, C*H*Me$_2$), 1.97 (s, 30, Cp*), 1.24 (s, 24, CH*Me*$_2$), 1.23 (s, 12, CH*Me*$_2$), 1.09 (br, 6, WMe), 0.30 (br, 6, WMe). The low-temperature limit spectrum (CD$_2$Cl$_2$, 500 MHz) was obtained at −40 °C; δ 6.89, 6.88 (TIPT, H$_m$, 4:1 ratio), 3.35 (br, sept, 2, C*H*Me$_2$), 2.95 (br, sept, 2, C*H*Me$_2$), 2.83 (sept, 2, C*H*Me$_2$), 1.95, 1.92 (s, 30, Cp*, 4:1 ratio), 1.05, 1.00 (4:1 ratio, each resonance is split into two, WMe), 0.27, 0.19 (1:4 ratio, WMe). Anal. Calcd for $WC_{27}H_{44}SN$: C, 54.18; H, 7.41; N, 2.34; S, 5.36. Found: C, 53.88; H, 7.22; N, 2.35; S, 5.41.

(b) From [WCp*Me$_2$Cl]$_2$(μ-N$_2$). [WCp*Me$_2$Cl]$_2$(μ-N$_2$) (0.055 g, 0.069 mmol) was suspended in 10 mL of ether. A solution of LiTIPT (0.036 g, 0.15 mmol) in 5 mL of ether was added to the stirred suspension. After 40 min the reaction mixture was filtered, and the solvent was removed in vacuo. The resulting orange residue was recrystallized from a minimum amount of ether layered with pentane: yield 0.027 g (33%).

[WCp*Me$_2$(SMes)]$_2$(μ-N$_2$) (2f). [WCp*Me$_2$(OTf)]$_2$(μ-N$_2$) (0.20 g, 0.195 mmol) was suspended in 30 mL of ether. NaSMes (0.065 g, 2.1 equiv) in a mixture of 12 mL of ether and 2 mL of THF was added all at once to the stirred suspension. The resulting red-orange solution was filtered after 45 min, and ether was removed from the filtrate to leave a red-brown solid that was recrystallized from a mixture of ether and pentane, yield 0.125 g (63%): ^{1}H NMR (C$_6$D$_6$) δ 6.95 (s, 4, H$_m$), 2.54 (s, 12, Me$_0$), 2.24 (s, 6, Me$_p$), 1.70 (s, 30, Cp*), 1.0 (br, 12, WMe); ^{1}H NMR (CD$_2$Cl$_2$) 6.84 (s, 4, H$_m$), 2.27 (s, 6, Me$_p$), 2.18 (s, br, 12, Me$_0$), 1.96 (s, C$_5$Me$_5$), 0.50 (br, 12, WMe). ^{1}H variable temperature data were collected on the 300 MHz NMR in CD$_2$Cl$_2$ and toluene-d_8. The low-temperature limit spectrum was obtained at −60 °C (CD$_2$Cl$_2$) δ 6.82, 6.75, (s, phenyl H's, 2:1 ratio), 2.24, 2.22, (s, 6 H, mesityl, 1:2 ratio), 2.08, 2.06 (s, 12 H, mesityl, 2:1 ratio), 1.91, 1.89, (s, 30 H, C$_5$Me$_5$, peaks too close to determine ratio; assume 2:1), 0.99, 0.94 (s, 6 H, WMe, 1:2 ratio), 0.04, −0.06, (s, 6 H, WMe, 1:2 ratio); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) 142.2 (s, C$_{ipso}$), 134.8 (d, *C*$_6$H$_2$ (CH$_3$)$_3$), 129.0 (*C*$_6$H$_2$ (CH$_3$)$_3$), 127.0 (*C*$_6$H$_2$ (CH$_3$)$_3$), 113.0 (s, *C*$_5$Me$_5$), 30.6 (q, *o*-C$_6$H$_2$ (*CH*$_3$)$_3$), 23.2 (br, WMe), 20.9 (q, *p*-C$_6$H$_2$ (*CH*$_3$)$_3$), 11.4 (q, C$_5$*Me*$_5$). Anal. Calcd for $WC_{21}H_{32}SN$: C, 49.03; H, 6.27; S, 6.23; N, 2.72. Found: C, 49.34; H, 6.41; S, 5.99; N, 2.74.

[WCp*Me$_2$(SC$_6$F$_5$)]$_2$(μ-N$_2$) (2c). [WCp*Me$_3$]$_2$(μ-N$_2$) (0.15 g, 0.2 mmol) was dissolved in 20 mL of dichloromethane. A solution of C$_6$F$_5$SH (0.159 g, 0.79 mmol) in methylene chloride (10 mL) was added. After 16 h the solvent was removed from the reaction mixture, leaving a dark red solid that was recrystallized from dichloromethane layered with pentane at −40 °C, recrystallized yield 0.18 g (58%): ^{1}H NMR (CD$_2$Cl$_2$) δ 1.99 (C$_5$Me$_5$), 0.74 (WMe); ^{19}F (CD$_2$Cl$_2$) δ −132.6 (dd, 2, F$_0$), −159.45 (t, 1, F$_p$), −164.65 (td, 2, F$_m$). Anal. Calcd for $WC_{18}H_{21}SF_5N$: C, 38.45; H, 3.76; N, 2.49; S, 5.70. Found: C, 38.32; H, 3.83; N, 2.59; S, 5.90.

[WCp*Me(O$_2$C$_6$Br$_4$)]$_2$(μ-N$_2$) (4b). [WCp*Me$_3$]$_2$(μ-N$_2$) (0.06 g, 0.079 mmol) was dissolved in 8 mL of dichloromethane, and a solution of tetrabromocatechol (0.071 g, 2.1 equiv) in 4 mL of dichloromethane was added. After 2 h the solvent was removed in vacuo to yield a red-black solid. Crystals were obtained from dichloromethane layered with pentane, recrystallized yield 0.077 g (62.5%): ^{1}H NMR (CD$_2$Cl$_2$) δ 2.05 (Cp*), 2.02 (Cp*), 1.27 (WMe), 1.22 (WMe). Due to the insolubility of this complex it was not possible to obtain a ^{13}C{^{1}H} NMR spectrum. Anal. Calcd for $WC_{17}H_{18}O_2Br_4N$: C, 26.46; H, 2.35; N, 1.81. Found: C, 26.63; H, 2.54; N, 1.79.

[WCp*Me(O$_2$C$_6$F$_{12}$)]$_2$(μ-N$_2$) (4a). A solution of [WCp*Me(OTf)$_2$]$_2$(μ-N$_2$) (0.043 g, 0.033 mmol) in 7 mL of diethyl ether was cooled to −40 °C, and Li$_2$PFP (PFP = perfluoropinacolate) (0.024 g, 2.1 equiv) in 2 mL of cold ether was added. The mixture was stirred for 8–10 min or until all starting material dissolved. Solvent was removed in vacuo, and the resulting solid was recrystallized from a minimum amount of diethyl ether layered with pentane to yield red-black, shiny crystals: ^{1}H NMR (CD$_2$Cl$_2$) δ 2.08 (Cp*), 1.24 (WMe).

{[WCp*Me$_2$(CH$_3$CN)]$_2$(μ-N$_2$)}$^{2+}$(BF$_4^-$)$_2$. [WCp*Me$_3$]$_2$(μ-N$_2$) (0.042 g, 0.056 mmol) was cooled to −35 °C in 4 mL of diethyl ether and CH$_3$CN (approximately 50 equiv). HBF$_4$·OEt$_2$ (12.8 μL, 2.1 equiv) was added to the cold, stirring solution. A red solid precipitate formed almost immediately. The mixture was stirred for 5 min. The solid was isolated and dried in vacuo: ^{1}H NMR (CD_2Cl_2) δ 2.51 (br, 3, CH_3CN), 2.2 (s, 15, C_5Me_5), 1.2 (s, 6, WMe); ^{13}C NMR (CD_2Cl_2) δ 117.4 (C_5Me_5), 110.2 (CH_3CN), 33.4 (WCH_3), 11.3 ($C_5\mathit{Me}_5$), 4.25 ($\mathit{C}H_3CN$).

X-ray Crystal Structure of $[WCp^*Me_2SMes]_2(\mu\text{-}N_2)$ (2f). Data were collected at −65 °C on an Enraf-Nonius CAD4 diffractometer equipped with a liquid nitrogen low-temperature device and using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). A total of 21 931 reflections were collected, 7188 of which were unique. Equivalent reflections were merged. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time declined by 28%. A linear correction factor was applied to the data to account for this phenomenon. The structure was solved by direct methods.[23] Refinement was by full-matrix least squares using TEXSAN. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å). Final R_1 = 0.050 and R_2 = 0.067. Crystal data can be found in Table I.

X-ray Crystal Structure of $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ (2d). Data were collected at 23 °C on a Rigaku AFC6 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and a 12 KW rotating anode generator. A total of 4476 reflections were collected, 4209 of which were unique. Equivalent reflections were merged. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability. Therefore, no decay correction was applied. The structure was solved by the Patterson method. Refinement was by full-matrix least squares using TEXSAN. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å). Final R_1 = 0.057 and R_2 = 0.077. Crystal data can be found in Table I.

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Registry No. 1, 96999-48-3; **2a**, 126017-96-7; **2b**, 126017-97-8; **2c**, 126018-01-7; **2d**, 126018-02-8; **2e**, 126018-05-1; **2f**, 126018-04-0; **2g**, 126018-03-9; **3a**, 126017-98-9; **3b**, 126018-00-6; **4a**, 126035-21-0; **4b**, 126018-06-2; $WCp^*Me_3(OTf)$, 126017-94-5; WCp^*Me_4, 96055-89-9; $[WCp^*Me_4]^+PF_6^-$, 96999-45-0; $WCp^*Me_3(NNH_2)$, 96999-47-2; WCp^*Cl_4, 96055-85-5; $WCp^*Me_3(CH_2)$, 108713-51-5; WCp^*Me_5, 108713-47-9; $[WCp^*Me_3]_2(\mu\text{-}^{15}N_2)$, 126017-95-6; $\{[WCp^*Me_2(CH_3CN)]_2(\mu\text{-}N_2)\}^{2+}(BF_4^-)_2$, 126018-08-4; ^{15}N, 14390-96-6.

Supplementary Material Available: A fully labeled drawing and an ORTEP drawing and tables of final positional parameters and anisotropic thermal parameters for $[WCp^*Me_2(OC_6F_5)]_2(\mu\text{-}N_2)$ and $[WCp^*Me_2(SMes)]_2(\mu\text{-}N_2)$ (16 pages); tables of observed and calculated structure factors (72 pages). Ordering information is given on any current masthead page.

Preparation and Characterization of Two High Oxidation State Molybdenum Dinitrogen Complexes: $[MoCp^*Me_3]_2(\mu\text{-}N_2)$ and $[MoCp^*Me_3](\mu\text{-}N_2)[WCp'Me_3]$

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Abstract: $[MoCp^*Cl_4]_2$ ($Cp^* = C_5Me_5$) is alkylated by MeMgCl in tetrahydrofuran to give red microcrystalline $MoCp^*Me_4$ in ~70% yield. $MoCp^*Me_4$ reacts with 1 equiv of $HOSO_2CF_3$ in ether to give purple microcrystalline $MoCp^*Me_3(OSO_2CF_3)$ in ~85% yield. Triflate can be displaced readily from $MoCp^*Me_3(OSO_2CF_3)$ by adding LiOR (OR = pentafluorophenoxide, 2,6-diisopropylphenoxide, 2,6-dimethoxyphenoxide, 2,4,6-trimethoxyphenoxide, 2,6-dimethyl-4-methoxyphenoxide, and catecholate) in ether to yield complexes of the type $MoCp^*Me_3(OR)$ ($MoCp^*Me_2(cat)$ in the case of catecholate) in 50–80% yield. Cyclic voltammograms of the $MoCp^*Me_3(OR)$ complexes display quasi-reversible oxidation waves in the region 0.29 to −0.50 V, and the complexes can be oxidized chemically (with the exception of OR = pentafluorophenoxide and catecholate) by $[FeCp_2][PF_6]$ in methylene chloride to give complexes of the type $[MoCp^*Me_3(OR)][PF_6]$ as orange-brown microcrystalline powders in 80–90% yield. Addition of 3 equiv of hydrazine to $[MoCp^*Me_3(OR)][PF_6]$ in ether provides $[MoCp^*Me_3]_2(\mu\text{-}N_2)$ in low yield after purification by filtration through alumina and recrystallization from ether. $[MoCp^*Me_3]_2(\mu\text{-}N_2)$ belongs to the space group $P2_1/n$ with a = 12.895 (5) Å, b = 16.443 (6) Å, c = 14.556 (5) Å, β = 115.87 (3)°, V = 2777 (4) Å^3, Z = 4. Final R = 0.032 and R_w = 0.043. It contains two pseudo-square-pyramidal molybdenum atoms (axial Cp*), one of which is twisted by ~90° with respect to the other. Mo–N–N angles are nearly linear (176.7 (2)° and 172.0 (2)°), Mo–N bonds are fairly short (1.819 (2) Å and 1.821 (3) Å), and N–N is 1.236 (3) Å. $[MoCp^*Me_3](\mu\text{-}N_2)[WCp'Me_3]$ can be prepared by treating $WCp'Me_3(NNH_2)$ ($Cp' = C_5Me_4Et$) with $[MoCp^*Me_3(OR)][PF_6]$ in ether in the presence of NEt_3 and is isolated by recrystallization from ether/pentane; it is contaminated with $[WCp'Me_3]_2(\mu\text{-}N_2)$. $[MoCp^*Me_3](\mu\text{-}N_2)[WCp'Me_3]$ belongs to the space group $P2_1/n$ with a = 13.46 (2) Å, b = 16.46 (2) Å, c = 14.48 (2) Å, β = 116.92 (9)°, V = 2861 (6) Å^3, Z = 4. Final R = 0.031 and R_w = 0.043. The structure is nearly identical with that of $[MoCp^*Me_3]_2(\mu\text{-}N_2)$. It contains pseudo-square-pyramidal molybdenum and tungsten atoms (Cp* and Cp′ axial), one of which is twisted by ~90° with respect to the other. Mo–N(1)–N(2) and W–N(2)–N(1) are nearly linear at 176.6 (4) and 174.1 (4)°, respectively, Mo–N(1) and W–N(2) are 1.816 (5) and 1.816 (7) Å, respectively, and N(1)–N(2) is 1.235 (7) Å. Addition of excess acid to $[MoCp^*Me_3](\mu\text{-}N_2)[WCp'Me_3]$ in the presence of excess zinc amalgam converts 90% of the coordinated dinitrogen ligand into ammonia (1.80 equiv), whereas $[MoCp^*Me_3]_2(\mu\text{-}N_2)$ and $[WCp^*Me_3]_2(\mu\text{-}N_2)$ under similar conditions yield less than half of the of the available nitrogen as ammonia.

In the previous paper[1] we described some W=N—N=W complexes that contain a highly reduced bridging dinitrogen ("hydrazido(4−)") ligand with a relatively long N-N bond (~1.30 Å) and short W-N bonds (~1.75 Å),[2] including $[WCp^*Me_3]_2(\mu\text{-}N_2)$ and derivatives of the type $[WCp^*Me_2X]_2(\mu\text{-}N_2)$ (X = Cl, OSO_2CF_3, thiolate, phenoxide). Since molybdenum-containing nitrogenases are the most common and most active, and since calculations indicate that the Mo–N

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