Synthesis and Characterization of a Series of (Pentamethylcyclopentadienyl)tungsten(V) and -(VI) Amino, Amido, Imido, and Bridging Nitrido Complexes and Molybdenum Analogues

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Ammonia adds reversibly to $[Cp^*WMe_4]PF_6$ (1) to give unstable $[Cp^*WMe_4(NH_3)]PF_6$ (2), which is readily deprotonated to form $Cp^*WMe_4(NH_2)$ (**3a**). Excess methylamine reacts with 1 to give $Cp^*WMe_4(NHMe)$; bulkier amines such as *tert*-butylamine simply deprotonate 1. Aniline reacts with 1 to yield $[Cp^*WMe(NHPh)(NPh)]PF_6$ (**5**), which is readily deprotonated to give $Cp^*WMe(NPh)_2$. Reaction of $Cp^*WMe(NPh)_2$ with anhydrous triflic acid gives $Cp^*WMe(OTf)_2(NPh)$, whereas aqueous HCl yields $Cp^*WMe(O)_2$. $Cp^*WMe_3(NPh)$ is formed upon alkylation of $Cp^*WMe(OTf)_2(NPh)$. Ammonia adds to $Cp^*WMe_3(OTf)$ to form two isolable adducts, $[Cp^*WMe_3(NH_3)]OTf$ and $[Cp^*WMe_3(NH_3)_2]OTf$. Deprotonation of either yields $Cp^*WMe_3(NH_2)$ (**8**). Oxidation of 8 in the presence of a base yields $Cp^*WMe_3(NH)$ (**9a**). **9a** is deprotonated by alkyllithium reagents to give $[Cp^*WMe_3(NLi)]_x$ (**9b**), which reacts with water, MeOTf, or Me_3SiCl to give $Cp^*WMe_3(NR)$ (R = H, Me, $SiMe_3$), respectively. Protonation of **9a** or oxidation of 8 is proposed to form transient $[Cp^*WMe_3(NH_2)]^+$ (**4**), which decomposes to $\{[Cp^*WMe_3]_2(\mu\text{-}N)\}^+$ and NH_4^+. Molybdenum analogues that have been prepared include $[Cp^*MoMe_3(NH_3)]OTf$, $[Cp^*MoMe_3(NH_3)_2]OTf$, $Cp^*MoMe_3(NH_2)$, $Cp^*MoMe_3(NH)$, and $[Cp^*MoMe_3(NLi)]_x$.

Introduction

For more than 20 years inorganic chemists have been fascinated by the coordination chemistry of dinitrogen.[1] The likelihood that dinitrogen is bound and reduced at one or more transition metals in nitrogenase enzymes,[2-4] most efficiently in those that contain molybdenum,[2] suggests that it should be possible to reduce dinitrogen under mild conditions using nonbiological transition metal catalysts. There are several reports in the literature of catalytic reduction of dinitrogen using relatively strong reducing agents.[5]

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.[6] The traditional explanation is that back-bonding to molecular nitrogen thereby is maximized. Complexes of the type $M(N_2)_2L_4$ (M = Mo or W; L = phosphine) contain dinitrogen ligands with N-N bonds only slightly longer than that in unbound N_2 (1.0976 Å).[7] The nitrogen ligand in these complexes can be protonated by strong acids to yield either hydrazido(2-) species[8] (M = NNH_2), or less than stoichiometric amounts of ammonia and hydrazine, the ratio depending on the complex and reaction conditions.[9]

In contrast, the chemistry of relatively high oxidation state dinitrogen complexes (d^0 to d^2) is in its infancy. Among the earliest "high oxidation state" dinitrogen complexes are those of the type $[Cp^*_2M(N_2)]_2(\mu\text{-}N_2)$ (Cp^* = η^5-C_5Me_5; M = Ti(II),[10a] Zr(II),[10b] and Hf(II)[10c]). Bimetallic complexes such as $(PMe_2Ph)_4ClRe(\mu\text{-}N_2)MCl_4(OMe)$ are known in which Re, in a relatively low oxidation state, and M = W or Mo, in a relatively high oxidation state, are both bound to a bridging dinitrogen ligand.[6a,d] More recently, μ-dinitrogen complexes of niobium(V) or tantalum(V) have been synthesized that contain a dinitrogen ligand in a highly reduced hydrazido(4-) state (N_2^{4-}),[11] as evidenced

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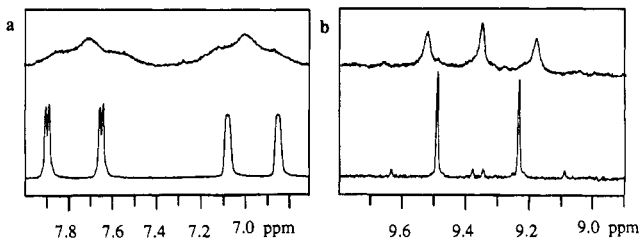

Figure 1. ^1H NMR of ^{14}N (top) and ^{15}N (bottom) isotopomers of (a) $Cp^*WMe_4(NH_2)$ (**3a**) and (b) $Cp^*WMe_3(NH)$ (**9a**).

by the relatively long N–N bonds (~1.30 Å).[12] Most recently, it has been found that reduction of $Cp^*WMe_3(OTf)$ (OTf = OSO_2CF_3) under molecular nitrogen yields $[Cp^*WMe_3]_2(\mu\text{-}N_2)$, a hydrazido(4–) complex, in greater than 90% yield.[13a] The proposed mechanism involves activation of dinitrogen by "Cp^*WMe_3" to give "$Cp^*WMe_3(N_2)$", followed by rapid electrophilic attack on coordinated dinitrogen by $Cp^*WMe_3(OTf)$ and reduction of "$\{[Cp^*WMe_3]_2(\mu\text{-}N_2)\}^{+}$" to $[Cp^*WMe_3]_2(\mu\text{-}N_2)$.[13a]

$[Cp^*WMe_3]_2(\mu\text{-}N_2)$ reacts with relatively acidic phenols (C_6H_5OH) and strong acids (CF_3SO_3H or HCl) to give derivatives of the type $[Cp^*WMe_2X]_2(\mu\text{-}N_2)$ (X = Cl, SO_3CF_3, etc.) and can be reduced to give ammonia in moderate yields (~50%) in the presence of [(2,6-lutidine)H]Cl.[13b] The mechanism of reduction is believed to consist of hydrolysis of one end of the molecule to give $Cp^*WMe_3(NNH_2)$, a known species that can be reduced in the presence of protons to give ammonia in greater than 90% yield.[14] $Cp^*Me_3W{=}N{-}N{=}MoCp^*Me_3$ also is reduced in the presence of an excess of protons to give nearly 2 equiv of ammonia, but it is known to react readily with water to give $Cp^*WMe_3(NNH_2)$.[15] An important intermediate in the reduction of $Cp^*WMe_3(NNH_2)$ is proposed to be the as yet unobserved $Cp^*WMe_3(NH_2NH_2)$, which decomposes to give ammonia and $Cp^*WMe_3(NH)$.[14] In fact, hydrazine can be reduced catalytically to ammonia in the presence of protons by a variety of complexes, including $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]^+$.[14] Therefore the search for a functional model for dinitrogen reduction is centered on monometallic species having the "Cp^*WMe_3" core.

The final steps in the reduction of $Cp^*WMe_3(NNH_2)$ must involve imido, amido, and amino complexes, e.g., $Cp^*WMe_3(NH)$, $Cp^*WMe_3(NH_2)$, and $[Cp^*WMe_3(NH_3)]^+$. Therefore some knowledge is required of the chemistry of these potential intermediates and related substituted derivatives. The parent (NH_x) species are of interest in their own right because of the paucity of high oxidation state complexes that contain unsubstituted NH_x ligands.[16] In this paper we report the synthesis and characterization of a variety of amino, amido, imido, and nitrido complexes that contain the "Cp^*MM_x" core (M = W, x = 3 or 4, or M = Mo, x = 3). The chemistry of related N_2H_x and $N_2H_xR_y$ species will be reported separately.

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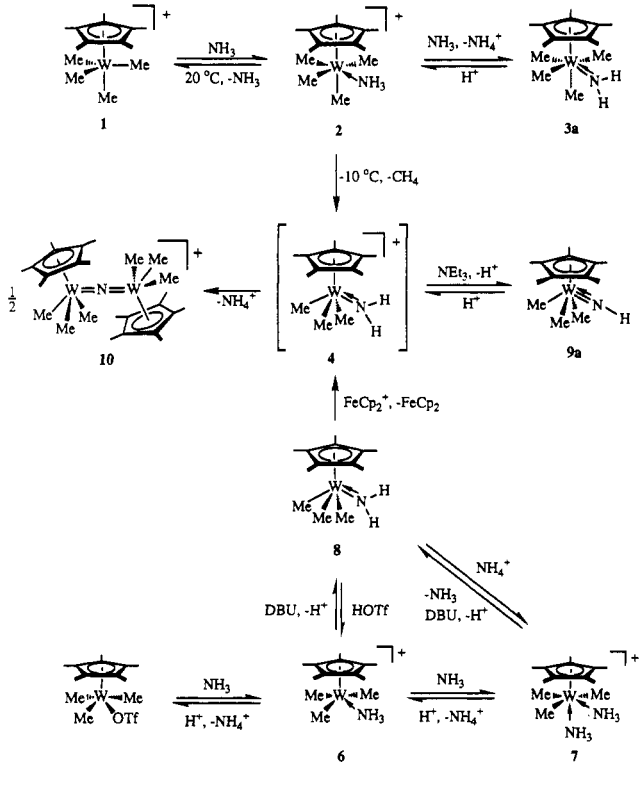
Scheme I



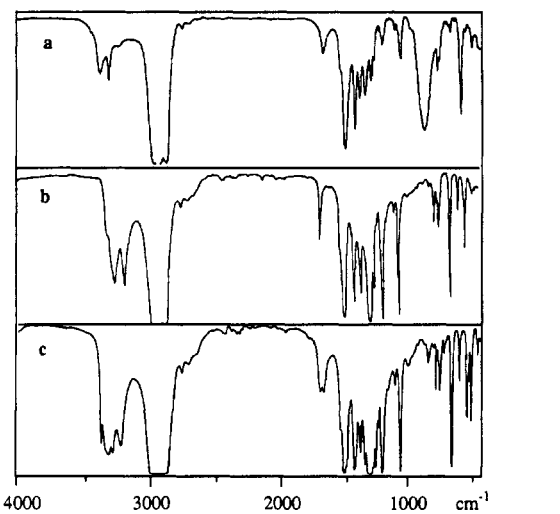


Figure 2. Infrared spectra of (a) $[Cp^*WMe_4(NH_3)]PF_6$ (**2**), (b) $[Cp^*WMe_3(NH_3)]OTf$ (**6**), and (c) $[Cp^*WMe_3(NH_3)_2]OTf$ (**7**).

Results

Reactions between $[Cp^*WMe_4]PF_6$ and Amines. $[Cp^*WMe_4]PF_6$ (**1**) reacts with DBU (1,8-diazobicyclo-[5.4.0]undec-7-ene, $pK_b < 0$) or $NH_2(t\text{-}Bu)$ (pK_b = 3.32) at low temperature to afford the unstable methylene complex $Cp^*WMe_3(CH_2)$.[17] However, ammonia coordinates reversibly to **1** in solution to give $[Cp^*WMe_4(NH_3)]PF_6$ (**2**, Scheme I) and then deprotonates **2** below room temperature to yield yellow crystalline $Cp^*WMe_4(NH_2)$ (**3a**). **2** can be prepared in a reaction between solid **1** and gaseous ammonia in vacuo; its IR spectrum (Figure 2a) is very similar to that of other ammonia adducts described later. A solution of **2** evolves methane at room temperature to give what we propose to be transient

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Table I. IR and ^{15}N NMR Spectroscopic Data for Related Tungsten Imido and Amido Complexes[a]

compd	ν(WNR)	ν(W^{15}NR)	$\Delta\nu$	δ(W^{15}N)	$^1J_{NW}$
Cp*WMe$_3$(NH)[b] (**9a**)	939	914	25	388.0	113
Cp*WMe$_3$(ND)[b]	910				
Cp*WMe$_3$(NCH$_3$) (**9c**)	1315	1283	32	387.7	115
Cp*WMe$_3$(N^{13}CH$_3$)	1301				
[Cp*WMe$_3$(NLi)]$_x$ (**9b**)	993	968	25	678.5	54
Cp*WMe$_3$(NSiMe$_3$) (**9d**)	1147	1116	31	454.3	88
Cp*WMe$_3$(NPh) (**9e**)	1364	1341	23	394.4	113
[Cp*WMe(NPh)-(NHPh)]PF$_6$ (**5**)	1350	1327	23	380.0	128
				264.9	74
Cp*WMe(NPh)$_2$[c]	1342	1320	22	380.7	121
Cp*WMe(OTf)$_2$(NPh)				435.2	121
Cp*WMe$_3$(NH$_2$) (**8**)	632	612	20		
Cp*WMe$_4$(NH$_2$)[d] (**3a**)				210.6	45

[a] IR spectra obtained in KBr/Nujol mull; frequencies and isotopic shifts in cm^{-1}; resolution ±2 cm^{-1}. ^{15}N NMR spectra obtained at room temperature; chemical shifts in ppm downfield from liquid ammonia (0 ppm) and referenced to external ^{15}NH$_2$Ph (56.5 ppm); coupling constants in Hz. [b] In CCl_4 $\nu(^{14}NH)$ = 3438, $\nu(^{15}NH)$ = 3431, $\nu(^{14}ND)$ = 2558 cm^{-1}. [c] A second unassigned absorption shifts from 974 to 966 cm^{-1}. [d] $\nu(^{14}NH_2)$ = 3417 and 3340 cm^{-1}, $\delta(^{14}NH_2)$ = 1579 cm^{-1}; $\nu(^{15}NH_2)$ = 3410 and 3338 cm^{-1}; $\delta(^{15}NH_2)$ = 1567 cm^{-1}.

[Cp*WMe$_3$(NH$_2$)]PF$_6$ (**4**; Scheme I), a molecule that is discussed in the next section. Note that **2** is isoelectronic with Cp*WMe$_5$, and loss of methane from it may be related to the decomposition of Cp*WMe$_5$ to Cp*WMe$_3$(CH$_2$).[17] In each case an α-hydrogen abstraction process could be invoked. Addition of triflic acid to **2** yields **1**.

Good yields of **3a** (~85%) can be obtained if a large excess of ammonia is added to **1** in solution at room temperature while the solution is stirred vigorously. (Competing reactions (see later) cause problems if only stoichiometric amounts of ammonia are employed.) NMR and IR studies suggest that Cp*WMe$_4$(NH$_2$) (**3a**) is pseudooctahedral with an axial methyl group trans to the Cp* ligand. In the proton NMR spectrum, the two amido protons are inequivalent (7.77 and 6.96 ppm), each giving rise to a broadened triplet (Figure 1a top). In Cp*WMe$_4$(^{15}NH$_2$) two doublets are observed (Figure 1a bottom; $^1J_{H_aH_b}$ = 4.6 Hz, $^2J_{HW} \approx$ 9 Hz). The most accessible orbital for forming a W–N dative π-bond lies between the basal ligands in the square pyramid (~d_{xy}).[18] Therefore one amido proton probably points toward the Cp* ring, and the other points away. It is interesting to note that the amido proton that gives rise to the 6.96 ppm resonance in **3a**-^{15}**N** is coupled to protons in the axial methyl group by $^4J_{HH} \approx$ 1.5 Hz. In Cp*WMe$_4$(NHMe) (**3b**, see below) where the more sterically demanding alkyl group is believed to point away from the Cp* ring, no coupling between the NH proton and the axial methyl group is observed. Therefore, the amido proton that points away from the Cp* ring is believed to be the one coupled to the axial methyl group. In the ^{15}N NMR spectrum of **3a** the amido nitrogen resonance is found 210.6 ppm downfield of liquid ammonia with $^1J_{^{15}N^{183}W}$ = 45 Hz (Table I) and $^1J_{^{15}NH}$ = 75 and 69 Hz. The IR spectrum of **3a** has sharp absorptions at 3417, 3340, and 1579 cm^{-1} that are ascribed to asymmetric and symmetric NH$_2$ stretching modes and an NH$_2$ bending mode, respectively (Figure 3b). **3a** is remarkably stable; variable-temperature proton NMR spectra reveal no sign of decomposition or of rotation about the W–N bond up to 100 °C in pyridine-d_5. The decomposition that has been noted sporadically in solution at lower temperatures is believed to be catalyzed by traces of acid impurities. (See Scheme I and below.) Excess ^{15}NH$_3$ readily exchanges with **3a** to give **3a**-^{15}**N**. Addition of excess triflic acid to **3a** at room temperature yields **1** and ammonium triflate in high yield (77%), [Cp*WMe$_4$-(NH$_3$)]$^+$ most likely being formed initially.

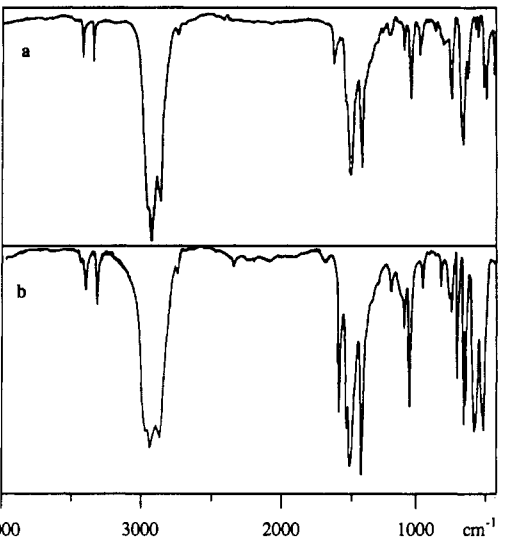

Figure 3. Infrared spectra of (a) Cp*WMe$_3$(NH$_2$) (**8**) and (b) Cp*WMe$_4$(NH$_2$) (**3a**).

Methylamine reacts with **1** to form Cp*WMe$_4$(NHMe) (**3b**, eq 1), probably via formation of [Cp*WMe$_4$(NH$_2$Me)]$^+$ followed by deprotonation by free amine. (Rapid deprotonation of **1** by NH$_2$-*t*-Bu,[17] even at −78 °C, might be

$$[Cp^*WMe_4]PF_6 \xrightarrow[-[NH_3Me]PF_6]{2\ NH_2Me} \underset{\mathbf{3b}}{\text{Cp*WMe}_4(NHMe)} \quad (1)$$

1

ascribed to an inability to form the initial cationic amine adduct.) On the basis of modeling studies (Chem 3D) the alkyl group in **3b** must point away from the Cp* ring in order to minimize steric interactions. NMR spectra of **3b** are invariant at temperatures up to 100 °C in pyridine-d_5.

Cp*WMe$_3$(NPh) is not formed upon adding aniline to [Cp*WMe$_4$]PF$_6$ (**1**). We presume that aniline will add to give [Cp*WMe$_4$(NH$_2$Ph)]PF$_6$ initially but that aniline is not small enough and sufficiently basic (p$K_b \approx$ 9.40) to deprotonate coordinated aniline before methane is lost to give [Cp*WMe$_3$(NHPh)]PF$_6$. At room temperature a second equivalent of aniline must then coordinate to [Cp*WMe$_3$(NHPh)]$^+$ and another 2 equiv of methane lost to yield yellow, crystalline [Cp*WMe(NPh)(NHPh)]PF$_6$ (**5**, eq 2) over a period of 2.5 h. ^{15}N NMR and IR data are

$$\underset{\mathbf{1}}{[Cp^*WMe_4]PF_6} \xrightarrow[-3CH_4]{2NH_2Ph} \underset{\mathbf{5}}{[Cp^*WMe(NPh)(NHPh)]PF_6} \xrightarrow[-[NEt_3H]PF_6]{NEt_3} Cp^*WMe(NPh)_2 \quad (2)$$

all consistent with the formulation of **5** (Table I). Bright orange Cp*WMe(NPh)$_2$ is formed quantitatively upon deprotonating **5** (eq 2). The imido ligands are equivalent on the NMR time scale and the chemical shift and coupling constants are in keeping with other imido compounds in which a W–N triple bond is suspected (Table I), although in valence bond terms it is not possible to form two pseudo triple W–N bonds in this circumstance (20-electron

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count). Addition of excess triflic acid to $Cp^*WMe(NPh)_2$ yields anilinium triflate and yellow $Cp^*WMe(OTf)_2(NPh)$ (eq 3). Yellow crystalline $Cp^*WMe_3(NPh)$ (**9e**), a member

$$Cp^*WMe(NPh)_2 \xrightarrow[-[NH_3Ph]OTf]{3HOTf} Cp^*WMe(OTf)_2(NPh) \xrightarrow[-2LiOTf]{2LiMe} Cp^*WMe_3(NPh) \quad (3)$$

of a class of molecules discussed later, was made by alkylating $Cp^*WMe(OTf)_2(NPh)$ (eq 3). ^{15}N NMR and IR data for $Cp^*WMe_3(NPh)$ are entirely those expected (Table I). Addition of aqueous acid to $Cp^*WMe(NPh)_2$ instead of anhydrous HOTf yields the known $Cp^*WMe(O)_2$ (eq 4).[19]

$$Cp^*WMe(NPh)_2 \xrightarrow[-2[NH_3Ph]Cl]{HCl/H_2O} Cp^*WMe(O)_2 \quad (4)$$

Reactions Involving Compounds Having the Cp^*WMe_3 Core. Compounds that contain the Cp^*WMe_3 core are more suitable than those that contain the Cp^*WMe_4 core for the reduction of dinitrogen, as demonstrated by the formation of $[Cp^*WMe_3]_2(\mu\text{-}N_2)$ from dinitrogen and $Cp^*WMe_3(OTf)$, as well as the ability of complexes such as $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]^+$ to catalytically reduce hydrazine to ammonia.[14] An important feature of complexes that contain the Cp^*WMe_3 core is that two coordination sites are available for stabilizing a variety of N_2H_x and NH_y ligands. A convenient starting material for complexes of this type is $Cp^*WMe_3(OTf)$.[13a] $Cp^*WMe_3(OTf)$ is believed to be a square-pyramidal complex, similar to that of the structurally characterized $(\eta^5\text{-}C_5Et_3Me_2)WMe_4$.[20]

$Cp^*WMe_3(OTf)$ reacts with ammonia to form two cationic adducts, yellow $[Cp^*WMe_3(NH_3)]OTf$ (**6**) or orange-red $[Cp^*WMe_3(NH_3)_2]OTf$ (**7**, Scheme I). ESR spectra for **6** and **7** are not especially informative; each consists of a single broad absorption centered at $\langle g \rangle$ = 1.998 ($\Delta\nu_{1/2}$ = 55 G) and $\langle g \rangle$ = 2.006 ($\Delta\nu_{1/2}$ = 35 G), respectively. We believe that **6** most likely is a square pyramid (d^1 $TaCp^*Cl_3(PMe_3)$ is a structurally characterized square pyramid[21]) and that the second ammonia in **7** is coordinated through the d_{z^2} orbital trans to the Cp^* ligand, consistent with the recently determined X-ray crystal structure of $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]OTf$.[22] IR spectra of **6** and **7** contain absorptions characteristic of NH_2 stretching and bending modes (Figure 2).[23] Ammonia is not removed readily from either **6** or **7** in vacuo, and recrystallization from tetrahydrofuran does not result in replacement of the coordinated ammonia with THF. Both **6** and **7** are soluble only in polar solvents such as tetrahydrofuran or dichloromethane. Their IR spectra suggest that they are salts; absorptions by covalently bound triflate ligands are observed at energies (e.g., in $Cp^*WMe_3(OTf)$ and $Cp^*WMe_2(OTf)(\mu\text{-}N_2)WCp^*Me_3$) significantly lower than absorptions by ionic triflate. In addition, **6** and **7** exhibit limiting equivalent conductivities in nitromethane of Λ_0 = 93 and 96 Ω^{-1} mol^{-1} cm^2, respectively, consistent with their being 1:1 electrolytes. Both **6** and **7** are extremely sensitive to oxygen, forming green-blue, paramagnetic decomposition products that have not been characterized. Dissociation of ammonia in solution from $[Cp^*WMe_3(NH_3)_2]OTf$ (**7**) is demonstrated by the quantitative reaction between **7** and an equimolar quantity of $Cp^*WMe_3(OTf)$ in THF in 5 min at room temperature to give **6** quantitatively. Similarly, according to IR spectra, 1 equiv of hydrazine reacts with **7** within a few minutes to yield $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]OTf$.[14] Addition of excess hydrazine results in deprotonation of $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]OTf$, a reaction that will be discussed in detail in a later publication.

The final complex in a dinitrogen reduction cycle is likely to be a mono ammonia adduct such as **6**. A significant question is how ammonia is removed from the metal. Interestingly, both **6** and **7** are converted into $Cp^*WMe_3(OTf)$ and ammonium triflate quantitatively by triflic acid in tetrahydrofuran (Scheme I). The most plausible explanation is that ammonia is protonated after dissociation from the metal in each case.

Either **6** or **7** can be deprotonated by 1 equiv of DBU in ether to form yellow, crystalline $Cp^*WMe_3(NH_2)$ (**8**) in high yield (Scheme I). Interestingly, ammonia itself is not a sufficiently strong base to deprotonate either **6** or **7**. (Ammonia coordinated to W(VI) (in **2**) therefore must be considerably more acidic than ammonia coordinated to W(V) in **6**, in spite of the possibility of some assistance by the metal in **6** through an agostic interaction of H_α in the coordinated ammonia.) Triethylamine will deprotonate **6**, but an equilibrium appears to result. The reversibility of these deprotonation reactions is further demonstrated by the addition of 1 equiv of HOTf or excess $[NH_4]OTf$ to $Cp^*WMe_3(NH_2)$ (**8**) to give $[Cp^*WMe_3(NH_3)]OTf$ (**6**) or $[Cp^*WMe_3(NH_3)_2]OTf$ (**7**), respectively (Scheme I). We propose that **8** is a square pyramid in which the amide group is sp^2-hybridized and turned so as to allow a dative π-bond to form using the d_{xy} orbital. (Use of the d_{z^2} orbital would result in significantly less overlap.[18]) Therefore the plane of the NH_2 ligand should be oriented perpendicular to the plane of the Cp* ligand. The ESR spectrum of **8** has an absorption at $\langle g \rangle$ = 2.005 ($\Delta\nu_{1/2}$ = 43 G), no hyperfine coupling to nitrogen is observable at room temperature. Its IR spectrum shows NH_2 vibrations at 3406, 3321, and 1543 cm^{-1} (cf., 3417, 3340, and 1579 cm^{-1} in $Cp^*WMe_4(NH_2)$; Figure 3). **8** is extremely sensitive to oxygen, even at −40 °C under an inert atmosphere, forming a green decomposition product that is insoluble in pentane. ^{15}N-labeled ammonia readily exchanges with **8**, as shown by oxidation and deprotonation of recovered **8**, to give statistically labeled $Cp^*WMe_3(NH)$ (see below), as determined by proton NMR spectroscopy. This exchange reaction could easily involve formation of intermediate $Cp^*WMe_3(NH_2)(^{15}NH_3)$.

Oxidation of $Cp^*WMe_3(NH_2)$ in the presence of a base such as triethylamine gives $Cp^*WMe_3(NH)$ (**9a**) in high yield. We propose that $[Cp^*WMe_3(NH_2)]^+$ (**4**) forms initially and is rapidly deprotonated. A variation of this reaction starts with **7** (eq 5); **7** should first be deprotonated

$$\underset{\mathbf{7}}{[Cp^*WMe_3(NH_3)_2]OTf} \xrightarrow[-[NEt_3H]OTf - [NEt_3H]PF_6]{\text{excess } NEt_3,\ [FeCp_2]PF_6} \underset{\mathbf{9a}}{Cp^*WMe_3(NH)} + FeCp_2 \quad (5)$$

in situ to form **8**. Unfortunately, we have not found a simple method of separating **9a** from ferrocene, so **9a** cannot be prepared in pure form by this method. $Cp^*WMe_3(N\text{-}t\text{-}Bu)$ also can be prepared (mixed with ferrocene) by adding excess *tert*-butylamine and 1 equiv of $[FeCp_2]PF_6$ to $Cp^*WMe_3(OTf)$; $[Cp^*WMe_3(NH_2\text{-}t\text{-}Bu)]^+$ is the most likely intermediate, even though it

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cannot be observed, which is then deprotonated, oxidized, and deprotonated again.

Addition of *n*-BuLi to an ether solution containing **9a** and ferrocene yields a precipitate of pale yellow, crystalline "Cp*WMe_3(NLi)" (**9b**) in 75% yield (eq 6). Since no solvent is present in the proton NMR spectrum of **9b** and

$$\underset{\mathbf{9a}}{Cp^*WMe_3(NH)} \xrightarrow[-\text{butane}]{n\text{-BuLi}} (1/x)\underset{\mathbf{9b}}{[Cp^*WMe_3(NLi)]_x} \qquad (6)$$

since it is only slightly soluble in pentane and ether, it is believed to have an oligomeric structure, $[Cp^*WMe_3(NLi)]_x$ (eq 6). (The structure and NMR studies of this complex and related bimetallic species will be discussed elsewhere.[24]) ^{15}N NMR studies of **9b** in pyridine-d_5 and THF-d_8 suggest that the oligomeric structure is degraded (lithium is solvated), while in C_6D_6 it remains intact.[24]

Addition of 1 equiv of water, MeOTf, or $SiMe_3Cl$ to **9b** yields **9a**, **9c**, or **9d** (eq 7). Isotopically labeled compounds can be prepared readily. (See Table I for IR and ^{15}N NMR

$$\underset{\mathbf{9b}}{[Cp^*WMe_3(NLi)]_x} \xrightarrow{H_2O} \underset{\mathbf{9a}}{Cp^*WMe_3(NH)} \quad \xrightarrow{MeOTf} \underset{\mathbf{9c}}{Cp^*WMe_3(NMe)} \quad \xrightarrow{SiMe_3Cl} \underset{\mathbf{9d}}{Cp^*WMe_3(NSiMe_3)} \qquad (7)$$

data.) The imido proton resonance in Cp*WMe_3(NH) (**9a**) is an unusual 1:1:1 triplet ($^1J_{H^{14}N}$ = 55 Hz; Figure 1b top). Resolved coupling to ^{14}N usually is observed only when the electric field gradient around nitrogen is low, i.e., in a symmetric environment.[25] Therefore it is surprising that coupling is observed in a species whose symmetry is as low as it must be in **9a**. In all other circumstances where coupling has been observed, the complexes are axially symmetric (Cp*Ir(N-*t*-Bu)[26a] ($^3J_{H^{14}N}$ = 1.6 Hz), $[Fe(CO)_3](\mu_3\text{-}CO)(\mu_3\text{-}NH)$[26b] ($^1J_{H^{14}N}$ = 57 Hz), and $[WF_5(NR)]^-$[26c]). The second requirement for observing coupling to ^{14}N is a balance of electronegativities on either side of the nitrogen.[27] Changing R in Cp*WMe_3(NR) from H to Me, *t*-Bu, or $SiMe_3$ results in a greatly reduced coupling ($^nJ_{H^{14}N}$ is not observable in those cases), most likely because of an increase in the electric field gradient at nitrogen. One conclusion that can be derived from the observation of ^{14}N coupling in **9a** is that the W≡N—H geometry *must* be linear, and the complex therefore monomeric. In accord with the gyromagnetic ratio of the two isotopes ($|\gamma(^{15}N)/\gamma(^{14}N)|$ = 1.40), a doublet with the expected coupling ($^1J_{H^{15}N}$ = 77 Hz) is observed for **9a**-^{15}N (Figure 1b). This value for $^1J_{H^{15}N}$ is comparable to that (72–75 Hz) observed in compounds of the type $[MX(^{15}NH)(dppe)_2]X$ (M = Mo, W; X = Cl, Br).[28] The ^{15}N NMR chemical shift of the imido nitrogen atom in **9a** is 388.0 ppm and coupling constants ($^1J_{NW}$ = 113 Hz and $^2J_{HW}$ = 83 Hz) are all consistent with an sp-hybridized nitrogen triply bonded to tungsten. The IR spectrum of **9a** in the solid state exhibits

Table II. Trends in ^{15}N NMR Chemical Shifts and Coupling Constants[a]

W—N (sp^3)	δ 30–90	$^1J_{NW}$ < 5
W=N (sp^2)	δ 200–260	$^1J_{NW}$ = 45–75
W≡N (sp)	δ 350–450	$^1J_{NW}$ = 110–130

[a] Chemical shifts (ppm) downfield of liquid ammonia (0 ppm) in Cp*WMe_nL (*n* = 3,4; L = hydrazido, amido, imido, and nitrido) complexes reported here. Coupling constants in Hz.

absorptions at 3439, 3406, 3386, and 3359 cm^{-1}, but in solution only an absorption at 3438 cm^{-1} is observed. The ^{15}N chemical shift of 454.3 ppm in Cp*$WMe_3(^{15}NSiMe_3)$ is significantly downfield of what it is in analogous imido complexes, an effect that could be ascribed to the presence of the electropositive silicon. The value for $^1J_{NW}$ (88 Hz) in **9d** is less than one would expect for a W–N triple bond (110–130 Hz, Table II), consistent with competition between silicon and tungsten for the nitrogen lone pair and consequent reduction of the W–N pseudo triple bond order.

The reaction between **9a** and D_2O yields Cp*WMe_3(ND) within minutes; Cp*WMe_3(O) is formed much more slowly. We propose that traces of acid catalyze the first process (i.e., $[Cp^*WMe_3(NHD)]^+$ is an intermediate) and speculate that nucleophilic attack by water on $[Cp^*WMe_3(ND_2)]^+$ followed by proton transfer from oxygen to nitrogen produces a hydroxo complex, which then loses a proton to give the oxo complex (eq 8). These proposals are consistent

$$\underset{\mathbf{9a}}{Cp^*WMe_3(NH)} \rightleftharpoons^{+D^+}_{} Cp^*WMe_3(NHD)^+ \rightleftharpoons^{-H^+} Cp^*WMe_3(ND)$$
$$\downarrow D_2O \qquad (8)$$
$$Cp^*WMe_3(OD_2)(NHD)^+ \xrightarrow{-NHD_3^+} Cp^*WMe_3(O)$$

with the fact that no $^{14}N/^{15}N$ exchange is observed by proton NMR spectroscopy upon heating **9a** in the presence of 2.5 equiv of ammonia-^{15}N at ~60 °C for 3 days in THF-d_8. However, addition of a catalytic amount of [(lutidine)H]OTf (0.07 equiv) to the reaction mixture gave **9a**-^{15}N (~80% of theory) under identical conditions. An extension of this reaction is exchange of one imido ligand for another. Cp*WMe_3(NMe) (**9b**) is formed in ~85% yield from **9a**, excess methylamine, and 0.25 equiv of [(lutidine)H]OTf as a catalyst (eq 9) upon heating the mixture overnight at 60 °C in dichloromethane.

$$Cp^*WMe_3(NH) + \text{excess } NH_2Me \xrightarrow[CH_2Cl_2]{\text{cat. [LutH]OTf}} Cp^*WMe_3(NMe) + NH_3Me^+ \qquad (9)$$

We noted earlier that when a solution of $[Cp^*WMe_4(NH_3)]PF_6$ (**2**) is allowed to warm in the absence of a large excess of ammonia, methane is eliminated to generate what is believed to be unstable and as yet unobserved $[Cp^*WMe_3(NH_2)]PF_6$ (**4**). Decomposition of **4** yields deep red $\{[Cp^*WMe_3]_2(\mu\text{-}N)\}PF_6$ (**10**, eq 10) by loss of ammonium ion. The ^{15}N NMR spectrum of **10** (δ(N) = 634.9 ppm) is consistent with a positively charged, multiply-bonded "nitride" or iminium-like nitrogen atom. The value of $^1J_{NW}$ (63 Hz) is intermediate between a typical value in a W≡N triple bond (115 Hz) and that for a W—N single bond (<5 Hz; Table II), consistent with each tungsten being doubly bound to an sp-hybridized nitrogen

$$\underset{\mathbf{1}}{[Cp^*WMe_4]PF_6} \xrightarrow[-CH_4,\ -1/2\ NH_4^+]{+\ NH_3} 1/2\ \underset{\mathbf{10}}{[Me_3W{\equiv}N{=}WMe_3]^+PF_6^-} \qquad (10)$$

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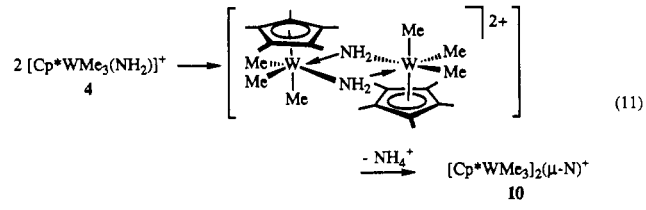
atom. The ^{183}W satellites comprise 28% of the peak intensity in **10a**, verifying the W=N=W connectivity. (This and related bimetallic species will be discussed in more detail elsewhere.[24]) Oxidation of $Cp^*WMe_3(NH_2)$ using $[FeCp_2]PF_6$ or protonation of $Cp^*WMe_3(NH)$ also yield **10**, presumably via formation and decomposition of **4**. Note that $[Cp^*WMe_3(NH_2)]^+$ is isoelectronic with $Cp^*WMe_3(CH_2)$, which has an agostic C—H bond and is unstable at room temperature.[17] Since an overall positive charge does not discourage the decomposition of a cationic rhenium methylene complex to give 0.5 equiv of a cationic ethylene complex,[29] we would not expect the positive charge on **4** to prevent bimolecular decomposition via a complex having two bridging NH_2 ligands, as shown in eq 11. **10** also has been prepared by oxidation of the mixed



(11)

$$[Cp^*WMe_3(NLi)]_x + \underset{\mathbf{9b}}{} Cp^*WMe_3(OTf) \xrightarrow{-LiOTf} [Cp^*WMe_3]_2(\mu\text{-N}) \quad (12)$$

$$[Cp^*WMe_4]PF_6 + Cp^*WMe_3(NH) \xrightarrow[\mathbf{9a}]{-CH_4} \underset{\mathbf{10}}{\{[Cp^*WMe_3]_2(\mu\text{-N})\}^+} \quad (13)$$

valence complex, $[Cp^*WMe_3]_2(\mu\text{-N})$ (eq 12; it will be reported and discussed in more detail elsewhere[24]), or by treating $[Cp^*WMe_4]PF_6$ (**1**) with $Cp^*WMe_3(NH)$ (**9a**; eq 13). The most likely mechanism of reaction 13 is initial attack by the imido nitrogen atom in **9a** on the metal in **1**, followed by proton transfer from NH to a methyl group.

Protonation of $Cp^*WMe_3(NMe)$ (**9c**) probably yields $[Cp^*WMe_3(NHMe)]^+$ as an intermediate, but since a μ-nitride cannot form in this circumstance, methane is lost from $[Cp^*WMe_3(NHMe)]^+$ to give what we propose to be square-pyramidal *trans*-$Cp^*WMe_2(OTf)(NMe)$. Over a period of hours, $Cp^*WMe_2(OTf)(NMe)$ reacts with triflic acid to form *cis*-$Cp^*WMe(OTf)_2(NMe)$ (eq 14), which is stable to further reaction with triflic acid.

$$\underset{\mathbf{9c}}{Cp^*WMe_3(NMe)} \xrightarrow[-CH_4]{HOTf} Cp^*WMe_2(OTf)(NMe) \xrightarrow[-CH_4]{HOTf} Cp^*WMe(OTf)_2(NMe) \quad (14)$$

Molybdenum Complexes. Although in the past we have found that some of the chemistry of complexes containing the Cp^*MoMe_3 core is similar to the chemistry of analogous tungsten complexes, there are some significant differences.[13b] For example, CV studies show that Cp^*MoMe_4 is oxidized irreversibly at 0.10 V and chemical oxidation of Cp^*MoMe_4 using $[FeCp_2]PF_6$ to give $[Cp^*MoMe_4]PF_6$ was not successful. $[Cp^*MoMe_3]_2(\mu\text{-}N_2)$ can be prepared, although not directly from dinitrogen as in the case of the analogous tungsten complex. Nevertheless, high oxidation state complexes containing the Cp^*MoMe_3 core have been shown to catalytically reduce hydrazine to ammonia in yields comparable to yields employing analogous tungsten complexes.[14] For this reason we sought to prepare some Mo complexes analogous to those that contain the Cp^*WMe_3 core described so far here.

$Cp^*MoMe_3(OTf)$ reacts with ammonia to form two stable cationic adducts in good yield, $[Cp^*MoMe_3(NH_3)_x]OTf$ where x = 1 (**11**) or 2 (**12**). Both **11** and **12** are dark red crystalline solids. Ammonia is not removed from either **11** or **12** in vacuo nor is it displaced by THF upon recrystallization. ESR studies of **11** and **12** show a single broad absorption centered at $\langle g \rangle$ = 2.008 ($\Delta\nu_{1/2}$ = 42 G, A_{Mo} = 40.4 G) and $\langle g \rangle$ = 2.006 ($\Delta\nu_{1/2}$ = 32 G, A_{Mo} = 37 G), respectively, typical of Mo(V) complexes. Their structures are believed to be analogous to the W species (**6** and **7**, Scheme I), as the IR spectra are identical. The reactivities of **11** and **12** are also very similar to those of their W analogues. Addition of 1 or 2 equiv of triflic acid to either produces $Cp^*MoMe_3(OTf)$ and the ammonium salt quantitatively, and the reaction between 1 equiv of **12** and 1 equiv of $Cp^*MoMe_3(OTf)$ produces **11** in good yield. **11** and **12** are also extremely oxygen sensitive, forming green-blue decomposition products.

Deprotonation of **11** and **12** by DBU produces red, pentane-soluble $Cp^*MoMe_3(NH_2)$ (**13**; cf. **8**, Scheme I). **11** and **12** also can be deprotonated by triethylamine, although the yield of **13** is much lower. Unfortunately, **13** is not as stable as its tungsten analogoue, being extremely sensitive to oxygen, and could not be isolated in analytically pure form. ESR spectra ($\langle g \rangle$ = 2.007, $\Delta\nu_{1/2}$ = 28 G) and IR spectra of **13** are virtually identical to those for $Cp^*WMe_3(NH_2)$.

Oxidation of **13** by $[FeCp_2]PF_6$ in the presence of either DBU or triethylamine produces a mixture of $FeCp_2$ and $Cp^*MoMe_3(NH)$ (**14**). However, **14** is produced in only low yield by this route, perhaps because the proposed intermediate $[Cp^*MoMe_3(NH_2)]PF_6$ is much less stable than its W analogue. The proton NMR spectrum of **14** shows the unusual 1:1:1 triplet for the imido proton ($^1J_{H^{14}N}$ = 52 Hz; cf. **9a**), while its IR spectra show an MoN absorption at 925 cm^{-1} and an N-H absorption at 3381 cm^{-1} (cf. 939 and 3438 cm^{-1} for **9a**; Table I). There is no evidence for formation of a bridging nitrido complex analogous to **10**.

Deprotonation of **14** using $Li[N(TMS)_2]$ produces $Cp^*MoMe_3(NLi)$ (**15**). However, the best route to prepare **15** is by treating $Cp^*MoMe_3(OTf)$ with excess LiN_2H_3 in THF. We propose that $Cp^*MoMe_3(N_2H_3)$ is an intermediate and that it undergoes a disproportionation reaction to form $Cp^*MoMe_3(N_2H_4)$ in which the N-N bond is cleaved to yield **14** and ammonia.[14] **14** is then deprotonated by excess LiN_2H_3 to form $[Cp^*MoMe_3(NLi)]_x$ in 50% isolated yield. **15** is a yellow solid that is soluble in ether and reacts with electrophiles to produce a variety of substituted imido complexes analogous to those described that contain tungsten. (Except for $Cp^*MoMe_3(NMe)$ (**16**) these compounds were not fully characterized.) Unlike the tungsten analogue, **15** decomposes readily in C_6D_6 upon heating to 50 °C.

We conclude that while several Mo analogues of the Cp^*WMe_3 complexes discussed earlier can be prepared, the yield and stability of these complexes are noticeably lower than those of the W complexes, perhaps in part because of the tendency for Mo to reduce more readily than W. For this reason complete studies of potential intermediates possessing the Cp^*MoMe_3 core were not carried out.

Infrared Studies of Imido Complexes. A transition-metal imido complex typically has an absorption in its IR spectrum between 1250 and 1350 cm^{-1}.[16a] This is not likely to be a pure M-N stretch for two reasons: (i)

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Table III. Percent W–N Contribution to the Isotopic Shift of the ν(WNX) Vibration[a]

$Cp^*WMe_3(NH)$ (9a)	90	$Cp^*WMe_3(NSiMe_3)$ (9d)	50
$[Cp^*WMe_3(NLi)]_x$ (9b)	70	$Cp^*WMe_3(NPh)$ (9e)	10
$Cp^*WMe_3(NCH_3)$ (9c)	55		

[a] Error ~5%.

what is expected to be a stronger bond in metal–nitride (M≡N) complexes absorbs at lower energies (950–1050 cm^{-1}); and (ii) the isotopic shift upon substitution of ^{15}N for ^{14}N in imido complexes is generally less than that calculated for a pure M–N stretch. The higher than expected stretching frequency and the smaller than expected isotropic shift can be explained if the M–N and N–R vibrations are strongly coupled. The availability of a variety of isotopically labeled imido complexes allows us to test the validity and the extent of M–N and N–R oscillator coupling.

Isotropic shifts of ν(MNR) can be used to determine the approximate relative contributions of pure ν(MN) and pure ν(NR). For example, in $Cp^*WMe_3(NR)$ (R = H, Me) substitution of ^{15}N for ^{14}N will affect both of the M–N and the N–R components, while replacing H with D or $^{12}CH_3$ with $^{13}CH_3$ will directly affect only the N–R contribution. Since ν(WNC) = 1315 cm^{-1} for $Cp^*WMe_3(NCH_3)$, substitution of ^{15}N for ^{14}N would result in a shift of 41 cm^{-1} to 1274 cm^{-1} if the stretch were solely ν(WN). Similarly, ^{15}N substitution would cause a shift of 20 cm^{-1} to 1295 cm^{-1} if the stretch were solely ν(NC). The actual isotopic shift is 32 cm^{-1}. If we assume that ν(WN) and ν(NC) are the only major contributors to the isotopic shift, the $^{14/15}N$ data can be explained if ν(WNC) is a combination of 55% ν(WN) and 45% ν(NC). Using the $^{12/13}CH_3$ data as a check, one obtains values of 51% ν(WN) and 49% ν(NC).

Similar calculations can be carried out for $Cp^*WMe_3(NH)$ since there are also two variables (contributions by ν(WN) and ν(NH)) and three data points (ν($W^{14}NH$), ν($W^{15}NH$), and ν(WND)). The calculated contributions (ν(WN):ν(NH)) are 83%:17% if $^{14/15}N$ data are used, or 89%:11% if H/D data are used. Since $^{14/15}N$ substitution would result in a small theoretical isotopic shift contribution of only 2 cm^{-1} for ν(^{14}NH)–ν(^{15}NH), whereas H/D interchange could lead to a maximum shift of 253 cm^{-1}, it is more accurate to use the latter result (89%:11%).

The results of similar calculations for other imido complexes are shown in Table III. The vibrational assignment of phenyl imido complexes should be affected by π conjugation of the ring with the imido nitrogen atom. In fact calculations on $Cp^*WMe_3(NPh)$ indicate that the absorption that is observed to shift from 1364 to 1341 cm^{-1} is predominantly (ca. 90%) ν(NC) in character. The comparatively low frequency for ν(WNSi) in $Cp^*WMe_3(NSiMe_3)$ (1147 cm^{-1}) can be ascribed in part to the larger mass of silicon vs carbon. Also, ^{15}N NMR data suggest electronic delocalization across the W–N–Si backbone, thereby lowering the W–N bond order relative to that in the alkyl imido compounds, and thus lowering ν(WN). The concomitant increase in ν(NSi) partially offsets the decrease in ν(WN). Values between 1100 and 1150 cm^{-1} have been reported for ν(WNSi) previously, with other vibrational modes for $SiMe_3$ at ~1250, 850, and 750 cm^{-1}.[30] This semiquantitative approach can be used to predict isotopic shifts in other imido complexes. For example, an imido complex that has been isotopically labeled and examined by IR is $[Os(NMe)(CH_2SiMe_3)_4]^-$.[31] The values reported for ν($Os^{14}N^{12}C$), ν($Os^{15}N^{12}C$), ν($Os^{14}N^{13}C$), and ν($Os^{15}N^{13}C$) are 1281, 1269, 1250, and 1235 cm^{-1}, respectively. Any two values yields a ratio of ~55:45 for ν(OsN):ν(NC); the other vibrational frequencies can then be calculated within 2 cm^{-1}. Note that the oscillator ratio is nearly identical to that for the tungsten imido complexes. However, it has not proven reliable to calculate the expected frequency of an imido stretch, rather than simply the isotopic shift, on the basis of the molar fraction of the base M–N frequency and a base N–C frequency. It is sometimes difficult to identify imido vibrations in IR spectra, since some common assumptions are not strictly correct. One incorrect assumption is that only the M–N and N–X components contribute to the final vibration. As has been demonstrated for $[F_5W(NR)]^-$ complexes,[32] changing R from Me to *t*-Bu causes a decrease in the stretching frequency, i.e., other vibrations (e.g., C–C) are also coupled to the N–X vibration.

Discussion

The stability of the d^1 alkyl complexes $[Cp^*WMe_3(NH_3)_x]OTf$ (*x* = 1 (**6**) or 2 (**7**)) toward loss of methane is at first surprising. For example, reactions between Cp^*TiMe_3, Cp^*TaMe_4, or $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ and ammonia, which are likely to proceed via intermediate ammonia adducts (as well as amido and imido complexes), yield $[Cp^*Ti(\mu\text{-}NH)]_3(\mu_3\text{-}N)$,[33] $[Cp^*TaMe(\mu\text{-}N)]_3$,[34] or $[(t\text{-}BuCH_2)_2TaN]_5(NH_3)$,[35] respectively. The high reactivity of titanium and tantalum can be ascribed to steric and electronic unsaturation of intermediates. Bimolecular alkane elimination reactions also are likely to be fast and NH_x ligands bound to the electrophilic d^0 metals relatively acidic. In contrast, **6** and **7** are comparatively crowded and have a higher electron count. It is interesting to note that bound ammonia is clearly more acidic in d^0 $[Cp^*WMe_4(NH_3)]PF_6$ (**2**) than in **6** or **7**. Steric crowding and perhaps hybridization of the NH_y ligand appear to be important considerations since $Cp^*WMe_4(NHR)$ (R = H, Me) and $Cp^*WMe_3(NH)$ are extremely robust thermally.

Terminal NH_2 complexes are relatively rare. $Cp^*_2Sc(NH_2)$[36] and $Cp^*_2M(H)(NH_2)$ (M = Zr and Hf)[37] were prepared by adding ammonia to the corresponding hydride complexes, while $(t\text{-}Bu_3SiO)_3Ta(H)(NH_2)$ was formed by oxidative addition of ammonia to $Ta(OSi\text{-}t\text{-}Bu)_3$.[38] Lower oxidation state species are somewhat more common. For example, $[CpRe(NO)(PPh_3)(NH_3)]OTf$,[39] $[CpRu(NH_3)(Cy_2PCH_2CH_2PCy_2)]OTf$ (Cy = cyclohexyl),[40] and $[Pt(PCy_3)_2X(NH_3)]ClO_4$ (X = H, Me)[41] all have been deprotonated to yield the corresponding monomeric, neutral

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NH_2 complexes, while $M[HB\text{-}3,5\text{-}Me_2C_3HN_2)_3](NO)X(NH_2)$ (M = Mo, W; X = I, Br) complexes have been prepared by adding excess ammonia to the corresponding $M[HB\text{-}3,5\text{-}Me_2C_3HN_2)_3](NO)X_2$ complexes.[42] In several cases bulky ligands play a key role in preventing the formation of bridging amido complexes, a situation that is also true in **3a** and **8**.

Terminal NH complexes also are rare. $Cp^*_2Ta(NH)(H)$ is the product of oxidative addition of ammonia to "$Cp^*_2Ta(CH_3)$", which is present in small equilibrium concentration in a solution of $Cp^*_2Ta(CH_2)H$.[43] Another d^0 complex is $MoCl_2(O)(OPR_3)_2(NH)$,[44] also the first structurally characterized terminal NH complex, formed from $MoOCl_3$, N_3SiMe_3, R_3PO, and adventitious water. (The Mo=N—H angle is this 18e species (not counting lone pair donation) was found to be 157 (9)°.) No imido stretch ν(NH) was observed, and decomposition in solution prevented NMR data from being obtained. Complexes of the type $[MoX(dppe)_2(NH)]X$[45] were prepared by adding a variety of acids HX to $Mo(dppe)_2(N_3)(N)$; the bromide derivative was structurally characterized. The ν(NH) vibrations were broad (between 3220 and 3420 cm^{-1}), most likely because of hydrogen-bonding between the counterion and the imide proton. Imido proton resonances were not unambiguously identified in the proton NMR spectra but couplings of 69–75 Hz have been observed in the ^{15}N NMR spectra.

Generation of unstable cationic M(VI) amido complexes by oxidation of M(V) complexes, followed by deprotonation to give neutral M(VI) imido species, is not uncommon. A recent example is the electrochemical study of the reversible interconversion of $[M^{VI}(N)(tpy)Cl_2]^+$ and $[M^{III}(NH_3)(tpy)Cl_2]^+$ (M = Ru or Os).[46]

It is not surprising that $[Cp^*WMe_3(NLi)]_x$ reacts with electrophiles to form a variety of imido complexes, since terminal nitrido ligands are known to be alkylated in a variety of circumstances. For example, $[M(N)R_4]^-$ complexes (M = Ru or Os, R = Me or CH_2SiMe_3) react with electrophiles such as MeI and $SiMe_3X$ (X = Cl, OTf) to yield imido complexes.[31] Other nitrides that can be protonated or alkylated include $Mo(N)(S_2CNR_2)_3$[47] and $Mo(N)X(dppe)_2$.[45]

Bonding in square-pyramidal complexes containing the Cp^*MMe_3 core (M = Mo or W) appears to involve a σ orbital in the fourth position of the square pyramid, a $\pi(d_{xy})$ orbital that lies between the ligands approximately parallel to the Cp* ring, and what is essentially a d_{z^2} orbital normal to the Cp* plane that can function either as a σ orbital in a pseudooctahedron or as a π orbital toward a ligand in the fourth position of the square pyramid.[18] Both the d_{xy} and d_{z^2} orbitals could be involved in forming two π bonds to the metal in imido complexes. The only direct structural evidence that suggests formation of two π bonds is possible is the short W=N bond (1.75 (4) Å) in the hydrazido(4–) complex, $Cp^*Me_3W{=}N{-}N{=}WCp^*Me_3$.[48] $Cp^*Me_3W{=}NR$ species should be easily protonated, as we have found, since the π overlap in the π bond employing the d_{z^2} orbital should be relatively poor.[18] Stability of $Cp^*Me_3W{=}N{-}N{=}WCp^*Me_3$ to acids mght be ascribed to formation of delocalized π bonding throughout the W=N—N=W system. We might predict that Mo=NR complexes will be more readily protonated as a result of poorer N → Mo dative π bonding. Indeed $Cp^*Me_3W{=}N{-}N{=}MoCp^*Me_3$ reacts more readily with water (to yield $Cp^*Me_3W{=}NNH_2$ and $Cp^*Me_3Mo{=}O$) than does $Cp^*Me_3W{=}N{-}N{=}WCp^*Me_3$.[15]

Future publications will be concerned with hydrazido complexes that contain the Cp^*MMe_3 core, and in particular, with the mechanism of cleavage of the N–N bond. Long range goals include the design of systems that incorporate many of the features of the Cp^*MMe_3 systems, but do not contain alkyl ligands, are relatively stable toward protons, and therefore are better candidates as catalysts for the reduction of dinitrogen under mild conditions. The first new complexes of this type are hydrazine and hydrazido complexes that contain the $W(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[2,6\text{-}NC_5H_3(CH_2N(Tosyl))_2]$ core.[49]

Conclusions

The main findings of this work are the following: (i) one binding site in square-pyramidal five-coordinate complexes that contain the Cp^*MMe_3 core is well-suited for multiple bonding to amido and imido ligands; (ii) ammonia, NH_2, and NH complexes (d^0 and d^1) containing the Cp^*MMe_3 core can be relatively stable and therefore are viable intermediates toward the end of a hypothetical cycle in which dinitrogen is catalytically reduced; (iii) the methyl groups in Cp^*MMe_3 complexes are relatively stable toward α-hydrogen abstraction reactions and also are surprisingly resistant to protonation.

Experimental Section

Solvents were dried and degassed prior to use and distilled from molten sodium (toluene), sodium/benzophenone (diethyl ether, tetrahydrofuran, pentane), CaH_2 (dichloromethane), or P_2O_5 (acetonitrile). Pentane was washed with 5% HNO_3/H_2SO_4 and dried using tetraglyme to solvate the sodium. All preparations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox, under argon in Schlenk ware, or on a high vacuum line ($<10^{-4}$ Torr). Triflic acid was purchased from Aldrich and used directly from the sealed ampule.

NMR operating frequencies and reference standards are as follows: ^1H (300.1 MHz, $SiMe_4$ = 0 ppm), ^{13}C (75.0 MHz, $SiMe_4$ = 0 ppm), ^6Li (44.1 MHz, 1.0 M $LiCl/D_2O$ = 0 ppm), ^7Li (116.6 MHz, 1.0 M $LiCl/D_2O$ = 0 ppm), ^{15}N (30.4 MHz, NH_2Ph = 56.5 ppm),[25b] ^{19}F (282.2 MHz, $CFCl_3$ = 0 ppm). Proton and carbon NMR data were referenced using resonances for the partially deuterated NMR solvent. Other nuclei were referenced externally in the same solvent unless otherwise noted. Chemical shifts are in ppm, and coupling constants and line widths are in hertz. All spectra were acquired at room temperature unless otherwise noted. Nuclei other than proton and carbon were referenced externally. Deuterated solvents were dried by passage through alumina and storage over 4-Å molecular sieves. Infrared spectra were acquired on a Mattson Cygnus 100 FT-IR spectrometer, absorptions are reported in units of inverse centimeters. All spectra are Nujol mulls between KBr plates unless otherwise indicated; solution spectra were collected using KBr cells in the solvent indicated. ESR spectra were collected on a Bruker ESP 300 spectrometer in 3-mm quartz tubes at room temperature unless otherwise noted; the line width ($\Delta\nu_{1/2}$) is in parentheses in the solvent indicated. UV–visible measurements were obtained using a Hewlett-Packard 8452A photodiode array spectrophotometer in airtight quartz cuvettes in the solvent indicated. Absorptions (λ) are recorded

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in units of nanometers and molar absorptivities (ϵ) are in parentheses. Microanalyses (C, H, and N) were performed either by Schwartzkopf Laboratories, Woodside, NY, or in our own laboratory using a Perkin-Elmer PE2400 microanalyzer.

Solution conductivity measurements were performed in nitromethane that had been dried by passing it through alumina and stirring over $CaCl_2$ overnight followed by a second alumina filtration. Conductivity measurements of the pure solvent of 0.3–0.6 Ω^{-1} mol^{-1} cm^2 are characteristic of dry solvent. A YSI (Yellow Springs Instrument) conductivity cell (No. 3401, cell constant = 0.997) with platinized electrodes was used in conjunction with a conductivity bridge YSI-31. The conductivity cell is of the dip-type, but the gas outlet was sealed and the inverted cell used as the vessel itself (ca. 20 mL). Conductivities at three to five different concentrations (between ca. 0.5 and 5 mM) were measured by dilution of the original solution. Equivalent conductivity (Λ) was calculated by subtracting background solvent conductivity, multiplying by the cell constant, and dividing by the concentration of the solution. A plot of equivalent conductivity vs (concentration)$^{1/2}$ yielded straight lines with the y intercept being the conductivity at infinite dilution (Λ_0).[50]

Anhydrous ammonia (Matheson) was used as purchased and the amines NH_2Me (Matheson) and $NHMe_2$ (Matheson) were dried as liquids under pressure over sodium and distilled. 1,8-Diazobicyclo[5.4.0]undec-7-ene (DBU) was purchased from Aldrich. $[Cp^*WMe_4]PF_6$[17] and $Cp^*WMe_3(OTf)$[13a] were prepared as reported in the literature. ND_3, $^{15}NH_3$, and $^{13}CH_3I$ were used as purchased from Cambridge Isotopes, Cambridge, MA.

$[Cp^*WMe_4(NH_3)]PF_6$ (2). Excess gaseous ammonia was added to $[Cp^*WMe_4]PF_6$ in the solid state at room temperature. A small amount of yellow $Cp^*WMe_4(NH_2)$ was rinsed away with ether leaving beige $[Cp^*WMe_4(NH_3)]PF_6$: IR (Nujol) 3362 (m, NH_2), 3299 (m, NH_2), 3204 (vw, NH), 1624 (m, NH_2), 1342 (m), 1301 (m), 1253 (m), 1022 (m, CH_3), 845 (vs, PF_6), 740 (w), 558 (s, PF_6), 469 (w) cm^{-1}.

$Cp^*WMe_4(NH_2)$ (3a). (a) Excess ammonia was passed over a slurry of $[Cp^*WMe_4]PF_6$ (0.15 g, 0.29 mmol) in 25 mL of ether at room temperature. The solution rapidly became yellow, and after 5 min the solution was filtered to remove $[NH_4]PF_6$. The filtrate was reduced to dryness in vacuo to give yellow crystalline $Cp^*WMe_4(NH_2)$ (0.10 g, 0.25 mmol, 87%). Recrystallization from a minimum of tetrahydrofuran/pentane at −40 °C yields analytically pure yellow plates: ^{1}H NMR (CD_2Cl_2) δ 7.78 (br, 1 H, NH), 6.96 (br, 1 H, NH), 1.75 (s, 15 H, Cp*), 1.22 (s, 3 H, WMe_{ax}), 0.04 (s, 6 H, WMe_{cis}), −0.44 (s, 3 H, WMe_{trans}); ^{13}C NMR (C_6D_6) δ 113.15 (Cp*), 62.33 ($^1J_{CW}$ = 66, WMe_{ax}), 33.62 ($^1J_{CW}$ = 33, WMe_{trans}), 30.02 ($^1J_{CW}$ = 56, WMe_{cis}), 9.35 (Cp*); IR (Nujol) 3417 (m, NH_2), 3340 (m, NH_2), 1579 (w, NH_2), 1021 (m, CH_3), 956 (w), 642 (s), 604 (w), 493 (w), 479 (w) cm^{-1}. Anal. Calcd for $C_{14}H_{29}NW$: C, 42.54; H, 7.40; N, 3.54. Found: C, 42.57; H, 7.16; N, 3.25.

$Cp^*WMe_4(^{15}NH_2)$ was prepared similarly using $^{15}NH_3$: ^{1}H NMR (CD_2Cl_2) δ 7.78 (dd, $^2J_{HH}$ = 4.6, $^1J_{HN}$ = 75, $^2J_{HW}$ = 9.1, NH_a), 6.96 (ddq, $^2J_{HH}$ = 4.6, $^1J_{HN}$ = 69, $^4J_{HH}$ = 1.5, NH_b), 1.22 (d, $^4J_{HH}$ = 1.5, WMe_{ax})—selective irradiation of WMe_{ax} caused the NH resonance at 6.96 ppm to collapse to a doublet of doublets; ^{15}N NMR (CD_2Cl_2) δ 210.6 ($^1J_{NW}$ = 45, $^1J_{NH_{av}}$ = 72); IR (Nujol) 3410 (m, NH_2), 3338 (m, NH_2), 1567 (w, NH_2), 1024 (m, CH_3), 942 (w), 640 (m), 624 (sh), 600 (m), 493 (w), 479 (w) cm^{-1}.

Protonation of $Cp^*WMe_4(NH_2)$. Triflic acid (0.038 g, 0.25 mmol, 2.57 equiv) in 2 mL of ether was added to $Cp^*WMe_4(NH_2)$ (0.039 g, 0.099 mmol) in 5 mL of ether at room temperature. After 5 min pale yellow $[Cp^*WMe_4]OTf$ (0.040 g, 0.076 mmol, 77%) was filtered off: ^{1}H NMR (CD_2Cl_2, 20 °C) δ 2.07 (s, Cp*), 1.62 (br, Me); ^{1}H NMR (CD_2Cl_2, −40 °C) δ 3.28 (s, 3 H, WMe_{ax}), 2.01 (s, 15 H Cp*), 1.50 (s, 9 H, WMe_{eq}); IR (Nujol) 1503 (m), 1262 (vs, OTf), 1224 (m, OTf), 1156 (s), 1142 (s), 1030 (s, OTf), 638 (s, OTf), 572 (w), 516 (m) cm^{-1}. $[NH_4]OTf$ was identified by proton NMR spectroscopy in dimethyl-d_6 sulfoxide (δ 7.07 (br)).

$Cp^*WMe_4(NHMe)$ (3b). Excess methylamine (4.00 mmol, 5.00 equiv) was condensed onto a frozen, degassed slurry of $[Cp^*WMe_4]PF_6$ (0.42 g, 0.80 mmol) in 20 mL of ether. The reaction mixture was warmed slowly to room temperature, and the solvent was removed in vacuo. The residue was extracted with pentane. The filtrate was concentrated in vacuo and cooled to −40 °C to give tiny yellow needles of **3b** (0.29 g, 0.70 mmol, 89%). Recrystallization from a minimum of ether/pentane at −40 °C gave analytically pure yellow needles: ^{1}H NMR (CD_2Cl_2) δ 7.71 (br, 1 H, NH), 2.90 (d, $^3J_{HH}$ = 6.9, 3 H, NMe), 1.73 (s, 15 H, Cp*), 0.04 (s, 6 H, WMe_{cis}), −0.55 (s, 3 H, WMe_{trans}); ^{13}C NMR (C_6D_6) δ 113.23 (Cp*), 61.60 ($^1J_{CW}$ = 62, WMe_{ax}), 38.80 (NMe), 36.64 ($^1J_{CW}$ = 38, WMe_{trans}), 30.89 ($^1J_{CW}$ = 56, WMe_{cis}), 9.14 (Cp*); IR (Nujol) 3382 (m, NH) cm^{-1}. Anal. Calcd for $C_{15}H_{31}NW$: C, 44.02; H, 7.63; N, 3.42. Found: C, 44.29; H, 7.65; N, 3.19.

$[Cp^*WMe(NPh)(NHPh)]PF_6$ (5). A solution of aniline (0.18 g, 1.95 mmol, 2.10 equiv) in 5 mL of dichloromethane was added to a rapidly stirring solution of $[Cp^*WMe_4]PF_6$ (0.40 g, 0.76 mmol) in 40 mL of dichloromethane at room temperature. After 2.5 h the solvent was removed from the resulting fluorescent orange solution in vacuo and the residue was rinsed with ether to remove excess aniline. The residue was dissolved in a minimum of tetrahydrofuran (15 mL). Slow addition of ether (10 mL) precipitated $[Cp^*WMe(NPh)(NHPh)]PF_6$ (0.54 g, 0.81 mmol, 87%) as a yellow powder. Recrystallization from dichloromethane/ether gave analytically pure orange-yellow crystals: ^{1}H NMR (CD_2Cl_2) δ 9.69 (br, 1 H, NH), 7.50–6.95 (two sets of inequivalent phenyl resonances), 2.26 (s, 15 H, Cp*), 1.44 (s, $^2J_{HW}$ = 7.7, 3 H, WMe); ^{13}C NMR (CD_2Cl_2) δ 151.34, 150.62 (C_{ipso}), 130.61 (C_p), 130.25 (C_m or C_o), 129.82 (C_m or C_o), 128.73 (C_p), 127.19 (C_m or C_o), 121.90 (C_m or C_o), 120.16 (Cp*), 28.01 (WMe, $^1J_{CW}$ = 101, $^1J_{CH}$ = 132), 10.66 (Cp*, $^1J_{CH}$ = 129); ^{19}F NMR (CD_2Cl_2) δ −72.42 (d, $^1J_{FP}$ = 710); IR (Nujol) 3289 (m, NH), 1586 (w, Ph), 1350 (m, WNPh), 1244 (m), 1211 (m), 1069 (w), 1027 (m, CH_3), 844 (vs, PF_6), 768 (s), 687 (s), 557 (s, PF_6), 530 (w), 487 (m) cm^{-1}. Anal. Calcd for $C_{23}H_{29}F_6N_2PW$: C, 41.71; H, 4.41; N, 4.23. Found: C, 41.31; H, 4.36; N, 3.91.

$[Cp^*WMe(^{15}NPh)(^{15}NHPh)]PF_6$ was prepared by a similar method using $^{15}NH_2Ph$: ^{1}H NMR (CD_2C_2) δ 9.69 (d, $^1J_{NH}$ = 74, NH); ^{15}N NMR (CD_2Cl_2) δ 380.0 ($^1J_{NW}$ = 128, NPh), 264.9 (d, $^1J_{NW}$ = 74, NHPh); IR (Nujol) 3282 (m, ^{15}NH), 1586 (w, Ph), 1327 (m, W^{15}NPh), 1237 (m), 1206 (m), 1069 (w), 1025 (m, CH_3), 845 (vs, PF_6), 767 (s), 686 (s), 557 (s, PF_6), 484 (m) cm^{-1}.

$Cp^*WMe(NPh)_2$. Triethylamine (0.059 g, 0.58 mmol, 1.00 equiv) was added to $[Cp^*WMe(NPh)(NHPh)]PF_6$ (0.38 g, 0.58 mmol) in 10 mL of dichloromethane at room temperature. The solution became lighter orange, and after 15 min the solvent was removed in vacuo and the residue was extracted with ether to remove $[NEt_3H]PF_6$. Orange crystalline $Cp^*WMe(NPh)_2$ (0.28 g, 0.28 mmol, 94%) was isolated after drying the filtrate in vacuo. Recrystallization from a minimum of ether/pentane yields analytically pure orange crystals: ^{1}H NMR (CD_2Cl_2) δ 7.17 (tr, 4 H, H_m), 6.73 (tr, 2 H, H_p), 6.70 (d, 4 H, H_o), 2.10 (s, 15 H, Cp*), 1.00 (s, 3 H, WMe, $^2J_{WH}$ = 8.5); ^{13}C NMR (CD_2Cl_2) δ 158.63 (C_{ipso}), 128.39 (C_o, $^1J_{CH}$ = 157), 121.43 (C_p, $^1J_{CH}$ = 160), 121.29 (C_m, $^1J_{CH}$ = 161), 114.79 (Cp*), 10.95 (Cp*), 7.72 (WMe, $^1J_{CW}$ = 114); IR (Nujol) cm^{-1} 1582 (s, Ph), 1342 (s, WNPh), 1162 (w), 1065 (w), 1024 (w), 998 (w), 974 (m, W^{15}NC), 751 (m, Ph), 687 (m, Ph), 516 (w); UV-VIS (THF) 214, 266, 304 (sh), 354, 380 (sh), 402 (sh). Anal. Calcd for $C_{23}H_{28}N_2W$: C, 53.50; H, 5.47; N, 5.43. Found: C, 53.75; H, 5.36; N, 5.34.

$Cp^*WMe(^{15}NPh)_2$ was prepared by a similar method using $[Cp^*WMe(^{15}NPh)(^{15}NHPh)]PF_6$: ^{15}N NMR ($CD_2Cl_2$) δ 380.7 ($^1J_{NW}$ = 121); IR (Nujol) 1583 (s, Ph), 1320 (s, W^{15}NPh), 1163 (w), 1066 (w), 1022 (w), 995 (w), 966 (m, W^{15}NC), 751 (m, Ph), 687 (m, Ph), 514 (w) cm^{-1}.

$Cp^*WMe(OTf)_2(NPh)$. Excess triflic acid (0.11 g, 0.71 mmol, 3.50 equiv) in 2 mL of ether was slowly added to $Cp^*WMe(NPh)_2$ (0.10 g, 0.20 mmol) in 10 mL of ether at room temperature. A yellow precipitate formed rapidly which was filtered off after 10 min. Extraction with tetrahydrofuran separated the insoluble $[NH_3Ph]OTf$ from soluble $Cp^*WMe(OTf)_2(NPh)$ (0.12 g, 0.16 mmol, 80%), which was isolated as a yellow powder upon removing the solvents from the filtrate in vacuo. Recrystallization from a minimum of dichloromethane/ether gave analytically pure yellow microcrystals: ^{1}H NMR (CD_2Cl_2) δ 7.45 (tr, 2 H, H_m), 7.27 (d, 2 H, H_o), 7.26 (tr, 1 H, H_p), 2.25 (s, 15 H, Cp*), 1.56 (s, 3 H, WMe, $^2J_{HW}$ = 5.3); ^{13}C NMR (CD_2Cl_2) δ 131.26 (Ph), 129.09 (Ph), 126.68 (Ph), 123.56 (Cp*), 44.26 (WMe), 11.07 (Cp*), no ipso carbon located; IR (Nujol) 1349 (s), 1240 (s, OTf), 1197 (s, OTf),

(50) Meites, L.; Thomas, H. C. *Advanced Analytical Chemistry*; McGraw-Hill: New York, 1958.

1003 (s, OTf), 970 (s), 767 (s, Ph), 688 (m, Ph), 630 (s, OTf), 514 (m) cm^{-1}; ^{19}F NMR (CD_2Cl_2) δ -77.05, -78.09.

$Cp^*WMe(OTf)_2(^{15}NPh)$ was prepared by a similar method using $Cp^*WMe(^{15}NPh)_2$: ^{15}N NMR (CD_2Cl_2) δ 435.2 ($^1J_{NW}$ = 121); IR (Nujol) 1345 (s), 1239 (s, OTf), 1191 (s, OTf), 1004 (s, OTf), 968 (s), 760 (s, Ph), 686 (m, Ph), 637 (s), 629 (s, OTf), 518 (w), 501 (w) cm^{-1}.

$Cp^*WMe_3(NPh)$ (9e). Excess LiMe in ether was added to $Cp^*WMe(OTf)_2(NPh)$ in ether at room temperature. The yellow solution immediately paled. After 5 min the solvent was removed in vacuo and the residue was extracted with pentane. The filtrate was taken to dryness in vacuo to give yellow $Cp^*WMe_3(NPh)$. Recrystallization from ether/pentane at -40 °C gave analytically pure pale yellow plates: ^1H NMR (CD_2Cl_2) δ 7.20 (tr, 2 H, H_m), 7.02 (tr, 1 H, H_p), 6.86 (d, 2 H, H_o), 1.87 (s, 15 H, Cp*), 0.70 (s, 6 H, WMe_{cis}), -0.01 (s, 3 H, WMe_{trans}); ^{13}C NMR (C_6D_6) δ 157.95 (C_{ipso}), 128.75 (C_o), 123.85 (C_p), 121.73 (C_m), 110.30 (Cp*), 32.43 ($^1J_{CW}$ = 68, WMe_{trans}), 25.24 ($^1J_{CW}$ = 56, WMe_{cis}), 10.40 (Cp*); IR (Nujol) cm^{-1} 1582 (s, Ph), 1364 (m, WNC), 1069 (m), 1025 (CH_3), 760 (m, Ph), 691 (m, Ph), 491 (m). Anal. Calcd for $C_{19}H_{29}NW$: C, 50.12; H, 6.42; N, 3.08. Found: C, 49.74; H, 6.46; N, 3.30.

$Cp^*WMe_3(^{15}NPh)$ was prepared by a similar method using $Cp^*WMe(OTf)_2(^{15}NPh)$: ^{13}C NMR (C_6D_6) δ 157.95 ($^1J_{CN}$ = 8.0, C_{ipso}), 128.75 ($^2J_{CN}$ = 2.1, C_o); ^{15}N NMR (C_6D_6) δ 394.4 ($^1J_{NW}$ = 113); IR (Nujol) cm^{-1} 1582 (s, Ph), 1341 (m, $W^{15}NC$), 1068 (m), 1022 (CH_3), 979 (m), 760 (s, Ph), 691 (m, Ph), 493 (m).

$[Cp^*WMe_3(NH_3)]OTf$ (6). Ammonia (0.56 mmol, 1.02 equiv) was condensed onto a frozen, degassed solution of $Cp^*WMe_3(OTf)$ (0.28 g, 0.55 mmol) in 20 mL of ether. A yellow precipitate formed upon warming the mixture to room temperature. After 15 min yellow $[Cp^*WMe_3(NH_3)]OTf$ (0.25 g, 0.47 mmol, 85%) was filtered off and rinsed with ether. Recrystallization from tetrahydrofuran/ether gave analytically pure yellow needles: ESR (CH_2Cl_2) $\langle g \rangle$ = 1.998 (55 G); IR (Nujol) 3249 (s, NH_2), 3171 (s, NH_2), 1644 (m, NH_2), 1326 (s), 1259 (vs, OTf), 1228 (m), 1163 (s), 1036 (s, OTf), 760 (w), 638 (s, OTf), 576 (w), 519 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{27}F_3NO_3SW$: C, 31.71; H, 5.13; N, 2.64. Found: C, 31.44; H, 4.90; N, 2.46.

$[Cp^*WMe_3(^{15}NH_3)]OTf$ was prepared by a similar method using $^{15}NH_3$: IR (Nujol) 3241 (s, NH_2), 3167 (s, NH_2), 1641 (m, NH_2), 1320 (m), 1268 (vs, OTf), 1258 (vs, OTf), 1227 (m), 1163 (s), 1035 (s, OTf), 759 (w), 638 (s, OTf), 576 (w), 519 (m) cm^{-1}.

An alternative method of preparing **6** is the following: $Cp^*WMe_3(OTf)$ (0.038 g, 0.074 mmol, 1.04 equiv) in 2 mL of tetrahydrofuran was added to $[Cp^*WMe_3(NH_3)_2]OTf$ (0.039 g, 0.071 mmol) in 5 mL of tetrahydrofuran at room temperature. After 5 min pentane was added to precipitate yellow microcrystalline $[Cp^*WMe_3(NH_3)]OTf$ (0.070 g, 0.13 mmol, 93%).

Protonation of $[Cp^*WMe_3(NH_3)]OTf$. Triflic acid (0.028 g, 0.19 mmol, 1.24 equiv) in 2 mL of ether was added to a light orange slurry of $[Cp^*WMe_3(NH_3)_2]OTf$ (0.080 g, 0.19 mmol) in 10 mL of ether. Within 2 min most of the $[Cp^*WMe_3(NH_3)_2]OTf$ disappeared and the solution became orange. After 10 min white insoluble $[NH_4]OTf$ (0.025 g, 0.15 mmol, 99%) was isolated by filtration and rinsed with ether. $[NH_4]OTf$ was identified by proton NMR in dimethyl-d_6 sulfoxide (δ 7.07 (br)). The filtrate was taken to dryness in vacuo, and yellow-orange crystals of $Cp^*WMe_3(OTf)$ (0.12 g, 0.24 mmol, 74%) were isolated upon crystallization of the residue from a minimum of a mixture of tetrahydrofuran by addition of pentane. Its IR spectrum was identical to that of authentic material.

$[Cp^*WMe_3(NH_3)_2]OTf$ (7). Excess ammonia (6.00 mmol, 2.50 equiv) was condensed onto a frozen, degassed solution of $Cp^*WMe_3(OTf)$ (1.23 g, 2.40 mmol) in 40 mL of ether. The mixture was warmed to room temperature and after 30 min orange $[Cp^*WMe_3(NH_3)_2]OTf$ (1.24 g, 2.26 mmol, 94%) was isolated by filtration. Recrystallization from tetrahydrofuran/ether at -40 °C gave analytically pure red-orange crystals: ESR (CH_2Cl_2) $\langle g \rangle$ = 2.006 (35 G); IR (Nujol) 3355 (s, NH_2), 3303 (s, NH_2), 3268 (s, NH_2), 3205 (s, NH_2), 1649 (m, NH_2), 1623 (m, NH_2), 1338 (s), 1303 (s), 1263 (vs, OTf), 1224 (s), 1171 (s), 1030 (s, OTf), 637 (s, OTf), 573 (w), 515 (m), 482 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{30}F_3N_2O_3SW$: C, 30.72; H, 5.52; N, 5.12. Found: C, 31.11; H, 5.38; N, 4.92.

$[Cp^*WMe_3(^{15}NH_3)_2]OTf$ was prepared by a similar method using $^{15}NH_3$.

$[Cp^*WMe_3(ND_3)_2]OTf$ was prepared by a similar method using ND_3 containing some NH_2D and NHD_2: IR (Nujol) ν(NHD) 2498, 2464, 2456, 2432 cm^{-1}; IR (Nujol) $\nu(ND_2)$ 2377, 2348, 2329, 2317, and 1164 (s), 1036 (s, OTf), 1014 (m), 1000 (m), 638 (s, OTf), 573 (w), 515 (w), 479 (w) cm^{-1}.

Protonation of $[Cp^*WMe_3(NH_3)_2]OTf$. Triflic acid (0.051 g, 0.34 mmol, 1.06 equiv) in 2 mL of ether was added to a light orange slurry of $[Cp^*WMe_3(NH_3)_2]OTf$ (0.18 g, 0.32 mmol) in 10 mL of ether. The color changed slowly to yellow after stirring for 1 h at room temperature. The precipitate was filtered off and rinsed with ether. Extraction with dichloromethane left white insoluble $[NH_4]OTf$ (0.039 g, 0.23 mmol, 73%). The filtrate was reduced to dryness in vacuo to give yellow crystals of $[Cp^*WMe_3(NH_3)]OTf$ (0.12 g, 0.24 mmol, 74%) upon recrystallization from a minimum of tetrahydrofuran by adding ether.

$Cp^*WMe_3(NH_2)$ (8). DBU (0.052 g, 0.34 mmol, 0.97 equiv) in 5 mL of ether was added to $[Cp^*WMe_3(NH_3)_2]OTf$ (0.19 g, 0.35 mmol) in 15 mL of ether. The solution was stirred vigorously for 10 min and then taken to dryness in vacuo. The residue was extracted with pentane, and the solvent was removed in vacuo to yield yellow crystalline $Cp^*WMe_3(NH_2)$ (0.12 g, 0.31 mmol, 91%). Recrystallization from a concentrated pentane solution at -40 °C gave analytically pure yellow crystals: ESR (THF) $\langle g \rangle$ = 2.005 (43 G); IR (Nujol) 3406 (m, NH_2), 3321 (m, NH_2), 1543 (w, NH_2), 1028 (m, CH_3), 681 (m), 632 (m), 556 (m), 485 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{26}NW$: C, 41.07; H, 6.89; N, 3.68. Found: C, 40.97; H, 7.18; N, 3.18.

$Cp^*WMe_3(^{15}NH_2)$ was prepared similarly from $[Cp^*WMe_3(^{15}NH_3)_2]OTf$: IR (Nujol) 3389 (w, NH_2), 3310 (w, NH_2), 1538 (w, NH_2), 1028 (m, CH_3), 676 (w), 626 (w), 612 (m), 555 (m), 485 (m) cm^{-1}.

Protonation of $Cp^*WMe_3(NH_2)$. Triflic acid (0.022 g, 0.12 mmol, 0.71 equiv) in 2 mL of ether was added to $Cp^*WMe_3(NH_2)$ (0.065 g, 0.17 mmol) in 5 mL of ether at -40 °C. A yellow precipitate formed quickly and after 10 min was isolated by filtration and rinsed with ether. The solvent was removed from the filtrate in vacuo, and the product was identified as $[Cp^*WMe_3(NH_3)]OTf$ (0.052 g, 0.094 mmol, 77%) by its IR spectrum.

Addition of $[NH_4]OTf$ to $Cp^*WMe_3(NH_2)$. Ammonium triflate (0.024 g, 0.14 mmol, 1.22 equiv) in 2 mL of tetrahydrofuran was added to $Cp^*WMe_3(NH_2)$ (0.045 g, 0.12 mmol) in 5 mL of tetrahydrofuran. The reaction was stirred at room temperature for 1 h and excess pentane was added to give a yellow precipitate. The precipitate was extracted with dichloromethane. The dichloromethane was removed from the filtrate in vacuo to give yellow $[Cp^*WMe_3(NH_3)]OTf$ (identified by IR spectroscopy). The remaining reddish residue was extracted with tetrahydrofuran, and pentane was added to the filtrate to precipitate light orange $[Cp^*WMe_3(NH_3)_2]OTf$ (identified by IR spectroscopy).

$Cp^*WMe_3(NH)$ (9a). (a) Excess triethylamine (145 μL, 1.44 mmol, 5.00 equiv) in 5 mL of dichloromethane was added to $[Cp^*WMe_3(NH_3)_2]OTf$ (0.16 g, 0.29 mmol) in 15 mL of dichloromethane at room temperature. After 30 s $[FeCp_2]PF_6$ (0.10 g, 0.31 mmol, 1.06 equiv) was added and the reaction mixture was stirred until all $[FeCp_2]PF_6$ had disappeared (~10 min). The solvent was removed in vacuo, and the residue was extracted with ether. Removal of the ether from the filtrate in vacuo left a yellow-orange 1:1 mixture of $Cp^*WMe_3(NH)$ and $FeCp_2$ (0.16 g, 0.28 mmol, 97%).

(b) Water (10 μL, 0.56 mmol, 3.01 equiv) was added to $[Cp^*WMe_3(NLi)]_x$ (0.071 g, 0.18 mmol) in 10 mL of ether. After 5 min LiOH was filtered off and $Cp^*WMe_3(NH)$ (0.045 g, 0.12 mmol, 65%) was obtained upon removing the ether in vacuo. Recrystallization from ether/pentane at -40 °C gave analytically pure ivory crystals: ^1H NMR (CD_2Cl_2) δ 9.35 (1:1:1, $^1J_{H^{14}N}$ = 55, 1 H, NH), 1.86 (s, 15 H, Cp*), 0.62 (s, 6 H, WMe_{cis}), -0.11 (s, 3 H, WMe_{trans}); ^{13}C NMR (CD_2Cl_2) δ 111.02 (Cp*), 29.34 ($^1J_{CW}$ = 68, WMe_{trans}), 21.94 ($^1J_{CW}$ = 57, WMe_{cis}), 10.81 (Cp*); IR (CCl_4) 3438 (s, NH), 939 (s, WNH) cm^{-1}; IR (Nujol) 3439 (m, NH), 3406 (w, NH), 3386 (w, NH), 3359 (s, NH), 1026 (m, CH_3), 939 (s, WNH), 923 (m, WNH), 767 (w), 722 (w), 551 (w), 487 (w) cm^{-1}. Anal. Calcd for $C_{13}H_{25}NW$: C, 41.18; H, 6.64; N, 3.69. Found: C, 41.01; H, 6.59; N, 3.76.

$Cp^*WMe_3(^{15}NH)$ was prepared similarly from $[Cp^*WMe_3(^{15}NLi)]_x$: ^1H NMR δ 9.35 (d, $^1J_{HN}$ = 77, $^2J_{HW}$ = 83, NH); ^{15}N NMR (CD_2Cl_2) δ 388.0 ($^1J_{NW}$ = 113); IR (CCl_4) 3431 (s, ^{15}NH),

911 (s, $W^{15}NH$) cm^{-1}; IR (Nujol) 3431 (m, ^{15}NH), 3399 (w, ^{15}NH), 3377 (w, ^{15}NH), 3357 (w, ^{15}NH), 1028 (m, CH_3), 914 (s, $W^{15}NH$), 901 (m, $W^{15}NH$) cm^{-1}.

$Cp^*WMe_3(ND)$ was prepared similarly from $[Cp^*WMe_3(NLi)]_x$ and D_2O: IR (CCl_4) 2558 (s, ND), 910 (s, WND) cm^{-1}; IR (Nujol) 2560 (w, ND), 2535 (m, ND), 2523 (m, ND), 2503 (m, ND), 1027 (m, CH_3), 910 (s, WND), 904 (s, WND), 765 (w), 724 (w), 497 (w) cm^{-1}.

$[Cp^*WMe_3(NLi)]_x$ (9b). A solution of *n*-butyllithium (1.85 mmol, 1.10 equiv) in 2 mL of ether was added to $Cp^*WMe_3(NH)$ (0.95 g, 1.68 mmol) in 20 mL of ether. After 15 min pale yellow, crystalline **9b** (0.47 g, 1.22 mmol, 73%) was filtered off and rinsed with cold ether. Recrystallization from a minimum of tetrahydrofuran layered with pentane at −40 °C gave an analytically pure white powder: ^1H NMR (CD_2Cl_2) δ 1.80 (s, 15 H, Cp*), 0.32 (s, 6 H, WMe_2), −0.42 (s, 3 H, WMe_{trans}); ^{13}C NMR (THF-d_8) δ 108.04 (Cp*), 24.34 ($^1J_{CW}$ = 78, WMe_{trans}), 19.06 ($^1J_{CW}$ = 70, WMe_{cis}), 11.17 (Cp*); IR (Nujol) 993 (s, WNLi), 742 (w), 495 (w) cm^{-1}. Anal. Calcd for $C_{13}H_{24}LiNW$: C, 40.54; H, 6.28; N, 3.64. Found: C, 41.32; H, 6.24; N, 3.41.

$[Cp^*WMe_3(^{15}NLi)]_x$ was prepared similarly from $Cp^*WMe_3(^{15}NH)$: ^{15}N NMR (THF-d_8) δ 678.5 ($^1J_{NW}$ = 54); ^{15}H NMR (pyridine-d_5) δ 679.0 ($^1J_{NW}$ = 54); IR (Nujol) 968 (s, $W^{15}NLi$), 743 (w), 496 (w) cm^{-1}.

$Cp^*WMe_3(NMe)$ (9c). Excess methyl triflate (0.15 g, 0.91 mmol, 2.04 equiv) was added to a slurry of $[Cp^*WMe_3(NLi)]_x$ (0.17 g, 0.44 mmol) in 10 mL of ether at room temperature. The starting material dissolved to give a pale yellow solution. After 20 min the solvents were removed in vacuo and the residue was extracted with pentane. The extract was taken to dryness to yield pale yellow, crystalline $Cp^*WMe_3(NMe)$ (0.14 g, 0.37 mmol, 83%). Recrystallization from a minimum of ether by addition of pentane at −40 °C gave analytically pure pale yellow needles: ^1H NMR (CD_2Cl_2) δ 2.98 (s, 3 H, NMe), 1.79 (s, 15 H, Cp*), 0.37 (s, 6 H, WMe_{cis}), −0.29 (s, 3 H, WMe_{trans}); ^{13}C NMR (CD_2Cl_2) δ 109.26 (Cp*), 49.92 (NMe), 28.21 ($^1J_{CW}$ = 69, WMe_{trans}), 21.82 ($^1J_{CW}$ = 58, WMe_{cis}), 9.67 (Cp*); IR (Nujol) 1315 (s, WNC), 1027 (m, CH_3), 490 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{27}NW$: C, 42.76; H, 6.92; N, 3.56. Found: C, 43.04; H, 7.30; N, 3.37.

$Cp^*WMe_3(^{15}NMe)$ was prepared similarly using $[Cp^*WMe_3(^{15}NLi)]_x$: ^1H NMR (CD_2Cl_2) δ 2.98 (d, $^2J_{HN}$ = 3.2, $^3J_{HW}$ = 5.4, NMe); ^{13}C NMR (CD_2Cl_2) δ 49.92 ($^1J_{CN}$ = 4.6, NMe); ^{15}N NMR (C_6D_6) δ 387.7 ($^1J_{NW}$ = 115); IR (Nujol) 1283 (s, $W^{15}NC$), 1029 (m, CH_3), 491 (m) cm^{-1}.

$Cp^*WMe_3(N^{13}CH_3)$ was prepared by adding an excess of $^{13}CH_3I$ (0.50 g, mmol, equiv) to a slurry of $[Cp^*WMe_3(NLi)]_x$ (0. g, 0. mmol) in 5 mL of ether. After 14 h the solvent was removed in vacuo and the residue was extracted with pentane. The pentane was removed in vacuo to give a mixture of 65% $Cp^*WMe_3(N^{13}CH_3)$, 25% $Cp^*WMe_3(NH)$, and 10% $[Cp^*WMe_3(NLi)]_x$: ^1H NMR (CD_2Cl_2) δ 2.98 (d, $^1J_{HC}$ = 119, $N^{13}CH_3$); IR (Nujol) 1301 (s, $WN^{13}C$) cm^{-1}.

$Cp^*WMe_3(NMe)$ also has been prepared by condensing excess methylamine (2.90 mmol, 20.0 equiv) onto a frozen solution of $Cp^*WMe_3(NH)$ (0.055 g, 0.14 mmol) and [(lutidine)H]OTf (0.010 g, 0.039 mmol, 0.28 equiv) in 5 mL of dichloromethane. A mixture of methylammonium chloride and triflate (0.049 g) was filtered off. (^1H NMR (dimethyl-d_6 sulfoxide) δ 8.06 (br, 3 H, NH), 2.30 (s, 3 H, NMe)). The light yellow filtrate was reduced to dryness in vacuo, and the residue was extracted with ether. Pale yellow crystals of $Cp^*WMe_3(NMe)$ (0.049 g, 0.12 mmol, 86%) were isolated upon addition of pentane and cooling to −40 °C.

$Cp^*WMe_2(OTf)(NMe)$. Triflic acid (0.043 g, 0.29 mmol, 0.94 equiv) in 2 mL of ether was added to $Cp^*WMe_3(NMe)$ (0.12 g, 0.30 mmol) in 10 mL of ether at room temperature, resulting in vigorous gas evolution. After 15 min the solvent was removed in vacuo and the residue was rinsed with pentane, leaving $Cp^*WMe_2(OTf)(NMe)$ (0.12 g, 0.23 mmol, 81%) as a pale yellow powder. Recrystallization from dichloromethane/ether yields analytically pure pale yellow plates: ^1H NMR (CD_2Cl_2) δ 3.74 (s, $^3J_{HW}$ = 7.5, 3 H, NMe), 1.98 (s, 15 H, Cp*), 0.84 (s, 6 H, WMe_{cis}); ^{13}C NMR (CD_2Cl_2) δ 119.38 (q, $^1J_{CF}$ = 317, OTf), 115.75 (Cp), 49.19 (NMe), 36.88 ($^1J_{CW}$ = 60, WMe_{cis}), 10.65 (Cp*); ^{19}F NMR (CD_2Cl_2) δ −78.98. Anal. Calcd for $C_{14}H_{24}F_3NO_3SW$: C, 31.89; H, 4.59; N, 2.66. Found: C, 32.07; H, 4.54; N, 2.44.

$Cp^*WMe(OTf)_2(NMe)$. Triflic acid (0.13 g, 0.86 mmol, 2.10 equiv) in 2 mL of ether was added to $Cp^*WMe_3(NMe)$ (0.16 g, 0.41 mmol) in 10 mL of ether at room temperature, resulting in gas evolution. After 18 h the solvent was removed in vacuo, leaving a pale yellow powder of $Cp^*WMe(OTf)_2(NMe)$ (0.124 g, 0.064 mmol, 46%). Recrystallization from a minimum of dichloromethane/ether yields analytically pure pale yellow crystals: ^1H NMR (CD_2Cl_2) δ 4.62 (s, $^3J_{HW}$ = 9.9, 3 H, NMe), 2.22 (s, 15 H, Cp*), 1.34 (s, 3 H, WMe); ^{13}C NMR (CD_2Cl_2) δ 122.66 (Cp*), 122.15 (q, $^1J_{CF}$ = 321, OTf), 119.61 (q, $^1J_{CF}$ = 322, OTf), 41.62 ($^1J_{CW}$ = 64, WMe), 10.77 (Cp*); ^{19}F NMR (CD_2Cl_2) δ −77.10 (OTf), −78.30 (OTf); IR (Nujol) 1354 (s), 1342 (s), 1301 (m), 1235 (s, OTf), 1183 (vs, OTf), 1001 (s, OTf), 974 (s, OTf), 797 (w), 762 (w), 630 (s, OTf), 595 (m), 572 (w), 516 (w) cm^{-1}. Anal. Calcd for $C_{14}H_{21}F_6NO_6S_2W$: C, 25.43; H, 3.20; N, 2.12. Found: C, 25.63; H, 3.09; N, 2.02.

$Cp^*WMe_3(NSiMe_3)$ (9d). Excess trimethylsilyl chloride (0.19 g, 1.76 mmol, 5.00 equiv) was added to a slurry of $[Cp^*WMe_3(NLi)]_x$ (0.14 g, 0.35 mmol) in 10 mL of ether at room temperature. After 30 min LiCl (0.015 g, 0.35 mmol, 1.00 equiv) was filtered off and the solvent was removed in vacuo. Extraction of the residue with pentane gives analytically pure $Cp^*WMe_3(NSiMe_3)$ (0.15 g, 0.34 mmol, 96%) as a beige oil upon removal of solvent, which becomes a crystalline solid upon cooling: ^1H NMR (CD_2Cl_2) δ 1.83 (s, 15 H, Cp*), 0.63 (s, 6 H, WMe_{cis}), −0.20 (s, 3 H, WMe_{trans}), −0.05 (s, 9 H, $SiMe_3$, J_{HSi} = 6.7); ^{13}C NMR (C_6D_6) δ 110.41 (Cp*), 31.77 ($^1J_{CW}$ = 61, WMe_{trans}), 24.78 ($^1J_{CW}$ = 60, WMe_{cis}), 10.96 (Cp*), −0.04 ($SiMe_3$, J_{CSi} = 57); IR (neat) 1246 (m, $SiMe_3$), 1147 (s, WNSi), 1028 (m, CH_3), 841 (s, $SiMe_3$), 752 (m, $SiMe_3$), 631 (m), 498 (cm) cm^{-1}. Anal. Calcd for $C_{16}H_{33}NSiW$: C, 42.58; H, 7.57; N, 3.10. Found: C, 42.91; H, 7.69; N, 2.91.

$Cp^*WMe_3(^{15}NSiMe_3)$ was prepared similarly from $[Cp^*WMe_3(^{15}NLi)]_x$: ^1H NMR δ 0.63 (d, $^3J_{HN}$ = 0.9, $^2J_{HW}$ = 5.7, WMe_{cis}), −0.05 (d, $^3J_{HN}$ = 0.9, $^4J_{HW}$ = 6.9, $SiMe_3$), −0.20 (s, $^3J_{HN} \approx 0$; $^2J_{HW}$ = 5.7, WMe_{trans}); ^{15}N NMR (C_6D_6) δ 454.3 ($^1J_{NW}$ = 88); IR (neat) 1245 (m, $SiMe_3$), 1116 (s, $W^{15}NSi$), 1034 (m, CH_3), 841 (s, $SiMe_3$), 750 (m, $SiMe_3$), 633 (m), 496 (m) cm^{-1}.

$Cp^*WMe_3(N\text{-}t\text{-}Bu)$. Excess *tert*-butylamine (165 μL, 1.57 mmol, 5.00 equiv) was added to a solution of $Cp^*WMe_3(OTf)$ (0.16 g, 0.31 mmol) in 15 mL of dichloromethane at −40 °C; the solution turned dark green immediately. $[FeCp_2]PF_6$ (0.11 g, 0.34 mmol, 1.10 equiv) was then added, and the solution turned orange in a few minutes. After 20 min the solvent was removed in vacuo. The yellow, crystalline residue was extracted with ether, the mixture was filtered, and the ether was removed from the filtrate in vacuo. The resulting residue was shown by NMR analysis to be a mixture of $Cp^*WMe_3(N\text{-}t\text{-}Bu)$ (0.075 g, 0.17 mmol, 55%) and $FeCp_2$ (0.075 g, 0.34 mmol, ca. 100%): ^1H NMR (C_6D_6) δ 1.60 (s, 15 H, Cp*), 1.08 (s, 9 H, *t*-Bu), 0.87 (s, 6 H, WMe_{cis}), 0.30 (s, 3 H, WMe_{trans}); ^{13}C NMR (C_6D_6) δ 109.63 (Cp*), 69.58 (−*NC*Me_3), 28.75 (−NC*Me*$_3$), 27.66 (WMe_{trans}, $^1J_{CW}$ = 70), 21.33 (WMe_{cis}, $^1J_{CW}$ = 58), 10.87 (Cp*); IR (Nujol) 1285 (s, WNC) cm^{-1}.

$\{[Cp^*WMe_3]_2(\mu\text{-}N)\}PF_6$ (10). (a) Solid $[FeCp_2]PF_6$ (0.041 g, 0.12 mmol) was added to a slurry of $[Cp^*WMe_3]_2(\mu$-N) (0.082 g, 0.11 mmol) in 10 mL of dichloromethane. The solution turned red, and after 15 min the solvent was removed in vacuo and $FeCp_2$ was removed from the filtrate by extraction with ether. Analytically pure deep red $\{[Cp^*WMe_3]_2(\mu$-N)$\}PF_6$ (0.075 g, 0.084 mmol, 77%) was crystallized from dichloromethane by addition of ether and cooling the solution to −40 °C: ^1H NMR (CD_2Cl_2) δ 1.98 (15 H, Cp*), 1.32 (6 H, WMe_{cis}), 1.02 (3 H, WMe_{trans}); ^{13}C NMR (CD_2Cl_2) δ 115.85 (Cp*), 57.23 ($^1J_{CW}$ = 47, WMe_{trans}), 51.95 ($^1J_{CW}$ = 52, WMe_{cis}), 11.08 (Cp*); ^{19}F NMR (CD_2Cl_2) δ −73.35 ($^1J_{FP}$ = 706); IR (Nujol) 1169 (m), 1029 (m, PF_6, CH_3), 999 (s, WNW), 877 (m), 843 (s, PF_6), 714 (m), 558 (m, PF_6), 494 (m), 453 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{48}F_6NPW_2$: C, 35.19; H, 5.45; N, 1.58. Found: C, 34.86; H, 5.22; N, 1.42.

$\{[Cp^*WMe_3]_2(\mu\text{-}^{15}N)\}PF_6$ was prepared similarly using $[Cp^*WMe_3]_2(\mu\text{-}^{15}N)$: ^{15}N NMR δ 634.9 ($^1J_{NW}$ = 63, ^{183}W satellites = 28% of peak area); IR (Nujol) 1169 (m), 1025 (m, PF_6, CH_3), 969 (s, $W^{15}NW$), 878 (m), 838 (s, PF_6), 713 (m), 558 (m, PF_6), 493 (m), 453 (w) cm^{-1}.

(b) $Cp^*WMe_3(NH)$ (0.057 g, 0.15 mmol) in 1 mL of dichloromethane was added to a slurry of $[Cp^*WMe_4]PF_6$ (0.078 g, 0.15 mmol) in 2 mL of dichloromethane. After 1.5 h the solution had become deep red and the solvent was removed in vacuo. Pre-

cipitation from dichloromethane/ether yielded $\{[Cp^*WMe_3]_2(\mu\text{-}N)\}PF_6$ (0.098 g, 0.11 mmol, 74%).

Generation and Decomposition of $[Cp^*WMe_3(NH_2)]PF_6$ (4). (a) Ammonia (0.13 mmol, 1.00 equiv) was condensed onto a degassed frozen slurry of $[Cp^*WMe_4]PF_6$ (0.070 g, 0.13 mmol) in 10 mL of dichloromethane. The solution was warmed to −78 °C and then slowly to room temperature. After 30 min the solvent was removed in vacuo from the orange-red solution. Extraction with dichloromethane yielded a mixture of $[Cp^*WMe_4]PF_6$ (~10%) and dark red $\{[Cp^*WMe_3]_2(\mu\text{-}N)\}PF_6$ (~90%).

(b) Solid $[FeCp_2]PF_6$ (0.029 g, 0.088 mmol, 0.98) was added to $Cp^*WMe_3(NH_2)$ (0.034 g, 0.089 mmol) in 5 mL of dichloromethane at −40 °C and allowed to warm to room temperature. After 45 min the orange-red solution was filtered and addition of ether resulted in precipitation of dark red $\{[Cp^*WMe_3]_2(\mu\text{-}N)\}PF_6$ (0.057 g, 0.065 mmol, 74%).

$[Cp^*MoMe_3(NH_3)]OTf$ (11). $Cp^*MoMe_3(OTf)$ (0.50 g, 1.18 mmol) was dissolved in 20 mL of ether to give a red-purple solution. Ammonia (1.06 mmol, 0.90 equiv) was condensed into the reaction flask and the reaction mixture was allowed to warm to room temperature in a water bath while it was stirred. A red solid formed almost immediately. After 20 min the red $[Cp^*MoMe_3(NH_3)]OTf$ (0.35 g, 0.78 mmol, 83%) was filtered off: EPR (CH_2Cl_2) $\langle g\rangle = 2.006$ ($\Delta\nu_{1/2} = 42$ G, $A_{Mo} = 40$ G); IR (Nujol) 3238 (s, NH_2), 3172 (s, NH_2), 1632 (s, NH_2), 1370 (s), 1260 (s, OTf), 1152 (s), 1031 (s), 727 (m), 636 (s, OTf), 573 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{27}NSO_3F_3Mo$: C, 38.01; H, 6.15; N, 3.17. Found: C, 37.42; H, 6.40; N, 3.16.

$[Cp^*MoMe_3(NH_3)_2]OTf$ (12). The procedure was the same as for $[Cp^*MoMe_3(NH_3)]OTf$ but using 2 equiv of ammonia. Orange $[Cp^*MoMe_3(NH_3)_2]OTf$ (0.56 g, 1.21 mmol, 86%) was filtered off: EPR (CH_2Cl_2) $\langle g\rangle = 2.007$ ($\Delta\nu_{1/2} = 32$ G, $A_{Mo} = 37$ G); IR (Nujol) 3360 (m, NH_2), 3321 (s, NH_2), 3260 (s, NH_2), 3202 (m, NH_2), 1628 (m, NH_2), 1617 (m, NH_2), 1270 (s, OTf), 1020 (s), 619 (m, OTf), 572 (m), 503 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{30}N_2OS_3F_3Mo$: C, 36.60; H, 6.58; N, 6.01. Found: C, 36.38; H, 6.55; N, 6.19.

$Cp^*MoMe_3(NH_2)$ (13). $[Cp^*MoMe_3(NH_3)_2]OTf$ (0.50 g, 1.09 mmol) was stirred in 15 mL of cold ether (−40 °C) to give an orange suspension. DBU (163 μL, 1.09 mmol, 1 equiv) was added to the reaction which became a dark homogeneous red and was stirred for 10 min. The red solution was decanted away from a brown oil, and the solvent was removed in vauco. The resulting red/brown film was washed with pentane, and the red solution was decanted and taken to dryness to give red-brown $Cp^*MoMe_3(NH_2)$ (0.23 g, 0.77 mmol, 71%): EPR (CH_2Cl_2) $\langle g\rangle = 2.007$ ($\Delta\nu_{1/2} = 28$ G); IR (Nujol) 3374 (w, NH_2), 3318 (w, NH_2), 1570 (m, NH_2), 1020 (s), 703 (m), 483 (m) cm^{-1}.

$Cp^*MoMe_3(NH)$ (14). $[Cp^*MoMe_3(DOMP)]PF_6$ (0.33 g, 0.57 mmol; DOMP = *O*-2,6-$C_6H_3(OMe)_2$) was suspended in 15 mL of ether with triethylamine (160 μL, 1.15 mmol, 2 equiv). Ammonia (1.15 mmol, 2 equiv) was condensed into the reaction flask, and the reaction mixture was warmed to room temperature. The reaction mixture turned red and was stirred for 1.5 h. The red solution was filtered, leaving behind brown $[NEt_3H]PF_6$. The solvent was removed in vacuo to produce an orange-white solid. The solid was extracted with cold pentane, and a dark orange solution was filtered off. The solvent was removed in vacuo to give an orange-white solid that was a mixture of orange $Cp^*MoMe_3(NH)$ and white DOMPH: ^1H NMR (C_6D_6) 6.68 (t, 1 H, $J_{HN} = 52$), 1.50 (s, 15 H), 1.15 (s, 6 H), 0.48 (s, 3 H); ^{13}C (C_6D_6) 110.8 (s, Me_5C), 29.8 (q, Mo–Me_{cis}), 25.0 (q, Mo–Me_{trans}), 10.4 (q, Me_5C); IR (Nujol) 3341 (s, NH), 925 (m, MoNH) cm^{-1}.

LiN_2H_3. A solution of *n*-butyllithium (14.20 mmol, 1.00 equiv) in hexane was slowly added to a mixture of hydrazine (0.46 g, 14.20 mmol) in 50 mL of ether at room temperature. After 30 min fluffy white LiN_2H_3 (0.51 g, 13.46 mmol, 95%) was filtered off, rinsed with ether, and dried in vacuo.

$[Cp^*MoMe_3(NLi)]_x$ (15). LiN_2H_3 (0.15 g, 3.70 mmol) was suspended in 50 mL of THF. $Cp^*MoMe_3(OTf)$ (0.20 g, 0.47 mmol) was added slowly over a period of 10 min. The initially dark purple reaction mixture turned quickly to orange-yellow. After 1.5 h the reaction mixture was filtered to yield a dark orange-yellow filtrate and a white solid (excess LiN_2H_3). The solvent was removed from the filtrate to give an orange-brown residue. The residue was extracted with pentane and the orange-yellow solution was decanted away from LiOTf. The solvent was removed in vacuo to give orange-yellow $[Cp^*MoMe_3(NLi)]_x$ (0.08 g, 0.22 mmol, 46%): ^1H NMR (C_6D_6) δ 1.73 (s, 15 H, Cp*), 0.68 (s, 6 H, Mo–Me_c), −0.05 (s, 3 H, Mo–Me_t); ^{13}C NMR (C_6D_6) δ 110.0 (s, Me_5C), 23.6 (q, Mo–Me_{cis}), 18.7 (q, Mo–Me_{trans}), 10.8 (q, Me_5C); IR (Nujol) 979 (m, MoNLi), 790 (m), 480 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{24}NLiMo$: C, 52.53; H, 8.14; N, 4.71. Found: C, 52.30; H, 8.20; N, 4.50.

$Cp^*MoMe_3(NMe)$ (16). $[Cp^*MoMe_3(NLi)]_x$ (0.15 g, 0.50 mmol) was dissolved in 25 mL of ether and methyl triflate (57 μL, 0.50 mmol, 1 equiv) was added. After the reaction was stirred for 1 h, the reaction mixture was worked up as described above to give light yellow $Cp^*MoMe_3(NMe)$ (0.13 g, 0.43 mmol, 84%): ^1H NMR (CD_2Cl_2) 3.60 (s, 3 H), 1.70 (s, 15 H), 0.47 (s, 6 H), 0.34 (s, 3 H); ^{13}C NMR (CD_2Cl_2) δ 110.4 (s, Me_5C), 54.7 (q, N–*Me*), 27.1 (q, Mo–Me_{cis}), 24.3 (q, Mo–Me_{trans}), 10.3 (q, Me_5C); IR (Nujol) 1280 (s), 1028 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{27}NMo$: C, 55.08; H, 8.91; N, 4.59. Found: C, 54.91; H, 9.31; N, 4.21.

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