(CO), 136.5, 131.1, 128.1, 126.7, 109.5, 107.8 (C=C, Ar), 62.5, 50.9 (NC), 33.4, 32.2, 30.6, 26.1, 23.3, 22.9 ($6CH_2$). Anal. Calcd for $C_{21}H_{21}NO_4Cr$: C, 62.53; H, 5.21; N, 3.47. Found: C, 62.47; H, 5.20; N, 3.45.

Ylide Complex 23b ($C_{21}H_{21}NO_4Cr$) was obtained from **9b** in refluxing benzene: yield, 40%, yellow powder: mp 175 °C dec; IR ($CHCl_3$) 1960, 1880, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.15, 5.75, 5.58, 5.05 (m, 5 H, Ar), 5.35 (d, 1 H), 4.05 (m, 1 H), 3.70 (m, 1 H), 3.15 (m, 1 H), 3.0 (m, 1 H), 2.85 (m, 1 H), 2.35 (m, 1 H), 1.95 (m, 2 H), 1.75 (m, 2 H), 1.65 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8 (CO), 112.8, 107.2, 96.0, 95.5, 89.4, 89.1, 87.6 (C=C, ArCr), 57.1, 49.3, 33.9, 30.3, 22.4, 21.3, 21.1; HRMS calcd for $C_{21}H_{21}NO_4Cr$ (M^+) 403.0875, found m/e 403.0885.

Ylide Complex 23c ($C_{20}H_{19}NO_4Cr$). Carbene complex **9c** (1 g) was refluxed in anhydrous benzene (50 mL). After 10 min, the solution turned deep red. Refluxing for an additional 10 h gave, after cooling to room temperature, complex **20c** (0.34 g, 40%) as a yellow powder: mp 175 °C dec; IR (CH_2Cl_2) 1960, 1880, 1700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.18 (d, 1 H), 5.66 (d, 1 H), 5.54 (m, 2 H), 5.29 (d, 1 H), 4.99 (m, 1 H), 3.98 (m, 2 H), 3.25 (m, 2 H), 2.92 (m, 1 H), 2.75 (m, 2 H), 2.11 (m, 4 H), 1.79 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 233.2 (CO), 170.9 (CO), 143.8, 107.9, 96.9, 95.4, 92.3, 92.1, 91.6, 56.7, 52.5, 33.6, 25.2, 24.8, 24.6; HRMS calcd for $C_{20}H_{19}NO_4Cr^+$ (M^+) 389.0720, found m/e 389.0721.

Pyrrolinones 25-27. Complex **9d** (2 g, 0.004 mol) was refluxed in anhydrous benzene (50 mL) for 12 h. After evaporation of the solvent, the residue was chromatographed on silica gel with petroleum ether/methylene chloride as eluents. Appropriate fractions were collected and evaporated to give first compound **27** (0.58 g, 45%) as an oil, then complex **25** (0.03 g, 2%) as yellow crystals, and finally compound **26** as an oil (0.11 g, 9%). **27**: IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR (200 MHz, C_6H_6) δ 7.65, 7.10 (m, 10 H), 3.63 (d, 1 H, PhCH), 3.08 (d, 1 H, PhCH), 2.42 (s, 3 H, NCH_3), 2.32 (m, 2 H), 1.73 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.5 (CO), 145.8, 139.8, 136.8, 129.5-126.3, 122.2 (C=C, Ar), 59.9, 42.9, 27.7, 27.3, 25.4, 24.3; HRMS calcd for $C_{21}H_{21}NO$ (M^+) 303.1623, found m/e 303.1624. **25**: mp 160 °C; IR ($CHCl_3$) 1965, 1895, 1690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (m, 5 H), 5.91, 5.49, 5.28 (m, 5 H, ArCr), 3.30 (d, 1 H, CHPh), 3.10 (d, 1 H, CHPh), 2.60 (s, 3 H, NCH_3), 2.63 (m, 2 H), 2.40 (m, 1 H), 2.20 (m, 1 H), 2.06 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.72 (CO), 180.05 (CO), 147.8, 135.7, 129.6-126.8, 119.6, 110.6 (C=C, Ar), 93.4, 92.9, 92.7, 91.7, 91.5 (ArCr), 57.8, 45.2, 29.6, 28.9, 27.3, 25.2, 24.6; MS $C_{24}H_{21}NO_4Cr^+$ 439, found 439. **26**: IR ($CHCl_3$) 1670 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53, 7.33, 7.26, 7.18, 7.11, 7.00 (m, 10 H), 3.08 (s, 3 H, NMe), 3.07 (2 doublets, 2 H, CH_2Ph), 2.84 (m, 1 H), 2.59 (m, 1 H), 2.33 (m, 1 H), 2.19 (m, 1 H), 2.03 (m, 1 H), 1.41 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.6 (CO), 163.6, 135.5, 132.0, 129.0-126.9 (C=C, Ar), 72.8, 39.5, 32.7, 26.4, 25.6, 23.7; HRMS calcd for $C_{21}H_{21}NO$ (M^+) 303.1623, found m/e 303.1624.

Acknowledgment. Professor N. Platzer is gratefully acknowledged for high-field NMR and CNRS for financial support.

Supplementary Material Available: Crystal structure data (Tables S1-S39) for **11a**, **18d**, **19c**, **21b**, **23a**, and **25** including complete lists of interatomic distances (Tables S7-S12) and bond angles (Tables S13-S22), fractional parameters (Tables S23-S28), and anisotropic thermal parameters (Tables S29-S33) (33 pages); tables of observed and calculated structure factors (Tables S34-S39) (36 pages). Ordering information is given on any current masthead page.

Diamagnetic (Pentamethylcyclopentadienyl)tungsten Complexes Containing Unsubstituted, Monomethyl, or 1,1-Dimethyl Hydrazine or Hydrazido Ligands

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Abstract: Hydrazine adducts are formed upon adding hydrazine, methylhydrazine, or 1,1-dimethylhydrazine to $[Cp^*WMe_4]PF_6$. They are readily deprotonated to yield hydrazido(1-) complexes of the type $Cp^*WMe_4[\eta^2$-hydrazido(1-)], or they decompose by loss of methane to yield complexes of the type $\{Cp^*WMe_3[\eta^2$-hydrazido(1-)]$\}^+$. $\{Cp^*WMe_3[\eta^2$-hydrazido(1-)]$\}^+$ complexes are deprotonated at low temperature to give complexes of the type $Cp^*WMe_3[\eta^2$-hydrazido(2-)], which rearrange readily to complexes of the type $Cp^*WMe_3[\eta^1$-hydrazido(2-)] above approximately -20 °C. Addition of acid to complexes of the type $Cp^*WMe_3(\eta^1$-NNRR') yields $[Cp^*WMe_3(NNRR'H)]^+$ complexes first. Loss of a proton from N_β followed by addition of a proton to N_α yields the thermodynamically preferred $[Cp^*WMe_3(\eta^2$-NHNRR')$]^+$ complexes. $[Cp^*WMe_3(\eta^2$-$NHNH_2)]Cl$ decomposes much more readily than the triflate salt by losing methane to give *trans*-$Cp^*WMe_2Cl(\eta^1$-$NNH_2)$. Methylation of $Cp^*WMe_3(\eta^1$-$NNMe_2)$ yields $[Cp^*WMe_3(NNMe_3)]^+$; $[Cp^*WMe_3(NNMe_3)]^+$ also is obtained upon methylating $Cp^*WMe_3(\eta^1$-$NNH_2)$ in the presence of a base. $Cp^*WMe_3(\eta^1$-$NNH_2)$ reacts with $[Cp^*WMe_3(\eta^2$-$NHNH_2)]^+$ to yield $[Cp^*WMe_3]_2(\mu$-$N_2)$ and $[N_2H_5]^+$, while $Cp^*WMe_3(\eta^1$-$NNH_2)$ decomposes to $Cp^*WMe_3(\mu$-NNH)$Cp^*WMe_2(\mu$-NN)Cp^*WMe_3. These findings are discussed in relation to the proposal that both nitrogen atoms of an N_2H_x intermediate must bind to the metal in preparation for formation of a d^2 η^2-N_2H_4 complex in which the N-N bond is cleaved to yield 1 equiv of ammonia.

Introduction

Dinitrogen is reduced to ammonia by various nitrogenases, those containing molybdenum or vanadium having the highest activity.[1-11] Over the last 25 years, inorganic chemists have elucidated modes of bonding of both dinitrogen and partially reduced dinitrogen (N_2H_x) ligands to transition metals and have been gathering evidence in support of mechanisms by which dinitrogen can be reduced to ammonia.[1,8,12,13] However, important pieces

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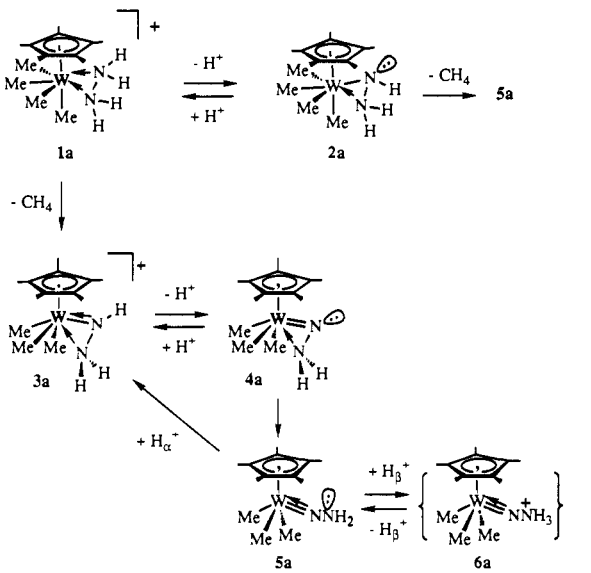
of the mechanistic puzzle are still missing, two of them being the manner in which the N–N bond is cleaved and how formation of free hydrazine is avoided.[8,13] There have been (rare) reports in the literature of the catalytic reduction of dinitrogen,[14–17] but in no case has the catalytically active transition metal complex been identified or the mechanism elucidated conclusively.

We have been interested for several years in the chemistry of high-oxidation-state transition metal complexes that is relevant to the reduction of dinitrogen to ammonia. Dinitrogen most commonly is activated by "electron-rich" metals in relatively low oxidation states, to give either monometallic dinitrogen complexes ([M]←N≡N) or bimetallic dinitrogen complexes ([M]←N≡N→[M]).[1,8,12,13] The synthesis of bimetallic hydrazido(4–) complexes ([M]=N—N=[M]; N—N ~ 1.30 Å) from dinitrogen and tantalum d^2 metal centers[18] suggested that metals are not typically viewed as electron-rich could significantly lengthen the N—N bond in a μ-dinitrogen ligand, perhaps because metal–nitrogen π bonding is an important component of dinitrogen reduction. (In contrast, by this criterion a d^2 metal such as Zr(II) does not reduce a μ-dinitrogen ligand as efficiently.[19,20]) Perhaps the most dramatic example of hydrazido(4–) complex formation is the synthesis of $[Cp^*WMe_3]_2(\mu\text{-}N_2)$ by reduction of Cp^*WMe_3(triflate) ($Cp^* = \eta^5\text{-}C_5Me_5$) in the presence of dinitrogen.[21] The mechanism is believed to consist of formation of an unobservable $Cp^*WMe_3(\eta^1\text{-}N_2)$ complex in which the dinitrogen ligand is strongly polarized and consequently attacked by Cp^*WMe_3(triflate) to form the W–N–N–W backbone. Loss of triflate ion and addition of a second external electron then yield $[Cp^*WMe_3]_2(\mu\text{-}N_2)$. An analogous reduction of Cp^*MoMe_3(triflate) under dinitrogen yields no $[Cp^*MoMe_3]_2(\mu\text{-}N_2)$, although $[Cp^*MoMe_3]_2(\mu\text{-}N_2)$ can be prepared by other methods, as can analogous "mixed metal" (W/Mo or W/Ta species).[22] μ-N_2 species can be reduced in the presence of protons to yield ammonia, the best yields being obtained from the W/Mo complex.

Recently we have found that several bimetallic hydrazido(3–) and hydrazido(4–) complexes containing the Cp^*WMe_3 core are hydrolyzed readily to give known monomeric species such as $Cp^*WMe_3(\eta^1\text{-}NNH_2)$[23] and have shown that ammonia can be obtained in high yield upon reducing this and other monomeric N_2H_x species (x = 2–4) that contain the Cp^*WMe_3 core, i.e., $Cp^*WMe_3(\eta^1\text{-}NNH_2)$ and $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]^+$.[24] We also have found that hydrazine can been reduced catalytically to give ammonia in high yield in the presence of protons and various N_2H_x species.[24] Consequently, we have begun to focus on monometallic mechanisms of N–N bond cleavage in N_2H_x complexes. The key, as yet unobserved, d^2 intermediate in which the N–N bond is believed to be cleaved in each case is $Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)$. Plausible products that might be formed after cleavage of the N–N bond that have been observed include $Cp^*WMe_3(NH)$, $Cp^*WMe_3(NH_2)$, and $[Cp^*WMe_3(NH_3)_x]^+$ (x = 1 or 2).[25]

The original method of preparing $[Cp^*WMe_3(N_2H_x)]^{n+}$ complexes involved reactions between hydrazine and $[Cp^*WMe_4]^+$.[23] It was proposed that excess hydrazine reacts with $[Cp^*WMe_4]^+$ to give $Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ (**2a**; Scheme I), via formation and deprotonation of $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]^+$ (**1a**). An X-ray study of **2a** showed it to be a pseudopentagonal bipyramid containing the two nitrogen atoms in the pentagonal plane with the lone NH proton pointing away from the Cp* ligand.[23] Two independent molecules were present. In one molecule the two NH_2 protons were hydrogen bonded to two THF molecules and the NH lone pair was interacting with the NH or an NH_2 proton in the other molecule. Protonation of $Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ gave **1a**, according to NMR studies, although this complex was thought to be unstable and was not isolated and fully characterized. The structure of **1a** was proposed to be analogous to that of **2a**.

Scheme I[a]



[a] Compound in braces has not been observed.

Methane is lost from $Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ (**2a**) to yield $Cp^*WMe_3(\eta^1\text{-}NNH_2)$ (**5a**; Scheme I).[23] NMR studies in CD_2Cl_2 showed that the reaction was first order in **2a** but the rate was somewhat variable (k = 6–8 × 10^{-4} s^{-1} at 35 °C). Protonation of **5a** yielded $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]^+$ (**3a**; Scheme I), a reaction that was proposed to proceed via unobservable **6a** (Scheme I) followed by a shift of a proton from N_β to N_α. An X-ray study of **3a**[23] (the triflate salt) showed that the center of the $NHNH_2$ ligand occupies what is approximately a basal position in a square pyramid and the N–W–N plane is perpendicular to the plane of the Cp* ring. The NH nitrogen atom is nearly planar (the NH proton was located) and the M–NH bond is short (1.86 (1) Å) as a consequence of donation of the NH electron pair into the d_{xy} orbital that lies parallel to the Cp* ring. The NH_2 nitrogen atom is bound to the metal through the d_{z^2} orbital. Deprotonation of **3a** gave **5a** (Scheme I).

In this paper we report further studies of reactions between $[Cp^*WMe_4]^+$ and hydrazine, along with additional studies involving methylhydrazine and 1,1-dimethylhydrazine. (Studies involving 1,2-disubstituted hydrazines will be reported separately.[26]) We will be most concerned with structures and rearrangements of various diamagnetic $[Cp^*WMe_m(\text{hydrazido})]^{n+}$ complexes (m = 3 or 4, n = 0 or 1), especially those in which two nitrogen atoms are bound to the metal, since we now believe that η^2-coordination may be a required step for efficient cleavage of the N–N bond in systems of this type. (In "low-oxidation-state" systems there is much evidence that end-on coordination is sufficient;[27,28] i.e., in general, more than one mechanism of N–N cleavage is likely to be operative.) These studies are intended to

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help us understand in greater detail how dinitrogen might be reduced beyond the hydrazido(2-) stage at a high-oxidation-state tungsten center. In subsequent papers we will discuss related paramagnetic species that contain the Cp^*MMe_3 core, where M is either W or Mo, and studies aimed at elucidating further the details of N-N bond cleavage in systems of this general type.

Results

Hydrazine and Hydrazido(1-) Complexes Containing the Cp^*WMe_4 Core. In complexes that contain the Cp^*WMe_4 core, in which a methyl group is bound trans to the Cp* ligand, only two orbitals are available for bonding to a mono- or bidentate ligand to give a pseudooctahedral species.[29] One is a σ type hybrid orbital, and the other is a π type orbital (approximately d_{xy}) that lies between the ligands approximately parallel to the Cp* ring. This situation contrasts with that found in complexes that contain the Cp^*WMe_3 core to be described later, where three orbitals (d_{z^2} being the third) are available.

In contrast to what we believed initially, $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6$ (**1a**-PF_6; Scheme I) forms quantitatively upon adding 1 equiv of hydrazine to $[Cp^*WMe_4]PF_6$ in THF at room temperature, and it can be isolated readily. It is likely that some **2a** forms by deprotonation of **1a**, but **2a** must be reprotonated readily by $[N_2H_5]^+$. $[Cp^*WMe_4(\eta^2\text{-}N_2H_4)]PF_6$ contains 2 equiv of THF when first crystallized at low temperature. We propose that 2 equiv of THF in **1a** are hydrogen bonded to the η^2-N_2H_4 ligand, as they are to the η^2-N_2H_3 ligand in **2a**,[23] although details are not known at this stage. As in the case of **2a**, solid **1a**-PF_6 loses THF slowly at 1 atm and 25 °C.

Deprotonation of **1a** by hydrazine or triethylamine gives **2a** in high yield, while protonation of the hydrazine ligand in **1a** by triflic acid yields $[Cp^*WMe_4]^+$. (Similar protonations of $[Cp^*WMe_4(NH_3)]^+$ and $[Cp^*WMe_3(NH_3)_x]^+$ (x = 1 or 2) have been observed.[25]) Protonation of hydrazine in **1a** should be possible only if one end of the η^2-NH_2NH_2 ligand dissociates from tungsten to give an η^1-NH_2NH_2 complex, a process that seems feasible on the basis of the fact that one ammonia in $[Cp^*WMe_3(NH_3)_2]^+$[25] is quite labile. The resulting $[NH_2NH_3]^+$ ion is then likely to dissociate readily from the positively charged tungsten center. Since a bidentate binding mode for hydrazine has now been established in an X-ray study of the somewhat less crowded W(V) complex, $[Cp^*WMe_3(\eta^2\text{-}N_2H_4)]^+$,[30] and for the hydrazido(1-) ligand in $Cp^*WMe_4(\eta^2\text{-}NHNH_2)$,[23] we believe it most likely that the hydrazine ligand in **1a** is bound in an η^2 fashion to yield an 18 electron complex, as we proposed in the earlier study,[23] which is consistent with ^{15}N NMR studies at -80 °C (see below). However, it should be kept in mind throughout this study that in solution 18-electron complexes that contain η^2-N_2H_x ligands are likely to be in equilibrium with 16-electron complexes that contain η^1-N_2H_x ligands, chemistry could arise from either form, and the η^1-N_2H_x complexes are likely to be the most reactive in protonation reactions.

Other spectroscopic data for **1a**, some of it not reported previously, and other $N_2H_xMe_y$ complexes discussed later (Schemes I-IV) are listed in Tables II-V. There are some differences between NMR spectra of salts that contain different anions, e.g., PF_6^- vs triflate, presumably because ion pairing and/or hydrogen bonding of the anion to hydrazine protons is not negligible. The IR spectrum of **1a**-PF_6 (Figure 2a) does not contain sharp NH stretches (in contrast to IR spectra of related neutral compounds; Figure 2c,d), perhaps because the hydrogen bonding in the solid state, especially in the presence of residual THF.

The ^{15}N NMR spectrum of $[Cp^*WMe_4(\eta^2\text{-}^{15}NH_2{}^{15}NH_2)]PF_6$ at -80 °C revealed only one type of nitrogen atom resonance at 29.7 ppm (Table V), consistent with η^2 coordination of the hydrazine ligand. Variable-temperature proton NMR spectra of **1a**-$^{15}N_2$ (the PF_6^- salt) are shown in Figure 1. The doublet resonances can be assigned to two sets of η^2-hydrazine protons, one set that points toward the Cp* ligand and another set that points away from the Cp* ligand; we do not know which is which. Selective homonuclear decoupling of the NH resonance at 4.37 ppm (at 20 °C) results in a nearly total elimination of the NH resonance at 4.98 ppm, a result that is consistent with exchange of the "upper" and "lower" sets of hydrazine protons in **1a** on the NMR time scale at that temperature. The fact that the resonance at higher field is significantly broader at 30 °C than the resonance at lower field could be ascribed to loss of coupling between that set of protons and ^{15}N as a result of proton exchange that is faster than interconversion of the two sets of protons. Spectra at higher temperatures could not be obtained due to elimination of methane from **1a** to give $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]^+$ (**3a**; Scheme I; see below), while hydrazine cannot be added to **1a** in order to study exchange because hydrazine deprotonates **1a** to give **2a**.

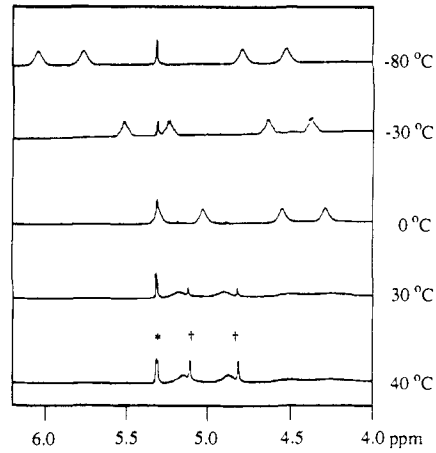

Figure 1. Variable-temperature proton NMR spectra of $[Cp^*WMe_4(\eta^2\text{-}^{15}NH_2{}^{15}NH_2)]PF_6$ (**1a**-$^{15}N_2$): ✱ = $CHDCl_2$; † = $[Cp^*WMe_3(\eta^2\text{-}^{15}NH^{15}NH_2)]PF_6$ (**3a**-PF_6-$^{15}N_2$).

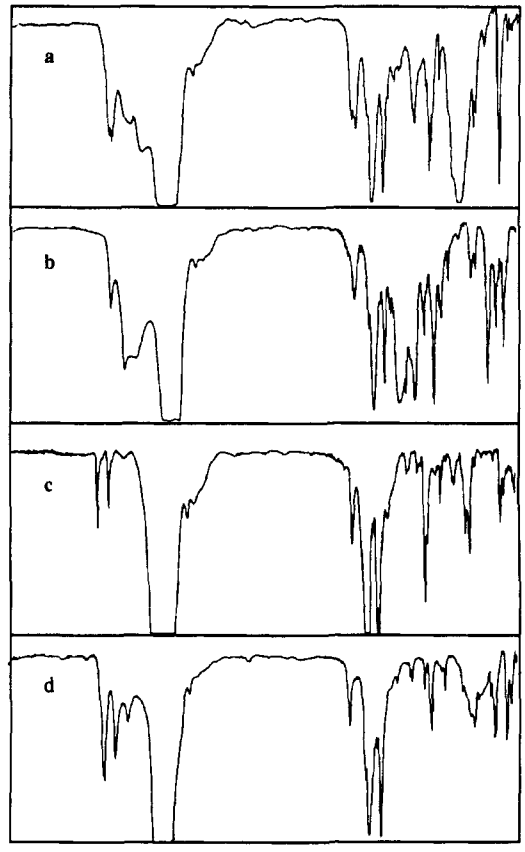

Figure 2. Infrared spectra of (a) $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6$ (**1a**-PF_6), (b) $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$ (**3a**-OTf), (c) $Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ (**2a**), and (d) $Cp^*WMe_3(\eta^1\text{-}NNH_2)$ (**5a**) (Nujol mull; KBr plates).

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Table I. Rates of Elimination of Methane or Rearrangement in $N_2H_xMe_y$ Complexes[a]

sample	solvent	T (°C)	conc (mM)[b]	k (10^{-4} s^{-1})	$t_{1/2}$ (min)	time (min)[c]
$[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6\cdot 2THF$ (**1a**-PF_6)	THF-d_8	40	(10)	0.54	210	155
	CD_2Cl_2	40		24	4.8	20
+ 4.2[LutH]OTf	THF-d_8	40	12	0.37	310	110
+ 5.1LiCl	THF-d_8	40	19	2.3	51	70
$[Cp^*WMe_4(\eta^2\text{-}NHMeNH_2)]$OTf (**1b**-OTf)	CD_2Cl_2	35	62	29	4	24
$Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ (**2a**)	py-d_5	40	38	1.5	76	100
	THF-d_8	40	8.1	3.2	36	110
	THF-d_8	40	63	3.1	38	150
	THF-d_8	40	(250)	3.0	30	50
	CD_2Cl_2[d]	40	38	12	9.5	23
+ 7.4DBU	THF-d_8	40	8.5	2.0	53	70
+ 0.07[LutH]OTf	THF-d_8	40	8.5	2.5	45	80
+ 0.36[LutH]OTf	THF-d_8	40	8.5	1.7–1.1	68–100	80
$Cp^*WMe_4(\eta^2\text{-}NMeNH_2)$ (**2b**)	CD_2Cl_2	35	53	1.5	77	320
	C_6D_6	28	84	0.57	202	320
+ 0.1NEt_3	C_6D_6	28	84	0.58	199	330
+ 0.1HOTf	C_6D_6	28	84	0.84	138	300
$Cp^*WMe_4(\eta^2\text{-}NHNHMe)$ (**2b'**)	CD_2Cl_2	35	10	1.4	80	320
$Cp^*WMe_3(\eta^2\text{-}NNH_2)$ (**4a**) + 7.8DBU + [DBUH]OTf	CD_2Cl_2	−20		4.1	28	20
+ 7.8DBU + [DBUH]OTf	CD_2Cl_2	−10		18	6.5	20
+ 3.1DBU + [DBUH]OTf	THF-d_8	−20	28	1.0	110	110
+ 3.1DBU + [DBUH]OTf	THF-d_8	−10	28	5.7	20	55
+ 21DBU + [DBUH]OTf	THF-d_8	−10	22	7.0	16	65
$Cp^*WMe_3(\eta^2\text{-}NNMeH)$ (**4b**) + 1.5NEt_3 + $[NEt_3H]$OTf	CD_2Cl_2	−25	200	8.4	14	43

[a] Reactions were monitored by proton NMR, and data were treated in the normal manner in order to determine k. The observation time in the majority of cases was between 1 and 4 half-lives, and linear coefficients of first-order plots were 0.99 to 1.00. [b] Concentrations in parentheses are approximate. [c] Observation time. [d] At 35 °C and 70 mM, $t_{1/2}$ = 16 min and $k = 7.3 \times 10^{-4}$ s^{-1}; see ref 23.

Table II. Infrared NH Vibrations for $N_2H_xMe_y$ Complexes[a]

compd	ν(NH)[b]	$\delta(NH_2)$
$[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6$ (**1a**-PF_6)	3326 m, 3306 m, 3176 br, 3094 br	1602 m, 1577 m
$[Cp^*WMe_4(\eta^2\text{-}NH_2NHMe)]$OTf (**1b**-OTf)	3255 m, 3205 m, 3120 m	1591 m
$Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ (**2a**)	3369 m, 3287 m, 3176 w	1556 m
$Cp^*WMe_4(\eta^2\text{-}NMeNH_2)$ (**2b**/**2b'**)	3294 m, 3216 w	1560 m
$[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]$OTf (**3a**-OTf)	3321 w, 3231 m, 3152 sh	1589 m
$[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]$OTf (**3b**-OTf)	3246 m, 3121 m (2442 m, 2291 m)[b]	1625 m
$Cp^*WMe_3(\eta^1\text{-}NNH_2)$ (**5a**)	3330 m, 3250 m, 3165 w[c]	1596 m
$Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (**5b**)	3286 m (2428 w)	
$[Cp^*WMe_3(NNH_2Me)]$OTf (**6b**-OTf)	2730 m, 2489 m	1593 m
$[Cp^*WMe_3(NNHMe_2)]$OTf (**6c**-OTf)	2720 m, 2670 m, 2602 m	

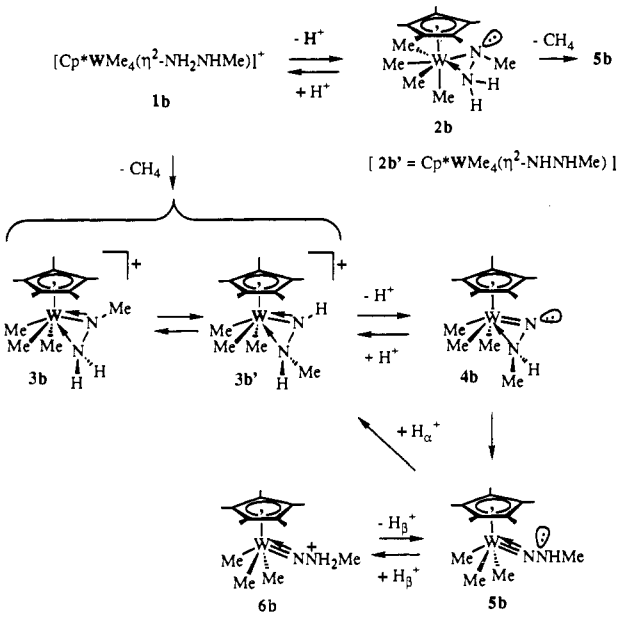
[a] Spectra were acquired as Nujol mulls between KBr plates. Frequencies are reported in cm^{-1}: w = weak, m = medium, sh = shoulder, br = broad. [b] Values in parentheses are for the deuterated $N_2D_xMe_y$ complexes. [c] Peak not present in solution spectrum.

In the absence of a base, **1a** loses methane slowly to give $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]^+$ (**3a**; to be discussed in a later section), a reaction that was not noted in the earlier study.[23] In THF-d_8 at 40 °C, methane is eliminated in a reaction that is first order in **1a** with a half-life of 3.5 h, but in CD_2Cl_2 the half-life is only approximately 5 min (Table I). Addition of over 4 equiv of [2,6-lutidineH]OTf slowed the rate of decomposition of **1a** in THF by approximately 50%, while addition of LiCl increased the rate of decomposition by approximately a factor of 4. Methane is eliminated from **1a** even in the solid state. After 3 days at 25 °C, a sample of previously pure **1a** contains approximately 50% **3a**. These data suggest that methane is eliminated from **1a** in an intramolecular fashion. We suspect that hydrogen bonding between the hydrazine protons and solvent or the anion may be significant.[31] Unfortunately, details of the decomposition reaction, e.g., whether methane is evolved from a complex in which the hydrazine is η^1 or η^2, or which methyl group removes which proton, could not be determined.

In an earlier study, **2a** was observed to decompose to **5a**.[23] Since we know that **3a** is deprotonated to give **5a**[23] and now know that **1a** can be transformed into **3a**, decomposition of **2a** to **5a** could be catalyzed by acid. A redetermination of the first-order rate of decomposition of **2a** in CD_2Cl_2 yielded a value of 12×10^{-4} s^{-1} at 40 °C (Table I), consistent with the values of $6–8 \times 10^{-4}$ s^{-1} that were obtained at 35 °C.[23] Since dichloromethane can contain traces of HCl, we were especially interested in the rate of decomposition of **2a** in other solvents or in the presence of bases. In THF-d_8, the reaction is also first order in **2a** over a 30-fold concentration range (Table I) and approximately 4 times slower than it is in CD_2Cl_2, while, in pyridine-d_5, the rate again drops by a factor of 2. Therefore the rate of decomposition of **2a** in pyridine is approximately $^1/_{10}$th of what it is in CD_2Cl_2. However, decomposition of **2a** in THF-d_8 in the presence of DBU was only slightly slower than decomposition in THF-d_8 alone, while decomposition in THF-d_8 in the presence of [2,6-lutidinium]OTf was significantly slower. It should be noted that the observed rates of conversion of **2a** to **5a** in THF (without added acid or base) are almost an order of magnitude faster than the rate of conversion of **1a** to **3a** in THF. This finding is consistent with the fact that addition of a proton source to **2a** *slows* the rate of its decomposition (Table I). Therefore we are relatively confident that the fastest conversion of **2a** to **5a** (in THF) is intramolecular, *not* acid catalyzed (via **1a** and **3a**). In dichloromethane, this conclusion is not warranted, since the rates of decomposition of **2a** and **1a** differ only by a factor of approximately 2 in dichloromethane. If the proton attached to N_α in **2a** were the one removed, then an "η^2-NNH_2" complex (**4a**; Scheme I) would be the first product, while if the proton attached to N_β were the one removed, the first formed product would be a diazene complex, $Cp^*WMe_3(\eta^2\text{-}NHNH)$. (A diazene complex is viable since $Cp^*WMe_3(\eta^2\text{-}MeNNMe)$ has been isolated recently and structurally characterized.[26]) Of course **5a** also could form directly from **2a**, perhaps after the η^2-$NHNH_2$ ligand in **2a** becomes an η^1-$NHNH_2$ ligand. ($Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ was proposed to be in equilibrium with $Cp^*WMe_4(\eta^1\text{-}NHNH_2)$ on the basis of proton NMR studies.[23])

(31) Bultitude, J.; Larkworthy, L. F.; Povey, D. C.; Smith, G. W.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1748.

Scheme II



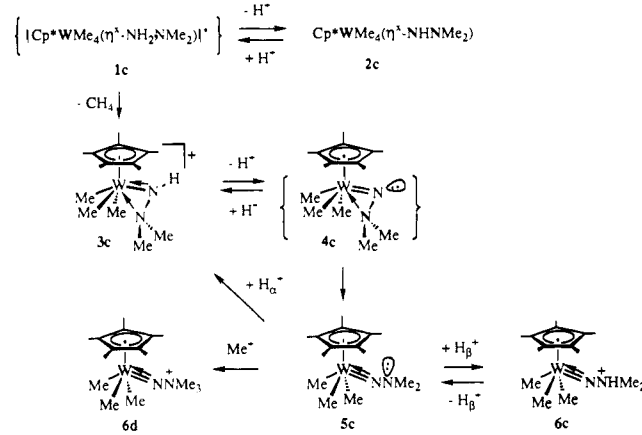
These findings concerning the decomposition of **2a** should be compared with those obtained for the related amido complex $Cp^*WMe_4(NHMe)$, which does *not* decompose to $Cp^*WMe_3(NMe)$ upon heating in CD_3NO_2 to 90 °C but *does* eliminate methane to yield $Cp^*WMe_3(NMe)$ in an acid-catalyzed reaction, probably via unobservable $[Cp^*WMe_4(NH_2Me)]^+$.[25]

Addition of at least 2 equiv of methylhydrazine to $[Cp^*WMe_4]^+$ at −40 °C yields what we propose is largely $Cp^*WMe_4(\eta^2\text{-}NMeNH_2)$ (**2b**) (Scheme II) after warming the mixture to room temperature. However, a minor amount (ca. 15%) of the product consists of what we propose is $Cp^*WMe_4(\eta^2\text{-}NHNHMe)$ (**2b′**) on the basis of NMR spectra. The presence of an NH_2 bending mode in the IR spectrum at 1560 cm^{-1} is consistent with the major product being **2b**, while a doublet for the $N_\beta Me$ group and the NH_α proton ($^2J_{HH}$ = 5.1 Hz) in the minor product is consistent with it being **2b′**. NMR evidence suggests that the two hydrazido protons in **2b**, which are inequivalent at low temperatures, exchange on the NMR time scale at room temperature and that the two methyl groups cis to the η^2-$NMeNH_2$ ligand exchange. A plausible intermediate would be $Cp^*WMe_4(\eta^1\text{-}NMeNH_2)$, in which a plane of symmetry is present.

Both **2b** and **2b′** decompose to $Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (**5b**). We find that **2b** decomposes cleanly to **5b** in benzene-d_6 at 28 °C in a first-order manner at a rate that does not change in the presence of 0.1 equiv of NEt_3 or triflic acid (Table I). At 35 °C in CD_2Cl_2 **2b** decomposes to **5b** at about one-fourth the rate at which **2a** decomposes to **5a**. Qualitatively, the decomposition of **2b** in THF or diethyl ether in a typical preparation of **5b** at room temperature requires at least twice the time that is required for **2a** to decompose to **5a** in THF. The rate of decomposition of **2b′** to **5b** was found to be essentially identical to the rate of decomposition of **2b** to **5b** in CD_2Cl_2 at 35 °C. Therefore we have to consider three possible "direct" mechanisms of forming **5b**: (i) **2b** is converted relatively rapidly into **2b′**, which is converted into $Cp^*WMe_4(\eta^1\text{-}NHNHMe)$, which is then deprotonated at N_α; (ii) **5b** is formed from **2b′** via **4b** (see below); (iii) **5b** is formed from **2b** via "$Cp^*WMe_3(\eta^2\text{-}HNNMe)$". In discussions of reactions that follow we will refer only to **2b**, although **2b′** is likely to be in rapid equilibrium (on the chemical time scale) with **2b**.

The proposed intermediate (**1b**) formed upon adding methylhydrazine to $[Cp^*WMe_4]^+$ can be prepared (as the triflate salt) by adding triflic acid to **2b**. The methyl groups on the metal in **1b** are all inequivalent, as are all the NH protons. For reasons analogous to those we gave above for **1a**, we believe that the lowest energy state for **1b** is that in which methylhydrazine is bound to the metal in an η^2 fashion, but whether the methyl group points toward the Cp* ligand or away from the Cp* ligand or how readily

Scheme III[a]



[a] Compound in braces has not been observed.

the η^1-NH_2NHMe complex is formed has not been established. Triethylamine cleanly deprotonates isolated **1b** at room temperature to give **2b**, while **1b** decomposes to yield **3b** cleanly in a first-order reaction. The rate of decomposition of **1b** to **3b** (to be described later) at 35 °C in CD_2Cl_2 was found to be approximately 20 times faster than the rate of decomposition of **2b** to **5b** (Table I and Scheme II). Since **3b** is readily deprotonated to yield **5b** (see later), the acid-catalyzed loss of methane from **2b** to give **5b** (via **1b** and **3b**; Scheme II) could compete with the intramolecular conversion of **2b** to **5b** in CD_2Cl_2, the solvent in which the rate of decomposition of **1a** was approximately twice the rate of decomposition of **2a** (Scheme I).

If methylhydrazine is added to $[Cp^*WMe_4]^+$ at room temperature instead of −40 °C, $[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]^+$ (**3b**) is isolated in good yield (Scheme II). Evidently unimolecular elimination of methane from **1b** under those conditions competes successfully with bimolecular deprotonation of **1b** by methylhydrazine to yield **2b**.

Excess 1,1-dimethylhydrazine reacts with $[Cp^*WMe_4]PF_6$ at −40 °C in dichloromethane to form $Cp^*WMe_4(\eta^x\text{-}NHNMe_2)$ (**2c**; x = 1 or 2; Scheme III).[32] The most consistent explanation is that **2c** is formed via deprotonation of **1c**. However, in this case we also should consider the possibility that $[Cp^*WMe_4]^+$ first is deprotonated by 1,1-dimethylhydrazine to give $Cp^*WMe_3(CH_2)$, since deprotonation of $[Cp^*WMe_4]^+$ is favored relative to adduct formation when relatively bulky, more basic amine ligands (e.g., *tert*-butylamine) are added to $[Cp^*WMe_4]^+$ (instead of ammonia, for example), and that formation of **2c** therefore involves transfer of a proton from 1,1-dimethylhydrazine to the methylene carbon atom in $Cp^*WMe_3(CH_2)$.[33] In **2c**, the bidentate mode of binding would appear to be less likely for steric reasons than in the other cases we have discussed so far. An η^1 mode of bonding is also consistent with the similarities between proton NMR data, carbon NMR data, and IR data for **2c** and data for $Cp^*WMe_4(NHMe)$.[25] Therefore, although a bidentate mode of bonding has been established in other η^2-NHNRR′ complexes,[34,35] it is not a foregone conclusion in **2c**. Interestingly, **2c** is remarkably stable (as is $Cp^*WMe_4(NHMe)$[25]), showing no sign of decomposition upon being heated to 50 °C. This result might be taken as evidence that a proton cannot be lost from an η^2-$NHNMe_2$ or η^1-$NHNMe_2$ ligand to give **5c** (see later) directly in an intramolecular process and therefore that formation of a diazene intermediate (which in this particular case is not possible) is the preferred mode of intramolecular loss of methane from complexes

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Table III. Proton NMR Data for $N_2H_xMe_y$ Complexes[a]

compd	$N_\alpha H$[c]	$N_\beta H$	$N_\alpha Me$	$N_\beta Me$[d]	Cp*	WMe_{cis}	WMe_{trans}	WMe_{ax}
$[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]OTf$[b] (**1a**-OTf)	5.25	5.02			1.72	0.31	0.06	0.52
$[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6$ (**1a**-PF_6)	4.98	4.37						
$[Cp^*WMe_4(\eta^2\text{-}NH_2NHMe)]OTf$ (**1b**-OTf)	4.37	5.73, 5.13		2.97 (5.0)	1.74	0.38, 0.33	0.09	0.66
$Cp^*WMe_4(\eta^2\text{-}NHNH_2)$[b,e] (**2a**)	3.53	2.44, 2.07			1.25	−0.30, −0.39	−0.55	−0.41
$Cp^*WMe_4(\eta^2\text{-}NMeNH_2)$[f,g] (**2b**)		3.45, 3.30	3.06		1.44	−0.19, −0.25	−0.01	0.10
$Cp^*WMe_4(\eta^2\text{-}NHNHMe)$ (**2b'**)	2.4	2.4		2.6	1.50	−0.02	−0.60	−0.12
$Cp^*WMe_4(\eta^x\text{-}NHNMe_2)$ (**2c**)	7.24			2.19	1.72	0.07	−0.53	1.38
$[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$[b] (**3a**-OTf)	11.72 (18)	5.08			2.04	0.45	0.33	
$[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]PF_6$ (**3a**-PF_6)	10.39	5.02			2.05	0.49	0.37	
$[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]Cl$ (**3a**-Cl)	14.00	6.70			2.03	0.42	0.22	
$[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$ (**3b**-OTf)		5.56	3.46		2.01	0.47	0.30	
$[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]PF_6$ (**3b**-PF_6)		4.86	3.40		2.01	0.45	0.30	
$[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]OTf$ (**3b'**-OTf)	11.77 (17)	5.08		2.94 (4.8)	2.04	0.47, 0.44	0.33	
$[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]PF_6$ (**3b'**-PF_6)	10.12	4.65		2.94 (4.8)	2.04	0.47, 0.44	0.33	
$[Cp^*WMe_3(\eta^2\text{-}NHNMe_2)]OTf$ (**3c**-OTf)	12.52 (13)			2.88	2.01	0.59	0.50	
$Cp^*WMe_3(\eta^2\text{-}NNH_2)$[g] (**4a**)		5.21			1.79	−0.60	−0.32	
$Cp^*WMe_3(\eta^2\text{-}NNHMe)$[g] (**4b**)		4.95		2.87 (5.1)	1.77	−0.59	−0.34	
$Cp^*WMe_3(\eta^1\text{-}NNH_2)$[b] (**5a**)		5.45			1.78	0.25	−0.29	
$Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (**5b**)		5.46		2.88 (4.8)	1.81	0.27	−0.30	
$Cp^*WMe_3(\eta^1\text{-}NNMe_2)$ (**5c**)				2.80	1.82	0.31	−0.30	
$[Cp^*WMe_3(NNH_2Me)]OTf$[f,g] (**6b**-OTf)		11.10		2.98	1.93	0.72	0.01	
$[Cp^*WMe_3(NNHMe_2)]OTf$ (**6c**-OTf)		11.90		3.07 (4.8)	1.92	0.77	0.09	
$[Cp^*WMe_3(NNMe_3)]OTf$ (**6d**-OTf)				3.48	1.93	0.81	0.15	
$Cp^*WMe_2Cl(\eta^1\text{-}NNH_2)$ (**7**)		6.10			1.89	0.56		

[a] Spectra acquired in CD_2Cl_2 at 25 °C; coupling constants in Hz. [b] See ref 21. [c] $^3J_{HW}$ in parentheses. [d] Doublet, $^3J_{HH}$ in parentheses. [e] $T = -100$ °C. [f] THF-d_8. [g] $T = -40$ °C.

Table IV. Carbon NMR Data for $N_2H_xMe_y$ Complexes[a]

compd	Cp*	WMe_{cis}	WMe_{trans}	WMe_{ax}	$N_\alpha Me$	$N_\beta Me$
$[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6$ (**1a**-PF_6)	112.13, 8.98	24.87 (47)	39.32 (57)	55.34 (68)		
$[Cp^*WMe_4(\eta^2\text{-}NH_2NHMe)]OTf$[b] (**1b**-OTf)	112.85, 9.12	26.79 (48), 25.32 (46)	40.60 (56)	56.17 (70)		33.09
$Cp^*WMe_4(\eta^2\text{-}NHNH_2)$[d] (**2a**)	109.60, 9.11	23.69 (48)	34.72 (49)	55.58 (69)		
$Cp^*WMe_4(\eta^2\text{-}NMeNH_2)$[d,e] (**2b**)	110.81, 9.48	25.97 (46), 24.69 (53)	38.78 (46)	51.70 (74)	37.34	
$Cp^*WMe_4(\eta^x\text{-}NHNMe_2)$[f] (**2c**)	112.95, 10.04	30.65 (56)	38.16 (43)	62.50 (60)		47.47
$[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$ (**3a**-OTf)	116.71, 10.47	32.91 (50)	30.06 (51)			
$[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]PF_6$ (**3a**-PF_6)	116.7, 10.7	33.6	30.6			
$[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]Cl$ (**3a**-Cl)[e]	115.23, 10.75	31.40 (49)	27.77 (52)			
$[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$[c] (**3b**-OTf)	114.82, 10.63	32.94 (52)	29.30 (47)		44.30	
$[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]OTf$[b] (**3b'**-OTf)	115.94, 10.63	35.99, 35.69	29.54			32.94
$[Cp^*WMe_3(\eta^2\text{-}NHNMe_2)]OTf$[c] (**3c**-OTf)	115.27, 10.65	38.55 (52)	31.10 (49)			48.40
$Cp^*WMe_3(\eta^2\text{-}NNH_2)$[c] (**4a**)	111.17, 9.89	22.42 (57)	20.90 (57)			
$Cp^*WMe_3(\eta^2\text{-}NNHMe)$[c] (**4b**)	111.07, 9.93	24.19 (55), 23.23 (60)	20.19 (57)			36.92
$Cp^*WMe_3(\eta^1\text{-}NNH_2)$[f] (**5a**)	108.05, 10.15	21.12 (57)	29.55 (73)			
$Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (**5b**)	108.89, 10.54	18.89 (57)	28.32 (73)			36.84
$Cp^*WMe_3(\eta^1\text{-}NNMe_2)$ (**5c**)	108.83, 10.91	17.87 (56)	28.15 (74)			44.28
$[Cp^*WMe_3(NNHMe_2)]OTf$[c] (**6c**-OTf)	111.85, 10.53	23.44 (52)	31.37 (68)			46.37
$[Cp^*WMe_3(NNMe_3)]OTf$ (**6d**-OTf)	113.59, 11.13	25.55 (52)	33.95 (69)			58.56

[a] Spectra acquired in CD_2Cl_2 at 25 °C, unless otherwise noted. ($^1J_{CW}$ in Hz in parentheses). [b] $T = -30$ °C. [c] $T = -40$ °C. [d] THF-d_8. [e] T = −20 °C. [f] C_6D_6.

of type **2**. With data for **2c** in hand, we can now say that the trend in stabilities of complexes of type **2** toward loss of methane is **2c** ≫ **2b** > **2a**.

In contrast to the thermal stability of **2c**, an acid-catalyzed decomposition of **2c** must be rapid, since when 1,1-dimethylhydrazine is added to $[Cp^*WMe_4]^+$ in dichloromethane at 25 °C, $Cp^*WMe_3(\eta^1\text{-}NNMe_2)$ (**5c**; see below) is formed quantitatively in 5 min. Therefore $[Cp^*WMe_4(\eta^2\text{-}NH_2NMe_2)]^+$ must be very unstable toward loss of methane to give **3c**, which is then deprotonated readily to give **5c** (Scheme III; see later). These results suggest that the trend in stabilities of hydrazine adducts of the general type $[Cp^*WMe_4(N_2H_xMe_y)]^+$ that we have discussed so far here ($y = 0$–2; $x = 4 - y$) toward loss of methane appears to be **1c** ≪ **1b** < **1a**, virtually the opposite of the stabilities noted above for compounds **2a**–**c**.

Hydrazido(1−) Complexes Containing the Cp^*WMe_3 Core. In complexes that contain the Cp^*WMe_3 core, three orbitals are available for bonding to an $N_2H_xMe_y$ fragment.[29] One is an orbital that can be used only for σ bonding in a square pyramidal or pseudooctahedral species that is trans to the central methyl group. Another (approximately d_{xy}) lies between the ligands more or less parallel to the Cp* ligand and is most often used only for π bonding or for forming a σ bonding hybrid with the first orbital. The third (approximately d_{z^2}) can be used either for σ bonding or for π bonding, depending on the manner in which the ligand approaches the metal and the orientation of the potential π bonding orbital on that ligand. The structure of **3a**[23] is consistent with this bonding picture. A double bond is formed between N_α and the metal, the d_{xy} orbital being used to form the π component of the double bond, while the d_{z^2} orbital accepts an electron pair from N_β. The results of a recent X-ray structure of $Cp^*WMe_3(\eta^2\text{-}MeNNMe)$[26] have led to the conclusion that the d_{xy} and d_{z^2} orbitals are remarkably similar in their ability to form a π bond to a ligand.

Compound **3a** (Scheme I) can be prepared either by allowing **1a** to decompose in dichloromethane or by protonating **5a**.[23] An important characteristic of the proton NMR spectrum of **3a** is the downfield chemical shift of the resonance for H_α at 11.7 ppm (triflate salt), a shift that is consistent with a positive charge being located on N_α; a complex in which a W=N bond is present and a positive charge is located on the nitrogen atom is, of course, a valid resonance structure for **3a** and is consistent with $^2J_{HW}$ = 18 Hz being observed in $[Cp^*WMe_3(\eta^2\text{-}^{15}NH^{15}NH_2)]^+$. As shown by the data in Table III, the chemical shifts of the hydrazido(1−) protons, especially H_α, depend to a significant degree on the nature of the anion, as one might expect if ion pairing and/or hydrogen bonding interactions differ in the various salts. The IR spectrum

Table V. ^{15}N NMR Data[a]

compd	T (°C)	$\delta(N_\alpha)$	$\delta(N_\beta)$	$^1J_{NN}$	$^1J_{N_\alpha W}$	$^{1,2}J_{N_\beta W}$	$^2J_{HNW}$	$^1J_{N_\alpha H}$	$^1J_{N_\beta H}$	$^2J_{N_\alpha N_\beta H}$
$[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6$ (**1a**-PF_6)	−80	29.7	29.7		<5	<5	<5, <5	80, 83	80, 83	
$Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ (**2a**)	−80	88.2	40.0	12	<5	<5	<5, <5	58	84	
$[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$ (**3a**-OTf)	−30	242.0	31.0	10	36	<5	18.5, <3	93	89	<1
$[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$ (**3b**-OTf)	−20	247.2	44.2	11					88	
$Cp^*WMe_3(\eta^2\text{-}NNH_2)$ (**4a**)[b]	−40	507.6	68.8[c]	13	10	<12	<8		87	<2
$Cp^*WMe_3(\eta^2\text{-}NNHMe)$ (**4b**)	−60	501.3	66.0	12					82	
$Cp^*WMe_3(\eta^1\text{-}NNH_2)$ (**5a**)[b]	25	382.0	131.6[c]	10.5	129	14			77	2
$Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (**5b**)	−20	387.4	136.5	10					82	
$[Cp^*WMe_3(NNMe_3)]OTf$ (**6d**-OTf)	0	352.9	117.7[c]	8.5	138	22				
$Cp^*_3W_3Me_8N_4H$ (**8**)	NMR (δ): 434.4 and 431.5 (10) (WNNW); 409.5 (W*N*NHW); 216.8 (WN*N*HW)									

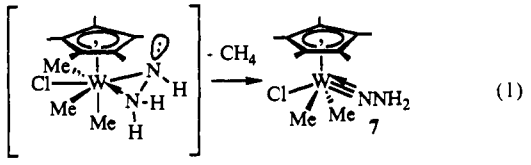
[a] Spectra obtained in CD_2Cl_2 and referenced to liquid ammonia (0 ppm), unless otherwise noted. [b] THF-d_8. [c] Inverted due to NOE of attached proton.

of **3a** (triflate salt; Figure 2b) contains broad N–H stretches, consistent with hydrogen bonding. ^{15}N NMR data for **3a**, which were not reported in the earlier study,[23] are listed in Table V. N_α in **3a** is coupled to ^{183}W with J = 36 Hz, consistent with the multiple character of the tungsten–N_α bond. Surprisingly, coupling between N_β and tungsten is too small to observe (estimated to be ≤5 Hz). Coupling between nitrogen and tungsten also is too small to observe in **1a** at −80 °C, where hydrazine is not likely to be dissociating rapidly from the metal, a process that could lead to decoupling of ^{15}N from ^{183}W.

A chloride salt of **3a** can be prepared by treating **5a** with HCl at −40 °C in ether (eq 1). However, $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]Cl$ is relatively unstable in solvents in which it dissolves. For example,

$$Cp^*WMe_3(\eta^1\text{-}NNH_2) \xrightarrow[\text{ether}]{\text{HCl, -40°}} [Cp^*WMe_3(\eta^2\text{-}NHNH_2)]Cl \xrightarrow{CH_2Cl_2}$$

5a **3a**-Cl



(1)

when it is dissolved in dichloromethane, it is converted into *trans*-$Cp^*WMe_2Cl(\eta^1\text{-}NNH_2)$ (**7**) in a few minutes at 25 °C. Addition of LiCl to a THF solution of $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$ also yields **7**. One possible explanation of these results is that chloride ion attacks the metal to form a higher coordinate neutral complex (analogous to **2a**) from which methane is eliminated more readily in an intramolecular fashion, although more subtle roles for the anion, e.g., assisting transfer of a proton from nitrogen to a methyl group on the metal, must also be considered.

The main product of adding methylhydrazine to $[Cp^*WMe_4]^+$ at room temperature is **3b** (Scheme II). However, the most reliable method of preparing **3b** (as the triflate salt) is to protonate **5b**. The location of the methyl group on N_α in **3b** is unambiguous, since no characteristic downfield resonance for a proton bound to N_α is found. A resonance at 11.77 ppm ($^2J_{HW}$ = 17 Hz) can be observed (irreproducibly), either upon decomposition of **1b** or upon protonation of **5b**, that we ascribed to H_α in $[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]^+$ (**3b′**). However, **3b′** is readily transformed into **3b** under either set of reaction conditions. The mechanism by which **3b′** is converted into **3b** is speculative. Formation of a methyldiazene intermediate, "$Cp^*WMe_3(\eta^2\text{-}NHNMe)$", by loss of a proton from N_β (eq 2) is an attractive possibility, and one

$$[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]^+ \xrightarrow{-H_\beta^+} Cp^*WMe_3(\eta^2\text{-}NHNMe) \xrightarrow{+H_\alpha^+} [Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]^+$$

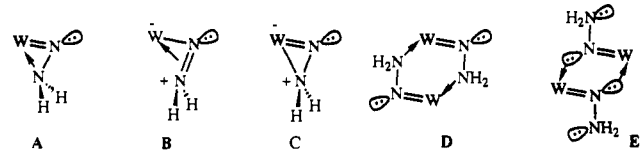
3b′ **3b**

(2)

perhaps even should consider the possibility of a W(VI) hydrido intermediate, i.e., "$Cp^*WMe_3(H)(\eta^2\text{-}HN{=}NMe)$". We have drawn the structure of **3b** in Scheme II to be analogous to that of **3a** on the basis of the fact that the two β protons are equivalent by NMR. At 20 °C an NMR spectrum of **3b′** reveals two broadened resonances for the two inequivalent cis WMe ligands, consistent with their interconversion on the NMR time scale.

The synthesis of **3c** (Scheme III) is the least straightforward of those of the complexes of this type, and in fact, so far it has been observed only in solution. There are three problems. The first is that addition of 1,1-dimethylhydrazine to $[Cp^*WMe_4]^+$ yields **5c**, rather than **3c**. **3c** is much less stable than **3a** or **3b** in solution, decomposing to a molecule whose NMR spectra are consistent with it being *trans*-$Cp^*WMe_2(OTf)(\eta^1\text{-}NNMe_2)$ (cf. *trans*-$Cp^*WMe_2Cl(\eta^1\text{-}NNH_2)$ above). The reason **3c** is so much less stable than **3a** or **3b** perhaps can be ascribed to a more facile formation of $[Cp^*WMe_3(\eta^1\text{-}NHNMe_2)]^+$. The third is that protonation of **5c** yields **6c** (see later), which rearranges too slowly to **3c** to compete with decomposition of **3c** to *trans*-$Cp^*WMe_2(OTf)(\eta^1\text{-}NNMe_2)$. However, there seems to be little doubt of the identity of **3c** on the basis of its NMR spectrum, the most characteristic feature being an NH_α resonance at 12.52 ppm ($^2J_{HW}$ = 13 Hz) in the proton NMR spectrum of its triflate salt.

Deprotonation of Hydrazido(1−) Complexes Containing the Cp^*WMe_3 Core. Deprotonation of **3a** to give **5a** is not as straightforward as we believed initially.[23] Upon adding DBU or triethylamine to **3a** in CD_2Cl_2 at −80 °C, a complex (**4a**; Scheme I) is formed that contains two equivalent NH protons, that is protonated at low temperatures to give **3a** quantitatively, and that starts to rearrange quantitatively to **5a** above approximately −20 °C. The ^{15}N NMR spectrum of the analogous complex prepared from **3a**-$^{15}N_2$ shows clearly that both protons in this intermediate are attached to the *same* nitrogen atom and that the chemical shift of that nitrogen atom is 68.8 ppm with no observable coupling to tungsten (<12 Hz; Table V). The value for J_{NN} (13 Hz) is still approximately what would be expected for an N–N single bond. The nitrogen atom that has no protons attached to it gives rise to a resonance at 507.6 ppm with J_{NW} = 10 Hz. It is known that the N_α resonance in "bent" η^1-hydrazido complexes is found at much lower fields relative to the N_β resonance.[36] For example, in $W(CO)_5(NNMe_2)$, the N_α resonance is found at 796 ppm and the N_β resonance at 297 ppm with $^1J_{NN}$ = 13 Hz.[37] Therefore we propose that **4a** contains an unusual type of η^2 ligand. The proposal we favor is that the intermediate is some combination of a "bent hydrazido(2−)" complex (A, **4a** in Scheme I), a W(IV)



η^2-isodiazene complex (B), or a W(VI) resonance form of B (C). Each is possible if the same three orbitals in the Cp^*WMe_3 core

(36) Mason, J. *Chem. Rev.* **1981**, *81*, 205.
(37) Sleiman, H. F.; Arndtsen, B. A.; McElwee-White, L. *Organometallics* **1991**, *10*, 541.

that we have been discussing in other circumstances are used to stabilize the η^2-NNH_2 ligand. Since this compound contains a plane of symmetry, we propose that N_α is bound to the metal in a basal position and N_β in an axial position trans to the Cp* ligand. Version A is perhaps the most reasonable on electronic grounds, since no formal charge separation is involved. In A the electron lone pair on the β nitrogen atom is coordinated to the tungsten through what is approximately a d_{z^2} orbital, while the W=N double bond is formed using the d_{xy} orbital. Unfortunately, the data in hand do not prove that this peculiar intermediate is a monomer. For example, D and E are not out of the question, even though dimers have not yet been observed in complexes containing the Cp^*WMe_3 core, and one might expect to see some evidence that N_α in E is coupled to more than one tungsten atom. There also has been no report of dimeric hydrazido complexes of type D or E.[1] Actually no proposal accounts for the relatively small value for $J_{N_\alpha W}$ (10 Hz; Table V), as if the metal–N_α bond were little more than a single bond. Since formation of a monomeric complex (some combination of A, B, and C) involves the least motion or reorganization of ligands, we will assume that **4a** is a monomer that contains an η^2-NNH_2 ligand and will chose form A to depict it.

Above −20 °C, **4a** rearranges quantitatively to **5a**. In the presence of DBU (and [DBUH]OTf that is formed upon deprotonation of **3a**), the conversion of **4a** to **5a** is first order with a half-life of approximately 5 min at −10 °C in CD_2Cl_2 (Table I). In THF-d_8 under similar conditions, the rate of decomposition is slower by a factor of approximately 4. We propose that the conversion of **4a** to **5a** consists simply of dissociation of N_β from the metal in **4a** followed by or concomitant with association of the electron pair on N_α with the metal to give a pseudo triple bond. Relatively facile dissociation of N_β would be consistent with the likelihood that various η^2-hydrazido(1−) ligands that we have discussed so far in this paper also equilibrate readily with η^1-hydrazido(1−) forms.

A potentially important question is whether the proton that is removed from **3a** actually is removed from N_α. Although that is the most direct way to from **4a**, we cannot be certain that is in fact the case. Addition of DOTf (1 equiv) to **4a** that had been isolated by filtration at −78 °C in diethyl ether yielded a precipitate of **3a**-d_1, whose proton NMR spectrum (at room temperature) in CD_2Cl_2 revealed that deuterium had scrambled between N_α and N_β at some stage.

Deprotonation of **3b** at low temperature yields a species that appears to be analogous to **4a**, according to its proton NMR spectrum, namely $Cp^*WMe_3(\eta^2$-NNHMe) (**4b**). Although the two methyl groups cis to the imido ligand are equivalent in the proton NMR spectrum at −40 °C, they are inequivalent in the carbon NMR spectrum, consistent with structure **4b** shown in Scheme II. The most straightforward way to form **4b** would seem to be via deprotonation of **3b′** at N_α, assuming that **3b′** is formed rapidly from **3b**, even below −20 °C. However, again we cannot exclude a more convoluted mechanism in which $Cp^*WMe_3(\eta^2$-NHNMe) is formed by loss of H_β from **3b** or **3b′** and then rearranges to give **4b**.

We felt that ^{15}N NMR studies of **4b** were required in order to prove more conclusively that it is analogous to **4a**. ^{15}N-labeled **5b** was prepared from $Cp^*WMe_3(\eta^1$-$^{15}N^{15}NH_2)$ as shown in eqs 3 and 4. The lithiation reaction shown in eq 3 is known, as is

$$Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NH_2) + LiR \rightarrow RH + Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NHLi) \quad (3)$$

$$Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NHLi) + MeI \rightarrow LiI + Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NHMe) \quad (4)$$

the reaction of the monolithio derivative with Me_3SiCl to give $Cp^*WMe_3(\eta^1$-NNH(TMS)).[38] The methylation reaction shown in eq 4 proceeded smoothly, although it is difficult to prevent some dilithiation in the first step to give $Cp^*WMe_3(\eta^1$-$^{15}N^{15}NLi_2)$ and consequently dimethylation in the second step to give $Cp^*WMe_3(\eta^1$-$^{15}N^{15}NMe_2)$. In practice, the presence of $Cp^*WMe_3(\eta^1$-$^{15}N^{15}NMe_2)$ and/or its protonation products presents no problems in terms of ^1H and ^{15}N NMR analysis. Protonation of $Cp^*WMe_3(\eta^1$-$^{15}N^{15}NMe)$ yielded $[Cp^*WMe_3(\eta^2$-$^{15}NMe^{15}NH_2)]^+$. (^{15}N NMR data (Table V) are those expected.) Deprotonation of $[Cp^*WMe_3(\eta^2$-$^{15}NMe^{15}NH_2)]^+$ at −80 °C yielded **4b**-$^{15}N_2$. An ^{15}N NMR spectrum of **4b** revealed an N_α resonance at 501 ppm and an N_β resonance at 66 ppm with an NN coupling of 11 Hz. Therefore we can conclude that **4b** is analogous to **4a**.

Above −20 °C, **4b** rearranges to **5b**. The rate of first-order conversion of $Cp^*WMe_3(\eta^2$-NNMeH) to $Cp^*WMe_3(\eta^1$-NNMeH) at −25 °C in CD_2Cl_2 (Table I) was faster than the rate of conversion of $Cp^*WMe_3(\eta^2$-$NNH_2)$ to $Cp^*WMe_3(\eta^1$-$NNH_2)$ at −20 °C by a factor of approximately 2. A more facile opening of **4b** to **5b** (relative to that of **4a** to **5a**) is what one would expect from increased steric congestion about the metal.

Attempts to deprotonate **3c** with DBU at low temperature yielded only **5c**. Perhaps for steric reasons, **4c**, which has not been observed, is considerably less stable than **4b** and therefore "opens" relatively rapidly to **5c**.

Protonation and Alkylation of Hydrazido(2−) Complexes. Protonation of $Cp^*WMe_3(\eta^1$-$NNH_2)$ (**5a**; Scheme I) at −40 °C with triflic acid has been shown to yield $[Cp^*WMe_3(\eta^2$-$NHNH_2)]^+$ (**3a**).[23] We had reported earlier that addition of 1 equiv of D^+ to **5a** at low temperature yielded **3a** in which H and D had scrambled between N_α and N_β. At that time, we proposed that the more accessible terminal nitrogen atom in **5a** is the kinetic site of protonation to give unobservable $[Cp^*WMe_3(NNH_3)]^+$ (**6a**; the η^1 descriptor is redundant in this circumstance) and that a 1,2 proton migration (H_β to N_α) then gives **3a**. Initial protonation on N_β is reasonable on the basis of the fact that the electron pair on N_α is involved in forming the triple bond to tungsten and is likely to be much less basic in a kinetic sense than the electron pair on N_β. However, 1,2 proton migration would seem to be difficult if the W=NNH_3 system were linear (as has been observed in the structurally-characterized analogous Mo=$NNMe_3$ compound[30] and complexes such as $[WCl(NNH_3)(PMe_3)_4]Cl_2$[39]) even if a β proton somehow could be activated intramolecularly by the d^0 metal. A more sensible alternative is the proposition that N_β in **5a** is protonated most readily, but *reversibly*, and that the electron pair on N_α is then protonated relatively more slowly (but still rapidly) to give **3a** more or less directly. This proposal is analogous to that concerning kinetically-preferred protonation at N_β in "low-oxidation-state" species.[1] One could propose that $[Cp^*WMe_3(\eta^1$-$NHNH_2)]^+$ is formed first upon protonating N_α in **5a**, but we know that it would be disfavored relative to the η^2-$NHNH_2$ form **3a**. It should be noted that deprotonation of **3a** at low temperature by DBU to give **4a** does *not* preclude direct addition of a proton from triflic acid to the electron pair on N_α in **5a**, since protonation and deprotonation steps take place under significantly different conditions; i.e., they are clearly not the reverse of one another. Therefore it is not necessary to propose that **4a** must form from **5a** *before* a proton adds to give **3a**, although the possibility that under some conditions **4a** may form from **5a** is intriguing. The situation is further confused by the possibility, as mentioned earlier, that under some circumstances a proton may be lost from N_β in **3a** to yield an intermediate, as yet unobserved, diazene complex, $Cp^*WMe_3(\eta^2$-NHNH).

$Cp^*WMe_3(\eta^1$-NNHMe) (**5b**) can be prepared either by deprotonating $[Cp^*WMe_3(\eta^2$-$NMeNH_2)]^+$ (**3b**) with triethylamine in THF or by allowing **2b** to decompose in solution (Scheme II). At −40 °C in ether, **5b** is protonated by triflic acid to give a beige, crystalline compound as a precipitate that we propose is $[Cp^*WMe_3(\eta^1$-$NNH_2Me)]OTf$ (**6b**). In order to isolate **6b**, the temperature must be kept strictly at or below −40 °C, and a minimum amount of solvent must be used in order to participate the product as soon as possible after it is formed. The IR spectrum of **6b** shows two low-energy, medium-intensity NH stretches at 2730 and 2489 cm^{-1} and an NH_2 bend at 1593 cm^{-1}. The bending

(38) Glassman, T. E.; Liu, A. H.; Schrock, R. R. *Inorg. Chem.* **1991**, *30*, 4723.

mode verifies that both NH's are on the same nitrogen atom, and the low NH stretching energies and breadth of the absorptions are consistent with some hydrogen bonding to the counterion, as observed in $[WCl(NNH_3)(PMe_3)_4]Cl_2$ (NH stretches at 3420 (w) and 2500 (v br) cm^{-1}).[39] The proton NMR spectrum of **6b** (in THF-d_8 at −40 °C) reveals resonances for the NH_2 protons at 11.10 ppm and the NMe protons at 2.98 ppm, both consistent with the terminal nitrogen atom being positively charged. Addition of D_2O to $Cp^*WMe_3(\eta^1$-NNHMe) yields $Cp^*WMe_3(\eta^1$-NNDMe) readily, a type of reaction that is relatively common for a variety of hydrazido(2−) complexes[40] and one that is consistent with facile protonation/deprotonation of the lone pair on N_β. Decomposition of **6b** in solution gives a mixture of **3b** and **3b′** (Scheme II) initially and then with time solely **3b**. We propose that **6b** loses a β proton to give **5b**, that **5b** is then reprotonated at N_α to give **3b′**, and that **3b′** is then transformed into **3b**, perhaps via an η^2-MeNNH intermediate.

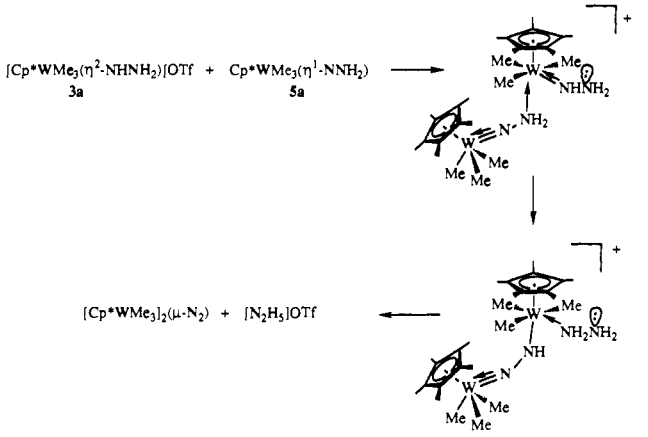
Addition of triflic acid to **5c** yields a pale-yellow microcrystalline complex whose IR and NMR spectra are consistent with it being **6c** (Scheme III). In solution, **6c** decomposes slowly to give **3c**, most likely we feel via loss of H^+ from N_β and reprotonation at N_α, but the instability of **3c**, as we noted above, prevents the decomposition of **6c** to **3c** from being a high-yield reaction.

Other evidence for faster addition of an electrophile to N_β in η^1-hydrazido(2−) complexes consists of methylation reactions. Methylation of **5c** yields $[Cp^*WMe_3(NNMe_3)]^+$ (**6d**), a stable compound that can be fully characterized. An X-ray structure of the analogous Mo complex showed that the Mo=NNMe$_3$ backbone is linear.[30] Addition of MeOTf to **5a** in ether yields a 2:1 mixture of **3a** and $[Cp^*WMe_3(NNMe_3)]OTf$ (**6d**-OTf), presumably via repeated cycles of methylation at N_β followed by deprotonation of N_β by **5a**. This reaction has been used to prepare **6d**-$^{15}N_2$. The ^{15}N NMR spectrum of **6d**-$^{15}N_2$ reveals a resonance for N_α at 352.9 ppm ($^1J_{NW}$ = 138 Hz, $^1J_{NN}$ = 8.5 Hz) and for N_β at 117.7 ppm ($^2J_{NW}$ = 22 Hz, $^1J_{NN}$ = 8.5 Hz). It is similar to the spectrum of **5a**-$^{15}N_2$ in that $J_{N_\alpha W}$ is large and $J_{N_\beta W}$ is significant, even thoguh N_β is not bonded directly to the metal. These data should be compared with the ^{15}N data for *trans*-$[WCl(^{15}N^{15}NH_3)(PMe_3)_4]Cl_2$ (δN_α = 288.5 ppm; δN_β = 126.4 ppm[39]).

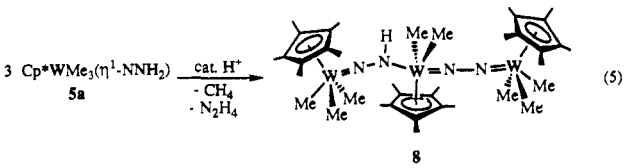
Some Intermolecular Decomposition Pathways of Unsubstituted Hydrazido Complexes. The chemistry of N_2H_x complexes is likely to be complicated by intermolecular reactions, hydrogen bonding, and proton-transfer reactions for steric reasons much more so than analogous chemistry involving $N_2H_xMe_y$ complexes. In this section, we present some examples of reactions that complicate the chemistry of N_2H_x complexes. Some of the reactions of this type, along with those in which one of the methyl groups in a Cp^*WMe_3 complex is lost as methane, are expected to be detrimental in any system in which dinitrogen might be reduced to ammonia and reveal the potential importance of preventing bimolecular decomposition reactions that produce multimetallic species with no special properties that might aid reduction of dinitrogen.[38]

Proton exchange between $[Cp^*WMe_4(\eta^2$-$NH_2NH_2)]^+$ (**1a**) and $Cp^*WMe_4(\eta^2$-NHNH$_2$) (**2a**) is degenerate and was shown to be a low-energy process; even at −80 °C in CD_2Cl_2, the chemical shifts were the weighted average of the two compounds.[23] However, proton transfer between $Cp^*WMe_3(\eta^1$-NNH$_2$) (**5a**) and $[Cp^*WMe_3(\eta^2$-NHNH$_2)]^+$ (**3a**) leads to the known,[21] relatively stable μ-hydrazido(4−) complex, $[Cp^*WMe_3]_2(\mu$-$N_2)$. The reaction is over in minutes in dichloromethane, but is much slower in tetrahydrofuran. One plausible mechanism is shown in Scheme IV. The proposed first step consists of formation of $[Cp^*WMe_3(\eta^1$-NHNH$_2)]^+$ from $[Cp^*WMe_3(\eta^2$-NHNH$_2)]^+$ followed by nucleophilic attack by N_β in $Cp^*WMe_3(\eta^1$-NNH$_2$) on $[Cp^*WMe_3(\eta^1$-NHNH$_2)]^+$. Two proton transfers to the hydrazido ligand then yield hydrazinium triflate and $[Cp^*WMe_3]_2(\mu$-$N_2)$.

Scheme IV



$Cp^*WMe_3(\eta^1$-NNH$_2$) (**5a**) is known to decompose slowly in solution.[23] We have now identified the decomposition product as the trinuclear, hydrazido(3−), hydrazido(4−) complex **8** shown in eq 5. Large dark-red needles of **8** can be obtained by allowing



(5)

an acetonitrile solution of **5a** to stand undisturbed for a period of days to weeks. Clean decomposition also occurs in ethereal solvents, although more slowly; however, **8** is not produced cleanly in aromatic solvents or in dichloromethane. The connectivity in the WNNWNNW backbone was established in an X-ray study, but disorder prevented establishing to which nitrogen atom the proton is attached. An alternative, W(N*H*N)W(NN)W, seems less sensible on the basis of the chemistry that we have been observing in complexes of this general type. Protonation of **8** with excess HOTf initially forms **5a** and $Cp^*WMe_2(OTf)(\mu$-$N_2)$-Cp^*WMe_3[38] (eq 6), a result that is consistent with the W(NN-*H*)W(NN)W connectivity. Proton and ^{13}C NMR spectra of **8** show the expected 2:2:2:1:1 ratio of WMe resonances. In the ^{15}N NMR spectrum of **8**-$^{15}N_4$, the W(μ-NN)W nitrogen resonances are found at 434.4 and 431.5 ppm ($^1J_{NN}$ = 10 Hz), and the W(μ-$N_\alpha N_\beta$H)W resonances are found at 409.5 ppm ($^1J_{NN}$ = 11.5 Hz, $^2J_{NH}$ = 2 Hz, N_α) and 216.8 ppm ($^1J_{NN}$ = 11.5 Hz, $^1J_{NH}$ = 76 Hz, N_β). A W=N stretch is found at 863 cm^{-1} in the infrared spectrum, but no N–H stretch is observed in solution or in a Nujol mull.

$$Cp^*WMe_3(\mu\text{-NNH})WCp^*Me_2(\mu\text{-}N_2)WCp^*Me_3 \xrightarrow{HOTf} \underset{\mathbf{8}}{} Cp^*WMe_3(\eta^1\text{-NNH}_2) + \underset{\mathbf{5a}}{} Cp^*WMe_2(OTf)(\mu\text{-}N_2)WCp^*Me_3 \quad (6)$$

Addition of NEt_3 to an acetonitrile solution of **5a** inhibits its decomposition, a result that suggests that the decomposition may be catalyzed by protons. The reaction is exceptionally slow in freshly dried ether or THF. Methane can be observed as a product in the proton NMR spectrum. A speculative mechanism that is based on reactions that we have discussed so far consists of protonation of **5a** by HX to give $[Cp^*WMe_3(\eta^2$-NHNH$_2)]X$ (**3a**-X), which then slowly eliminates methane to yield $Cp^*WMe_2(X)(\eta^1$-NNH$_2)$. $Cp^*WMe_2(X)(\eta^1$-NNH$_2)$ reacts with **3a** to yield $Cp^*WMe_2(X)(\mu$-$N_2)Cp^*WMe_3$, which finally reacts with a third equivalent of **5a** (the reverse of the reaction shown in eq 6) to yield **8**. The net reaction does not consume protons. As one might expect in "condensation" reactions of this type, methylated hydrazido(2−) derivatives are relatively stable; for

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example, $Cp^*WMe_3(\eta^1$-NNHMe) (**5b**) decomposes only slightly over a period of 3 weeks in C_6D_6.

Discussion

Monomeric complexes that contain η^2-bound hydrazido(1−) or hydrazine ligands are relatively rare, especially those that contain unsubstituted hydrazido or hydrazine ligands. Examples of unsubstituted hydrazido(1−) complexes other than those discussed here include Mo{HB(3,5-dimethylpyrazolyl)$_3$}(NO)I(NHNH$_2$),[41] $Cp^*_2Sc(\eta^2$-NHNH$_2$),[42] $[(MeC(CH_2PPh_2)_3)Co(\eta^2$-NHNH$_2$)]$^+$,[43] M(NHNH$_2$)(NO)[ethylenedithiobis(2-benzenethiolato)] (M = Mo or W),[44] and W[N-2,6-$C_6H_3(i$-Pr)$_2$][2,6-$NC_5H_3(CH_2$N-tosyl)$_2$](Cl)(η^2-NHNH$_2$).[45] The last three have been structurally characterized. Examples of structurally-characterized monomeric complexes that contain a substituted η^2-hydrazido(1−) ligand are not much more common.[34,35,46-50] Monomeric complexes other than those discussed here that contain unsubstituted η^2-hydrazine ligands include $\{[MeC(CH_2PPh_2)_3]Co(\eta^2$-$NH_2NH_2)\}^{2+}$,[43] $[Cp^*WMe_3(\eta^2$-$NH_2NH_2)]^+$,[24] and [W[N-2,6-$C_6H_3(i$-Pr)$_2$][2,6-$NC_5H_3(CH_2$N-tosyl)$_2$](Cl)(η^2-NH$_2$NH$_2$)]$^+$.[51] The few monomeric complexes that contain substituted η^2-hydrazine ligands whose structures have been confirmed include $[VCl_2(\eta^2$-$NH_2NMePh)_2(NNMePh)]Cl$[31] and $[CpMo(NO)I(\eta^2$-$NH_2NHPh)]^+$.[48] It has been assumed in the past that hydrazine and hydrazido ligands, especially unsubstituted ligands, are highly reducing and would not be found bound to a reducible d^0 metal.[52] Our results show clearly that this is not the case for certain W(VI) complexes in many circumstances.

All of the hydrazine and hydrazido complexes discussed here are W(VI) 18-electron species when the hydrazine or hydrazido ligands are bound to the metal in an η^2 fashion. With the exception of $Cp^*WMe_4(\eta^x$-NHNMe$_2$) (where x is probably 1), complexes that contain the Cp^*WMe_4 core are not as stable toward elimination of methane as those that contain the Cp^*WMe_3 core. The relative stability of W(VI) complexes that contain the Cp^*WMe_3 core toward loss of methane nevertheless is surprising in view of the W(VI) oxidation state and what one might assume to be relatively polar W–carbon bonds. Although the majority of $N_2H_xMe_y$ ligands are coordinated in an η^2 fashion in the lowest energy form of a Cp^*WMe_3 complex, there is abundant evidence that $[Cp^*WMe_3(\eta^1$-$N_2H_xMe_y)]^{n+}$ species form and are relatively reactive intermediates in much of the chemistry discussed here. (It has been recognized for several years that complexes that contain η^1-hydrazido ligands would be inherently more reactive than those with η^2-hydrazido ligands in some reactions, e.g., protonations.[1]) It seems likely that many of what are likely to be relatively common *inter*molecular decomposition reactions will involve η^1-$N_2H_xMe_y$ species rather than η^2-$N_2H_xMe_y$ species, since an electron pair is then available on the hydrazine or hydrazido ligand and the electron count of the metal in complexes discussed here would be 16.

There is much evidence that hydrogen bonding will be common in N_2H_x systems of the type described here, especially cationic species. (Hydrogen bonding has been observed in several circumstances in X-ray studies of hydrazido and hydrazine complexes.[31]) It remains to be seen how important hydrogen bonding will be in solution chemistry. However, it is clear even at this stage that the presence of anions such as chloride (versus triflate) can lead to rather different chemistry, so noncoordinating anions may be more desirable in order to predict and control chemistry of the type described here.

One of the central issues in dinitrogen reduction mechanisms is how the N–N bond is cleaved. Our hypothesis is that it is cleaved in the Cp^*WMe_3 system in $Cp^*WMe_3(\eta^2$-$NH_2NH_2)$.[24] *If* a W=NNH$_2$ complex is part of the sequence of a dinitrogen reduction, then an important issue is at what point the two nitrogen atoms become bound to a single metal. The evidence we have accumulated here suggests that η^2-coordination occurs upon protonation of the α nitrogen atom; it is still an intriguing possibility that the η^1-NNH$_2$ ligand must become an η^2-NNH$_2$ ligand first in order to free the lone pair on the α nitrogen atom to receive the proton. There are many other reports of protonation or alkylation at the α nitrogen atom in η^1-NNH_xR_y complexes, usually of metals in lower oxidation states,[53] but η^2-coordination as a required step for N–N bond cleavage so far has been deemphasized relative to processes that involve η^1-intermediates.[1,54] It also is interesting to note that ammonia is formed most efficiently in Chatt-type ($M(N_2)_2L_4$) systems (M = Mo or W; L = a phosphine) in which the L ligands are labile, a result which is consistent with required η^2-coordination of N_2H_x in intermediates, although other explanations have been preferred. In the Cp^*WMe_3 system, successive addition of an electron, a proton, and an electron to $[Cp^*WMe_3(\eta^2$-NHNH$_2$)]$^+$ would complete the formation of the crucial intermediate, $Cp^*WMe_3(\eta^2$-$NH_2NH_2)$. In discussions of the mechanism of N–N bond cleavage in systems involving lower oxidation-state metals, it is proposed that bound hydrazine yields free hydrazine; i.e., bound hydrazine is *not* an intermediate in the production of ammonia. In contrast we propose that bound hydrazine *is* required for efficient cleavage of the N–N bond.[24]

Many potentially important details of the hydrazido chemistry reported here are missing. Several times in this work we raised the possibility that diazene complexes of the type Cp^*WMe_3-(η^2-diazene) might be involved in various reactions involving rearrangement of N_2H_x ligands. $Cp^*WMe_3(\eta^2$-MeNNMe) has now been prepared (by deprotonation of $[Cp^*WMe_3(\eta^2$-MeNNHMe)]$^+$) and structurally characterized.[26] An interesting feature of the structure, in addition to the fact that the dimethyldiazene is significantly reduced to the 1,2-dimethylhydrazido(2−) ion, is that one of the nitrogen atoms is sp^2-hybridized and forms a double bond to the metal using the d_{z^2} orbital (instead of the d_{xy} orbital). As a result of this extra stabilization of the coordinated dimethyldiazene ligand, $Cp^*WMe_3(\eta^2$-HN=NH) now should at least be considered as a plausible intermediate in a dinitrogen reduction scheme. However, it is not at all obvious why Nature would choose η^2-diazene complexes as the common type of intermediate in a variety of reactions, when simpler pathways would seem more economical. In future studies, we hope to explore in more detail questions concerning the role of η^2-N_2H_x intermediates in Cp^*WMe_3 and related high-oxidation-state systems and further explore possible connections between high-oxidation-state N_2H_x chemistry and reduction of dinitrogen by nitrogenases.

Experimental Section

General Procedures. Solvents were dried and degassed prior to use and distilled from molten sodium (toluene), sodium/benzophenone (ether, tetrahydrofuran, pentane), calcium hydride (dichloromethane), or P_2O_5 (acetonitrile). (Pentane was first washed with 5% HNO_3/H_2SO_4 and dried using tetraglyme to solvate the sodium.) All preparations were

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conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox, under argon when using Schlenk techniques, or on a high-vacuum line ($<10^{-4}$ Torr).

NMR operating frequencies and reference standards for heteronuclei on the scale of ^1H (300 MHz, $SiMe_4$ = 0 ppm) are as follows: ^{13}C (75.5 MHz, $SiMe_4$ = 0 ppm), ^{15}N (30.40 MHz, NH_2Ph = 56.5 ppm), and ^{19}F (282.21 MHz, $CFCl_3$ = 0 ppm). Proton and carbon spectra were referenced using the partially deuterated solvent as an internal reference. Other nuclei were referenced externally to the compounds indicated in the same solvent where possible. Chemical shifts are in ppm, and coupling constants and line widths are in Hertz. All spectra were acquired at room temperature unless otherwise noted. Deuterated solvents were dried by passage through alumina and storage over 4-Å molecular sieves.

IR absorptions are reported in units of cm^{-1}. All spectra were recorded as Nujol mulls between KBr plates, unless otherwise indicated. Solution spectra were recorded using airtight KBr cells. Microanalyses were performed either by Schwartzkopf Laboratories, Woodside, NY, or in our own laboratory using a Perkin–Elmer PE2400 microanalyzer.

$[Cp^*WMe_4]PF_6$ was prepared according to the literature procedure.[33] NH_2NHMe (Aldrich) and NH_2NMe_2 (Aldrich) were distilled from CaH_2 and stored over 4-Å sieves. Hydrazine (Aldrich) was dried over 3-Å sieves. Hydrazine-$^{15}N_2$ and NHMeNHMe were isolated by liquid ammonia extraction of $^{15}N_2H_4{\cdot}H_2SO_4$ (MSD Isotopes: Montreal, Canada) and NHMeNHMe·2HCl (Aldrich), respectively. Methyl triflate, trifluoromethanesulfonic anhydride, and triflic acid (Aldrich) were used as purchased. A 30% (w/w) solution of DOTf in ether was prepared by vacuum transferring 1 equiv of D_2O into a flask containing Tf_2O in ether.

Preparation of Compounds. $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6{\cdot}2THF$ (1a-PF_6). A solution of hydrazine (0.096 g, 3.00 mmol, 1.07 equiv) in 15 mL of tetrahydrofuran was added to a slurry of $[Cp^*WMe_4]PF_6$ (1.47 g, 2.81 mmol) in 40 mL of THF at room temperature. The solution became pale-yellow, and $[Cp^*WMe_4]PF_6$ dissolved over a period of ca. 10 min. The solvent was removed in vacuo, and the residue was recrystallized from THF/pentane to yield ivory, crystalline $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6{\cdot}2THF$ (1.47 g, 2.10 mmol, 75%). Anal. Calcd for $C_{22}H_{47}F_6N_2O_2PW$: C, 37.73; H, 6.76; N, 3.10. Found: C, 37.19; H, 6.74; N, 3.49.

$[Cp^*WMe_4(\eta^2\text{-}^{15}NH_2{}^{15}NH_2)]PF_6{\cdot}2THF$ was prepared similarly from hydrazine-$^{15}N_2$: ^1H NMR (CD_2Cl_2) δ 4.98 (d, $^1J_{HN}$ = 80, 2 H, NH), 4.37 (d, $^1J_{HN}$ = 83, 2 H, NH).

Protonation of 1a. A solution of triflic acid (0.027 g, 0.18 mmol, 4.39 equiv) in 2 mL of dichloromethane was added to a solution of $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6{\cdot}\sim$1.5THF (0.026 g, 0.039 mmol) in 5 mL of dichloromethane at −20 °C. After 15 min, a white precipitate was filtered off and the solvent was removed from the yellow filtrate to yield a mixture of $[Cp^*WMe_4]PF_6$ and $[Cp^*WMe_4]OTf$ (0.022 g, 0.042 mmol, ca. 100%).

$[Cp^*WMe_4(\eta^2\text{-}NH_2NHMe)]OTf$ (1b-OTf). A solution of triflic acid (0.013 g, 0.087 mmol, 0.97 equiv) in 2 mL of ether was added to a solution of **2b** (0.038 g, 0.090 mmol) in 5 mL of ether at −40 °C. After 15 min at −40 °C, white, microcrystalline $[Cp^*WMe_4(\eta^2\text{-}NH_2NHMe)]OTf$ (0.050 g, 0.087 mmol, 97%) was filtered off and rinsed with cold ether: ^{19}F NMR (CD_2Cl_2, −30 °C) δ −78.5.

$Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ (2a). This synthesis is a slight modification of that already published.[23] A solution of triethylamine (0.26 g, 2.62 mmol, 2.00 equiv) in 5 mL of ether was added to a rapidly stirred slurry of $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6$ (0.73 g, 1.31 mmol) in 15 mL of ether at −20 °C. The solution became light-yellow, and some tan solid was present. After 5 min, $[NEt_3H]PF_6$ was filtered off and rinsed with ether. The pale-yellow filtrate was taken to dryness in vacuo to yield ivory $Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ (0.52 g, 1.26 mmol, 96%). Recrystallization of the crude product from ether/pentane at −40 °C gave analytically pure material. Anal. Calcd for $C_{14}H_{30}N_2W$: C, 40.99; H, 7.37; N, 6.83. Found: C, 40.92; H, 6.94; N, 6.70.

$Cp^*WMe_4(\eta^2\text{-}^{15}NH^{15}NH_2)$ was prepared similarly from $[Cp^*WMe_4(\eta^2\text{-}^{15}NH_2{}^{15}NH_2)]PF_6{\cdot}2THF$.

$Cp^*WMe_4(\eta^2\text{-}NMeNH_2)$ (2b). A solution of methylhydrazine (0.051 g, 1.11 mmol, 3.82 equiv) in 2 mL of ether was added to a rapidly stirring slurry of $[Cp^*WMe_4]PF_6$ (0.15 g, 0.29 mmol) in 5 mL of ether at −40 °C. The solution became light-yellow, and a tan goo formed. After 2 min, the solution was filtered and the filtrate was taken to dryness in vacuo. The residue was extracted with ether, and the mixture was filtered. Ether was removed from the filtrate in vacuo to yield pale-yellow $Cp^*WMe_4(\eta^2\text{-}NMeNH_2)$ (0.090 g, 0.21 mmol, 73%). The crude product was recrystallized from THF/pentane at −40 °C to yield an off-white powder. Selective irradiation of the WMe_{cis} group at −0.19 ppm resulted in the loss of nearly all intensity for the other WMe_{cis} peak at −0.15 ppm, consistent with interchange of the two cis methyl groups on the NMR time scale. Anal. Calcd for $C_{15}H_{32}N_2W$: C, 42.46; H, 7.60; N, 6.60. Found: C, 42.76; H, 7.67; N, 6.72.

$Cp^*WMe_4(NHNMeH)$ (**2b′**) was also observed in the NMR spectra in approximately 15% yield. Isomerization of **2b′** to **2b** (or vice versa) was not observed at room temperature on the NMR time scale, but rapid interconversion on the chemical time scale could not be discounted.

$Cp^*WMe_4(\eta^x\text{-}NHNMe_2)$ (2c). A solution of 1,1-dimethylhydrazine (0.089 g, 1.48 mmol, 6.22 equiv) in 2 mL of dichloromethane was added to a rapidly stirred solution of $[Cp^*WMe_4]PF_6$ (0.12 g, 0.24 mmol) in 5 mL of dichloromethane at −40 °C. The solution became orange immediately. After 15 s, the solvent was removed quickly in vacuo. The residue was extracted twice with pentane, and the extract was taken to dryness to yield pale-yellow crystalline $Cp^*WMe_4(\eta^x\text{-}NHNMe_2)$ (0.083 g, 0.19 mmol, 80%) contaminated with ca. 10% $Cp^*WMe_3(\eta^1\text{-}NNMe_2)$. Recrystallization from pentane at −40 °C yielded light-yellow crystals of pure $Cp^*WMe_4(\eta^x\text{-}NHNMe_2)$. An NH stretch was not observable in the IR spectrum of this compound in Nujol.

$[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]Cl$ (3a-Cl). Addition of an ether solution of HCl (0.27 mmol, 1.05 equiv) to a solution of $Cp^*WMe_3(\eta^1\text{-}NNH_2)$ (0.10 g, 0.26 mmol) in 10 mL of ether at −40 °C results in the immediate precipitation of pale-yellow $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]Cl$ (0.099 g, 0.23 mmol, 89%). This compound is unstable in solution, decomposing readily to $Cp^*WMe_2Cl(\eta^1\text{-}NNH_2)$ by losing methane.

Observation of $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]PF_6$ (3a-PF_6). Thermal decomposition of a solution of $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6$ yields $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]PF_6$, although the preferred method of preparing **3a** (as the triflate salt) is by protonating **5a**: ^{19}F NMR (CD_2Cl_2) δ −71.74 (d, $^1J_{FP}$ = 713).

$[Cp^*WMe_3(\eta^2\text{-}^{15}NH^{15}NH_2)]PF_6$ was prepared similarly from $[Cp^*WMe_3(\eta^2\text{-}^{15}NH_2{}^{15}NH_2)]PF_6$: ^1H NMR (CD_2Cl_2) δ 10.39 (d, $^1J_{HN}$ = 93, $^2J_{HW}$ = 18, 1 H, NH), 5.04 (d, $^1J_{HN}$ = 89, 2 H, NH_2).

Preparation of $[Cp^*WMe_3(\eta^2\text{-}^{15}NH^{15}NH_2)]OTf$. This compound was prepared by protonating $Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NH_2)$, as described in the literature for $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$:[23] ^1H NMR (CD_2Cl_2) δ 11.82 ($^1J_{HN}$ = 93, $^2J_{HW}$ = 18.5, 1 H, NH), 5.21 (tr, $^1J_{HN}$ = 89, $^2J_{HW}$ < 5, 2 H, NH_2); IR (Nujol, cm^{-1}) 3312 (m, NH), 3225 (s, NH), 3146 (br,m, NH), 1585 (m, NH_2).

$[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]PF_6$ (3b-PF_6). Monomethylhydrazine was added to a solution of $[Cp^*WMe_4]PF_6$ in 10 mL of tetrahydrofuran. After 5 min, the solvent was removed in vacuo and the residue was rinsed with ether to yield a mixture of products that consisted primarily of $[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]PF_6$, according to its proton NMR spectrum.

$[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$ (3b-OTf). A solution of triflic acid (0.081 g, 0.54 mmol, 1.03 equiv) in 2 mL of ether was added slowly to a solution of $Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (0.21 g, 0.52 mmol) in 15 mL of ether at −20 °C. After 15 min, yellow, crystalline $[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$ (0.19 g, 0.34 mmol, 64%) was filtered off and rinsed with ether. Recrystallization of the crude product from tetrahydrofuran/ether at −40 °C yielded analytically pure yellow needles. This method is not always reproducible. It is most successful if fresh $Cp^*WMe_3(\eta^1\text{-}NNHMe)$ and triflic acid are employed, but the yield also varies with temperature and rate of addition of acid: ^{19}F NMR (CD_2Cl_2) δ −79.0. Anal. Calcd for $C_{15}H_{29}F_3N_2O_3SW$: C, 32.27; H, 5.24; N, 5.02. Found: C, 32.54; H, 5.09; N, 4.92.

$[Cp^*WMe_3(\eta^2\text{-}NMeND_2)]OTf$ was prepared similarly from $Cp^*WMe_3(\eta^1\text{-}NNDMe)$ and DOTf. No hydrazido(1−) protons were observed in the proton NMR spectrum.

$[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]OTf$ (3b′-OTf). Addition of a solution of triflic acid in 2 mL of ether to a solution of $Cp^*WMe_3(\eta^1\text{-}NNHMe)$ in 5 mL of ether at −40 °C yielded a beige to pale-yellow mixture of microcrystalline $[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]OTf$ and $[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$.

Some solutions of $[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]OTf$ in CD_2Cl_2 were stable at room temperature overnight. The addition of a catalytic amount of base to a solution containing a mixture of $[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]OTf$ and $[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$ in CD_2Cl_2 qualitatively accelerated the conversion of **3b′** to **3b**, while also yielding a trace of $Cp^*WMe_3(\eta^1\text{-}NNHMe)$.

Observation of $Cp^*WMe_3(\eta^2\text{-}NNH_2)$ (4a). An excess of triethylamine was transferred by high-vacuum line into a J. Young/Brunfeldt high-vacuum NMR tube that contained a frozen, degassed solution of $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$ in CD_2Cl_2 (or THF-d_8). The solution was warmed to −78 °C and mixed. The sample was then placed in a precooled NMR probe in order to observe **4a**. At temperatures greater than −20 °C, **4a** rapidly isomerized to **5a**.

Observation of $Cp^*WMe_3(\eta^2\text{-}NNHMe)$ (4b). An excess of triethylamine was transferred by high-vacuum line into a J. Young/Brunfeldt high-vacuum NMR tube that contained a frozen, degassed solution of $[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$ (or a mixture of $[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$ and $[Cp^*WMe_3(\eta^2\text{-}NHNHMe)]OTf$) in CD_2Cl_2 (or THF-d_8). The solution was warmed to −78 °C and mixed. The sample was then placed in a precooled NMR probe. At temperatures greater

than −20 °C, **4b** rapidly isomerized to **5b**.

$Cp^*WMe_3(\eta^1\text{-}NNH_2)$ (5a). This synthesis is a modified version of that which is published.[23] A solution of $Cp^*WMe_4(\eta^2\text{-}NHNH_2)$ (3.73 g, 9.10 mmol) in 100 mL of toluene was allowed to stand at room temperature for 3 h. Most of the toluene was removed in vacuo from the light-orange to red solution. Addition of excess pentane resulted in crystallization of $Cp^*WMe_3(\eta^1\text{-}NNH_2)$ (2.99 g, 7.58 mmol, 79%) as beige needles. Recrystallization from toluene/pentane at −40 °C yielded beige plates.

$Cp^*WMe_3(^{15}N^{15}NH_2)$ was prepared similarly from $Cp^*WMe_4(\eta^2\text{-}^{15}NH^{15}NH_2)$: ^1H NMR (C_6D_6) δ 4.59 (dd, $^1J_{HN}$ = 77, $^2J_{HN}$ = 2, 2 H, NH_2); IR (Nujol, cm^{-1}) 3336 (m, ^{15}NH), 3267 (m, ^{15}NH), 1596 (m, ^{15}NH).

$Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (5b). (a) A solution of $Cp^*WMe_4(\eta^2\text{-}NMeNH_2)$ (0.17 g, 0.41 mmol) in 10 mL of toluene was allowed to stand at room temperature overnight. The solvent was removed in vacuo, and the residue was extracted with pentane. The solvent was removed from the filtrate in vacuo to yield light-yellow, crystalline $Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (0.14 g, 0.34 mmol, 82%). Recrystallization from ether/pentane yielded analytically pure yellow crystals. Irradiation of the NH resonance in a proton NMR sample results in collapse of the NMe doublet to a singlet. Anal. Calcd for $C_{14}H_{28}N_2W$: C, 41.19; H, 6.91; N, 6.86. Found: C, 40.81; H, 7.15; N, 7.26.

$Cp^*WMe_3(\eta^1\text{-}NNDMe)$ was prepared by adding excess D_2O to a solution of $Cp^*WMe_3(\eta^1\text{-}NNHMe)$ in 3 mL of ether. After 10 min, the solvent was removed in vacuo.

(b) A solution of triethylamine (0.013 g, 0.13 mmol, 1.89 equiv) in 2 mL of tetrahydrofuran was added to a solution of $[Cp^*WMe_3(\eta^2\text{-}NMeNH_2)]OTf$ (0.038 g, 0.068 mmol) in 5 mL of tetrahydrofuran. The solution rapidly became a lighter yellow, and after 10 min, the solvent was removed in vacuo. The residue was extracted with pentane twice, and the pentane solution was reduced to dryness in vacuo to yield $Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (0.025 g, 0.061 mmol, 90%).

Preparation of $Cp^*WMe_3(\eta^2\text{-}^{15}N^{15}NMeH)$. $Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NH_2)$ was synthesized by previously discussed methods. $Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NHLi)$ was synthesized by deprotonation of **5a** using *n*-BuLi according to literature methods.[38] $Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NHLi)$ (0.102 g, 0.254 mmol) was dissolved in 10 mL of ether at −30 °C, and methyl iodide (0.016 mL, 0.254 mmol) was added. The reaction mixture became a light-yellow color over a 30-min period, and the solvent was removed in vacuo to produce an ivory solid. The solid was extracted with pentane, and the mixture was filtered to yield a yellow filtrate. The solvent was removed from the filtrate in vacuo to yield yellow $Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NMeH)$ as the major product in 73% yield (0.076 g, 0.185 mmol). $Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NMe_2)$ was also present in approximately 10% yield due to formation of $Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NLi_2)$ in the previous step. $[Cp^*WMe_3(\eta^2\text{-}^{15}NMe^{15}NH_2)]OTf$ and $Cp^*WMe_3(\eta^2\text{-}^{15}N^{15}NMeH)$ were formed by methods previously discussed for the formation of **3b** and **5b**.

$Cp^*WMe_3(\eta^1\text{-}NNMe_2)$ (5c). This procedure is a modification of that employed by Murray.[32] A solution of 1,1-dimethylhydrazine (0.096 g, 1.60 mmol, 4.90 equiv) in 2 mL of dichloromethane was added to a solution of $[Cp^*WMe_4]PF_6$ (0.17 g, 0.33 mmol) in 10 mL of dichloromethane at −20 °C. After the solution was stirred for 5 min, it became pale-orange and cloudy. The solvent was then removed in vacuo, and the residue was extracted twice with pentane. The pentane was removed from the filtrate in vacuo to yield yellow, crystalline $Cp^*WMe_3(\eta^1\text{-}NNMe_2)$ (0.10 g, 0.25 mmol, 76%). Recrystallization of the crude product from a minimum of ether/pentane at −40 °C yields analytically pure yellow crystals. Anal. Calcd for $C_{15}H_{30}N_2W$: C, 42.67; H, 7.16; N, 6.63. Found: C, 42.67; H, 7.36; N, 6.67.

$[Cp^*WMe_3(NNH_2Me)]OTf$ (6b-OTf). A solution of 1.0 equiv of triflic acid (17.5 μL, 0.198 mmol) in 2 mL of ether was added quickly to a solution of freshly prepared $Cp^*WMe_3(\eta^1\text{-}NNHMe)$ (0.081 g, 0.198 mmol) in 5 mL of ether at −40 °C. The solution was mixed quickly and stored at −40 °C. Beige, crystalline $[Cp^*WMe_3(NNH_2Me)]OTf$ (0.053 g, 0.095 mmol, 48%) should precipitate within seconds and must be filtered off onto a precooled glass frit. If a precipitate does not appear immediately or it appears to be yellow in color, then the product has probably isomerized to a mixture of **3b** and **3b'**.

$[Cp^*WMe_3(NNHMe_2)]OTf$ (6c-OTf). A solution of triflic acid (0.022 g, 0.15 mmol, 1.08 equiv) in 1 mL of ether was added to a solution of $Cp^*WMe_3(\eta^1\text{-}NNMe_2)$ (0.058 g, 0.14 mmol) in 5 mL of ether at −40 °C. A precipitate formed quickly, and the vial was immediately stored at −40 °C for 5 min. Pale-yellow microcrystalline $[Cp^*WMe_3(NNHMe_2)]OTf$ (0.059 g, 0.10 mmol, 73%) was filtered off onto a cold frit and rinsed with ether that had been cooled to −40 °C.

$[Cp^*WMe_3(NNMe_3)]OTf$ (6d-OTf). (a) A solution of methyltriflate (0.056 g, 0.34 mmol, 1.08 equiv) in 1 mL of ether was quickly added to a solution of $Cp^*WMe_3(\eta^1\text{-}NNMe_2)$ (0.13 g, 0.32 mmol) in 5 mL of ether at room temperature. After 10 min, the pale-yellow precipitate of $[Cp^*WMe_3(NNMe_3)]OTf$ (0.16 g, 0.26 mmol, 83%) was filtered off and rinsed with pentane. Recrystallization from tetrahydrofuran/ether at −40 °C yielded analytically pure pale-yellow needles. Anal. Calcd for $C_{17}H_{33}F_3N_2O_3SW$: C, 34.82; H, 5.67; N, 4.78. Found: C, 34.57; H, 5.56; N, 4.52.

(b) $[Cp^*WMe_3(^{15}N^{15}NMe_3)]OTf$ was prepared by adding excess MeOTf (1.30 g, 7.91 mmol, 8.21 equiv) and 2,6-di-*tert*-butylpyridine (1.10 g, 5.73 mmol, 5.94 equiv) in 4 mL of ether to $Cp^*WMe_3(\eta^1\text{-}^{15}N^{15}NH_2)$ (0.38 g, 0.96 mmol) in 20 mL of ether at room temperature. After 10 min, crystalline material began to form; after 1 h, a 2:1 pale-yellow mixture of [2,6-di-*tert*-butylpyridinium]OTf and $[Cp^*WMe_3(^{15}N^{15}NMe_3)]OTf$ (0.97 g, 0.76 mmol, 79%) was filtered off and rinsed with ether: ^1H NMR (CD_2Cl_2) δ 3.48 (dd, $^2J_{HN}$ = 1.3, 9 H, NMe); ^{13}C NMR (CD_2Cl_2) δ 58.56 (d, $^1J_{CN}$ = 4.5, NMe). [2,6-Di-*tert*-butylpyridinium]OTf: ^1H NMR (CD_2Cl_2) δ 12.10 (br, 1 H, NH), 8.40 (tr, 1 H, H_{para}), 7.78 (d, 2 H, H_{meta}), 1.60 (s, 18 H, *t*-Bu); ^{13}C NMR (CD_2Cl_2) δ 165.26 (C_{aryl}), 148.47 (C_{aryl}), 122.79 (C_{aryl}), 121.23 (q, $^1J_{CF}$ = 321, OTf), 37.26 ($-CMe_3$), 28.92 ($-CMe_3$).

***trans*-$Cp^*WMe_2Cl(\eta^1\text{-}NNH_2)$ (7).** (a) A solution of $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]Cl$ in 10 mL of dichloromethane was stirred for 15 min at room temperature. The solvent was removed in vacuo to yield $Cp^*WMe_2Cl(\eta^1\text{-}NNH_2)$ quantitatively.

(b) Solid lithium chloride (0.027 g, 0.064 mmol, 12.7 equiv) was added to a solution of $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$ (0.027 g, 0.050 mmol) in 5 mL of tetrahydrofuran at room temperature. After 1.5 h, the solution had faded to a pale yellow. The solvent was removed in vacuo, and the residue was extracted twice with dichloromethane to yield light-yellow, crystalline $Cp^*WMe_2Cl(\eta^1\text{-}NNH_2)$ (0.020 g, 0.048 mmol, 96%). Anal. Calcd for $C_{12}H_{23}ClN_2W$: C, 34.76; H, 5.59; N, 6.76. Found: C, 34.65; H, 5.12; N, 6.44.

$Cp^*WMe_3(\mu\text{-}NNH)Cp^*WMe_2(\mu\text{-}NN)Cp^*WMe_3$ (8). A solution of $Cp^*WMe_3(\eta^1\text{-}NNH_2)$ in acetonitrile slowly decomposes over a period of weeks under dinitrogen to form analytically pure, long, dark-red needles of $Cp^*WMe_3(\mu\text{-}NNH)Cp^*WMe_2\text{-}(\mu\text{-}NN)Cp^*WMe_3$: ^1H NMR (CD_2Cl_2) δ 7.81 (br, 1 H, NH), 1.74 (s, 15 H, Cp*), 1.64 (s, 15 H, Cp*), 1.59 (s, 15 H, Cp*), 1.03 (s, 6 H, WMe_{cis}), 0.89 (s, 6 H, WMe_{cis}), 0.85 (s, 6 H, WMe_{cis}), 0.74 (s, 3 H, WMe_{trans}), 0.59 (s, 3 H, WMe_{trans}); ^{13}C NMR (CD_2Cl_2) δ 111.89 (Cp*), 110.05 (Cp*), 107.00 (Cp*), 39.13 ($^1J_{CW}$ = 64, WMe_{cis}), 29.82 ($^1J_{CW}$ = 57, WMe_{trans}), 28.76 ($^1J_{CW}$ = 56, WMe_{trans}), 26.59 ($^1J_{CW}$ = 56, WMe_{cis}), 21.18 ($^1J_{CW}$ = 58, WMe_{trans}), 10.99 (Cp*), 10.98 (Cp*), 9.74 (Cp*). Anal. Calcd for $C_{38}H_{70}N_4W_3$: C, 40.23; H, 6.22; N, 4.94. Found: C, 40.68; H, 6.33; N, 5.07.

$Cp^*WMe_3(\mu\text{-}^{15}N^{15}NH)Cp^*WMe_2(\mu\text{-}^{15}N^{15}N)Cp^*WMe_3$ was prepared similarly from $Cp^*WMe_3(^{15}N^{15}NH_2)$: ^1H NMR (CD_2Cl_2) δ 7.55 (d, $^1J_{HN}$ = 76, $^2J_{HN}$ = 2, 1 H, NH); ^{15}N NMR (CD_2Cl_2) δ 434.4 (d, $^1J_{NN}$ = 10, WNNW), 431.5 (d, $^1J_{NN}$ = 10, WNNW), 409.5 (d, $^1J_{NN}$ = 11.5, W*N*NHW), 216.8 (d, $^1J_{NN}$ = 11.5 WN*N*HW).

Reaction of $Cp^*WMe_3(\eta^1\text{-}NNH_2)$ (5a) with $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$ (3a-OTf). A solution of $Cp^*WMe_3(\eta^1\text{-}NNH_2)$ (0.028 g, 0.071 mmol) in 2 mL of dichloromethane was added to $[Cp^*WMe_3(\eta^2\text{-}NHNH_2)]OTf$ (0.038 g, 0.070 mmol, 0.98 equiv) in 5 mL of dichloromethane at room temperature. The solution slowly became dark-red; after being stirred for 30 min, the solution was filtered to remove $[N_2H_5]^+$, and the solvent was removed from the filtrate in vacuo to yield 40% $[Cp^*WMe_3]_2(\mu\text{-}N_2)$, among other unidentified compounds, according to the ^1H NMR spectrum.

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