# Synthesis and Decomposition of Alkyl Complexes of Tungsten(IV) That Contain a [(Me₃SiNCH₂CH₂)₃N]³⁻ Ligand

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The synthesis of a variety of tungsten alkyl complexes of the type [N₃N]WR ([N₃N]³⁻ = [(Me₃SiNCH₂CH₂)₃N]³⁻; R = Me, Et, Bu, CH₂Ph, CH₂SiMe₃, CH₂CMe₃, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopentenyl) was attempted by alkylation of [N₃N]WCl complexes. Only the methyl, phenyl, and cyclopentenyl complexes could be isolated. The susceptibility of the [N₃N]WR complexes is similar to that of [N₃N]WCl; the effective moment is depressed as a consequence of a combination of spin−orbit effects and low-symmetry ligand-field components that result in zero-field splitting of the $d^2$ ground-state spin triplet. No linear alkyl complexes could be observed as a consequence of α,α-dehydrogenation to give molecular hydrogen and alkylidyne complexes, [N₃N]W≡CR′. [N₃N]W(cyclopropyl) evolves ethylene in a first-order process to give [N₃N]W≡CH, while [N₃N]W(cyclobutyl) is converted into the 1-tungstacyclopentene complex, [N₃N]W(CHCH₂CH₂CH₂), as confirmed in an X-ray study. [N₃N]W(CHCH₂CH₂CH₂) decomposes readily in a first-order manner to give [N₃N]W≡CCH₂CH₂CH₃. An attempt to prepare [N₃N]W(cyclopentyl) led to formation of [N₃N]W(cyclopentylidene)(H), as confirmed in an X-ray study. NMR studies suggest that [N₃N]W(cyclopentylidene)(H) is in equilibrium with [N₃N]W(cyclopentyl) where $\Delta H° = 11.8$-(6) kcal mol⁻¹ and $\Delta S° = 33(2)$ eu or $K_{eq} \approx 0.1$ at 46 °C. From these and other data it is concluded that the rate constant for α elimination in [N₃N]M(cyclopentyl) is approximately the same for Mo and W. The [N₃N]W(cyclopentenyl) complex is unstable, decomposing to give a complex containing a "bent imido" ligand, [(Me₃SiNCH₂CH₂)₂(NCH₂CH₂)N]W(1-(trimethylsilyl)cyclopentene), as confirmed in an X-ray study.

## Introduction

Triamidoamine ligands, [(RNCH₂CH₂)₃N]³⁻, in which R is a bulky substituent (usually SiMe₃[1] or C₆F₅[2]), can bind to a variety of transition metals,[3] especially in oxidation states 3+ or higher. Triamidoamine ligands usually bind to a transition metal in a tetradentate manner, thereby creating a sterically protected, 3-fold-symmetric "pocket" in which only three orbitals are available to bond to additional ligands in that pocket, two degenerate π orbitals (approximately $d_{xz}$ and $d_{yz}$) and a σ orbital (approximately $d_{z^2}$). We have been interested in the chemistry of Mo and W complexes that contain the [(Me₃SiNCH₂CH₂)₃N]³⁻ {[N₃N]³⁻} ligand from several perspectives, including dinitrogen fixation,[4,5] terminal chalcogenide complexes,[6−8] and new organometallic chemistry.[4,9,10]

In a recent paper,[11] we reported the synthesis of a variety of molybdenum alkyl complexes, [N₃N]MoR ([N₃N]³⁻ = [(Me₃SiNCH₂CH₂)₃N]³⁻; R = Me, Et, Bu, CH₂Ph, CH₂SiMe₃, CH₂CMe₃, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopentenyl). In general, such species are relatively stable, even when β protons are present in the alkyl. They are all Curie−Weiss $S = 1$ paramagnets down to 50 K, but below ∼50 K the effective moments undergo a sharp decrease as a consequence of what are proposed to be a combination of spin−orbit coupling and zero-field splitting effects. NMR spectra are temperature dependent as a consequence of a "locking" of the [N₃N]³⁻ ligand backbone in one $C_3$-symmetric conformation and as a consequence of Curie−Weiss behavior. The cyclopentyl and cyclohexyl complexes show another type of temperature-dependent behavior that can be ascribed to a rapid and reversible α-elimination process to give an unobservable cycloalkylidene hydride intermediate. It was shown that the rate of α-elimination for the cyclopentyl complex is more than 10⁶ times faster than the rate of β elimination, perhaps in part as a consequence of steric acceleration of the α-elimination process and concomitant steric deceleration of the β-elimination process.

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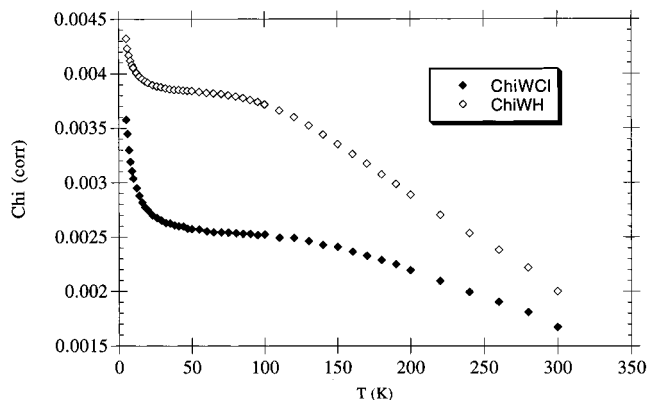
Among the linear alkyl complexes, only $[N_3N]Mo(CH_2CMe_3)$ decomposes cleanly (albeit slowly) to give $[N_3N]Mo\equiv CCMe_3$ and molecular hydrogen. Other decompositions of linear alkyl complexes are complicated by competing reactions, including $\beta$-hydride elimination to give the olefin and $[N_3N]MoH$. $\beta$-hydride elimination is the sole mode of decomposition of the cyclopentyl and cyclohexyl complexes, and $[N_3N]MoH$ can be isolated in high yield in each case. Other unusual decomposition reactions that involve C–C bond cleavages were also observed. For example, $[N_3N]Mo(cyclopropyl)$ evolved ethylene upon being heated to give $[N_3N]Mo\equiv CH$, while $[N_3N]Mo(cyclobutyl)$ was converted into $[N_3N]Mo\equiv CCH_2CH_2CH_3$, both quantitatively.

Attempts to prepare $[N_3N]WCH_2R$ complexes led to the surprising result that only $[N_3N]W\equiv CR$ complexes were formed when R was not a proton.[9] Moreover, attempts to prepare a cyclopentyl complex resulted in formation of the cyclopentylidene hydride complex, $[N_3N]W(C_5H_8)(H)$. The selective formation of $[N_3N]W-(C_5H_8)(D)$ from $Li-\alpha-DC_5H_8$ and $[N_3N]WCl$ at low temperatures suggested that $\alpha$ elimination is faster than $\beta$ elimination.[10] This paper contains the full report concerning tungsten alkyl complexes that contain the $[N_3N]^{3-}$ ligand. These results are contrasted with those obtained for the analogous Mo complexes, and an attempt is made to rationalize any significant differences.

## Results

**Tungsten Halide Complexes.** Addition of $WCl_4$-(dimethoxyethane) to $Li_3[N_3N]$[12] in THF yielded paramagnetic $[N_3N]WCl$ (**1**) in a maximum yield of ~25%. More typical yields are between 15 and 20%. Variations of this reaction so far have failed to increase the yield beyond 25%. As in the synthesis of $[N_3N]MoCl$, we suspect that loss of $Me_3SiCl$ and metal reduction are persistent problems, in part because related reactions between $(C_6F_5NHCH_2CH_2)_3N$ and $WCl_4$ in the presence of $NEt_3$ give $[(C_6F_5NCH_2CH_2)_3N]WCl$ in high yield.[2] The reaction between $[N_3N]WCl$ and TMSI yields $[N_3N]WI$, so other derivatives (Br, triflate, etc.) most likely could be prepared similarly. (It should be noted that $[N_3N]$-Mo(triflate) is a known compound that has been structurally characterized.[11])

A plot of the susceptibility of $[N_3N]WCl$ (along with that for $[N_3N]WH$, to be described later) versus $T$ is shown in Figure 1. The susceptibility of $[N_3N]WCl$ is much smaller at a given temperature than the susceptibility of $[N_3N]MoCl$,[11] especially at low temperatures. The effective moment, therefore, is lower than the expected spin-only value (2.83 $\mu_B$) near room temperature and decreases smoothly as $T$ approaches 5 K (Figure 2). In contrast, $[N_3N]MoCl$ is a Curie–Weiss $S = 1$ paramagnet down to 50 K, at which point the effective moment decreases sharply. The decrease in the effective magnetic moment was attributed to a combination of spin–orbit effects and low-symmetry ligand-field components that result in zero-field splitting of the $d^2$ ground-state spin triplet.[11,13] The effect is much larger for W than for Mo as a consequence of the larger spin–orbit coupling constant for $W^{4+}$ ($\lambda(W^{4+}) \approx$

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**Figure 1.** Plot of the molar susceptibility versus temperature for $[N_3N]WCl$ and $[N_3N]WH$.
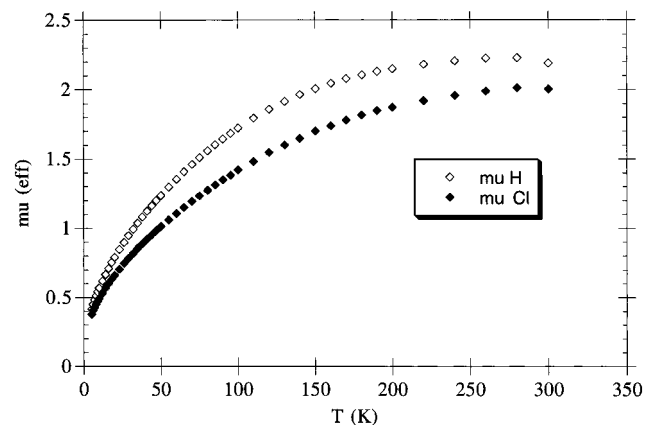


**Figure 2.** Plot of $\mu_{eff}$ versus temperature for $[N_3N]WCl$ and $[N_3N]WH$.

1050 cm$^{-1}$, while $\lambda(Mo^{4+}) \approx 475$ cm$^{-1}$.[13] The two electrons in the paramagnetic form of $[N_3N]WCl$ are believed to be in the degenerate $d_{xz}$ and $d_{yz}$ orbitals. Two measurements of the magnetic moment for $[N_3N]WCl$ in solution at 22 °C by the Evan's method gave values of 2.4 and 2.5 $\mu_B$, consistent with a magnetic moment for $[N_3N]WCl$ that is reduced from the spin-only value.

$^1$H NMR spectra of **1** show two characteristic upfield-shifted resonances for the methylene groups on the backbone of the triamidoamine ligand (at −29.83 and −75.44 ppm at 22 °C) and a TMS resonance at 8.30 ppm (at 22 °C). In general, $^1$H NMR resonances for tungsten complexes are narrower than those for molybdenum complexes, possibly as a consequence of the reduced magnetic moment for tungsten species in general. These spectra are temperature dependent in a manner analogous to that described for $[N_3N]MoCl$.[11] (See also $[N_3N]WMe$ below.) Two basic temperature-dependent processes are observed. The $[N_3N]^{3-}$ ligand's methylene and TMS resonances (to a lesser degree) shift to higher field and lower field, respectively, as the temperature is lowered. Second, at low temperature, four methylene backbone resonances are observed as a consequence of a process in which the WNCCN five-membered rings within the $[N_3N]^{3-}$ ligand system become locked in some "puckered" configuration that gives the molecule an overall $C_3$ symmetry.

An X-ray structure of $[N_3N]WCl$[14] revealed that it has a $C_3$-symmetric structure that is virtually identical to

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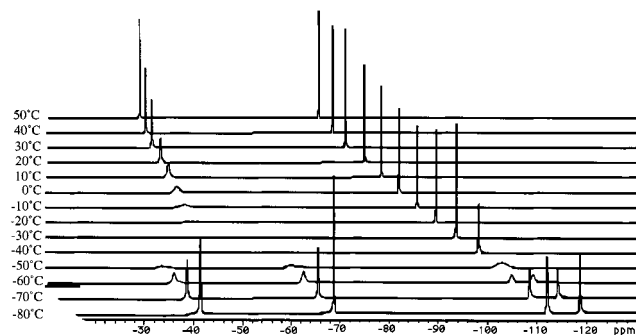
**Figure 3.** Variable-temperature $^1$H NMR spectra of the ligand backbone in [N$_3$N]WMe ($\sim$0.055M; toluene-$d_8$).

that of [N$_3$N]MoCl.[15] For example, W−N$_{eq}$ = 1.985(11) Å, N$_{eq}$−W−N$_{eq}$ = 117.66(6)°, and W−N$_{ax}$ = 2.182(6) Å. The trimethylsilyl groups are virtually "upright" with N$_{ax}$−W−N$_{eq}$−Si angles near 180°, which is typical of [N$_3$N]MX complexes in which the X group in the trigonal pocket has minimal steric demands.[3,11] X-ray studies of [N$_3$N]MoX (X = triflate, CH$_3$, cyclohexyl)[11] reveal that the degree of "tipping" of the trimethylsilyl substituents, as measured by the N$_{ax}$−Mo−N$_{eq}$−Si dihedral angle, depends on the steric bulk of X, i.e., the N$_{ax}$−Mo−N$_{eq}$−Si angles are smallest in [N$_3$N]Mo(cyclohexyl), in which the steric hindrance within the trigonal coordination pocket is most severe.

**Attempted Syntheses of Tungsten Linear Alkyl Complexes.** Addition of methyllithium to **1** in ether or THF yielded paramagnetic, orange [N$_3$N]W(CH$_3$) (**2**) in high yield. A variable-temperature $^1$H NMR spectrum of **2** is shown in Figure 3. The observed temperature-dependent processes are qualitatively the same as those observed for [N$_3$N]Mo(CH$_3$)[11] and described above for [N$_3$N]WCl. The activation energy ($\Delta G^{\ddagger}$) for the WN$_2$C$_2$ "ring-flipping" process that produces an effectively $C_{3v}$-symmetric species on the NMR time scale can be obtained from coalescence to give the upfield resonance at −50 °C (9.0(2) kcal/mol) or the lower field resonance at −30 °C (9.1(2) kcal/mol). A value of $\Delta G^{\ddagger}_{W}$ = 9.0 kcal mol$^{-1}$ is comparable to that estimated for [N$_3$N]Mo(CH$_3$) ($\Delta G^{\ddagger}_{Mo}$ = 8.4 kcal mol$^{-1}$).[11] We believe that the processes in which the ligand backbone begins to flip from one $C_3$ conformation to another have approximately the same activation energy for W and Mo because the process involves only conformational changes in the MN$_2$C$_2$ rings, i.e., N$_{ax}$ remains bound during the flipping process. One might expect that if dissociation of N$_{ax}$ from the metal is required, the barrier for a W complex would be significantly higher than for the analogous Mo complex as a consequence of a higher W−N$_{ax}$ bond strength. The effective magnetic moment of [N$_3$N]W(CH$_3$) in the solid state was found to decrease smoothly from $\sim$2 near room temperature to $\sim$0 at 5 K in a manner similar to that shown in Figure 2, and the magnetic moment at 25 °C in C$_6$D$_6$ was found to be 2.5 $\mu_B$ by the Evan's method.

[N$_3$N]W(CH$_3$) is not very stable. Upon heating **2** at temperatures between 25 °C and 80 °C it is converted quantitatively into pale yellow [N$_3$N]W≡CH (**3a**; eq 1). The dehydrogenation reaction could be monitored by UV-Vis spectroscopy in toluene by observing the disappearance of the absorption at 462 nm or by $^1$H NMR

**Table 1. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ Values for Decomposition Reactions**

| | $\Delta H^{\ddagger}$ (kcal mol$^{-1}$)[a] | $\Delta S^{\ddagger}$ (eu)[b] | $10^4 k$ (s$^{-1}$) at 341 $K$[c] |
|---|---|---|---|
| [N$_3$N]W(CH$_3$) (**2**) in toluene[d] | 19.9 | −14 | 10.0 |
| [N$_3$N]Mo(CH$_2$CMe$_3$) in toluene[e] | 25.9 | −7 | 0.048 |
| [N$_3$N]W(CHCH$_2$CH$_2$CH$_2$) in toluene[f] | 20.7 | −13 | 4.5 |
| [N$_3$N]Mo(cyclobutyl) in toluene[g] | 24.3 | 0 | 16.4 |
| [N$_3$N]W(C$_5$H$_8$)(H)[h] | 22.5 | −8 | 4.8 |

[a] Error $\approx$ 0.2 kcal. [b] Error $\approx$ 1 eu. [c] Calculated from exact values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ given in the Experimental Section. [d] $R$ = 0.995 for 13 runs between 300 and 341 K, 9 runs by $^1$H NMR, and 4 runs by visible spectroscopy. [e] See ref 11. [f] $R$ = 0.9998 for 4 runs by NMR between 313 and 343 K. [g] See ref 11. [h] $R$ = 0.9997 for 4 runs by NMR between 318 and 353 K.
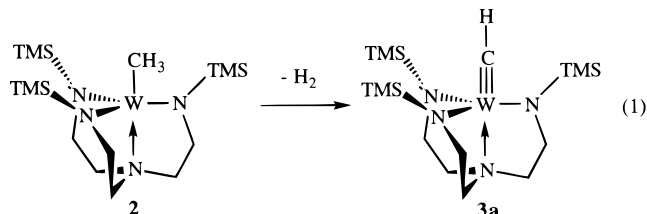


spectroscopy by following the decrease in the intensity of the TMS resonance.[9] The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained by combining these data (nine runs by NMR, four runs by visible spectroscopy) are listed in Table 1. (See Experimental Section for individual rate constants at temperature $T$.) A resonance at 4.5 ppm for molecular hydrogen could be observed in the $^1$H NMR spectrum during conversion of **2** to **3a**, but the low solubility of dihydrogen in toluene-$d_8$ did not allow the amount to be quantified accurately. By $^1$H NMR at 47 °C $k_H/k_D$ for [N$_3$N]W(CD$_3$) was determined to be 5.6 while at 68 °C $k_H/k_D$ = 5.3.[9] Isotope effects of this magnitude have been documented for $\alpha$-hydrogen abstraction reactions in high oxidation state tantalum complexes.[16,17] Loss of dihydrogen was judged to be essentially irreversible at 25 °C; no [N$_3$N]W≡CH was observed over a period of 14 days in a sample of [N$_3$N]W≡CD in C$_6$D$_6$ that had been placed under 2 atm of dihydrogen at 25 °C. The calculated value for the loss of dihydrogen from [N$_3$N]W-(CH$_3$) at 120 °C ($k_W$ = 8 × 10$^{-2}$ s$^{-1}$) should be compared with the (estimated) value for the loss of dihydrogen from [N$_3$N]Mo(CH$_3$) ($k_{Mo}$ < 8 × 10$^{-6}$ s$^{-1}$) at 120 °C.[11] (Although [N$_3$N]Mo≡CH is a known species that is formed upon decomposition of [N$_3$N]Mo(cyclopropyl),[11] no [N$_3$N]Mo≡CH was observed to form from [N$_3$N]Mo-(CH$_3$) at 120 °C over a period of 24 h; [N$_3$N]Mo(CH$_3$) simply slowly disappeared with time, and no decomposition products could be identified.[11]) Therefore, we can safely conclude that the rate of decomposition of [N$_3$N]W-(CH$_3$) to [N$_3$N]W≡CH is at least 4 orders of magnitude greater than the rate of decomposition of [N$_3$N]Mo(CH$_3$) to [N$_3$N]Mo≡CH. [N$_3$N]W≡CH is also the product of the attempted synthesis of [N$_3$N]W(cyclopropyl) (see below).

[N$_3$N]WCl reacts with LiCH$_2$R′ reagents (R′ = Me, Pr$^n$, SiMe$_3$, Bu$^t$) or KCH$_2$Ph in ether or THF at room temperature to yield the alkylidyne complexes, [N$_3$N]-W≡CR′, in high yield (eq 2). We presume that the alkyl

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$$\text{(2)}$$

R' = Me (**3b**), Pr (**3c**), Ph (**3d**),
SiMe$_3$ (**3e**), CMe$_3$ (**3f**)
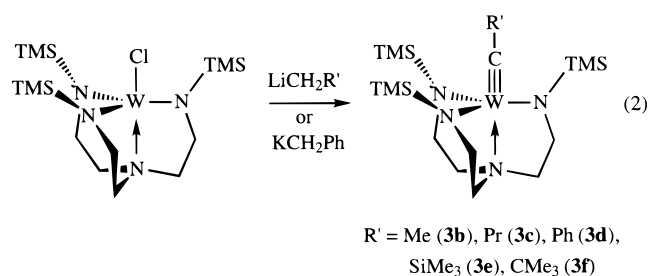
complexes, [N$_3$N]W(CH$_2$R′), are intermediates in these reactions, although they could not be observed. Reaction of [N$_3$N]WCl with LiCD$_2$CH$_2$CH$_2$CH$_3$ resulted in the production of [N$_3$N]W≡CCH$_2$CH$_2$CH$_3$ only, while the reaction between [N$_3$N]WCl and Li$^{13}$CH$_2$CH$_2$CH$_2$-CH$_3$ gave only [N$_3$N]W≡$^{13}$CCH$_2$CH$_2$CH$_3$. The value for $J_{C_2W}$ (242 Hz) in [N$_3$N]W≡$^{13}$CCH$_2$CH$_2$CH$_3$ could be obtained easily from the $^{13}$C NMR spectrum and is in the range normally observed in tungsten alkylidyne complexes.[18] These results suggest that dihydrogen is rapidly lost from the α-carbon atom in the intermediate butyl complex compared to the rate of any process that would lead to the metal "walking" to the other end of the C$_4$ chain or producing n-butyl groups in which H and D have been partially scrambled along the chain. For [N$_3$N]Mo(butyl), the overall rates of β elimination to give [N$_3$N]MoH and α,α-dehydrogenation to give [N$_3$N]Mo≡CCH$_2$CH$_2$CH$_3$ are comparable and relatively slow,[11] although there is still no significant degree of migration of the Mo along the butyl chain before the complex decomposes.

Addition of cyclopropyllithium to [N$_3$N]WCl at ca. −30 °C yields [N$_3$N]W≡CH quantitatively in less than ~1 min as the solution warms to room temperature (eq 3).



$$\text{(3)}$$
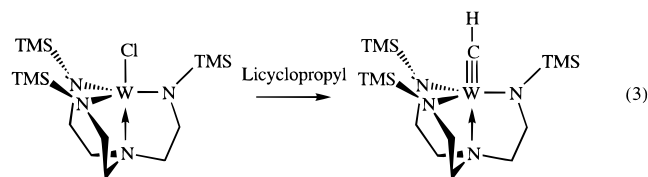
The reaction turns from the orange color characteristic of [N$_3$N]WCl to purple quickly upon addition of cyclopropyllithium, consistent with formation of [N$_3$N]W-(cyclopropyl). However, the purple color then fades rapidly as pale yellow [N$_3$N]W≡CH is formed. Although the reaction could be monitored by $^1$H NMR at −70 °C and evidence obtained for the formation of the cyclopropyl species in the form of characteristically high-field-shifted [N$_3$N]$^{3-}$ ligand resonances (comparable to the resonances obtained in the $^1$H NMR spectrum of [N$_3$N]Mo(cyclopropyl)[11]), accurate kinetic measurements were not possible. If we estimate the half-life for the decomposition of intermediate [N$_3$N]W(cyclopropyl) to be ~5 s at 243 K, then $k = 7 \times 10^{-3}$ s$^{-1}$ at 243 K. The rate constant for decomposition of [N$_3$N]Mo(cyclopropyl) can be calculated to be $4 \times 10^{-9}$ at 243 K.[11] Therefore, at 243 K, [N$_3$N]W(cyclopropyl) can be estimated to decompose roughly 6 orders of magnitude more rapidly than [N$_3$N]Mo(cyclopropyl).

[N$_3$N]WCl reacts with *trans*-2,3-dimethylcyclopropyllithium in ether at room temperature to give *trans*-2-butene and [N$_3$N]W≡CH quantitatively. No *cis*-2-butene could be observed by $^1$H NMR. The stereospecificity of this experiment suggests that the radical

shown in eq 4 is unlikely to be an intermediate in the ring opening, or if it is, its lifetime is too short for the configuration at the radical center to invert.



$$\text{(4)}$$
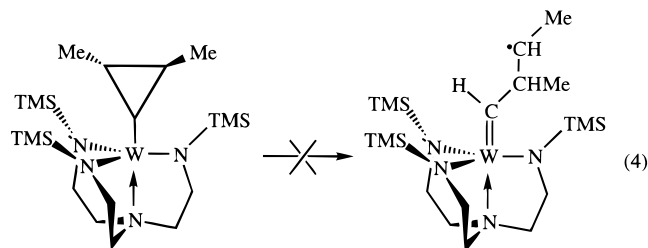
We propose that the cyclopropyl complexes decompose via C−C bond cleavage in the cyclopropyl ring to yield a metallacyclobutene complex (eq 5). One would expect



$$\xrightarrow[- CH_2=CH_2]{} \quad \textbf{3a} \qquad \text{(5)}$$
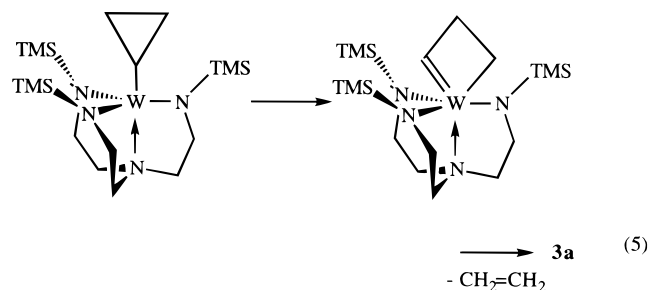
that a metallacyclobutene complex of this type would be unstable with respect to loss of ethylene to give the methylidyne complex, since reactions between olefins and high oxidation state alkylidyne complexes[18] are extremely rare.[19] This mechanism of formation of [N$_3$N]W≡CH is the same as that proposed for the formation of [N$_3$N]Mo≡CH.[11]

Addition of cyclobutyllithium to [N$_3$N]WCl yields a diamagnetic complex whose $^1$H and $^{13}$C NMR spectra are consistent with it being the "1-tungstacyclopentenyl" complex, [N$_3$N]W(CHCH$_2$CH$_2$CH$_3$), shown in eq 6. The



$$\text{(6)}$$
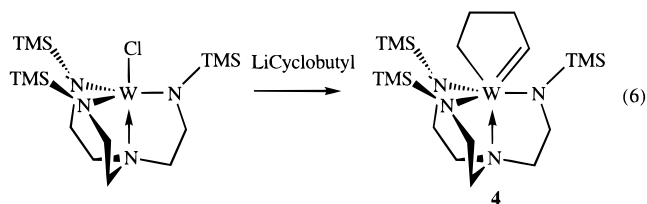
alkylidene proton in **4** appears in the $^1$H NMR spectrum as a triplet at 11.3 ppm, while in the $^{13}$C NMR spectrum C$_α$ appears at 265 ppm with $^1J_{CH} = 130$ Hz. The $^1$H NMR spectrum of **4** at room temperature is consistent with $C_{3v}$ symmetry, so the tungstacyclopentene ring must effectively "rotate" about the $z$ axis with respect to the ligand framework on the NMR time scale at 25 °C. We also can say that **4** is not in rapid equilibrium with [N$_3$N]W(cyclobutyl), since in that case only two sets of methylene protons in a ratio of 4:2 would be observed in the diamagnetic region. (Three methylene proton sets are observed in the $^1$H NMR spectrum of **4**.) It should be noted that an analogous reaction between [N$_3$N]MoCl and cyclobutyllithium yielded purple, paramagnetic [N$_3$N]Mo(cyclobutyl).[11] Therefore, the d$^0$ "alkyl-

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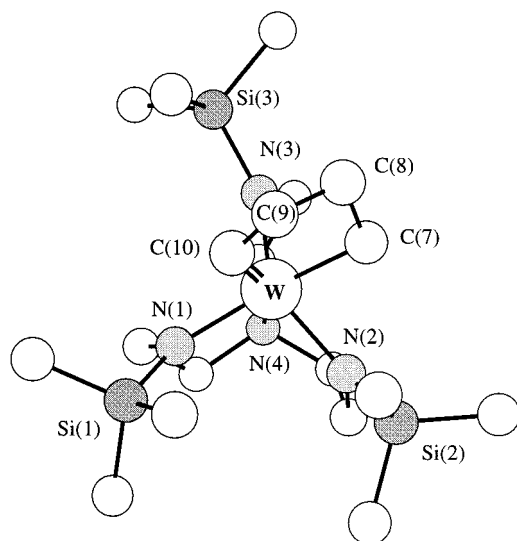
**Figure 4.** View of the structure of [N$_3$N]W(CHCH$_2$CH$_2$-CH$_2$) (**4**).

**Table 2. Selected Distances (Å) and Angles (deg) for [N$_3$N]W(CHCH$_2$CH$_2$CH$_2$) (4)**

| Distances | | | |
|---|---|---|---|
| W−N(1) | 2.015(5) | W−C(10) | 1.972(6) |
| W−N(2) | 2.033(5) | C(7)−C(8) | 1.527(8) |
| W−N(3) | 2.004(5) | C(8)−C(9) | 1.508(8) |
| W−N(4) | 2.395(5) | C(9)−C(10) | 1.509(8) |
| W−C(7) | 2.216(6) | | |

| Angles | | | |
|---|---|---|---|
| W−N(1)−Si(1) | 134.0(3) | N(1)−W−C(7) | 151.0(2) |
| W−N(2)−Si(2) | 133.1(3) | N(2)−W−C(7) | 77.9(2) |
| W−N(3)−Si(3) | 136.3(3) | N(3)−W−C(7) | 91.1(2) |
| N(4)−W−N(1)−Si(1) | 142[a] | N(1)−W−N(2) | 100.9(2) |
| N(4)−W−N(2)−Si(2) | 170[a] | N(2)−W−N(3) | 133.5(2) |
| N(4)−W−N(3)−Si(3) | 149[a] | N(1)−W−N(3) | 109.0(2) |
| W−C(7)−C(8) | 113.0(5) | C(10)−W−C(7) | 72.7(3) |
| C(7)−C(8)−C(9) | 104.8(5) | C(10)−W−N(1) | 83.8(2) |
| C(8)−C(9)−C(10) | 105.2(5) | C(10)−W−N(3) | 97.4(2) |
| W−C(10)−C(9) | 127.1(5) | C(10)−W−N(2) | 120.9(2) |
| C(7)−W−N(4) | 130.3(2) | C(10)−W−N(4) | 155.3(2) |

[a] Obtained from a Chem 3D model. The error is estimated to be ±1°.

idene/alkyl" tautomer (**4**) is lower in energy than [N$_3$N]W(cyclobutyl), whereas for Mo the reverse was proposed to be the case.[11]

An X-ray structure of **4** confirms its proposed nature (Figure 4, Table 2). The complex has a trigonal-monopyramidal [N$_3$N]W core typical of triamidoamine complexes of this general type.[3] The W−N(4) distance is relatively long, and two of the three trimethylsilyl substituents are twisted away from the "upright" orientation (N(4)−W−N$_{eq}$−Si = 180°), typical of complexes in which the trigonal coordination pocket is occupied by a relatively bulky group,[3,11] here the 1-tungstacyclopentene ring. (Similar effects have been observed in [N$_3$N]Mo(CD$_3$) versus [N$_3$N]Mo(cyclohexyl).[11]) The N(2)−W−N(3) angle (135.5(2)°) is opened up significantly compared to the other two as a consequence of the 1-tungstacyclopentene ring being oriented so that it lies roughly in the N(4)−W−N(1) plane with C(10) (the alkylidene carbon atom) pointing toward N(1) and C(7) pointing between N(2) and N(3). The W−C(10) and W−C(7) distances are typical of W(VI) W=C and W−C bonds, respectively. The W−C(10)−C(9) angle is larger than than the W−C(7)−C(8) angle, and the N(4)−W−C(10) angle is much larger than the N(4)−W−C(7) angle, as

one would expect. The structure of **4** should be compared with that for [N$_3$N]W(cyclopentylidene)(H) discussed below.

Compound **4** is converted quantitatively into [N$_3$N]W≡CCH$_2$CH$_2$CH$_3$ in a first-order reaction according to kinetic studies carried out by visible spectroscopy (Table 1; eq 7) at a rate that is approximately the same as the rate of conversion of [N$_3$N]Mo(cyclobutyl) into [N$_3$N]Mo≡CCH$_2$CH$_2$CH$_3$ (Table 1).[11] (The Mo analog of **4** was



$$(7)$$
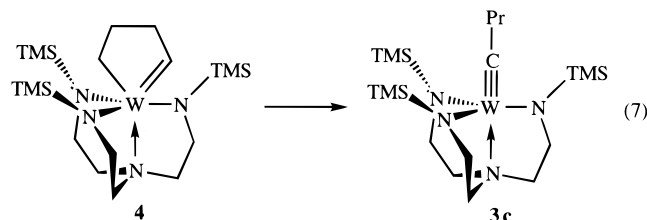
proposed to be an intermediate in the reaction in which [N$_3$N]Mo(cyclobutyl) is converted into [N$_3$N]Mo≡CCH$_2$CH$_2$CH$_3$.[11]) At this stage we can only presume that the alkylidene carbon atom in **4** becomes the alkylidyne C$_\alpha$ carbon atom in **3c**. In that case the reaction could be viewed as a type of α-hydrogen abstraction reaction from a d$^0$ alkyl/alkylidene complex to give a d$^0$ alkylidyne complex, a type of reaction that has been documented in tantalum alkylidene/alkylidyne chemistry,[17] and that is the origin of many high oxidation state alkylidyne complexes.[18] However, it is not clear how a concerted transfer of a proton from the alkylidene carbon to the alkyl carbon could take place given the 18-electron nature of **4** and the fact that the alkylidene proton points 180° away from the alkyl carbon atom to which it migrates. Therefore, we must consider the possibility that **3c** does not arise from **4** directly, but from some as yet unspecified intermediate, or that the rearrangement that gives **3c** involves the [N$_3$N]$^{3-}$ ligand in some manner. However, at this stage we cannot justify proposing any alternatives to a concerted transformation of **4** to **3c**.

The reaction of [N$_3$N]WCl with cyclopentyllithium in ether at room temperature produces yellow, crystalline [N$_3$N]W(C$_5$H$_8$)(H) (**5**) in high yield (eq 8). An X-ray



$$(8)$$
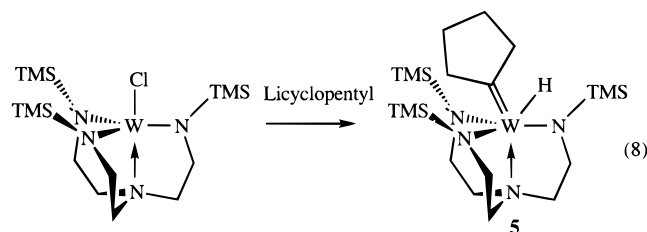
structural determination of **5** revealed the structure shown in Figure 5. (See Table 3 for selected distances and angles.) The W−C(1) bond length (1.97(1) Å) is statistically somewhat longer than that found in W(cyclopentylidene)(OCH$_2$CMe$_3$)$_2$Br$_2$ (1.890(5) Å) and its gallium tribromide adduct (1.896(9) Å),[20] perhaps because of the lower coordination number of, or greater electrophilicity of, the metal in W(cyclopentylidene)-(OCH$_2$CMe$_3$)$_2$Br$_2$. Nonetheless, it is in the range expected for a "d$^0$" alkylidene complex[17,21] and is identical

(20) Youinou, M. T.; Kress, J.; Fischer, J.; Aguero, A.; Osborn, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1488.
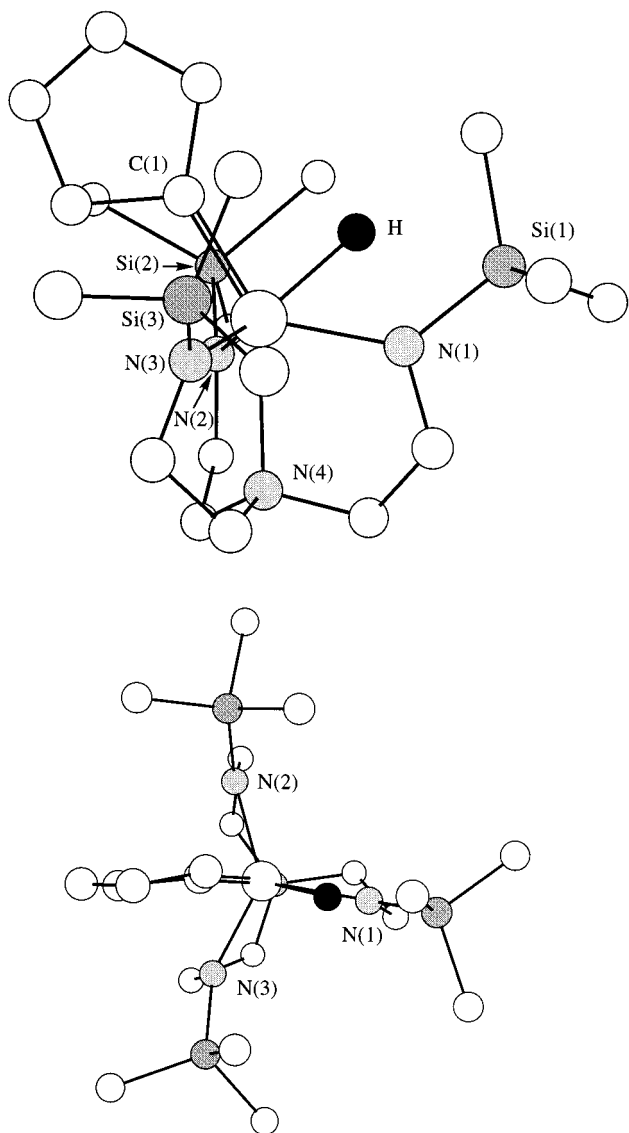
**Figure 5.** Two views of the structure of [N$_3$N]W(cyclopentylidene)(H) (**5**).

**Table 3. Selected Distances (Å) and Angles (deg) for [N$_3$N]W(cyclopentylidene)(H) (5)**

| Distances | | | |
|---|---|---|---|
| W−C(1) | 1.97(1) | W−N(3) | 2.045(9) |
| W−N(1) | 2.046(9) | W−N(4) | 2.346(9) |
| W−N(2) | 2.20(1) | | |

| Angles | | | |
|---|---|---|---|
| H−W−C(1) | 80(2)[a] | N(2)−W−N(3) | 125.7(4) |
| W−N(1)−Si(1) | 131.2(5) | N(1)−W−N(3) | 105.4(4) |
| W−N(2)−Si(2) | 122.3(5) | N(4)−W−N(1)−Si(1) | 179.9(7) |
| W−N(3)−Si(3) | 128.7(5) | N(4)−W−N(2)−Si(2) | 165.0(7) |
| N(1)−W−N(2) | 112.4(4) | N(4)−W−N(3)−Si(3) | 148.1(7) |

[a] Hydride does not survive refinement.

to the W−C(10) distance in **4**. The cyclopentylidene ring is oriented so that it lies approximately in a plane that passes through W, N(1), N(4), and Si(1). The N(2)−W−N(3) angle (125.7(4)°) is consequently slightly larger than the other two N$_{eq}$−W−N$_{eq}$ angles (cf. the N(2)−W−N(3) angle of 133.5(2)° in **4**). The cyclopentylidene ring is leaning slightly toward Si(3), and Si(3) is consequently tipped furthest from "vertical" (N(4)−W−N(3)−Si(3) = 148.1(7)°). Electron density ascribable to

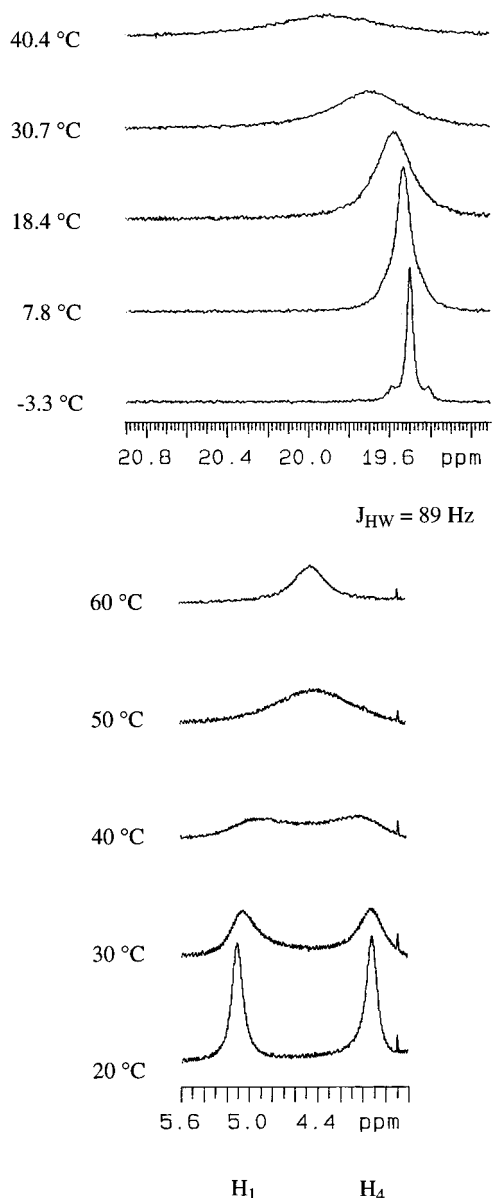(21) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

the hydride ligand was found approximately in the C(1)−W−N(1) plane 1.81 Å from the metal, but it would not survive refinement. The largest W−N−Si angle is actually W−N(1)−Si(1) (131.2(5)°), presumably as a consequence of the hydride pointing directly toward Si-(1). The W−N(4) distance (2.346(9) Å) is close to the W−N(4) distance in **4**. The position and observed orientation of the cyclopentylidene ligand is consistent with the nature of the three available bonding orbitals, i.e., formation of two σ bonding hybrid orbitals in either the d$_{xz}$ or d$_{yz}$ plane and a W=C π bond using the π orbital perpendicular to that plane. Although the Mo complex analogous to **5**, [N$_3$N]Mo(C$_5$H$_8$)(H), could not be observed directly, its formation was the most expeditious way to explain the interconversion of the exo and endo protons in the cyclopentyl ring in [N$_3$N]Mo-(cyclopentyl).[11]

The $^1$H NMR spectrum of **5** at 22 °C displayed a broad singlet at δ 0.22 ppm for the trimethylsilyl groups of the [N$_3$N]$^{3-}$ ligand, two triplets for the methylene groups on the [N$_3$N]$^{3-}$ ligand backbone, and a broad resonance for W−H at δ 19.6 ppm (Figure 6a). When the sample was cooled to −3 °C, the hydride resonance sharpened and W−H coupling (90 Hz) could be observed. At −40 °C, two singlets for the trimethylsilyl groups could be resolved in a ratio of 2:1, the methylene groups in the ligand become multiplets at δ 3.27 and 2.02 ppm, and the cyclopentylidene ligand displays three resonances at δ 5.18, 3.98, and 1.90 ppm in a ratio of 1:1:2. All data are consistent with a structure having mirror symmetry on the NMR time scale at −40 °C. (At −40 °C the WN$_2$C$_2$ "ring-flipping" process is still relatively fast on the NMR time scale). The resonances at 5.18, 3.98, and 1.90 ppm in a ratio of 1:1:2 are assigned to the methylene resonances 1−4 (eq 9) in the cyclopentylidene ring, two sets of which overlap. The low-



(9)
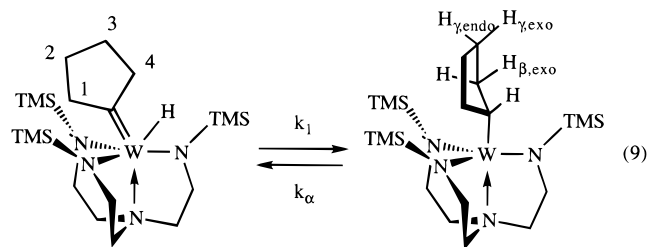
temperature $^{13}$C{$^1$H} NMR spectra of **5** are also consistent with mirror symmetry at low temperatures and reveal the cyclopentylidene α-carbon resonance at 268.4 ppm.

The temperature-dependent $^1$H NMR spectra of **5** reveal that the resolved cyclopentylidene methylene resonances at 5.18 and 3.98 ppm broaden and coalesce at high temperatures (Figure 6b). Therefore, we propose that these resonances can be assigned to protons 1 and 4 (eq 9) and the overlapping methylene resonances at 1.90 ppm (see also Figure 8) to protons on carbons 2 and 3; the overlapping resonances assigned to protons on carbons 2 and 3 also sharpen to a single resonance at higher temperatures. We propose that we are observing the consequences of an interconversion of [N$_3$N]W(cyclopentylidene)(H) and [N$_3$N]W(cyclopentyl) (eq 9). In [N$_3$N]W(cyclopentyl), which we presume would be a high-spin paramagnetic species analogous to [N$_3$N]Mo(cyclopentyl)[11] and [N$_3$N]WMe, the β protons

40.4 °C

30.7 °C

18.4 °C

7.8 °C

-3.3 °C

20.8   20.4   20.0   19.6   ppm

$J_{HW} = 89$ Hz

60 °C

50 °C

40 °C

30 °C

20 °C

5.6    5.0    4.4    ppm

H$_1$            H$_4$

**Figure 6.** Variable-temperature $^1$H NMR spectra of [N$_3$N]W(cyclopentylidene)(H). (a) hydride resonance; (b) $\beta$ protons of the cyclopentylidene ring. (H$_1$ and H$_4$ assignments are arbitrary.)
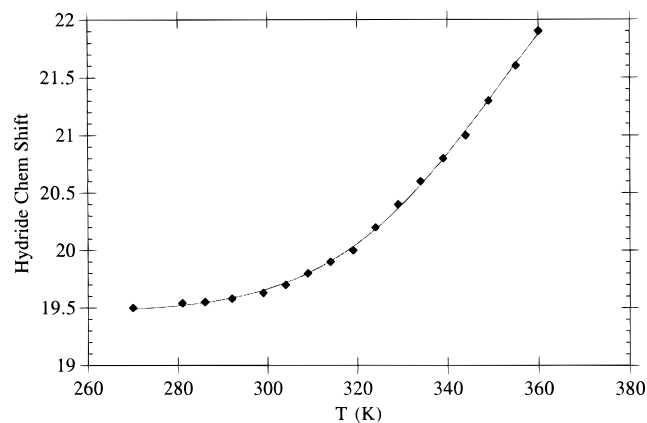


**Figure 7.** Plot of the chemical shift of the hydride in [N$_3$N]W(cyclopentylidene)(H) versus temperature.

on the same side of the ring as the metal (endo) would be equivalent and the $\beta$ protons on the opposite side of the ring (exo) would be equivalent. Therefore, all $\beta$

protons (on carbons 1 and 4) would become equivalent when the rate of interconversion of [N$_3$N]W(cyclopentylidene)(H) and [N$_3$N]W(cyclopentyl) becomes fast on the NMR time scale, as would all $\gamma$ protons (on carbons 2 and 3). A similar process was proposed to account for interconversion of the endo and exo protons in [N$_3$N]Mo(cyclopentyl), and the slower rate constant for that reaction (the equivalent of $k_\alpha$ in eq 9) was found to be $\sim 10^3$ at 22 °C.[11] In the tungsten system, $k_1$ is smaller than $k_\alpha$ and can be determined at 46 °C from the coalescence point of the resonances for methylene protons 1 and 4 (Figure 6b), assuming a chemical shift difference that is relatively independent of temperature. The value so obtained (at 46 °C) is $k_1 = 1.3 \times 10^3$ s$^{-1}$.

The other important feature of the temperature-dependent $^1$H NMR spectrum of **5** is that the hydride resonance shifts downfield and broadens as the temperature is increased (Figure 6a). Since paramagnetic [N$_3$N]W(cyclopentyl) is being accessed rapidly on the NMR time scale and since H$_\alpha$ could not be observed in [N$_3$N]Mo(cyclopentyl) or any similar alkyl complex,[11] the chemical shift and width of the H$_\alpha$ resonance in [N$_3$N]W-(C$_4$H$_8$)(H) in some temperature range should be affected accordingly, depending upon the magnitude of $k_1/k_\alpha$. (The hydride resonance should be affected the most, since it becomes attached to the $\alpha$ carbon atom in the cyclopentyl complex.) If we assume that the temperature dependence of the chemical shifts of the resonances in unobservable [N$_3$N]W(cyclopentyl) follow a 1/T dependence (as found for [N$_3$N]Mo(cyclopentyl)[11]) and that these resonances do not shift to any significant degree for any other reason, then we can determine the $\Delta G°$ for the equilibrium in eq 9 (i.e., the magnitude of the equilibrium constant $k_1/k_\alpha$) using the expression shown in eq 10,[22–24] where $\delta$ is the observed chemical shift of the hydride resonance in the spectrum of [N$_3$N]W-(cyclopentylidene)(H) at temperature $T$, $\delta_{dia}$ is the chemical shift of the hydride resonance in the spectrum of [N$_3$N]W(cyclopentylidene)(H) in the absence of any contact shift caused by equilibration of [N$_3$N]W(cyclopentylidene)(H) with [N$_3$N]W(cyclopentyl), and $C$ is a constant. From a plot of $\delta$ for the hydride ligand in

$$\delta = \delta_{dia} + \frac{C}{T\left(1 + e^{\left(\frac{\Delta H°}{RT} - \frac{\Delta S°}{R}\right)}\right)} \tag{10}$$

[N$_3$N]W(cyclopentylidene)(H) versus $T$ (Figure 7), we extract values of $\Delta H° = 11.8(6)$ kcal mol$^{-1}$, $\Delta S° = 33(2)$ eu, and $\delta_{dia} = 19.46$ ppm. Therefore, at a temperature of 46 °C, the equilibrium constant $k_1/k_\alpha$ is calculated to be 0.13 and $k_{\alpha W} = 1.0 \times 10^4$ s$^{-1}$. This value should be compared with that determined in the analogous Mo system,[11] $k_{\alpha Mo} = 10^3$ s$^{-1}$ at 22 °C. At 46 °C, $k_{\alpha Mo}$ could be as much as 1 order of magnitude larger than that at 22 °C. Thus, $k_{\alpha W}$ and $k_{\alpha Mo}$ *are approximately the same* at $\sim 46$ °C. Therefore, the fact that [N$_3$N]W(cyclopentylidene)(H) is the favored species for W while [N$_3$N]-Mo(cyclopentyl) is the favored species for Mo must be ascribed to a significantly smaller $k_{1W}$ than $k_{1Mo}$.

(22) Gütlich, P.; McGarvey, B. R.; Kläui, W. *Inorg. Chem.* **1980**, *19*, 3704.
(23) Smith, M. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 1119.
(24) Kläui, W.; Eberspach, W.; Gütlich, P. *Inorg. Chem.* **1987**, *26*, 3977.
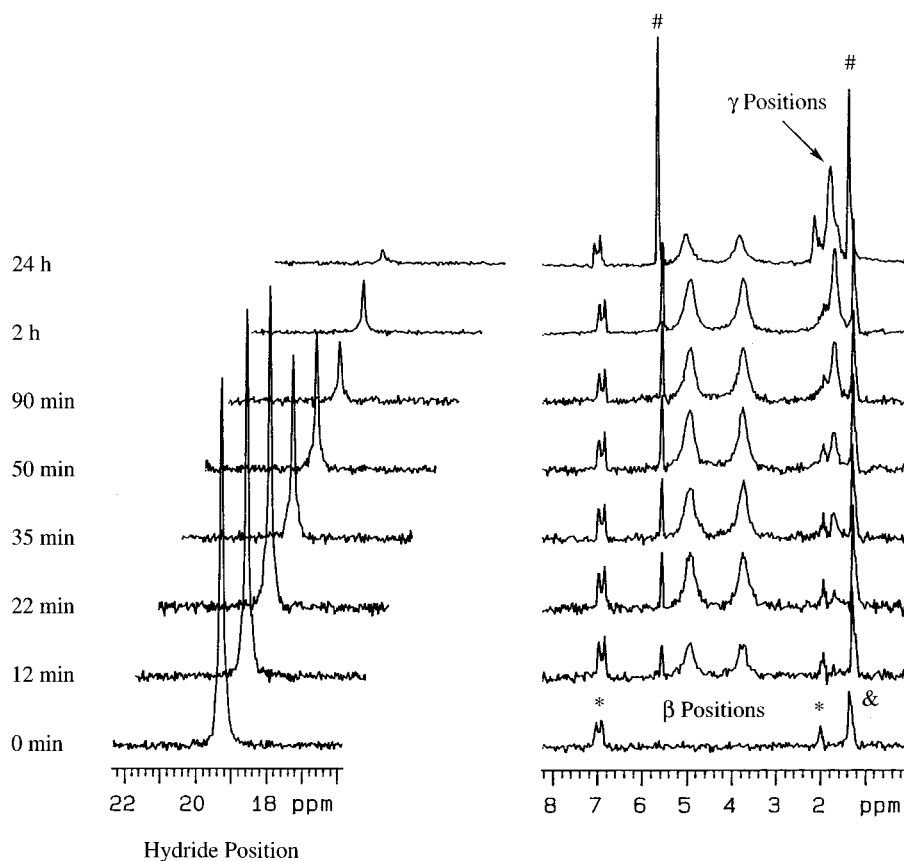
**Figure 8.** Stacked $^2$H NMR spectra in toluene showing the incorporation of deuterium from $[N_3N]W(C_5H_8)(D)$ into the $\beta$ and $\gamma$ ring positions over time (Peaks marked with * indicate the natural abundance of $^2$H in toluene; those marked with & cyclopentane-$d_1$ from trace hydrolysis; those marked with # cyclopentene-$d_1$ from decomposition of $[N_3N]W(C_5H_8)(D)$ to give $[N_3N]WH$).

Unfortunately, this conclusion cannot be confirmed, as there is no way to measure the magnitude of the equilibrium constant between observable $[N_3N]Mo$-(cyclopentyl) and unobserved $[N_3N]Mo$(cyclopentylidene)-(H) and, therefore, $k_{1Mo}$. If we assume that $k_1/k_\alpha$ in the Mo system is $>10^2$, then we can estimate that $k_{1Mo} > 10^5$ s$^{-1}$ at 22 °C. This value should be compared with $k_{1W} = 1.3 \times 10^3$ s$^{-1}$ at 46 °C. The fact that the $k_\alpha$ values for W and Mo are roughly the same while the $k_1$ values for W and Mo differ by approximately 3 orders of magnitude is somewhat surprising.

Addition of 1-$d$-cyclopentyllithium to $[N_3N]WCl$ at −60 °C followed by warming the sample to −13 °C resulted in formation of only $[N_3N]W(C_5H_8)(D)$, as determined by $^1$H and $^2$H NMR spectroscopy (eq 11).[10]
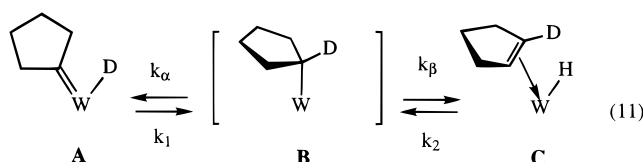


The $^2$H resonance in $[N_3N]W(C_5H_8)(D)$ disappears over a period of 24 h, and $^2$H intensity begins to appear in the cyclopentylidene $\beta$-methylene positions at ~3.8 and 5 ppm first (Figure 8). Only after a much longer period of time does D appear in the $\gamma$ positions (2 and 3 in eq 9) at ~2.0 ppm (Figure 8). We propose that D scrambles into the $\beta$ positions first as a consequence of reversible $\beta$-hydride elimination from the the cyclopentyl complex **B** (eq 11) to give **C**. (We show below that little
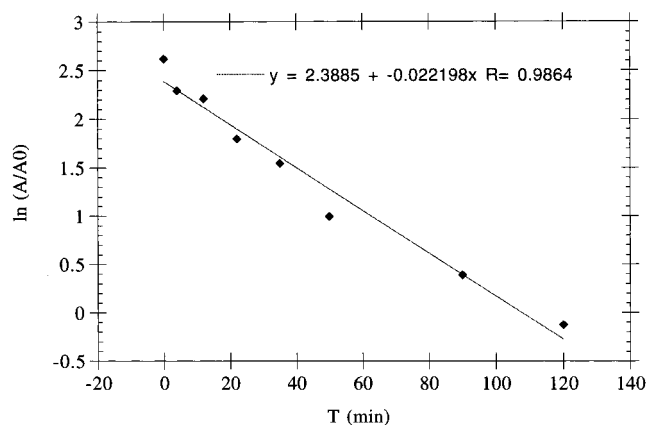


**Figure 9.** Plot of $\ln(A/A_0)$ versus time ($A$ = amount of deuterium present in the hydride site) during the incorporation of deuterium from $[N_3N]W(C_5H_8)(D)$ into the $\beta$ and $\gamma$ ring positions.

cyclopentene is lost from **C** at room temperature over a period of 24 h.) It takes more than 2 h for D to be evenly distributed between the $\beta$ and $\gamma$ positions since the one deuterium becomes distributed throughout four $\beta$ positions before it scrambles from the four $\beta$ positions to the four $\gamma$ positions. We can obtain a measure of the rate of scrambling of D into $\beta$ positions via **C** by plotting the decrease in intensity of the $^2$H resonance at 19.3 ppm in the $^2$H NMR spectrum of **A** at 22 °C (Figure 9). If we assume that the initial decrease is first order (the accuracy of the experiment is not great enough to confirm that that is the case), then the first-order rate constant at 22 °C is $k_{obs} = 3.7 \times 10^{-4}$ s$^{-1}$ ($t_{1/2} = 31$ min).

(A more accurate experiment would have to include the sequential nature of the scrambling reaction.) This value is much smaller than both $k_1$ and $k_\alpha$ (eq 11). Unfortunately, we cannot say which is larger, $k_\beta$ or $k_2$, and therefore cannot say which corresponds to $k_{obs}$. The observation that only $[N_3N]W(C_5H_8)(D)$ is formed upon adding 1-$d$-cyclopentyllithium to $[N_3N]WCl$ at $-60$ °C followed by warming to $-13$ °C would require only that $k_\beta < k_\alpha$, and that seems assured in view of the large values for $k_1$ and $k_\alpha$ relative to $k_{obs}$. It should be noted that in the Mo system $k_{\beta Mo}$ was estimated to be $\sim 7 \times 10^{-4}$ s$^{-1}$ at 22 °C. It also should be noted that after 24 h only $\sim 3\%$ of the original D (by NMR integration) is bound to the metal (Figure 8) instead of what one would predict ($^1/_9$ or $\sim 11\%$ of the original) if no equilibrium isotope effect were operative and no other H/D exchange were taking place that is slower than exchange into the cyclopentylidene ring. A substantial normal equilibrium isotope effect *should* be observed, as a proton should favor being bound to the metal versus carbon.[25–30] Although the residual WD ($\sim 3\%$) cannot be measured accurately by integration, the amount is, in fact, approximately what one would expect using plausible stretching frequencies for WH, WD, CH, and CD as a means of estimating the energy difference between the WD compound and the WH compound ($\sim 750$ cal). Therefore, there is no need to invoke any other exchange reaction that would further reduce the amount of WD or potentially alter the linearity of the plot shown in Figure 9.

$[N_3N]W(cyclopentylidene)(H)$ (**5**) decomposes readily at temperatures above $\sim 45$ °C to give cyclopentene and paramagnetic $[N_3N]WH$ (**6**). Compound **6** has NMR spectra and magnetic behavior (Figures 1 and 2) typical of d$^2$ complexes of the type $[N_3N]WX$. Warming the sample of **5**-$d_1$ discussed in the preceding paragraph above 45 °C yielded cyclopentene-$d_1$ in which deuterium was scrambled throughout all positions in the ring according to $^1$H and $^2$H NMR spectroscopy, as expected. The decomposition of **5** is proposed to proceed via formation and decomposition of the cyclopentyl complex by $\beta$-hydride elimination and loss of cyclopentene, eq 12. The decomposition of $[N_3N]W(cyclopentylidene)(H)$ was found by $^1$H NMR to follow a first-order dependence through three or more half-lives at 45 ($k = 4.8 \times 10^{-5}$ s$^{-1}$), 60 ($k = 2.3 \times 10^{-4}$ s$^{-1}$), and 80 °C ($k = 1.8 \times 10^{-3}$ and $2.0 \times 10^{-3}$ s$^{-1}$). An Eyring plot yielded $\Delta H^{\ddagger} = 22\,463$ cal/mol and $\Delta S^{\ddagger} = -7.84$ eu. The value for the loss of cyclopentene at 22 °C, therefore, can be calculated to be $2.3 \times 10^{-6}$ s$^{-1}$. This is approximately 2 orders of magnitude slower than the rate of deuterium scrambling ($k_{obs} = 3.7 \times 10^{-4}$ s$^{-1}$). Many attempts to synthesize $[N_3N]WH$ directly from $[N_3N]WCl$ using various hydride sources have failed, so that decomposition of **5** currently is the only practical method of forming **6**.

Addition of cyclohexyllithium to $[N_3N]WCl$ yielded $[N_3N]W(cyclohexylidene)H$, the NMR characteristics of

$$(12)$$
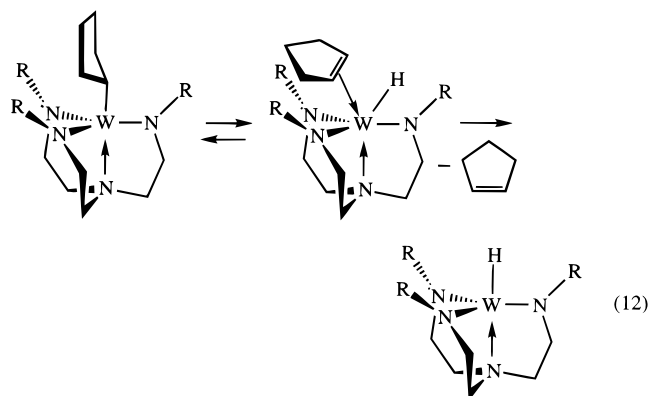
which are similar to those of $[N_3N]W(cyclopentylidene)H$. However, $[N_3N]W(cyclohexylidene)(H)$ does not decompose cleanly to $[N_3N]WH$, although some $[N_3N]WH$ is formed. The competitive side reaction or reactions have not been elucidated. Addition of cyclopentenyllithium to $[N_3N]WCl$ yielded $[N_3N]W(cyclopentenyl)$ (**2b**; eq 13), while addition of phenyllithium yielded $[N_3N]W(phenyl)$.

$$(13)$$

**2b**
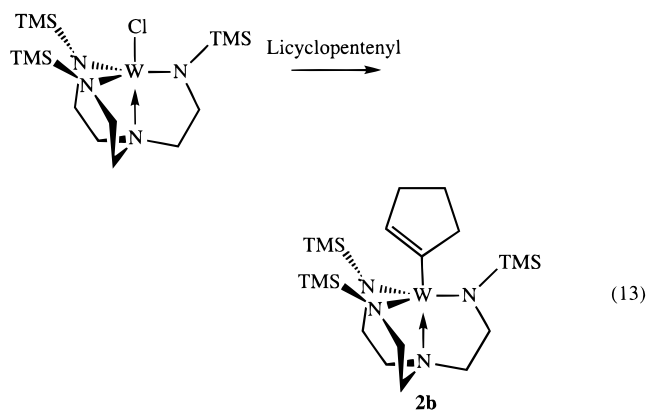
The behavior of the susceptibility and effective moment of $[N_3N]W(phenyl)$ versus temperature are analogous to the behavior of $[N_3N]WMe$, $[N_3N]WCl$, and $[N_3N]WH$. Compound **2b** is also a paramagnetic species, judging from its NMR spectra, although detailed susceptibility studies on it were not carried out. The paramagnetism of both $[N_3N]W(phenyl)$ and **2b** suggests that conjugation of the C=C $\pi$ system with one of the $\pi$ orbitals available for bonding in the trigonal pocket (d$_{xz}$ or d$_{yz}$) is not sufficient to break the degeneracy of the d$_{xz}$ and d$_{yz}$ orbitals in either compound. $[N_3N]WMe$, $[N_3N]WPh$, and **2b** are the only five-coordinate species so far that contain a W–C single bond.

Like $[N_3N]WMe$, **2b** was found to be unstable at room temperature. It decomposes cleanly to produce a diamagnetic species that has no symmetry. An X-ray structural study revealed that the product is that shown in eq 14; a trimethylsilyl group has migrated from an amido nitrogen to the cyclopentenyl ligand to form a 1-(trimethylsilyl)cyclopentene complex (**7**). Two views of **7** are shown in Figure 10, and some relevant bond distances and angles are listed in Table 4. The most notable aspect of this structure is the absence of a TMS group on one nitrogen, leading to a bent imido ligand (W–N(3)–C(5) = 135.7(6)°). (Bent imido ligands are somewhat unusual,[31,32] although they appear to be more

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(26) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.
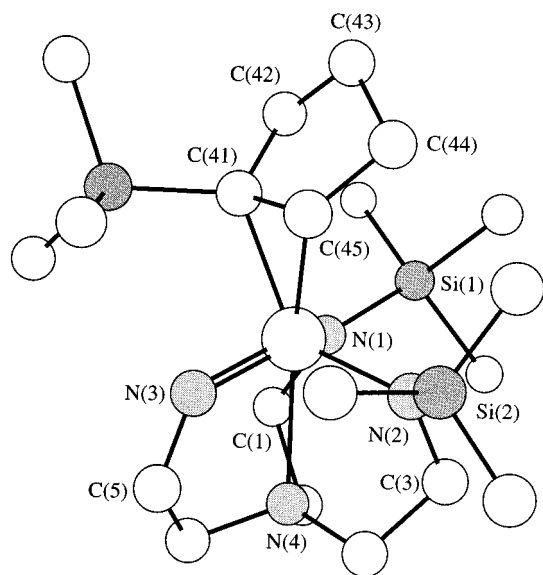(27) Faller, J. W.; Murray, H. H.; M., S. *J. Am. Chem. Soc.* **1980**, *102*, 2306.
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**Figure 10.** View of the structure of [(Me$_3$SiNCH$_2$CH$_2$)$_2$-NCH$_2$CH$_2$N)W(1-(trimethylsilyl)cyclopentene) (**7**).

**Table 4. Selected Distances (Å) and Angles (deg) for [(Me$_3$SiNCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$N]-W(1-(trimethylsilyl)cyclopentene) (7)**

| Distances | | | |
|---|---|---|---|
| W−C(41) | 2.198(8) | W−N(2) | 2.040(7) |
| W−C(45) | 2.200(8) | W−N(3) | 1.765(7) |
| W−N(1) | 2.005(7) | W−N(4) | 2.428(7) |
| C(41)−C(45) | 1.513(13) | C(43)−C(44) | 1.548(13) |
| C(41)−C(42) | 1.544(12) | C(44)−C(45) | 1.556(13) |
| C(42)−C(43) | 1.530(14) | | |

| Angles | | | |
|---|---|---|---|
| W−N(3)−C(5) | 135.7(6) | N(1)−W−N(2) | 105.5(3) |
| W−N(2)−C(3) | 110.3(6) | N(2)−W−N(3) | 105.8(3) |
| W−N(1)−C(1) | 112.2(5) | N(1)−W−N(3) | 128.3(3) |
| W−N(1)−Si(1) | 136.1(4) | N(4)−W−N(2)−Si(2) | 126.1(4) |
| W−N(2)−Si(2) | 127.2(4) | N(4)−W−N(1)−Si(1) | 132.6(4) |



$$\text{(14)}$$
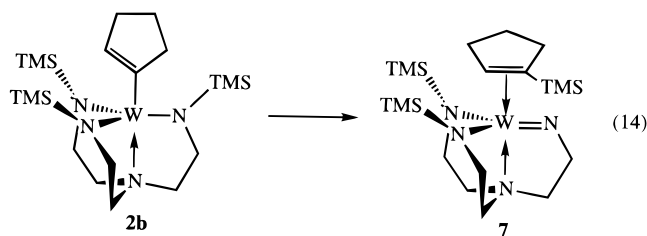
common when there is little alternative, i.e., when incorporated into some metal-containing ring,[33,34] as found here. Under these circumstances, a M=N−C value as low as 116.3(4)° has been observed.[34] The W−N(3)−C(5) angle is considerably larger than W−N(2)−C(3) or W−N(1)−C(1), which are more typical for [N$_3$N]M systems. The N(3)···Si(3) distance is 3.14 Å, consistent with a fully broken N−Si bond. All carbon atoms $\beta$ to the equatorial nitrogens serve as the "flap" in the MC$_2$N$_2$ rings, thereby leading to a pronounced tilt to the TMS groups, presumably in order to relieve steric interactions between the trimethylsilyl substituents and the cyclopentene ring. The W−N(4) bond length is also longer than in typical molecules having only a single cylindrically symmetric ligand in the axial

position, presumably again as a consequence of steric pressure in the apical pocket. The W−C(41) and W−C(45) distances are relatively short for W−C single bonds, while C(41)−C(45) is not much shorter than other C−C bonds in the cyclopentene ring, consistent with a "tungstacyclopropane" description for the W(olefin) bond. We presume at this stage that the TMS group migrates directly to the unsubstituted carbon atom in **2b** to give **7**.

## Discussion

In another paper,[11] we discuss how little is known concerning $\alpha$ elimination to give an alkylidene hydride[35] relative to $\beta$-hydride elimination to give an olefin hydride in transition metal alkyl chemistry. An equilibrium between an alkyl complex and alkylidene hydride has usually involved high oxidation state early transition metal alkyl complexes, i.e., those of tungsten[36−38] or tantalum[39−43] complexes. It was noted[43] in a paper concerning the decomposition of Cp*$_2$(H)-Ta=C=CH$_2$ that although "the generality of faster $\alpha$-H elimination versus $\beta$-H elimination is questionable, since the transition state for $\beta$-H elimination in this system is highly strained, whereas that for $\alpha$-H elimination is much less so." It has also been noted recently that competition between $\alpha$ abstraction and $\beta$ abstraction in dialkyltantalum species containing the [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]$^{3-}$ ([N$_3$N]$^{3-}$) ligand can be controlled by varying the size of the apical pocket, either by increasing the size of the alkyl[44] or by increasing the size of the silyl substituent from SiMe$_3$ to SiEt$_3$.[45] Most recently, it has been shown that $\alpha$ elimination in two [N$_3$N]Mo-(cycloalkyl) complexes is 6−7 orders of magnitude faster than $\beta$ elimination.[11] We now have the opportunity to compare several [N$_3$N]W(alkyl) complexes with the analogous [N$_3$N]Mo(alkyl) complexes.

The equilibrium shown in eq 15 lies to the right for M = Mo, with a magnitude of ∼10$^2$ or greater, and to the left for M = W with an estimated $K_{eq} \approx 0.04$ ($K_{eq}$ = [alkyl]/[alkylidene]) at 298 K. Differences in the magnitude of $K_{eq}$ of several orders of magnitude can be easily explained in terms of differences in M=C and M−H bond energies relative to the M−C bond energy, with greater differences being expected when M = W. For example, a change in $\Delta G°_{\text{alkylidene}} - \Delta G°_{\text{alkyl}}$ of only ca. −5 kcal mol$^{-1}$ translates into an increase in $K_{eq}$ of ∼10$^4$. Since the alkylidene ligand can be viewed as a dianion,

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$$(15)$$
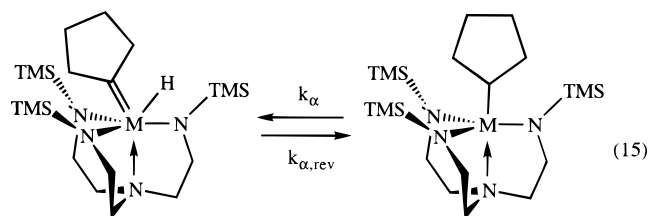
this finding also can be rationalized in terms of oxidation-state stabilities (W(VI) > Mo(VI)). The similar $k_\alpha$ values for Mo and W may be circumstantial. Another possibility, however, is that the transition state for α elimination is relatively early and $k_\alpha$, therefore, is relatively independent of the nature of the alkylidene hydride product.

We have documented that formation of $[N_3N]Mo\equiv CR$ complexes by what is essentially irreversible α,α dehydrogenation (eq 16) and $[N_3N]MoH$ by loss of olefin are slow and competitive, while α,α dehydrogenation in $[N_3N]W(CH_2R)$ complexes is many orders of magnitude more rapid than in an analogous $[N_3N]Mo(CH_2R)$ complex. On the basis of the data obtained for Mo and



$$(16)$$
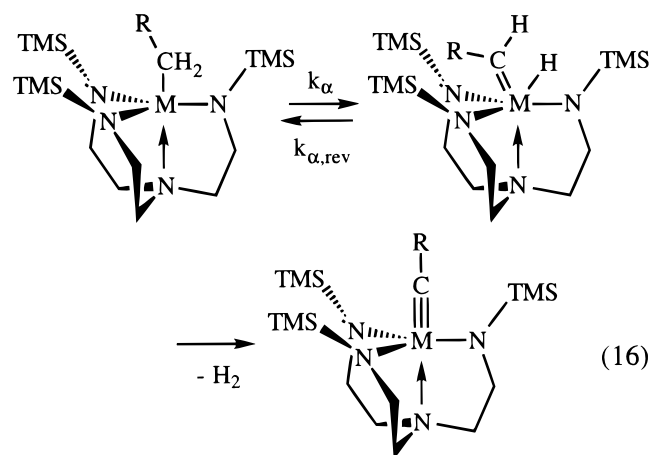
W cyclopentyl complexes we propose that the position of the equilibrium between $[N_3N]M(CH_2R)$ and $[N_3N]M(CHR)(H)$ is several orders of magnitude larger (toward the latter) when M = W than when M = Mo. The overall more facile α,α elimination when M = W (in analogous W and Mo complexes) could be ascribed largely to the higher concentration of $[N_3N]W(CHR)(H)$ versus $[N_3N]W(CH_2R)$, if we could say with some confidence that the rate of loss of molecular hydrogen from a given $[N_3N]W(CHR)(H)$ complex were at least as great as the rate of loss of molecular hydrogen from a given $[N_3N]Mo(CHR)(H)$ complex. Although we have no independent data that would suggest that an α-abstraction reaction is at least as fast for a third-row metal complex as it is for a second-row metal complex, it would not be surprising to find that to be the case. If the rate of loss of molecular hydrogen from a given $[N_3N]W(CHR)(H)$ complex were significantly *greater* than the rate of loss of molecular hydrogen from a given $[N_3N]Mo(CHR)(H)$ complex, then the overall rate of loss of molecular hydrogen from a given $[N_3N]W(CH_2R)$ complex relative to a $[N_3N]Mo(CH_2R)$ complex would only become that much faster. These arguments are all consistent with the preference for tungsten (versus Mo) to form a M(VI) species, which may ascribed in part to the likely stronger metal–carbon bonds in a W(VI)

species compared to its Mo(VI) analog. The 4–6 orders of magnitude difference in the rate of α,α dehydrogenation between analogous Mo and W complexes that we have been able to estimate in several circumstances, therefore, can be rationalized readily.

The chemistry of tungsten cyclopropyl and cyclobutyl complexes is similar to that of analogous Mo complexes, although the reactions (eqs 3, 4, and 5) are again simply much faster for tungsten compared to molybdenum. If we make the reasonable assumption that the cyclobutyl reactions proceed analogously for W and Mo, then it is interesting to note that $[N_3N]W(CHCH_2CH_2CH_2)$ (**4**) is formed rapidly from unobservable $[N_3N]W(\text{cyclobutyl})$ but $[N_3N]Mo(\text{cyclobutyl})$ is observable and intermediate $[N_3N]Mo(CHCH_2CH_2CH_2)$ is not observed when $[N_3N]Mo(\text{cyclobutyl})$ is converted into $[N_3N]Mo\equiv CCH_2CH_2CH_3$. These results could be circumstantial, as we know few details about how $[N_3N]M(CHCH_2CH_2CH_2)$ complexes are converted into $[N_3N]M\equiv CCH_2CH_2CH_3$ complexes. As shown in Table 1, the value of $\Delta H^\ddagger$ for $[N_3N]Mo(\text{cyclobutyl})$ is ~4 kcal mol$^{-1}$ higher than the value of $\Delta H^\ddagger$ for the decomposition of **4**. It seems likely that intermediate $[N_3N]Mo(CHCH_2CH_2CH_2)$ is higher in energy than $[N_3N]Mo(\text{cyclobutyl})$, while $[N_3N]W(CHCH_2CH_2CH_2)$ is clearly lower in energy than $[N_3N]W(\text{cyclobutyl})$, consistent with the observations discussed above with respect to the cyclopentyl complexes.

In the paper concerning molybdenum chemistry[11] and in an earlier communication,[10] we raised the possibility that the overall rate of a unimolecular reaction could be slowed significantly as a consequence of a small equilibrium constant for the equilibrium between the observed high-spin ground state and a "required" low-spin form with $^1A$ symmetry. However, so far all magnetic behavior is of a relatively classical type, and we have no evidence that a more readily accessible $^1A$ state is what leads to some dramatically faster reactions in the W systems compared to the analogous Mo system. We also still have not been able to eliminate the possibility that the $[N_3N]$ ligand is directly involved in proton-migration reactions of the type described here nor the possibility that the axial nitrogen atom does not remain strongly bound in all reactions. We hope to address some of these issues in the future through the synthesis of triamido/donor ligands with amido substituents different from those available so far and with donor atoms other than nitrogen.

## Experimental Section

**General Details.** All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox, using standard Schlenk techniques, or on a high-vacuum line (<10$^{-4}$ Torr). Pentane was washed with $HNO_3/H_2SO_4$ (5/95 v/v), sodium bicarbonate, and $H_2O$, stored over $CaCl_2$, and then distilled from sodium benzophenone under nitrogen. Reagent grade ether, tetrahydrofuran, and benzene were distilled from sodium benzophenone under nitrogen. Toluene was distilled from molten sodium. Methylene chloride was distilled from $CaH_2$. All solvents were stored in the drybox over activated 4 Å molecular sieves. Deuterated solvents were freeze−pump−thaw degassed and vacuum transferred from an appropriate drying agent. NMR spectra are recorded in $C_6D_6$ unless noted otherwise. $^1H$ and $^{13}C$ data are listed in parts per million (ppm) downfield from tetramethylsilane and were referenced using the residual protonated solvent peak. $^2H$ NMR spectra

were obtained at 46.0 MHz and referenced to external $C_6D_6$ (7.15 ppm). Coupling constants are given in Hertz, and routine coupling constants are not listed. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer in our own laboratory.

$LiCH_2CD_3$ was prepared by treatment of $CD_3CH_2Br$ (Cambridge Isotope Labs) with lithium metal. $Li^{13}CH_2CH_2CH_2CH_3$ was prepared by (i) treating $^{13}CO_2$ with $Pr^nMgCl$, (ii) reducing the acid with $LiAlH_4$ to the alcohol, (iii) chlorinating the alcohol with $SOCl_2$ in hexane, and (iv) treating the chloride with lithium in the usual manner; overall yield 20% (one synthesis).

All organic compounds were received from commercial suppliers and used as received. Triethylamine was distilled from $CaH_2$ and stored over 4 Å molecular sieves. $WCl_4(DME)$[46] was prepared according to a published procedure. Deuterated solvents were dried by passage through alumina or stirring over sodium benzophenone ketyl and storage over 4 Å molecular sieves. 1-$d$-Cyclopentyl lithium was prepared by reduction of cyclopentanone with lithium aluminum deuteride followed by treatment with $Ph_3Br_2$. $Li_3[N_3N]$ was prepared as reported in the literature.[12]

In the UV−vis studies, the following equation was employed to follow the disappearance of an alkyl species: $\ln[(\lambda_o - \lambda_\infty)/(\lambda - \lambda_\infty)] = kt$, where $\lambda_o$ = absorbance at wavelength $\lambda$ at time 0, $\lambda_\infty$ = absorbance at wavelength $\lambda$ at infinite time, and $\lambda$ = absorbance at wavelength $\lambda$ at time $t$.

**[N₃N]WCl (1).** $WCl_4(DME)$ (3.84 g, 9.23 mmol) dissolved in minimum DME was added to a THF (40 mL) solution of $Li_3[N_3N]$ (3.54 g, 9.23 mmol) at −40 °C. The reaction mixture was allowed to warm slowly to 25 °C and was stirred for 3 h. The resulting yellow-brown solution was evaporated to dryness *in vacuo*, and pentane (∼200 mL) and ether (∼20 mL) were added to the reaction residue. The mixture was stirred at room temperature for 3 h and filtered through a pad of Celite. The filtrate volume was reduced until a quantity of yellow solid formed. The yellow solid was collected by filtration, washed with cold pentane (2 × 3 mL), and dried *in vacuo*. The filtrate and pentane washes were combined, evaporated to dryness, and extracted with pentane (∼20 mL). The extract was chilled to −40 °C to afford another crop of yellow product; total yield, 1.38 g (26%): $^1H$ NMR $\delta$ 8.30 (br s, $SiMe_3$), −29.83 (br s, $NCH_2$, $w_{1/2} \approx 55$), −75.44 (br s, $NCH_2$, $w_{1/2} \approx 87$). Anal. Calcd for $C_{15}H_{39}N_4ClSi_3W$: C, 31.11; H, 6.79; N, 9.68. Found: C, 30.88; H, 6.64; N, 9.56. Two measurements of $\mu_{eff}$ by the Evan's method gave values of 2.4 and 2.5.

**[N₃N]WI.** Into a 20 mL flask was added 74 mg (0.13 mmol) of [N₃N]WCl and 5 mL of benzene. To this solution was added 28 mg of TMSI (0.14 mmol). The mixture was stirred at room temperature for 2 days. The volatile materials were removed *in vacuo* and the residue extracted with minimum pentane (5 mL). This solution was filtered, reduced in volume, and cooled to −40 °C to give yellow crystals; yield 32 mg (38%): $^1H$ NMR $\delta$ 17.7 (s, $NSiMe_3$), −29.5 (s, $NCH_2CH_2N$), −92.5 (s, $NCH_2CH_2N$). Anal. Calcd for $C_{15}H_{39}N_4Si_3WI$: C, 26.87; H, 5.86; N, 8.36. Found: C, 26.50; H, 5.68; N, 8.47.

**[N₃N]W(CH₃) (2a).** A solution of [N₃N]WCl (0.30 g, 0.52 mmol) in ether (∼40 mL) was treated with LiMe (0.41 g, 0.78 mmol, 1.4 M in ether) at 25 °C. The reaction mixture was stirred for 30 min, and the solvent was removed *in vacuo*. The orange reaction residue was extracted with pentane (∼80 mL), and the extract was filtered through a pad of Celite. The volume of the filtrate was reduced to ∼5 mL *in vacuo*, and the solution was chilled to −40 °C to yield orange crystals of the product; yield 0.25 g (86%): $^1H$ NMR $\delta$ 9.89 ($SiMe_3$), −31.43 ($NCH_2$, $w_{1/2} = 40$), −72.70 ($NCH_2$, $w_{1/2} = 23$); $\mu = 2.5$ BM at 25 °C (Evan's method). Anal. Calcd for $C_{16}H_{42}N_4Si_3W$: C, 34.40; H, 7.58; N, 10.03. Found: C, 34.73; H, 7.19; N, 9.84.

The conversion of [N₃N]W(CH₃) was measured by following the decrease in the intensity of the $SiMe_3$ resonance at 500

MHz in toluene-$d_8$ through at least two half-lives at a concentration of ∼0.020 M.[9] The values for $k$ ($\times 10^{-4}$ s$^{-1}$) at temperature $T$ (K) are as follows: 30.6 (351), 12.2, 11.8 (341), 4.35 (330), 1.56, 1.49, 1.50 (320), 0.644 (310), 0.251 (300).

The conversion was followed in toluene by UV−vis; the values for $k$ ($\times 10^{-4}$ s$^{-1}$) at temperature $T$ (K) are as follows: 0.105 (298), 1.28 (320), 9.66 (341), 10.50 (341).

A plot of $\ln(k/T)$ versus 1/T for all data gave $\Delta H^{\ddagger} = 19\,916$ cal/mol and $\Delta S^{\ddagger} = -13.87$ eu with $R = 0.995$.

**[N₃N]W(CD₃).** This compound was prepared in a manner analogous to that used to prepare **2a**; yield 0.22 g (75%): $^1H$ NMR (toluene-$d_8$) $\delta$ 10.05 ($SiMe_3$), −32.41 ($NCH_2$, $w_{1/2} = 58$), −73.17 ($NCH_2$, $w_{1/2} = 35$). Anal. Calcd for $C_{16}H_{39}N_4D_3Si_3W$: C, 34.22; H, 7.00; N, 9.98. Found: C, 33.57; H, 6.69; N, 9.91. In the preliminary communication,[10] it was reported that a resonance for $CD_3$ could be observed in the $^2H$ NMR spectrum of [N₃N]W(CD₃) in $C_6H_6$ at 7.5 ppm. This is incorrect. The resonance at 7.5 ppm is due to deuterium in $C_6H_6$ in natural abundance. We have not been able to locate the resonance in [N₃N]W(CD₃).

**[N₃N]W(phenyl) (2c).** Phenyllithium (12 mg, 0.14 mmol) was added to a cold solution of 45 mg (0.08 mmol) of [N₃N]-WCl in 5 mL of diethyl ether. The color changed immediately to red. The solution was stirred for 1 h at room temperature, and the solvent was removed *in vacuo*. The residue was extracted with pentane, and the volume of the solution was reduced to 2 mL *in vacuo*. The solution was kept at −30 °C for 2 h, and the red crystalline product was collected; yield 35 mg: $^1H$ NMR $\delta$ 58.1 (s, Ph), 14.6 (s, TMS), −30.0 (s, $CH_2$), −59.8 (s, $CH_2$). Anal. Calcd for $C_{21}H_{44}N_4WSi_3$: C, 40.64; H, 7.14; N, 9.03. Found: C, 40.28; H, 7.30; N, 8.89.

**[N₃N]W≡CH (3a). Method a:** [N₃N]W(CH₃) (0.20 g, 0.36 mmol) was dissolved in 30 mL of freshly distilled ether, and the solution was stirred at 25 °C for 3 days. The resulting light yellow solution was evaporated to dryness *in vacuo*, and the residue was dissolved in pentane (∼60 mL, freshly passed through alumina). The pentane solution was filtered, and the pentane was removed *in vacuo* to yield brownish, pale yellow crystals; yield 0.18 g (90%).

**Method b:** A toluene (∼20 mL) solution of [N₃N]W(CH₃) (0.40 g, 0.72 mmol) was freeze−pump−thawed four times on a high-vacuum line in a thick Pyrex glass reaction vessel. The reaction vessel was heated to 75 °C for 5 h, and the solvent was then removed *in vacuo*. The reaction residue was dissolved in pentane, and the extract was filtered. The pentane filtrate was concentrated to ∼3 mL and chilled to −40 °C for 1 h. The resulting white precipitate was filtered off and dried *in vacuo*; yield 0.35 g (90%): $^1H$ NMR $\delta$ 0.48 ($SiMe_3$), 2.06 ($NCH_2$), 3.46 ($NCH_2$), 7.08 (W≡CH, $^2J_{HW} = 81$); $^{13}C\{^1H\}$ NMR (toluene-$d_8$) $\delta$ 4.47 ($SiMe_3$), 51.66 ($NCH_2$), 52.50 ($NCH_2$), 272.6 (W≡C, $^1J_{CW} = 244$, $^1J_{CH} = 138$). Anal. Calcd for $C_{16}H_{40}N_4Si_3W$: C, 34.52; H, 7.24; N, 10.07. Found: C, 34.82 H, 6.64; N, 10.00.

**[N₃N]W≡CD.** The reaction procedure is similar to that used to prepare [N₃N]W≡CH, except [N₃N]W(CD₃) and a longer reaction time (∼10 days with method a; ∼24 h with method b) were used; 72% yield: $^1H$ NMR $\delta$ 0.49 ($SiMe_3$), 2.03 ($NCH_2$), 3.48 ($NCH_2$); $^{13}C\{^1H\}$ NMR $\delta$ 4.80 ($SiMe_3$), 51.96 ($NCH_2$), 52.25 ($NCH_2$), 231.15 (W≡C, $^1J_{CD} = 33$); $^2H$ NMR ($C_6H_6$) $\delta$ 7.4 (W≡CD).

The values for $k$ ($\times 10^{-4}$ s$^{-1}$) at temperature $T$ (K), determined as described for [N₃N]W≡CH, are as follows: 2.30 (341), 0.273 (320). (Taken from ref 10).

**[N₃N]W≡CCH₃ (3b).** An ether (∼25 mL) solution of [N₃N]-WCl (0.20 g, 0.345 mmol) was treated with LiEt (0.019 g, 0.52 mmol) at 25 °C. The reaction mixture turned light yellow as gas evolved. The resulting mixture was stirred for another 3 h and then evaporated to dryness *in vacuo*. The yellow reaction residue was extracted with pentane (∼60 mL), and the extract was filtered. The filtrate was concentrated to ∼5 mL *in vacuo* and chilled at −40 °C for several hours to yield light yellow crystals; yield 0.16 g (81%): $^1H$ NMR $\delta$ 0.49

(46) Persson, C.; Andersson, C. *Inorg. Chim. Acta* **1993**, *203*, 235.

(SiMe$_3$), 2.03 (NCH$_2$), 3.48 (NCH$_2$), 3.73 (W≡CCH$_3$, $^3J_{WH}$ = 7.9); $^{13}$C{$^1$H} NMR $\delta$ 4.91 (SiMe$_3$), 35.58 (C$CH_3$, $^1J_{CH}$ = 124), 52.06 (NCH$_2$), 52.31 (NCH$_2$), 274.33 (W≡$C$CH$_3$). Anal. Calcd for C$_{17}$H$_{42}$N$_4$Si$_3$W: C, 35.78; H, 7.42; N, 9.87. Found: C, 35.57; H, 7.81; N, 9.67.

**[N$_3$N]W≡C−Pr$^n$ (3c).** This compound was prepared in a manner analogous to that used to prepare **3b** from [N$_3$N]WCl (0.20 g, 0.345 mmol) and LiBu$^n$ (0.30 mL, 0.483 mmol, 1.6 M in hexane) at 25 °C; yield 0.15 g (73%): $^1$H NMR $\delta$ 0.53 (SiMe$_3$), 0.94 (t, 3, −CH$_2$CH$_2$C$H_3$), 2.00 (m, 2, −CH$_2$CH$_2$−), 2.04 (NCH$_2$), 3.51 (NCH$_2$), 4.23 (m, 2, −CH$_2$CH$_2$CH$_3$); $^{13}$C{$^1$H} NMR $\delta$ 281.9 (W≡C), 53.55 (W≡C$CH_2$−), 52.23 (NCH$_2$), 25.52 (−CH$_2$CH$_2$-CH$_3$), 14.82 (−CH$_2$CH$_2$CH$_3$), 5.06 (SiMe$_3$). Anal. Calcd for C$_{19}$H$_{46}$N$_4$Si$_3$W: C, 38.12 H, 7.74; N, 9.36. Found: C, 38.34; H, 8.03; N, 9.19.

**[N$_3$N]W≡CPh (3d).** KCH$_2$Ph (0.068 g, 0.52 mmol) was added to a THF (∼20 mL) solution of [N$_3$N]WCl (0.20 g, 0.345 mmol) at 25 °C, and the mixture was stirred for 5 h. The resulting yellow-orange mixture was evaporated to dryness *in vacuo*, and the residue was extracted with pentane (∼100 mL) and ether (∼10 mL). The extract was filtered through a pad of Celite, and the solvent was removed *in vacuo* to give a brown oil. The oil was dissolved in 5 mL of pentane, and the solution was chilled to −40 °C to obtain yellow crystals; yield 0.16 g (73%): $^1$H NMR $\delta$ 0.51 (SiMe$_3$), 2.10 (NCH$_2$), 3.54 (NCH$_2$), 6.88 (t, H$_{para}$), 7.36(t, H$_{meta}$), 7.44 (d, H$_{ortho}$); $^{13}$C{$^1$H} NMR $\delta$ 5.10 (SiMe$_3$), 52.39 (NCH$_2$), 52.63 (NCH$_2$), 125.12 (C$_{para}$), 126.82 (C$_{meta}$), 134.58 (C$_{ortho}$), 152.03 (C$_{ipso}$), 277.18 (W≡C).

**[N$_3$N]W≡CSiMe$_3$ (3e).** The reaction procedure is similar to the synthesis of [N$_3$N]W≡CCH$_3$, except LiCH$_2$SiMe$_3$ was employed instead of LiEt; yield 91%: $^1$H NMR $\delta$ 0.51 (CSiMe$_3$), 0.52 (SiMe$_3$), 1.98 (NCH$_2$), 3.47 (NCH$_2$); $^{13}$C{$^1$H} NMR $\delta$ 319.43 (W≡C), 52.57 (NCH$_2$), 52.50 (NCH$_2$), 5.97 (CSiMe$_3$), 5.01 (SiMe$_3$). Anal. Calcd for C$_{19}$H$_{48}$N$_4$Si$_4$W: C, 36.29; H, 7.69; N, 8.91. Found: C, 36.32; H, 7.52; N, 8.94.

**[N$_3$N]W≡C−Bu$^t$ (3f).** The reaction procedure is similar to the synthesis of [N$_3$N]W≡CCH$_3$, except LiCH$_2$−Bu$^t$ was employed; yield 88%: $^1$H NMR $\delta$ 0.46 (SiMe$_3$), 1.64 (CMe$_3$), 2.05 (NCH$_2$), 3.35 (NCH$_2$); $^{13}$C{$^1$H} NMR $\delta$ 297.93 (W≡C), 55.70 (NCH$_2$), 51.59 (CMe$_3$), 50.79 (NCH$_2$), 35.51 (C$Me_3$), 4.67 (SiMe$_3$). Anal. Calcd for C$_{20}$H$_{48}$N$_4$Si$_3$W: C, 39.20; H, 7.90; N, 9.14. Found: C, 39.09; H, 8.18; N, 8.88.

**[N$_3$N]W(CHCH$_2$CH$_2$CH$_2$) (4).** A solution of 126 mg (0.22 mmol) of [N$_3$N]WCl in 10 mL of diethyl ether was cooled to −40 °C, and a cold (−40 °C) solution of 17 mg (0.27 mmol) of cyclobutyllithium in 2 mL of diethyl ether was added. The color changed from orange to red. The solution was stored at −40 °C overnight. The solvent was removed *in vacuo*, and the residue was extracted with pentane. The extract's volume was reduced to 3 mL, and after 2 h red needles were collected by filtration; yield 86 mg (66%): $^1$H NMR $\delta$ 11.43 (t, $^3J_{HH}$ = 4.8, WCH), 5.24 (q, 2, WCHCH$_2$), 3.28 (t, 8, NCH$_2$ and WC$_4$-CH$_2$), 2.62 (t, 2, WC$_4$CH$_2$), 2.0 (NCH$_2$), 0.38 (TMS); $^{13}$C NMR 265 (d, $^1J_{CH}$ = 130, WCH), 92.79 (t, $^1J_{CH}$ = 120, WC$_4$ CH$_2$), 58.06 (NCH$_2$), 57.06 (t, $^1J_{CH}$ = 124, WC$_4$ CH$_2$), 52.69 (t, $^1J_{CH}$ = 135, NCH$_2$), 36.49 (t, $^1J_{CH}$ = 127, WC$_4$ CH$_2$), 3.38 (q, $^1J_{CH}$ = 119, TMS). Anal. Calcd for C$_{19}$H$_{46}$N$_4$Si$_3$W: C, 38.12; H, 7.74; N, 9.36. Found: C, 38.19; H, 7.83; N, 9.03.

The decomposition of [N$_3$N]W(CHCH$_2$CH$_2$CH$_2$) to give [N$_3$N]W≡CCH$_2$CH$_2$CH$_3$ was followed in toluene by UV−vis spectroscopy at 480 nm. The values for $k$ ($\times 10^{-4}$ s$^{-1}$) at temperature $T$ (K) that were obtained are 0.27 (313), 0.75 (323), 2.03 (333), 5.48 (343). A plot of ln($k/T$) versus 1/$T$ gave $\Delta H^{\ddagger}$ = 20 731 cal/mol and $\Delta S^{\ddagger}$ = −13.34 eu.

**[N$_3$N]W(C$_5$H$_8$)(H) (5).** A solution of [N$_3$N]WCl (0.20 g, 0.345 mmol) in ether (∼25 mL) was treated with LiC$_5$H$_9$ (0.05 g, 0.66 mmol) at 25 °C. The reaction turned light yellow immediately. The resulting mixture was stirred for 3 h, and the volatile components were removed *in vacuo*. The yellow reaction residue was extracted with pentane (∼80 mL), and the extract was filtered through Celite. The filtrate was concentrated to ∼3 mL and chilled at −40 °C for several hours

to yield yellow crystals; yield 0.21 g (99%): $^1$H NMR $\delta$ 0.22 (SiMe$_3$), 1.88 (m, 4, -CCH$_2$(C$H_2$)$_2$CH$_2$), 2.11 (NCH$_2$), 3.34 (NCH$_2$), 3.97 (br s, 2, -CC$H_2$(CH$_2$)$_2$CH$_2$), 5.11 (br s, 2, -CCH$_2$-(CH$_2$)$_2$C$H_2$), 19.66 (br s, 1, W−H); $^{13}$C{$^1$H} NMR (−40 °C; toluene-$d_8$) $\delta$ 3.95 (SiMe$_3$), 5.16 (SiMe$_3$), 28.40 (-CCH$_2$(CH$_2$)$_2$-CH$_2$), 30.47 (-CCH$_2$(CH$_2$)$_2$CH$_2$), 52.33 (NCH$_2$), 51.40 (NCH$_2$), 54.20 (NCH$_2$), 55.87 (NCH$_2$), 268.37 (W≡C). Anal. Calcd for C$_{20}$H$_{48}$N$_4$Si$_3$W: C, 39.20; H, 7.90; N, 9.14. Found: C, 39.04; H, 7.44; N, 9.14.

The decomposition of **5** was followed by $^1$H NMR through at least three half-lives at three temperatures: at 45 °C, $k$ = 4.8 × 10$^{-5}$ s$^{-1}$; at 60 °C, $k$ = 2.3 × 10$^{-4}$ s$^{-1}$; at 80 °C, $k$ = 1.8 × 10$^{-3}$ and 2.0 × 10$^{-3}$ s$^{-1}$. An Eyring plot yielded $\Delta H^{\ddagger}$ = 22 463 cal/mol and $\Delta S^{\ddagger}$ = −7.84 eu with $R$ = 0.9997.

**[N$_3$N]W(C$_6$H$_{10}$)(H).** To a cold solution (−40 °C) of 138 mg (0.24 mmol) of [N$_3$N]WCl in 10 mL of diethyl ether was added 37 mg (0.41 mmol) of cyclohexyllithium. The orange suspension was stirred for 1.5 h at 22 °C. The solvent was removed, and the residue was extracted with 10 mL of pentane and filtered through Celite. The solvent was reduced to 1 mL and cooled to −40 °C. After 12 h, orange needles were collected by filtration; yield 110 mg (74%): $^1$H NMR $\delta$ 3.1 (br s, CH$_2$), 1.92 (br s, CH$_2$), 1.80 (br m, Cy), 1.63 (br m, Cy), 0.41 (br s, TMS); $^1$H NMR (toluene-$d_8$, −40 °C) 19.4 (s, $^1J_{HW}$ = 102, WH), 4.53 (br s, 2, cy), 3.33 (br s, 2), 3.2 (br s, 2), 3.05 (br s, 2), 2.35 (br s, 2), 2.06 (br s, 4), 1.93 (br s, 2), 1.78 (br s, 4), 1.68 (br s, 2), 0.41 (s, 9, TMS), 0.18 (s, 18, TMS); $^{13}$C{$^1$H} NMR (toluene-$d_8$, −40 °C) 252.0 (s, WC), 57.6 (NCH$_2$), 54.2 (NCH$_2$), 53.8 (NCH$_2$), 51.1 (NCH$_2$), 30.4 (cyclohexyl CH$_2$), 27.4 (cyclohexyl CH$_2$), 24.5 (cyclohexyl CH$_2$), 23.7 (cyclohexyl CH$_2$), 4.1 (TMS), 3.8 (TMS). Anal. Calcd for C$_{21}$H$_{50}$N$_4$Si$_3$W: C, 40.88; H, 8.04; N, 8.94. Found: C, 40.53; H, 8.00; N, 8.83.

**[N$_3$N]WH (6).** [N$_3$N]W(C$_5$H$_8$)(H) 653 mg (1.06 mmol) and 10 mL of toluene were added to a 100 mL glass bomb that was then sealed and heated to 45 °C for 24 h. The volatile components were removed *in vacuo*, and the resulting yellow crystalline material was extracted with minimum pentane. The extract was filtered through a 1 cm plug of Celite, and the filtrate was reduced in volume by half and stored at −35 °C for 1 day. The resulting yellow-orange needles were collected by filtration; yield 501 mg (0.920 mmol, 87%): $^1$H NMR $\delta$ 17.7 (SiMe$_3$), −29.5 (NCH$_2$), −92.5 (NCH$_2$); IR (Nujol) cm$^{-1}$ 1766.3 ($\nu_{MH}$). Anal. Calcd for C$_{15}$H$_{40}$N$_4$Si$_3$W: C, 33.08; H, 7.40 N, 10.29 Found: C, 32.67; H, 7.44; N, 10.09.

**[N$_3$N]W(1-cyclopentenyl).** Cyclopentenyl lithium (714 $\mu$L of a 1.7 M solution, 1.21 mmol) was added to 471 mg (0.809 mmol) of [N$_3$N]WCl in 50 mL of ether. After 1 h, the volatile components of the reaction were removed *in vacuo* and the residue was extracted with 10 mL of pentane. The extract was filtered through Celite and cooled to −40 °C to give deep red crystals; yield 363 mg (0.550 mmol, 68%): $^1$H NMR $\delta$ 15.14 (TMS), 8.88 (CH$_2$), −30.57 (NCH$_2$), −54.81 (NCH$_2$). Anal. Calcd for C$_{20}$H$_{46}$N$_4$Si$_3$W: C, 39.33; H, 7.59; N, 9.17. Found: C, 39.72; H, 7.60; N, 9.09.

**[(Me$_3$SiNCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$N]W(1-(trimethylsilyl)cy-clopentene) (7).** A solution of [N$_3$N]W(1-pentenyl) (120 mg, 0.196 mmol) in 5 mL of benzene was stirred at room temperature for 24 h. The volatile components were removed *in vacuo* and the orange solid was extracted with minimum pentane (∼5 mL). The extract was cooled to −40 °C to yield 104 mg (0.171 mmol, 87%) of orange crystals: $^1$H NMR $\delta$ 5.05 (m, 1, W(TMSC$_5$H$_7$)), 4.09 (dd, 1, W(TMSC$_5$H$_7$)), 3.84 (m, 1, W-(TMSC$_5$H$_7$)), 3.53 (dt, 2), 3.25 (m, 4), 2.60 (m, 2), 2.47 (dd, 1, W(TMSC$_5$H$_7$)), 2.15 (m, 4), 2.08 (d, 1), 1.66 (m, 2), 0.329 (s, 18, TMS), 0.142 (s, 9, TMS); $^{13}$C NMR $\delta$ 83.8 (s, WCH, $J_{CW}$ = 38, $J_{CH}$ = 156), 70.4 (s, CTMS), 65.8 (s, CH$_2$, $J_{CW}$ = 18.3), 59.6 (s, CH$_2$), 57.9 (s, CH$_2$), 57.1 (s, CH$_2$), 54.3 (s, CH$_2$), 50.9 (s, CH$_2$), 40.5 (s, CH$_2$), 36.0 (s, CH$_2$), 34.9 (s, CH$_2$), 4.47 (s, TMS), 1.52 (s, TMS), −0.046 (s, TMS). Anal. Calcd for C$_{20}$H$_{46}$N$_4$-Si$_3$W: C, 39.33; H, 7.59; N, 9.17. Found: C, 39.68; H, 7.82; N, 9.21.

**X-ray Structure of [N₃N]W(CHCH₂CH₂CH₂) (4).** The structure was solved at 183 K using a Siemens SMART/CCD diffractometer, see Supporting Information. Empirical formula $C_{19}H_{46}N_4Si_3W$, fw = 598.71, space group *Pbca*, $a$ = 17.494(3) Å, $b$ = 15.860(4) Å, $c$ = 19.350(4) Å, $V$ = 5369(2) Å³, $Z$ = 8, $D_{calc}$ = 1.474 Mg/m³.

**X-ray Structure of [(Me₃SiNCH₂CH₂)₂(NCH₂CH₂)N]W-(1-(trimethylsilyl)cyclopentene) (7).** The structure was solved at 188 K using a Siemens SMART/CCD diffractometer, See Supporting Information. Empirical formula $C_{20}H_{46}N_4Si_3W$, fw = 610.71, space group $P2_1/n$, $a$ = 14.676(4) Å, $b$ = 11.402(4) Å, $c$ = 16.758(3) Å, $\beta$ = 107.366(14), $V$ = 2676.3(12) Å³, $Z$ = 4, $D_{calc}$ = 1.513 Mg/m³.

**Solid-State Magnetic Susceptibility Measurements.** SQUID experiments were performed at 5 KG on a Quantum Design 5.5 T instrument running MSRP2 software. Samples were prepared in an N₂-filled drybox. A gelatin capsule and a 2.2 × 1.9 cm piece of parafilm were weighed. The capsule was then loaded with the sample, and the parafilm was folded and packed on top using plastic tongs. The capsule was closed and weighed again to determine the sample mass. It was then suspended in a straw. The straw was placed in a plastic bottle with a screw cap, and the bottle was tightly sealed. At the instrument, the straw was quickly attached to the sample rod and transferred to the helium atmosphere. Measurements were taken in 1° intervals from 5 to 10 K, 2° intervals from 12 to 20 K, 3° intervals from 23 to 50 K, 5° intervals from 55

to 100 K, 10° intervals from 110 to 200 K, and 20° intervals from 220 to 300 K. A background measurement of an empty gel capsule, parafilm square, and straw was taken over the entire temperature range and subtracted from the experimental values at each temperature. The susceptibility at each temperature also was corrected for the diamagnetic contribution by the ligands using Pascal's constants.

**Supporting Information Available:** Labeled ORTEP diagrams and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for [N₃N]W(CHCH₂CH₂CH₂) and [(Me₃SiNCH₂CH₂)₂NCH₂CH₂N]W(1-(trimethylsilyl)cyclopentene) (12 pages). Ordering information is given on any current masthead page. Supporting information for the structure of [N₃N]W(C₅H₈)(H) can be found in the previous communication.[10]

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