

Tungsten and Molybdenum Alkyl or Aryl Complexes That Contain the $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ Ligand

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$[N_3N_F]W(OC_6F_5)$ and $[N_3N_F]W(O-3,5-Me_2C_6H_3)$ ($[N_3N_F]^{3-} = [(C_6F_5NCH_2CH_2)_3N]^{3-}$) can be prepared readily from $[N_3N_F]WCl$ in good yields. An X-ray study of the latter revealed an approximately trigonal structure with the phenoxide in the trigonal pocket. Alkylation of $[N_3N_F]WCl$ with $LiCH_2R$ ($R = Me, n-Pr, SiMe_3, CMe_3$) reagents in toluene at room temperature led to the evolution of molecular hydrogen and formation of the corresponding tungsten(VI) alkylidyne complexes, $[N_3N_F]W\equiv CR$ ($R = Me, n-Pr, SiMe_3, CMe_3$). The intermediate $[N_3N_F]W(CH_2SiMe_3)$ decomposed in a first-order manner to give $[N_3N_F]W\equiv CSiMe_3$ ($\Delta H^\ddagger = 20.3 \pm 0.2$ kcal/mol, $\Delta S^\ddagger = -7 \pm 1$ eu). An X-ray study of $[N_3N_F]W\equiv CSiMe_3$ showed it to have the expected, relatively undistorted, structure in which the W–C triple bond distance is 1.768(6) Å. Although attempts to prepare $[N_3N_F]WCH_3$ were not successful, $[N_3N_F]W\equiv CH$ could be prepared by reacting $[N_3N_F]WCl$ with cyclopropyllithium in toluene. $[N_3N_F]MoCl$ reacts with $LiCH_2SiMe_3$ or $LiCH_2CMe_3$ in toluene to yield $[N_3N_F]Mo(CH_2CMe_3)$ or $[N_3N_F]Mo(CH_2SiMe_3)$, respectively. Thermolysis of $[N_3N_F]Mo(CH_2CMe_3)$ produced $[N_3N_F]Mo\equiv CMe_3$ in a first-order reaction at 121 °C ($k = 7.9(5) \times 10^{-5} s^{-1}$). Several labeling experiments are consistent with the proposal that β -elimination competes with α -elimination and loss of molecular hydrogen in the $[N_3N_F]^{3-}$ system. $[N_3N_F]WI$ reacts with aryllithium reagents ($Ar = Ph, 3,5-Me_2C_6H_3$) to yield $[N_3N_F]WPh$ and $[N_3N_F]W(3,5-Me_2C_6H_3)$. The aryl complexes react with hydrogen (3 atm) in toluene at 40 °C to yield diamagnetic $[N_3N]WH_3$ and are cleanly oxidized by pyridine N-oxide. An X-ray study of $[N_3N_F]W(O)(3,5-Me_2C_6H_3)$ revealed it to have a pseudo-octahedral structure. $[N_3N_F]W(3,5-Me_2C_6H_3)$ reacts with trimethylsilyl azide to give $[N_3N_F]W(NSiMe_3)(3,5-Me_2C_6H_3)$.

Introduction

We recently reported the synthesis of a variety of molybdenum alkyl complexes that contain a trimethylsilyl-substituted triamidoamine, $[N_3N]MoR$ ($[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$; $R = Me, Et, Bu, CH_2Ph, CH_2SiMe_3, CH_2CMe_3, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopentenyl$).¹ In general, such species are relatively stable, even when β protons are present in the alkyl. NMR spectra of the cyclopentyl and cyclohexyl complexes show a 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 10^6 times faster than the rate of β -elimination, perhaps as a consequence of steric acceleration of the α -elimination process and concomitant steric inhibition of the β -elimination process. Among the linear alkyl complexes, only $[N_3N]Mo(CH_2CMe_3)$ decomposed cleanly (albeit slowly) to give $[N_3N]Mo\equiv CMe_3$ and molecular hydrogen. Other decompositions of linear alkyl complexes were complicated by competing reactions, including β -hydride elimination to give the olefin and $[N_3N]$ -

MoH. β -Hydride elimination was the sole mode of decomposition of the cyclopentyl and cyclohexyl complexes, and $[N_3N]MoH$ could be isolated in high yield in each case. Other unusual decomposition reactions that involved C–C bond cleavages were also observed. For example, $[N_3N]Mo(cyclopropyl)$ evolved ethylene 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.

Attempted syntheses of a variety of analogous $[N_3N]WR$ complexes ($R = Me, Et, Bu, CH_2Ph, CH_2SiMe_3, CH_2CMe_3, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopentenyl$) yielded only the methyl, phenyl, and cyclopentenyl complexes.² No linear alkyl complexes could be observed as a consequence of rapid α, α -dehydrogenation to give molecular hydrogen and alkylidyne complexes, $[N_3N]W\equiv CR'$. $[N_3N]W(cyclopropyl)$ evolved ethylene in a first-order process to give $[N_3N]W\equiv CH$, while $[N_3N]W(cyclobutyl)$ was converted into the 1-tungstacyclopentene complex, $[N_3N]W(CHCH_2CH_2CH_2)$, which upon further heating was converted into $[N_3N]W\equiv CCH_2CH_2CH_3$. An attempt to prepare $[N_3N]W(cyclopentyl)$ led to formation of $[N_3N]W(cyclopentylidene)(H)$. NMR studies suggested that $[N_3N]W$ -

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(cyclopentylidene)(H) is in equilibrium with $[\text{N}_3\text{N}]\text{W}$ -(cyclopentyl) with $K_{\text{eq}} \approx 0.1$ at 46 °C. From these and other data it was concluded that the rate constant for α -elimination in $[\text{N}_3\text{N}]\text{M}$ (cyclopentyl) is approximately the same for Mo and W, but the rate constant for the reverse reactions differ substantially. Although the differences between the chemistry of $[\text{N}_3\text{N}]\text{Mo}$ and $[\text{N}_3\text{N}]\text{W}$ complexes is dramatic, many of the differences can be accounted for on the basis of equilibria being altered by several orders of magnitude, which in turn can be explained simply in terms of relatively small bond-energy differences between Mo and W.

The only other triamidoamine ligand that has been employed to prepare a variety of complexes (of Ti,³ V,^{4,5} Mo,⁶ W,^{6,7} and Re⁸) is $[(\text{C}_6\text{F}_5\text{NHCH}_2\text{CH}_2)_3\text{N}]$ ($\text{H}_3\text{N}_3\text{NF}$).⁹ Generally, syntheses must employ the ligand in its protic form, as the trillithium salt cannot be isolated. Although some unusual $[\text{N}_3\text{NF}]\text{Mo}$ complexes that contain molecular nitrogen or its derivatives have been reported,⁶ no organometallic chemistry has been carried out that is analogous to that known for $[\text{N}_3\text{N}]\text{M}$ (M = Mo or W) complexes. In view of the unusual nature of many of the organometallic reactions noted above, we felt compelled to explore the possibility of preparing organometallic (alkyl or aryl) derivatives of $[\text{N}_3\text{NF}]\text{M}$ (M = Mo or W) complexes. These results (primarily for M = W) are reported here. A small portion of this work has appeared in a preliminary publication.⁷

Results

Synthesis of Tungsten Halide and Aryloxide Complexes. One limitation to the chemistry of molybdenum and tungsten $[\text{N}_3\text{N}]^{3-}$ complexes is that the $[\text{N}_3\text{N}]\text{MCl}$ starting materials can be prepared only in low yield (15–35%). That is not true for the analogous $[\text{N}_3\text{NF}]\text{MCl}$ (M = Mo, W) complexes. They can be prepared in 70–80% yields⁶ from $\text{H}_3[\text{N}_3\text{NF}]$, $\text{MoCl}_4(\text{THF})_2$ or $\text{WCl}_4(\text{SEt}_2)_2$, and triethylamine. We speculate that the syntheses of $[\text{N}_3\text{NF}]\text{MCl}$ (M = Mo, W) complexes proceed in high yield because of the decreased lability of the N– C_6F_5 bond relative to the N–SiR₃ bond and the less-reducing nature of $\text{H}_3[\text{N}_3\text{NF}]$ relative to Li_3N_3 that is employed to synthesize $[\text{N}_3\text{N}]\text{MCl}$ (M = Mo, W) complexes. The only significant improvement in the synthesis of $[\text{N}_3\text{NF}]\text{MCl}$ (M = Mo, W) complexes over that reported in an earlier publication⁶ is that more readily and conveniently prepared $\text{WCl}_4(\text{dimethoxyethane})$ can be employed in place of $\text{WCl}_4(\text{SEt}_2)_2$. $[\text{N}_3\text{NF}]\text{WI}$ could be prepared by treating $[\text{N}_3\text{NF}]\text{WCl}$ with Me_3SiI . In some of the chemistry described here, $[\text{N}_3\text{NF}]\text{WI}$ was found to be much more reactive than $[\text{N}_3\text{NF}]\text{WCl}$.

The magnetic behavior of d^2 $[\text{N}_3\text{NF}]\text{MoCl}$ or $[\text{N}_3\text{NF}]\text{WCl}$ is analogous to that noted for the corresponding $[\text{N}_3\text{N}]^{3-}$ complexes. The susceptibility of $[\text{N}_3\text{NF}]\text{MoCl}$

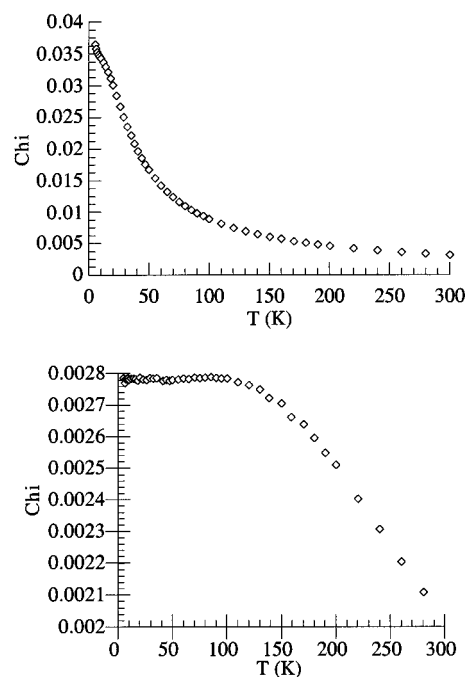


Figure 1. The corrected susceptibility of (a) $[\text{N}_3\text{NF}]\text{MoCl}$ and (b) $[\text{N}_3\text{NF}]\text{WCl}$ versus temperature between 300 and 5 K.

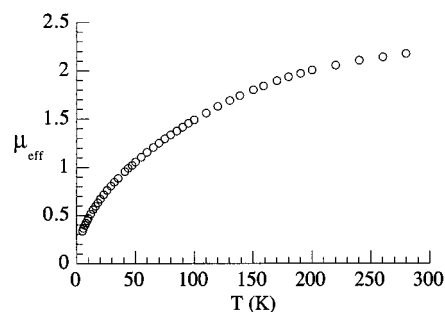


Figure 2. The magnetic moment of $[\text{N}_3\text{NF}]\text{WCl}$ versus temperature between 300 and 5 K.

(Figure 1a) follows Curie–Weiss behavior ($\chi = \mu^2/8(T + \theta)$) between 50 and 300 K ($\mu = 2.76$, $\theta = 6.8$ K, $\rho = 0.99999$), but below 50 K, the effective magnetic moment decreases sharply as a consequence of competition between spin–orbit effects and low-symmetry ligand-field components that result in zero-field splitting of the ground-state spin triplet of the d^2 configuration of Mo^{4+} .¹ We assume that the two electrons are in the set of degenerate nonbonding orbitals of π symmetry (approximately d_{xz} and d_{yz} if $\text{N}_{\text{ax}}\text{–Mo–Cl}$ is taken to be the z axis). The solid-state susceptibility of $[\text{N}_3\text{NF}]\text{WCl}$ (Figure 1b) is much smaller than that of $[\text{N}_3\text{NF}]\text{MoCl}$, and μ_{eff} (Figure 2) decreases smoothly from 300 to 5 K as a consequence of the larger spin–orbit coupling for the heavier metal. This is a relatively classical type of behavior¹⁰ that we now can say does not depend on whether the substituent on the nitrogen in a triamidoamine complex is trimethylsilyl^{1,2} or pentafluorophenyl.

Proton and fluorine spectra of paramagnetic $[\text{N}_3\text{NF}]^{3-}$ complexes typically show shifted resonances, analogous

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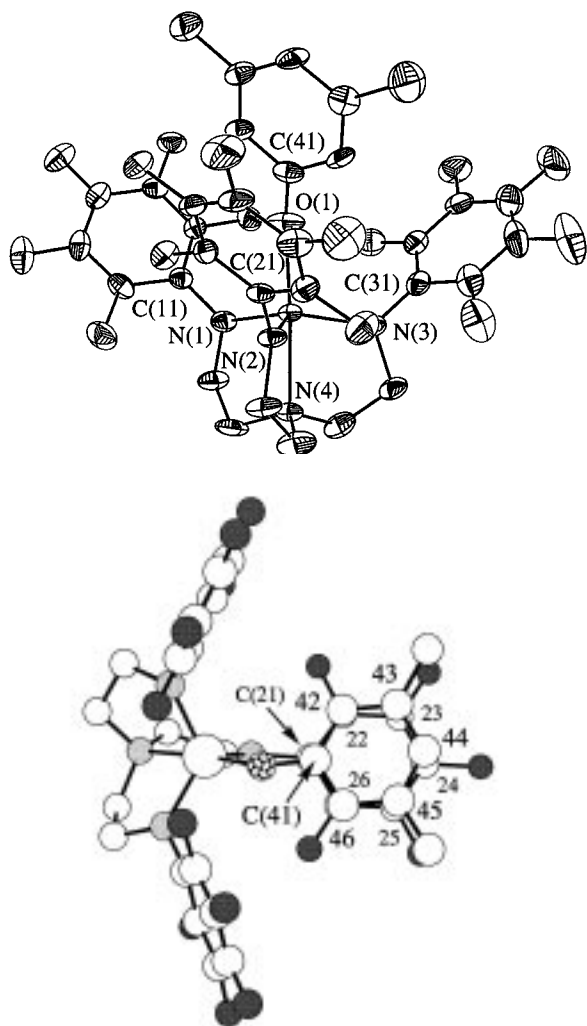


Figure 3. (a) ORTEP drawing of $[\text{N}_3\text{NF}]\text{W}(\text{O}-3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (**1b**). (b) A view of **1b** (Chem 3D) showing the relationship between $\text{Me}_2\text{C}_6\text{H}_3$ and the C_6F_5 rings.

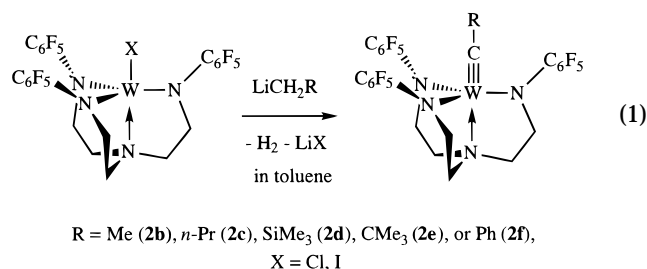
to what is observed for $[\text{N}_3\text{N}]^{3-}$ complexes.^{1,2} These spectra are temperature-dependent as a consequence of Curie–Weiss behavior and also as a consequence of a slowing down of equilibration of the backbone methylene resonances at low temperatures to give a structure with apparent C_3 symmetry. However, the low solubility of $[\text{N}_3\text{NF}]^{3-}$ complexes, in general, limited the feasibility of extensive low-temperature NMR spectroscopy. Therefore, only room-temperature NMR data are reported. Fluorine NMR is especially convenient for following reactions involving $[\text{N}_3\text{NF}]^{3-}$ complexes, as ^{19}F resonances even for paramagnetic species are generally well-resolved (though broad) and easily distinguished from the sharp resonances for diamagnetic species.

$[\text{N}_3\text{NF}]\text{WCl}$ reacts quickly with potassium pentafluorophenoxide or potassium 3,5-dimethylphenoxide in THF to provide $[\text{N}_3\text{NF}]\text{W}(\text{OC}_6\text{F}_5)$ (**1a**) and $[\text{N}_3\text{NF}]\text{W}(\text{O}-3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (**1b**) in good yields. The phenoxide complexes are paramagnetic, with contact-shifted ^1H and ^{19}F NMR spectra. All six magnetically inequivalent fluorines in **1a** (between -4 and -177 ppm) can be assigned unambiguously, a good demonstration of the utility of ^{19}F NMR in the synthesis and characterization of the paramagnetic complexes of the type presented

here. The magnetic moment for **1b** was measured in solution at 22°C using the Evans method and found to be $3.2 \mu_{\text{B}}$.

An X-ray study of **1b** revealed the structure shown in Figure 3a. Table 1 contains crystallographic data, while Table 2 contains selected bond lengths and angles. Selected bond distances and angles in $[\text{N}_3\text{NF}]\text{MoCl}$ ⁶ are listed in Table 2 for the purpose of comparison. The overall structure of **1b** is similar to that of $[\text{N}_3\text{NF}]\text{MoCl}$, i.e., a C_3 -symmetric structure in which the C_6F_5 rings form a bowl around the phenoxide. The three $\text{N}(4)\text{--M--N--C}$ dihedral angles (161.7° , 174.4° , and 178.2°), W--N_{ax} distance, W--N_{eq} distances, and $\text{N}_{\text{eq}}\text{--W--N}_{\text{eq}}$ angles are all similar to those in $[\text{N}_3\text{NF}]\text{MoCl}$, suggesting that the molecule is relatively strain-free.¹ The W--O distance ($1.991(7)$ Å) and $\text{W--O--C}(41)$ angle ($145.0(6)^\circ$) are typical of M--O bond distances and M--O--C bond angles in a variety of early transition metal alkoxides and aryloxides.¹¹ Interestingly, the orientation of the phenoxide ring in the pocket appears to be determined by a stacking interaction between the 3,5-xylyl ring and one of the C_6F_5 rings, with aryl carbon–fluorinated aryl carbon distances ranging from 3.153 to 3.915 Å (see Figure 3b and Table 2). The electrostatic interaction between the phenyl and perfluorophenyl rings has been recently shown to lead to $\pi\text{--}\pi$ stacking distances in the range of 3.4 to 3.6 Å.^{12–14}

Attempted Syntheses of Tungsten and Molybdenum Alkyl Complexes. Alkylation of $[\text{N}_3\text{NF}]\text{WCl}$ with LiCH_2R ($\text{R} = \text{Me}$, *n*-Pr, SiMe_3 , CMe_3) reagents in toluene at room temperature leads to the evolution of molecular hydrogen and formation of the corresponding tungsten(VI) alkylidyne complexes shown in eq 1.



$[\text{N}_3\text{NF}]\text{W}\equiv\text{CPh}$ can be prepared similarly from $[\text{N}_3\text{NF}]\text{WI}$, but the reaction between LiCH_2Ph and $[\text{N}_3\text{NF}]\text{WCl}$ appears to be slow and does not give a clean product. Dihydrogen was observed at 4.5 ppm in the ^1H NMR spectrum of a reaction between $[\text{N}_3\text{NF}]\text{WCl}$ and $\text{LiCH}_2\text{--SiMe}_3$ run in toluene- d_8 in a flame-sealed NMR tube. We presume that the first step in this process is formation of $[\text{N}_3\text{NF}]\text{WCH}_2\text{R}$ complexes, which then lose molecular hydrogen in a manner similar to that found for the analogous $[\text{N}_3\text{N}]^{3-}$ complexes.^{2,7} The light tan or brown products have been isolated in $50\text{--}70\%$ yields. The alkylation reactions proceed smoothly only in toluene, in which $[\text{N}_3\text{NF}]\text{WCl}$ and the products are only sparingly soluble. Attempts to alkylate $[\text{N}_3\text{NF}]\text{WCl}$ homogeneously in THF led only to decomposition, and

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Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for [N₃N_F]W(O-3,5-Me₂C₆H₃) (1b), [N₃N_F]W=CSiMe₃ (2d), and [N₃N_F]W(O)(3,5-Me₂C₆H₃) (4b)

	1b	2d	4b
empirical formula	C ₃₂ H ₂₁ F ₁₅ N ₄ O _W	C ₂₈ H ₂₃ N ₄ F ₁₅ Si _W	C ₃₂ H ₂₁ F ₁₅ N ₄ O _W
fw	946.38	912.43	946.38
diffractometer	Siemens SMART/CCD	Enraf-Nonius CAD-4	Siemens SMART/CCD
cryst dimens (mm)	0.50 × 0.15 × 0.15	0.28 × 0.280 × 0.240	n/a
cryst syst	monoclinic	monoclinic	monoclinic
a (Å)	15.2959(9)	9.285(2)	21.73(2)
b (Å)	13.8809(8)	28.268(5)	14.92(2)
c (Å)	15.5727(9)	12.054(2)	24.17(3)
β (deg)	98.9050(10)	100.25(2)	94.94(2)
V (Å ³)	3266.6(3)	3133(2)	7804(15)
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>I</i> 2/ <i>a</i>
Z	4	4	8
D _{calc} (Mg/m ³)	1.924	1.946	1.611
abs coeff (mm ⁻¹)	3.657	3.941	3.061
F ₀₀₀	1832	1768	3664
λ (Mo Kα) Å	0.710 73 Å	0.710 69 Å	0.710 73 Å
temp (K)	188 (2)	187	188 (2)
θ range for data collection (deg)	1.35–23.28	ω scans	1.61–18.75
no. of reflns coll'd	12 524	5512	8082
no. of indep reflns	4657		3030
R [I > 2σ(I)]	0.0522	0.032 ^a	0.0855
R _w [I > 2σ(I)]	0.1247 ^b	0.035 ^c	0.1761 ^b
GoF	1.128	1.37	1.160
ext coeff	0.0023(4)		0.00008(4)
largest diff peak and hole (e Å ⁻³)	2.056, -2.920	0.99, -0.96	0.819, -0.767

^a Based upon $I > 3\sigma(I)$. ^b $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^c $R_w = \{\sum[|w(F_o - |F_c|)^2|/\sum wF_o^2]\}^{1/2}$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) and Dihedral Angles (deg) for [N₃N_F]MoCl, ^a [N₃N_F]W(O-3,5-Me₂C₆H₃) (1b), and [N₃N_F]W=CSiMe₃ (2d)

	[N ₃ N _F]MoCl	1b	2d
W-N(1)	1.962(3)	1.990(6)	1.973(4)
W-N(2)	1.957(3)	1.968(7)	1.963(5)
W-N(3)	1.964(3)	1.975(7)	1.968(4)
W-N(4)	2.182(3)	2.195(7)	2.323(4)
W-N(1)-C	127.8(3)	121.5(5)	126.8(3)
W-N(2)-C	125.9(3)	125.1(5)	127.8(4)
W-N(3)-C	124.6(2)	127.8(6)	126.5(3)
N(1)-W-N(2)	119.0(1)	116.2(3)	116.4(2)
N(1)-W-N(3)	115.9(1)	119.8(3)	116.3(2)
N(2)-W-N(3)	117.4(1)	115.8(3)	114.8(2)
N(3)-W-N(4)	80.4(1)	80.3(3)	78.0(2)
N(4)-W-X	177.97(9)	176.3(3)	177.3(2)
N(4)-W-N(1)-C	168.4 ^b	161.7 ^b	172.8(5)
N(4)-W-N(2)-C	176.8 ^b	171.8 ^b	175.4(5)
N(4)-W-N(3)-C	171.6 ^b	174.4 ^b	173.3(5)
other		145.0(6) (W-O-C) 1.991(7) (W-O) 3.153 ^b (C(41)-C(26)) 3.318 ^b (C(41)-C(21)) 3.487 ^b (C(42)-C(21)) 3.398 ^b (C(46)-C(26)) 3.915 ^b (C(44)-C(25)) 3.609 ^b (C(42)-C(22))	176.9(4) (W-C-Si) 1.768(6) (W-C(19))

^a See ref 6. ^b Obtained from a Chem 3D model.

attempts to prepare a methylidyne complex (**2a**) analogous to [N₃N]W≡CH² in toluene employing LiMe in ether or MeMgCl in ether failed, even though **2a** can be prepared via another route (see below). Chemical shifts of the alkylidyne α carbon atom (281–296 ppm) and J_{CW} in [N₃N_F]W≡¹³CCH₂CH₂CH₃ (254 Hz) are typical of values found for other d⁰ alkylidyne complexes.¹⁵ [N₃N_F]W(O-3,5-Me₂C₆H₃) also reacts with butyllithium to yield [N₃N_F]W≡CCH₂CH₂CH₃ essentially quantitatively, we presume via intermediate [N₃N_F]W(butyl).

The reaction between LiCH₂SiMe₃ and [N₃N_F]WCl is qualitatively different from other alkylations. The

solution turns red initially but lightens to yellow only over the course of approximately 1 day at room temperature. After 2 days, [N₃N_F]W=CSiMe₃ was isolated in 72% yield. The reaction of [N₃N_F]WCl with LiCH₂-SiMe₃ at -10 °C for 1 h gave a red precipitate, which displayed ¹H and ¹⁹F NMR spectra indicative of a paramagnetic species, as expected for d² [N₃N_F]W(CH₂-SiMe₃) (**3a**). This complex decomposes in a first-order manner to give [N₃N_F]W=CSiMe₃. The transformation was followed by ¹⁹F NMR in THF (0.01 M in **3a**) at five temperatures from 16 to 53 °C. A plot of ln(*k*/*T*) versus 1/*T* (Figure 4) yielded a Δ*H*[‡] of 20.3 ± 0.2 kcal/mol and a Δ*S*[‡] of -7 ± 1 eu (*R* = 0.999). The rate constant at 298 K is calculated to be 2.3 × 10⁻⁴ s⁻¹ and the half-life 50 min. In comparison, the reaction between

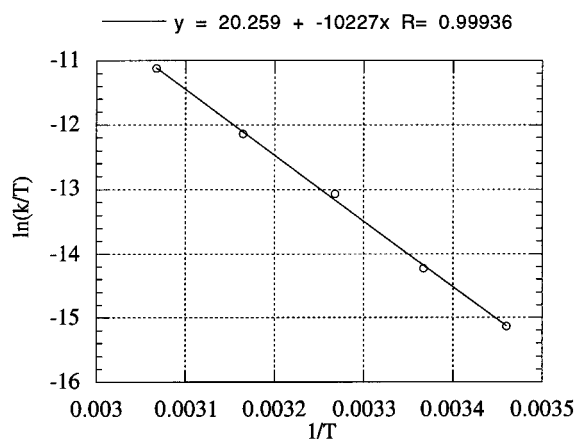


Figure 4. A plot of $\ln(k/T)$ vs $1/T$ for the decomposition of $[\text{N}_3\text{N}_\text{F}]\text{W}(\text{CH}_2\text{SiMe}_3)$.

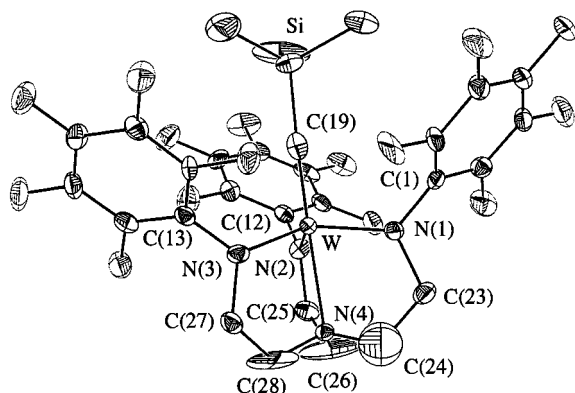
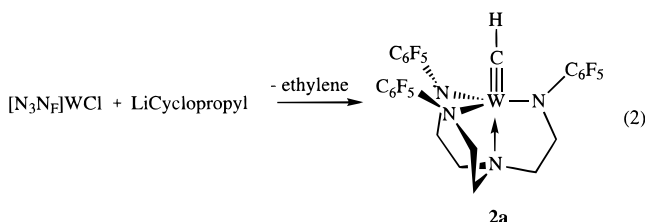


Figure 5. ORTEP drawing of $[\text{N}_3\text{N}_\text{F}]\text{W}\equiv\text{CSiMe}_3$.

$[\text{N}_3\text{N}]\text{WCl}$ and $\text{LiCH}_2\text{SiMe}_3$ yielded $[\text{N}_3\text{N}]\text{W}\equiv\text{CSiMe}_3$ within 2 h, and there is no evidence for intermediate $[\text{N}_3\text{N}]\text{W}(\text{CH}_2\text{SiMe}_3)$ at room temperature.²

An X-ray study of $[\text{N}_3\text{N}_\text{F}]\text{W}\equiv\text{CSiMe}_3$ (Tables 1 and 2; Figure 5) showed it to have the expected, relatively undistorted, structure. The W–C triple bond distance (1.768(6) Å) is in the range normally observed in tungsten alkylidyne complexes.¹⁵ The only significant structural difference between $[\text{N}_3\text{N}_\text{F}]\text{W}\equiv\text{CSiMe}_3$ and $[\text{N}_3\text{N}_\text{F}]\text{MoCl}$ or **1b** is the slightly longer W–N(4) distance (2.323(4) Å), as expected for a donor trans to a tungsten–carbon triple bond. All other bond distances and angles are similar to those in $[\text{N}_3\text{N}_\text{F}]\text{MoCl}$ or **1b** and deserve no further comment.

Although attempts to prepare $[\text{N}_3\text{N}_\text{F}]\text{WCH}_3$ were not successful, $[\text{N}_3\text{N}_\text{F}]\text{W}\equiv\text{CH}$ (**2a**) could be prepared by reacting $[\text{N}_3\text{N}_\text{F}]\text{WCl}$ with cyclopropyllithium in toluene. We presume that this reaction proceeds via a cyclopropyl

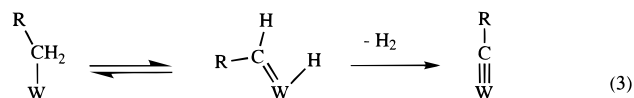


pyl complex that then loses ethylene (eq 2).² Light orange, microcrystalline **2a** displays a characteristic low-field ¹³C resonance¹⁵ for the methylidyne carbon at

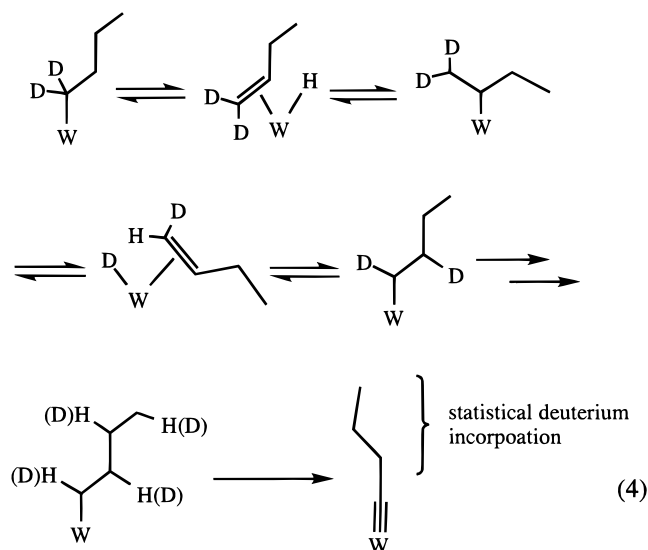
284.3 ppm and a resonance at 5.24 ppm (²J_{HW} = 76 Hz) in the ¹H NMR spectrum for the methylidyne proton.

$[\text{N}_3\text{N}_\text{F}]\text{MoCl}^6$ reacts with $\text{LiCH}_2\text{SiMe}_3$ or $\text{LiCH}_2\text{CMe}_3$ in toluene to yield $[\text{N}_3\text{N}_\text{F}]\text{Mo}(\text{CH}_2\text{CMe}_3)$ or $[\text{N}_3\text{N}_\text{F}]\text{Mo}(\text{CH}_2\text{SiMe}_3)$, respectively. These complexes are relatively stable toward loss of dihydrogen at room temperature, as observed for analogous $[\text{N}_3\text{N}]\text{MoR}$ complexes.¹ However, thermolysis of $[\text{N}_3\text{N}_\text{F}]\text{Mo}(\text{CH}_2\text{CMe}_3)$ yields $[\text{N}_3\text{N}_\text{F}]\text{Mo}\equiv\text{CCMe}_3$ in a first-order reaction at 121 °C. The rate constant at 121 °C in toluene is $7.9(5) \times 10^{-5} \text{ s}^{-1}$, as determined via UV–vis spectroscopy. This value should be compared to the rate constant for the decomposition of $[\text{N}_3\text{N}]\text{Mo}(\text{CH}_2\text{CMe}_3)$, which was found to be an order of magnitude larger ($9.41 \times 10^{-4} \text{ s}^{-1}$) at 121 °C.¹ If the same were true for decomposition of $[\text{N}_3\text{N}]\text{W}(\text{CH}_2\text{SiMe}_3)$ versus decomposition of $[\text{N}_3\text{N}_\text{F}]\text{W}(\text{CH}_2\text{SiMe}_3)$ (see above), then the half-life of $[\text{N}_3\text{N}]\text{W}(\text{CH}_2\text{SiMe}_3)$ would be only ~5 min (or less) at room temperature, which would account for the failure to observe intermediate $[\text{N}_3\text{N}]\text{W}(\text{CH}_2\text{SiMe}_3)$ during alkylation of $[\text{N}_3\text{N}]\text{WCl}$ with $\text{LiCH}_2\text{SiMe}_3$ at room temperature.^{2,7}

We believe that the loss of molecular hydrogen from $[\text{N}_3\text{N}_\text{F}]\text{W}^{3-}$ tungsten(IV) alkyl complexes consists of a reversible α -elimination to yield an unobserved alkylidene hydride complex, which then undergoes intramolecular α -abstraction of the alkylidene proton by the hydride, yielding dihydrogen and the alkylidyne (eq 3).



The reaction between $[\text{N}_3\text{N}_\text{F}]\text{WCl}$ and $\text{LiCD}_2\text{CH}_2\text{CH}_2\text{CH}_3$ led to the formation of **2c**, which contained a statistical amount of deuterium scrambled throughout the propyl chain. Therefore, we propose that β -elimination in intermediate $[\text{N}_3\text{N}_\text{F}]\text{W}(\text{CD}_2\text{CH}_2\text{CH}_2\text{CH}_3)$ gives an olefin hydride complex, which is then converted into an intermediate *sec*-butyl complex (eq 4). A series of



relatively rapid β -hydride elimination–migratory insertion reaction sequences leads to scrambling of H and D before a significant amount of the butyl complex is

converted into the butyldiyne complex. Loss of any olefin from an intermediate olefin hydride complex also must be relatively slow. Further support for this proposal was obtained by reacting $[\text{N}_3\text{N}_F]\text{WCl}$ with $\text{Li}^{13}\text{C}_2\text{H}_2\text{CH}_2\text{CH}_3$ to give **2c** with $\sim 50\%$ ^{13}C label at the alkylidyne carbon and $\sim 50\%$ ^{13}C label at the terminal carbon on the propyl chain. These results contrast strongly with those obtained in the analogous $[\text{N}_3\text{N}]\text{W}$ system. When $[\text{N}_3\text{N}]\text{WCl}$ is reacted with $\text{LiCD}_2\text{CH}_2\text{CH}_2\text{CH}_3$, D_2 gas is lost and the butyldiyne product contains only hydrogen, as evidenced by ^2H NMR.⁷ Similarly, when $[\text{N}_3\text{N}]\text{WCl}$ is reacted with $\text{Li}^{13}\text{C}_2\text{H}_2\text{CH}_2\text{CH}_3$, the product formed is labeled exclusively at the alkylidyne carbon atom.² These data are consistent with a relatively rapid loss of D_2 or H_2 by α,α -elimination compared to any scrambling ascribable to reversible β -hydride elimination processes in the $[\text{N}_3\text{N}]\text{W}$ system.

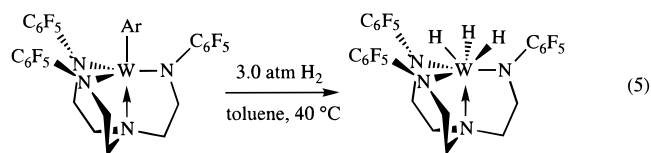
Several additional experiments were carried out in order to substantiate the mechanism shown in eq 4. $[\text{N}_3\text{N}_F]\text{WCl}$ reacts with *sec*-butyllithium to yield $[\text{N}_3\text{N}_F]\text{W}=\text{CCH}_2\text{CH}_2\text{CH}_3$. This result lends credence to the notion that the metal can "walk" along a *sec*-butyl chain to the end to produce a butyldiyne complex. We also found that $[\text{N}_3\text{N}_F]\text{WCl}$ reacts with LiCH_2CD_3 to yield $[\text{N}_3\text{N}_F]\text{W}=\text{CMe}$ (**2b**), in which H and D are scrambled in the methyl group. Apparently β -elimination again competes with α -elimination and loss of molecular hydrogen during the formation of **2b**. Although these results do not lead to the conclusion that β -elimination to give an olefin hydride is faster than α -elimination to give an alkylidene hydride, it does not seem possible that β -elimination is 10^6 times slower than α -elimination, as found in the $[\text{N}_3\text{N}]$ system.

Reactions between $[\text{N}_3\text{N}_F]\text{WCl}$ and cyclopentylolithium lead only to decomposition. This result could be the consequence of the instability of $[\text{N}_3\text{N}_F]\text{WH}$, the likely product of β -elimination. (The corresponding hydrides, $[\text{N}_3\text{N}]\text{MH}$, are eventually formed when $[\text{N}_3\text{N}]\text{MoCl}$ or $[\text{N}_3\text{N}]\text{WCl}$ reacts with cyclopentylolithium.) On the basis of these results, we cannot tell if $[\text{N}_3\text{N}_F]\text{W}(\text{cyclopentylidene})\text{H}$ is formed more rapidly than $[\text{N}_3\text{N}_F]\text{W}(\text{cyclopentene})\text{H}$ or not. If loss of cyclopentene from $[\text{N}_3\text{N}_F]\text{W}(\text{cyclopentene})\text{H}$ proceeds at a significant rate, then formation of $[\text{N}_3\text{N}_F]\text{WH}$ and subsequent decomposition would be the end result, even if $[\text{N}_3\text{N}_F]\text{W}(\text{cyclopentylidene})\text{H}$ were formed more rapidly than $[\text{N}_3\text{N}_F]\text{W}(\text{cyclopentene})\text{H}$.

As one might expect, it is possible to prepare aryl complexes. $[\text{N}_3\text{N}_F]\text{WI}$ reacts with aryllithium reagents ($\text{Ar} = \text{Ph}$, 3,5- $\text{Me}_2\text{C}_6\text{H}_3$) to yield $[\text{N}_3\text{N}_F]\text{WPh}$ (**3b**) and $[\text{N}_3\text{N}_F]\text{W}(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (**3c**) as red-orange paramagnetic solids. In these reactions, $[\text{N}_3\text{N}_F]\text{WCl}$ does not produce a good yield of product. As in the case of $[\text{N}_3\text{N}]\text{WPh}$,² conjugation of the metal d_{xz} or d_{yz} orbitals with the π system of the aryl rings is not enough to break the d_{xz}/d_{yz} degeneracy. The observed magnetic moment of **3c** in C_6D_6 solution at 22°C is $3.0 \pm 0.1 \mu_B$, close to the spin-only value for two unpaired electrons ($2.83 \mu_B$). ^1H NMR spectra of the complexes reveal ligand backbone resonances between -15 and -60 ppm, but resonances for the aryl protons are not observed. However, in **3c**, a sharp resonance that we assign to the aryl methyl groups is observed at -53.9 ppm. **3b** is only sparingly soluble in hydrocarbon solvents, whereas **3c** is soluble

enough in toluene to render extraction into this solvent, a viable method of separating it from most of the LiI side product. Nevertheless, contamination of **3b** and **3c** with LiI has prevented our obtaining satisfactory elemental analyses so far.

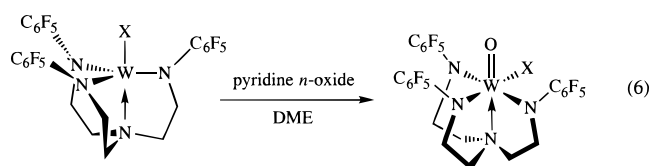
The failure to observe $[\text{N}_3\text{N}_F]\text{WH}$ led us to question whether *any* hydrido complexes, namely $[\text{N}_3\text{N}_F]\text{WH}_3$, an analogue of $[\text{N}_3\text{N}]\text{WH}_3$,¹⁶ could be prepared. In fact, the aryl complexes do react with hydrogen (3 atm) in toluene at 40°C to yield diamagnetic $[\text{N}_3\text{N}]\text{WH}_3$, eq 5. The



$\text{Ar} = \text{Ph}$ (**3b**), 3,5- $\text{Me}_2\text{C}_6\text{H}_3$ (**3c**)

hydride resonance of $[\text{N}_3\text{N}_F]\text{WH}_3$ is observed at 11.1 ppm in the ^1H NMR spectrum with $J_{\text{HW}} = 25$ Hz. The relaxation time of the hydride was determined to be 344 ± 5 ms at 22°C , which suggests that $[\text{N}_3\text{N}_F]\text{WH}_3$ is a classical hydride complex.¹⁷ An absorption at 1898 cm^{-1} is observed in the IR spectrum that we assign to the symmetric W–H stretch. The trideuteride could be prepared similarly employing D_2 . The ^1H NMR of $[\text{N}_3\text{N}_F]\text{WD}_3$ has no resonance at 11.1 ppm, while the ^2H NMR spectrum displays a resonance at 10.9 ppm. The IR spectrum of $[\text{N}_3\text{N}]\text{WD}_3$ shows no absorption at 1898 cm^{-1} ; we assign a new absorption at 1372 cm^{-1} to the symmetric W–D stretch.

Atom-Transfer Reactions of W(IV) Aryl Complexes. Both **3b** and **3c** are cleanly oxidized by pyridine N-oxide to yield diamagnetic $[\text{N}_3\text{N}_F]\text{W}(\text{O})(\text{Ph})$ (**4a**) or $[\text{N}_3\text{N}_F]\text{W}(\text{O})(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (**4b**), respectively, eq 6. No



$\text{X} = \text{Ph}$ (**4a**), 3,5- $\text{Me}_2\text{C}_6\text{H}_3$ (**4b**)

IR stretch for the oxo ligand could be identified in either complex because the region around 1000 cm^{-1} where a tungsten oxo stretch is normally observed¹⁸ contains many strong C–F absorptions. Room-temperature ^1H and ^{19}F NMR spectra for **4b** show a normal C_3v -symmetric ligand backbone. Compound **4b** does not react with TMSI at room temperature or with trimethylphosphine in C_6D_6 at 60°C for 14 h.

An X-ray structure of **4b** revealed it to have the structure proposed in eq 6 (Figure 6a and b). (The structure is of relatively low quality, as only the tungsten, fluorine, nitrogen, and oxygen atoms could be refined anisotropically. Therefore, bond lengths and angles in Table 3 will not be discussed in detail.) It is essentially a pseudo-octahedral species in which two of

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(18) Nugent, W. A.; Mayer, J. A. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

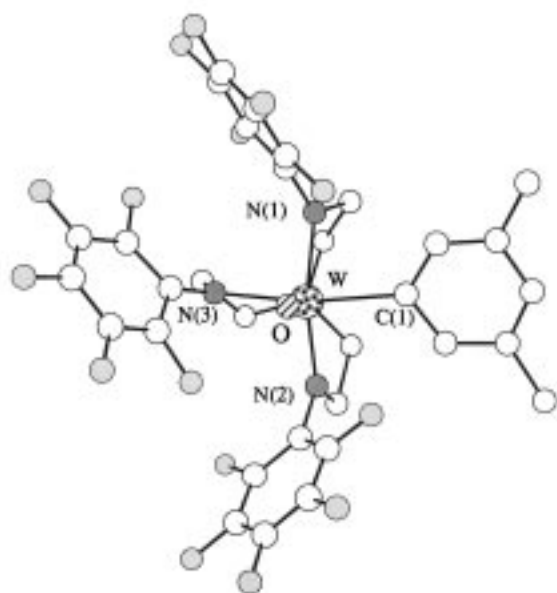
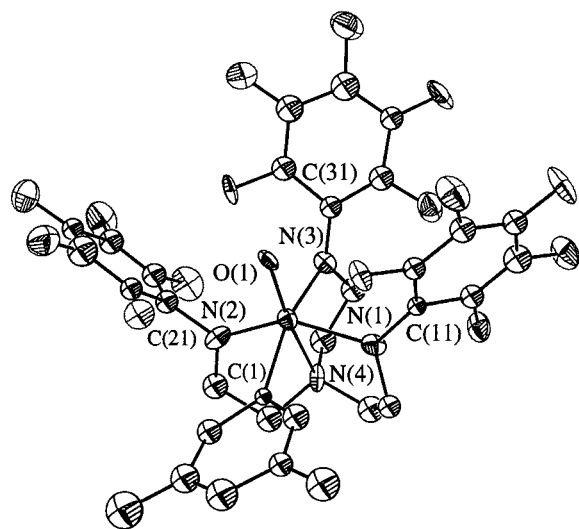


Figure 6. (a) ORTEP drawing of $[\text{N}_3\text{NF}]\text{W}(\text{O})(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (**4b**). (b) A top view (Chem 3D) of the structure of $[\text{N}_3\text{NF}]\text{W}(\text{O})(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (**4b**).

the “arms” of the $[\text{N}_3\text{NF}]^{3-}$ ligand have opened up to receive the 3,5-dimethylphenyl group approximately in the $\text{WN}(\text{amido})_3$ plane. The C_6F_5 groups on N(1) and N(2), therefore, are twisted from their usual “bowl-like” arrangement and are turned away from the dimethylphenyl ligand to a significant degree, as evidenced by two dihedral angles $\text{N}(4)\text{-W-N-C}$ that are considerably less than 180° ; the $\text{N}(4)\text{-W-N}(3)\text{-C}(31)$ angle is $\sim 180^\circ$, as one would expect. The $\text{N}(1)\text{-W-N}(2)$ angle is opened up from the $\sim 120^\circ$ value expected for a C_{3v} -symmetric $[\text{N}_3\text{NF}]$ complex to $146.0(7)^\circ$. This is the smallest angle for ligands “trans” to one another in the distorted octahedron, with the other two such angles, $\text{O-W-N}(4)$ and $\text{N}(3)\text{-W-C}(1)$, equal to $165.2(7)^\circ$ and $167.2(7)^\circ$, respectively. The tungsten–oxygen bond length ($1.685(14)$ Å) lies in the range normally observed for pseudo-triply-bonded tungsten oxo ligands.¹⁸ At room temperature, the structure must be fluxional on the NMR time scale, since NMR spectra are consistent with a C_{3v} -symmetric structure. However, the fluxional process cannot consist of rapid migration of the phenyl ring to and from the oxo ligand, since intermediate

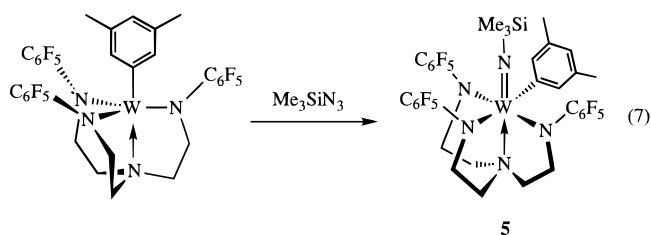
Table 3. Selected Bond Lengths (Å) and Angles (deg) and Dihedral Angles (deg) for $[\text{N}_3\text{NF}]\text{W}(\text{O})(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (**4b**)

Distances			
W–O(1)	1.685(14)	W–C(1)	2.23(2)
W–N(1)	2.06(2)	N(1)–C(11)	1.37(3)
W–N(2)	1.96(2)	N(2)–C(21)	1.45(3)
W–N(3)	2.13(2)	N(3)–C(31)	1.32(3)
W–N(4)	2.33(2)		
Angles			
O(1)–W–N(4)	165.2(7)	N(3)–W–N(1)	86.7(7)
N(1)–W–N(2)	146.0(7)	N(4)–W–N(3)	75.3(7)
C(1)–W–N(3)	167.2(7)	W–N(1)–C(11)	123.3(13)
O–W–C(1)	99.5(7)	W–N(2)–C(21)	124.7(14)
N(4)–W–N(1)	74.3(7)	N(3)–W–O(1)	90.2(7)
N(4)–W–N(2)	74.2(7)	N(2)–W–C(1)	88.2(7)
N(4)–W–C(1)	95.3(7)	N(3)–W–C(1)	167.2(7)
N(3)–W–N(2)	97.4(7)	N(1)–W–O(1)	108.4(7)
Dihedral Angles ^a			
N(4)–W–N(2)–C(21)	154.4	N(4)–W–N(3)–C(31)	178.5
N(4)–W–N(1)–C(11)	139.9		

^a Obtained from a Chem 3D model.

$[\text{N}_3\text{NF}]\text{W}(\text{O})(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (**1b**) would have to be formed. One would not expect a rapid and reversible migration to an oxo ligand to be fast in any case since, in general, it appears to be rare and/or slow.¹⁹

Nitrogen-atom transfer to $[\text{N}_3\text{NF}]\text{W}(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ can be accomplished with trimethylsilyl azide (eq 7). Unlike



4b, however, $[\text{N}_3\text{NF}]\text{W}(\text{NSiMe}_3)(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ does not show C_{3v} symmetry on the NMR time scale at room temperature, but C_s symmetry. A related molecule containing the $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ ligand, $[\text{N}_3\text{N}]\text{Mo}(\text{NSiMe}_3)(\text{Me})$, has been synthesized recently in our laboratories²⁰ and is also C_s -symmetric by NMR. Apparently, the imido group “locks” the structure in the lower symmetry on the NMR time scale. One reason for the relative rigidity of **5** could be the sterically crowded nature of the required intermediate with the imido and aryl groups in the trigonal pocket.¹⁶ However, it is also true that in a complex in which the three ligand amido nitrogens are $\sim 120^\circ$ to one another and form two W-N π bonds, the imido ligand, a traditionally strong π -bonding ligand, cannot be pseudo-triply-bound to the metal, since only three orbitals would be available for bonding to the imido and phenyl ligands.⁹ In **5**, two $\text{W-N}_{\text{imido}}$ π bonds and one of the two possible π bonds in the $\text{WN}(\text{amido})_3$ plane can form to yield an “18-electron” species.

Discussion

The main reason we sought to prepare organometallic species that contain $[\text{N}_3\text{NF}]^{3-}$ was to compare them with

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$[\text{N}_3\text{N}]^{3-}$ complexes. There are differences, to be sure, but many of the differences can be explained on steric grounds alone, i.e., how well the triamidoamine substituents "protect" the trigonal coordination pocket. The remaining differences can be explained in terms of some competing side reaction or decomposition of the final expected product (e.g., $[\text{N}_3\text{N}_\text{F}]\text{WH}$).

One of the main findings is that β -elimination in the $[\text{N}_3\text{N}_\text{F}]^{3-}$ system is probably *not* many orders of magnitude slower than α -elimination, as found in the $[\text{N}_3\text{N}]^{3-}$ Mo and W systems.^{1,2} Unfortunately, we only have circumstantial evidence on which to base this statement, since we have not measured the rate of α -elimination *per se* in the $[\text{N}_3\text{N}_\text{F}]\text{W}$ system, only the overall rate of loss of dihydrogen to give alkylidyne complexes. Therefore, it would seem that in the fluorinated system there is a more conventional kinetic preference for β -elimination over α -elimination.²¹ The fact that the rate of loss of dihydrogen from $[\text{N}_3\text{N}_\text{F}]\text{Mo}(\text{CH}_2\text{CMe}_3)$ and $[\text{N}_3\text{N}]\text{Mo}(\text{CH}_2\text{CMe}_3)$ differ by only 1 order of magnitude alone is somewhat surprising from an electronic standpoint. Although overall loss of dihydrogen consists of two steps, the slower loss of dihydrogen from $[\text{N}_3\text{N}_\text{F}]\text{Mo}(\text{CH}_2\text{CMe}_3)$ in fact is also consistent simply with less steric hindrance in the trigonal pocket that might accelerate an elimination process by increasing the Mo–C $_{\alpha}$ –C $_{\beta}$ angle. Perhaps for steric reasons alone the loss of molecular hydrogen from $[\text{N}_3\text{N}_\text{F}]\text{W}(n\text{-butyl})$ cannot compete with β -elimination that scrambles the labels in the butyl chain, i.e., a more "open" steric pocket does not accelerate an α -elimination, and does not sterically inhibit β -elimination to give an olefin hydride *and* allow formation of a *sec*-butyl intermediate required for scrambling within the butyl chain. At the same time, loss of 1-butene from the metal would *not* be sterically accelerated. It remains to be seen whether the results of cyclic voltammetry studies can be correlated with some of the chemistry observed here. These results also bring into question the correlation of redox behavior in silylated triamidoamine species with α,α -dehydrogenation to give alkylidyne complexes,²² as the observed trend also correlates with a steric effect. As mentioned earlier, a more open coordination pocket also explains the fact that β -elimination and loss of cyclopentene competes with α -elimination to give a cyclopentylidene hydride complex.

Other differences between the $[\text{N}_3\text{N}_\text{F}]^{3-}$ and the $[\text{N}_3\text{N}]^{3-}$ systems might be explained by reactions involving the C_6F_5 ring. For example, the C_6F_5 ring is almost certainly attacked by strong nucleophiles. Some of the peculiarities associated with the synthesis of alkyl complexes (e.g., the failure to observe smooth reactions with methylolithium or the need to use $[\text{N}_3\text{N}_\text{F}]\text{WI}$ to make aryl complexes) might be explained in terms of competitive attack on, or electron transfer to, the C_6F_5 ring. The failure to prepare alkyl derivatives in THF could be a consequence of THF-blocking attack at the metal relative to attack on the C_6F_5 ring. Finally, the apparent instability of $[\text{N}_3\text{N}_\text{F}]\text{WH}$ might be ascribed to

some intramolecular or intermolecular reaction involving a CF bond in the C_6F_5 ring.

Steric effects have been used in the past to rationalize preferential α versus β abstraction^{23,24} and elimination^{25–27} processes. The results presented here reinforce the notion that steric effects can dramatically alter the relative rates of α - and β -elimination or -abstraction processes. It remains to be seen to what extent the chemistry of complexes containing the triamidoamine ligand might be altered by electronic differences between substituents on the amido nitrogens. We are continuing to work toward a general synthesis of aryl-substituted triamidoamine ligands in order to begin to answer such questions.

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). Glassware was dried at 135 °C in an oven overnight. Pentane was distilled from sodium benzophenone (in the presence of tetraglyme) under nitrogen. Ether and THF were purified by sparging with nitrogen and passing through alumina columns.²⁸ Reagent-grade benzene was distilled from sodium benzophenone under nitrogen. Toluene was distilled from molten sodium. Acetonitrile was distilled from P_2O_5 . Methylene chloride was distilled from CaH_2 . All solvents were stored in the drybox over activated 4 Å molecular sieves. Deuterated solvents were degassed by freeze–pump–thaw cycles and vacuum transferred from an appropriate drying agent or sparged with argon and stored over molecular sieves. ^1H and ^{13}C data are listed in parts per million downfield from tetramethylsilane and were referenced using the solvent peak. ^{19}F NMR data are listed in parts per million downfield of CFCl_3 as an external standard. ^2H NMR spectra were obtained at 46.0 MHz and referenced to external C_6D_6 (7.15 ppm). ^{31}P NMR spectra are listed in parts per million downfield from H_3PO_4 . Coupling constants are given in hertz; routine coupling constants usually are not listed. Solution magnetic susceptibilities were measured by NMR using the Evans method.²⁹ Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer. Magnetic susceptibilities were measured in the solid state at 5 KG on a Quantum Design 5.5 T instrument running MSRP2 software as described elsewhere;¹ the data were corrected for the diamagnetic contribution by the ligands using Pascal's constants.

Preparation of Starting Materials. $[\text{N}_3\text{N}_\text{F}]\text{WCl}$, $[\text{N}_3\text{N}_\text{F}]\text{W}(\text{OTf})$, and $[\text{N}_3\text{N}_\text{F}]\text{MoCl}$ were synthesized as described in the literature,⁶ except that $\text{WCl}_4(\text{dme})$ ³⁰ was used instead of $\text{WCl}_4(\text{Et}_2\text{S})_2$. $\text{LiCD}_2\text{CH}_2\text{CH}_2\text{CH}_3$ was prepared by reduction of butyryl chloride with LiAlD_4 in ether followed by reaction with thionyl chloride in hexane in the presence of pyridine. The hexane/butyryl chloride mixture was dried and distilled together from P_2O_5 . Treatment of this solution with lithium wire gave $\text{CH}_3\text{CH}_2\text{CH}_2\text{CD}_2\text{Li}$ in ~15% overall yield. LiCH_2CD_3 was prepared by treatment of $\text{CD}_3\text{CH}_2\text{Br}$ (Cambridge Isotope Labs)

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with lithium wire. $\text{Li}^{13}\text{C}_2\text{H}_2\text{CH}_2\text{CH}_3$ was prepared from $^{13}\text{CO}_2$ by formation of the acid with *n*-PrMgCl, followed by LiAlH_4 reduction to the alcohol. Treatment with SOCl_2 in hexane in the presence of pyridine as for $\text{LiCD}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and subsequent reaction with lithium metal gave the ^{13}C -labeled butyllithium in 20% overall yield. Phenyllithium and 3,5-xylyllithium were prepared by treatment of the aryl bromide with BuLi in ether/hexane at -35°C . Ethyllithium was prepared by the literature procedure.³¹ (Trimethylsilyl)-methylolithium was purchased commercially as a solution in pentane, and the pentane was removed in vacuo. Cyclopropyllithium was synthesized from cyclopropyl bromide and lithium powder in ether. Neopentyllithium was prepared by the literature procedure.³²

$[\text{N}_3\text{N}_F]\text{WI}$. Trimethylsilyl iodide (216 μL , 1.52 mmol, 1.5 equiv) was added to a solution of $[\text{N}_3\text{N}_F]\text{WCl}$ (870 mg, 1.01 mmol) in 30 mL of dichloromethane. The reaction was stirred overnight, and the solvent was removed in vacuo. The yellow-brown residue was recrystallized from a mixture of dichloromethane and ether to give orange crystals; 755 mg (97% yield): ^1H NMR (C_6D_6) δ -25.5 (br s, $\Delta\nu_{1/2} = 156$, CH_2), -50.0 (br s, $\Delta\nu_{1/2} = 115$, CH_2); ^{19}F NMR (C_6D_6) δ -86.5 (F_o), -124.0 (F_m), -144.5 (F_p). Anal. Calcd for $\text{C}_{24}\text{H}_{12}\text{N}_4\text{F}_{15}\text{WI}$: C, 30.28; H, 1.27; N, 5.88. Found: C, 30.45; H, 1.32; N, 5.80.

$[\text{N}_3\text{N}_F]\text{W}(\text{OC}_6\text{F}_5)$ (1a). $[\text{N}_3\text{N}_F]\text{WOTf}$ (250 mg, 0.257 mmol) was covered with 8 mL of THF, and the mixture was cooled to -40°C . KOC_6F_5 (57 mg, 0.26 mmol) was added as a solid, and the reaction was warmed to room temperature and stirred for 6 h. The solvent was removed under reduced pressure, and the red residue was extracted with dichloromethane. The extract was reduced in volume, ether was layered on top of the solution, and the mixture was cooled to -40°C overnight. The red crystalline product was isolated by decanting the supernatant; yield 129 mg in two crops (50%): ^1H NMR (CD_3CN) δ -18.5 (br s, NCH_2N), -51.5 (s, NCH_2N); ^{19}F NMR (CD_3CN) δ -4.53 (s, 2, phenoxide F_o), -54.1 (s, 6, F_o), -100.4 (s, 2, phenoxide F_m), -125.9 (s, 6, F_m), -147.3 (s, 3, F_p), -170.8 (s, 1, phenoxide F_p). Anal. Calcd for $\text{C}_{30}\text{H}_{12}\text{N}_4\text{F}_{20}\text{OW}$: C, 35.74; H, 1.20; N, 5.56. Found: C, 35.92; H, 1.21; N, 5.72.

$[\text{N}_3\text{N}_F]\text{W}(\text{O}-3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (1b). Solid potassium 3,5-dimethylphenoxide (37 mg, 0.23 mmol) was added to a stirred -40°C solution of $[\text{N}_3\text{N}_F]\text{WCl}$ (200 mg, 0.232 mmol) in 10 mL of THF. The color of the reaction changed from orange to deep purple within seconds. After 3 h, the solvent was removed in vacuo and the residue was extracted with dichloromethane. The potassium salts were filtered off, and the extract was concentrated in vacuo. The concentrated solution was layered with pentane, and that mixture was cooled to -40°C for 15 h. Purple needles were isolated by decantation; yield 184 mg (84%): ^1H NMR (CD_3CN) δ -8.5 (s, 6, 3,5- $\text{Me}_2\text{C}_6\text{H}_3$), -15.1 (br s, $\Delta\nu_{1/2} = 46$, 6, NCH_2N), -27.8 (s, 1, H_{para}), -42.2 (br s, $\Delta\nu_{1/2} = 10$, 2, H_{ortho}), -47.6 (br s, $\Delta\nu_{1/2} = 23$, 6, NCH_2N); ^{19}F NMR (CD_3CN) δ -59.8 (br s, F_o), -123.4 (s, F_m), -142.6 (s, F_p); $\mu_{\text{obs}} = 3.2 \mu_{\text{B}}$ (Evans method). Anal. Calcd for $\text{C}_{32}\text{H}_{21}\text{N}_4\text{OF}_{15}\text{W}$: C, 40.61; H, 2.24; N, 5.92. Found: C, 40.79; H, 2.30; N, 5.73.

$[\text{N}_3\text{N}_F]\text{W}=\text{CH}$ (2a). $[\text{N}_3\text{N}_F]\text{WCl}$ (500 mg, 0.581 mmol) was dissolved in 40 mL of toluene by stirring the mixture for 1 h. A solution of cyclopropyllithium (84 mg, 0.56 mmol, 1 equiv) was prepared by adding 3 drops of THF to the solid lithium reagent followed by 2 mL of toluene. This solution was added dropwise to the solution containing $[\text{N}_3\text{N}_F]\text{WCl}$. The reaction mixture was stirred for 20 min, at which point 0.3 equiv of cyclopropyllithium (28 mg, 0.19 mmol) in 1 mL of toluene was added. After an additional 30 min, an ^{19}F NMR spectrum showed that the reaction was complete. The mixture was filtered through Celite, and the solvents were removed in

vacuo. Recrystallization from CH_2Cl_2 layered with pentane yielded several crops of orange microcrystals, which were isolated by decantation; yield 394 mg (81%): ^1H NMR (C_6D_6) δ 1.99 (t, 6, NCH_2 , 6), 3.29 (t, 6, NCH_2), 5.24 (s, $J_{\text{HW}} = 76$, 1, $\text{W}=\text{CH}$); ^{13}C NMR (CD_2Cl_2) δ 52.2 (t, NCH_2), 57.9 (t, NCH_2), 136.1, 137.0, 139.4, 140.2, 141.8, 145.1 (C_6F_5), 284.3 ($\text{W}=\text{C}-\text{H}$); ^{19}F NMR (C_6D_6) δ -150.9 (br s, F_o), -163.4 (t, F_p), -164.9 (br s, F_m).

$[\text{N}_3\text{N}_F]\text{W}=\text{CMe}$ (2b). Ethyllithium (31 mg, 0.842 mmol) was added as a solid to a room-temperature suspension of $[\text{N}_3\text{N}_F]\text{WCl}$ (0.50 g, 0.58 mmol) in 10 mL of toluene. Gas evolved immediately, and the reaction changed from orange to brown over a period of 30 min. After 45 min, the toluene was removed in vacuo and the residue was extracted with 10 mL of dichloromethane. The mixture was filtered through a short column of Celite, and the solvent was removed in vacuo. The crude product was recrystallized from a mixture of dichloromethane and ether at -40°C ; yield 249 mg (50%) in two crops: ^1H NMR (CDCl_3) δ 2.2 (t, $J_{\text{WH}} = 8.7$, 3, $\text{W}=\text{CMe}$), 3.1 (t, 6, NCH_2), 3.9 (t, 6, NCH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 30.1 ($\text{W}=\text{CMe}$), 51.8 (NCH_2), 56.8 (NCH_2), 135.6, 138.9, 140.7, 144.0 (C_6F_5), 286.3 ($\text{W}=\text{CMe}$); ^{19}F NMR (CDCl_3) δ -165.2 (t, F_m), -164.8 (t, F_p), -151.0 (d, F_o). Anal. Calcd for $\text{C}_{26}\text{H}_{15}\text{N}_4\text{F}_{15}\text{W}$: C, 36.64; H, 1.77; N, 6.57. Found: C, 36.71; H, 1.90; N, 6.42.

$[\text{N}_3\text{N}_F]\text{W}=\text{CCH}_2\text{CH}_2\text{CH}_3$ (2c). *n*-Butyllithium (0.581 mL, 1.45 mmol, 2.5 M in hexane) was added to a suspension of $[\text{N}_3\text{N}_F]\text{WCl}$ (1.00 g, 1.16 mmol) in 30 mL of toluene at room temperature. Within minutes, the color began to change from orange to brown and gas evolved. The reaction mixture was stirred for 3 h and filtered through Celite. The filtrate was reduced in volume in vacuo until crystals began to form and then cooled to -40°C overnight. The off-white microcrystalline product was filtered off and dried in vacuo. A second crop was obtained by further reducing the volume and cooling to -40°C ; total yield 0.673 g (66%): ^1H NMR (C_6D_6) δ 0.25 (t, 3, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 0.41 (sextet, 2, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.05 (t, 6, $\text{NCH}_2\text{CH}_2\text{N}$), 2.50 (t, 2, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.33 (t, 6, NCH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 12.94 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 22.29 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 46.71 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 51.22 (NCH_2), 56.92 (NCH_2), 136.2, 139.5, 141.4, 144.7 (br s, C_6F_5), 292.64 ($\text{W}=\text{C}$, $J_{\text{CW}} = 254$). Anal. Calcd for $\text{C}_{28}\text{H}_{19}\text{N}_4\text{F}_{15}\text{W}$: C, 38.20; H, 2.18; N, 6.36. Found: C, 38.33; H, 2.27; N, 6.32.

$[\text{N}_3\text{N}_F]\text{W}=\text{CSiMe}_3$ (2d). $\text{LiCH}_2\text{SiMe}_3$ (66 mg, 0.70 mmol) was added as a solid to a stirred suspension of $[\text{N}_3\text{N}_F]\text{WCl}$ (500 mg, 0.581 mmol) in 10 mL of toluene at room temperature. The reaction turned wine-red, and bubbling was observed. After 2 days of stirring, the reaction mixture was evaporated to dryness and the residue was extracted with dichloromethane. The extract was filtered through Celite, and the solvent was removed from the filtrate in vacuo to give the crude product as a pink residue. This residue was recrystallized by dissolving it in ~ 3 mL THF, layering $(\text{Me}_3\text{Si})_2\text{O}$ on top, and standing the solution in the refrigerator at -40°C . After 2 days, red crystals were filtered off; yield 0.381 g (72%): ^1H NMR (CDCl_3) δ -0.80 (s, 9, $-\text{SiCH}_3$), 3.03 (t, 6, NCH_2), 3.97 (t, 6, NCH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ -0.87 (SiCH_3), 51.13 (NCH_2), 57.35 (NCH_2), 136, 139, 142, 145 (br s, C_6F_5), 288.37 ($\text{W}=\text{C}$); ^{19}F NMR (C_6D_6) δ -165.24 (br s, F_m), -164.61 (t, F_p), -150.22 (br s, F_o). Anal. Calcd for $\text{C}_{28}\text{H}_{21}\text{N}_4\text{F}_{15}\text{SiW}$: C, 36.94; H, 2.32; N, 6.15. Found: C, 36.90; H, 2.42; N, 6.12.

$[\text{N}_3\text{N}_F]\text{W}=\text{CCMe}_3$ (2e). $\text{LiCH}_2\text{CMe}_3$ (79 mg, 1.02 mmol) was added as a solid to a stirred suspension of $[\text{N}_3\text{N}_F]\text{WCl}$ (500 mg, 0.581 mmol) in 20 mL toluene. Within seconds, gas was evolved and the color began to change from orange to light yellow. After 3.5 h, the toluene was removed in vacuo and the off-white residue dissolved in ~ 60 mL of 1,2-dimethoxyethane. The solution was filtered through Celite, and the volume was reduced in vacuo until microcrystals began to form. Cooling this solution to -40°C overnight gave the product as a light yellow powder. A second crop was obtained

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by concentrating the mother liquor and cooling to $-40\text{ }^{\circ}\text{C}$; total yield 0.317 g (61%): $^1\text{H NMR}$ (THF- d_6) δ 0.064 (s, 9, $\text{W}=\text{CC}(\text{CH}_3)_3$), 3.12 (t, 6, NCH_2), 3.94 (t, 6, NCH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_6) δ 29.90 ($\text{W}=\text{CC}(\text{CH}_3)_3$), 48.73 ($\text{W}=\text{CCMe}_3$), 52.54 (NCH_2), 58.35 (NCH_2), 137, 139, 143, 146 (C_6F_5), 296.07 ($\text{W}=\text{CCMe}_3$); $^{19}\text{F NMR}$ (C_6D_6) δ -165.3 (d, F_m), -164.6 (t, F_p), -150.7 (s, F_o). Anal. Calcd for $\text{C}_{29}\text{H}_{21}\text{N}_4\text{F}_{15}\text{W}$: C, 38.95; H, 2.37; N, 6.26. Found: C, 38.82; H, 2.18; N, 6.12.

$[\text{N}_3\text{N}_F]\text{W}=\text{CPh}$ (2f). LiCH_2Ph (325 mg, 1.70 mmol) was added as a solid to a stirred suspension of $[\text{N}_3\text{N}_F]\text{WI}$ (750 mg, 0.788 mmol) in 25 mL of toluene. The reaction darkened immediately and gas evolved. The reaction was stirred for 2 days, at which point the toluene was removed in vacuo. The residue was dissolved in dichloromethane, and the mixture was filtered through Celite. The solvent was removed in vacuo, the residue was dissolved in a minimum amount of dichloromethane, and the solution was cooled to $-40\text{ }^{\circ}\text{C}$ overnight, giving the product as an off-white solid; yield 337 mg (47%): $^1\text{H NMR}$ (C_6D_6) δ 2.09 (t, 6, NCH_2), 3.37 (t, 6, NCH_2), 6.09 (d, 2, H_o), 6.41 (t, 1, H_p), 6.70 (t, 2, H_m); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 52.7 (NCH_2), 58.0 (NCH_2), 127.2 (C_6H_5), 130.5 (C_6H_5), 136.2, 137.2, 139.5, 141.8, 145.0, 146.7 (C_6F_5), 281.6 ($\text{W}=\text{CPh}$); $^{19}\text{F NMR}$ (C_6D_6) δ -164.8 (t, F_m), -164.0 (t, F_p), -150.7 (d, F_o).

$[\text{N}_3\text{N}_F]\text{W}(\text{CH}_2\text{SiMe}_3)$ (3a). A solution of $\text{LiCH}_2\text{SiMe}_3$ (131 mg, 1.39 mmol, 1.2 equiv) in 40 mL of toluene was added via cannula to solid $[\text{N}_3\text{N}_F]\text{WCl}$ (1.00 g, 1.16 mmol) in a 100 mL Schlenk flask immersed in a $-10\text{ }^{\circ}\text{C}$ bath. The heterogeneous reaction mixture was stirred at this temperature for 1 h; the color changed gradually from orange to red. The red precipitate was filtered off and dried in vacuo; yield 908 mg (86%). The product could be recrystallized as red crystals from dichloromethane layered with pentane: $^1\text{H NMR}$ (C_6D_6) δ -0.82 (br s, 9, TMS), -18.3 (br s, 6, NCH_2), -52.1 (br s, 6, NCH_2); $^{19}\text{F NMR}$ (C_6D_6) δ -29 (br s, F_o), -112 (s, F_m), -140 (s, F_p).

The dehydrogenation of $[\text{N}_3\text{N}_F]\text{W}(\text{CH}_2\text{SiMe}_3)$ to give $[\text{N}_3\text{N}_F]\text{W}=\text{CSiMe}_3$ was followed by $^{19}\text{F NMR}$ at 470 MHz by monitoring the decrease in intensity of the meta fluorine resonance versus fluorobenzene as an internal standard. Runs were done in THF with an initial alkyl concentration of ~ 0.01 M and followed through 2–5 five half-lives. The values for k ($\times 10^{-4}\text{ s}^{-1}$) at temperature T (K) are as follows: 48.1 (326), 16.9 (316), 6.47 (306), 1.97 (297), 0.774 (289). A plot of $\ln(k/T)$ versus $1/T$ yielded $\Delta H^\ddagger = 20\text{ }250\text{ cal/mol}$ and $\Delta S^\ddagger = -6.937\text{ eu}$.

$[\text{N}_3\text{N}_F]\text{WPh}$ (3b). $[\text{N}_3\text{N}_F]\text{WI}$ (500 mg, 0.525 mmol) was dissolved in 10 mL of toluene by stirring the solution for 30 min. A solution of phenyllithium (59 mg, 0.63 mmol, 1.2 equiv) in 3 drops of THF followed by 5 mL of toluene was added dropwise to the iodide over a period of 15 min. The reaction was stirred for 7 h, at which point 0.3 equiv of phenyllithium (15 mg, 0.161 mmol) in 1 mL of toluene was added. The reaction was stirred for another 15 h. The solvents were removed in vacuo, and the residue was extracted with dichloromethane. The extract was filtered through Celite, and the dichloromethane was removed in vacuo to yield the crude product as an orange solid; yield 413 mg (87%). The crude product proved sufficiently pure for subsequent reactions. The product could be purified further by recrystallization from methylene chloride/pentane mixtures; yield 279 mg (59%): $^1\text{H NMR}$ (C_6D_6) δ -16.7 (br s, $\Delta\nu_{1/2} = 52$), NCH_2), -58.1 (br s, $\Delta\nu_{1/2} = 47$), NCH_2); $^{19}\text{F NMR}$ (toluene) δ 22.2 (br s, F_o), -120 (s, F_m), -139.6 (s, F_p).

$[\text{N}_3\text{N}_F]\text{W}(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (3c). $[\text{N}_3\text{N}_F]\text{WI}$ (985 mg, 1.03 mmol) was suspended in 20 mL of toluene, and a solution of 3,5-xylyllithium (139 mg, 1.24 mmol, 1.2 equiv in 5 drops of THF and 10 mL of toluene) was added dropwise. The reaction mixture was stirred for 2 h and then allowed to stand ~ 1 h, and the precipitated LiI was filtered off (74 mg). The toluene was removed in vacuo, and the residue was taken up in a

minimum amount of dichloromethane. The solution was allowed to stand for ~ 1 h and filtered through Celite to yield an additional 30 mg of LiI (78% of theory). The dichloromethane extract was layered with pentane, and the mixture was chilled to $-40\text{ }^{\circ}\text{C}$ for 15 h to give 590 mg of burgundy microcrystals. The volume was reduced in vacuo, and the process repeated to give a second crop (188 mg); total yield 778 mg (81%): $^1\text{H NMR}$ (C_6D_6) δ -16.5 (br s, $\Delta\nu_{1/2} = 64$, NCH_2), -53.9 (s, 3,5-dimethylphenyl), -59.0 (br s, $\Delta\nu_{1/2} = 54$, NCH_2); $^{19}\text{F NMR}$ (C_6D_6) δ 12.5 (br s, F_o), -120.2 (s, F_m), -136.0 (s, F_p); $\mu_{\text{eff}} = 3.0\text{ } \mu_{\text{B}}$ at $22\text{ }^{\circ}\text{C}$ (Evans method).

$[\text{N}_3\text{N}_F]\text{W}(\text{H}_3)$. A 300 mL glass bomb was charged with $[\text{N}_3\text{N}_F]\text{W}(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (400 mg, 0.430 mmol), a Teflon-coated stir bar, and 25 mL of toluene. The bomb was attached to a high-vacuum line and degassed using 3 freeze–pump–thaw cycles. It was then chilled to 77 K, and dihydrogen (640 mmHg, 39.9 mmol, 92 equiv) was introduced by vacuum transfer. The bomb was sealed, warmed to room temperature, and placed in a $40\text{ }^{\circ}\text{C}$ oil bath, and the reaction mixture was stirred for 15 h. The volatile components were removed under reduced pressure, and the crude product was recrystallized by layering a concentrated toluene solution with pentane and cooling to $-40\text{ }^{\circ}\text{C}$. The brown product was isolated in two crops; yield 214 mg (60%): $^1\text{H NMR}$ (C_6D_6) δ 11.1 (s, $^1J_{\text{HW}} = 25$, 3, WH_3 , T_1 ($22\text{ }^{\circ}\text{C}$) = 344(5) ms), 3.27 (t, 6, NCH_2), 2.28 (t, 6, NCH_2); $^{19}\text{F NMR}$ (C_6D_6) δ -152.6 (d, 6, F_o), -163.9 (t, 3, F_p), -165.7 (t, 6, F_m). Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{N}_4\text{F}_{15}\text{W}$: C, 34.80; H, 1.83; N, 6.76. Found: C, 34.48; H, 1.73; N, 6.42.

The trideuteride was prepared similarly, employing D_2 instead of H_2 .

$[\text{N}_3\text{N}_F]\text{W}(\text{O})(\text{C}_6\text{H}_5)$ (4a). Pyridine N-oxide (11 mg, 0.11 mmol) was added to a THF (5 mL) solution of $[\text{N}_3\text{N}_F]\text{WPh}$ (100 mg, 0.111 mmol). The reaction was stirred for 8 h, and the volatile components were removed in vacuo. The residue was recrystallized from DME layered with pentane at $-40\text{ }^{\circ}\text{C}$ to yield 69 mg of red crystals (68%) containing 1.5 equiv of dme, according to NMR data: $^1\text{H NMR}$ (CD_2Cl_2) δ 7.96 (d, 2, H_o), 7.20 (m, 3, H_m and H_p), 4.31 (t, 6, NCH_2N), 3.63 (s, 6, dme CH_2), 3.51 (t, 6, NCH_2N), 3.48 (s, 9, dme CH_3); $^{19}\text{F NMR}$ (CD_2Cl_2) δ -146.8 (s, 6, F_o), -163.7 (t, 3, F_p), -165.3 (t, 6, F_m).

$[\text{N}_3\text{N}_F]\text{W}(\text{O})(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (4b). $[\text{N}_3\text{N}_F]\text{W}(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ (150 mg, 0.161 mmol) was dissolved in 5 mL of dimethoxyethane. Pyridine N-oxide (15 mg, 0.16 mmol, 1 equiv) was added as a solid, and the reaction was stirred for 15 h. The solvent was removed in vacuo, and the red residue was recrystallized by layering a concentrated DME solution with pentane and cooling to $-40\text{ }^{\circ}\text{C}$ overnight. The red crystalline product was isolated by decantation of the mother liquor and drying in vacuo (95 mg, 62%): $^1\text{H NMR}$ (C_6D_6) δ 7.70 (s, 2, H_o), 6.72 (s, 1, H_p), 3.69 (t, 6, NCH_2), 2.58 (t, 6, NCH_2), 2.22 (s, 6, $\text{C}_6\text{H}_3\text{Me}_2$); $^{19}\text{F NMR}$ (dme) δ -146.8 (d, 6, F_o), -164.9 (t, 3, F_p), -166.7 (t, 6, F_m). Anal. Calcd for $\text{C}_{32}\text{H}_{21}\text{N}_4\text{F}_{15}\text{OW}$: C, 40.61; H, 2.24; N, 5.92. Found: C, 40.65; H, 2.09; N, 5.80.

$[\text{N}_3\text{N}_F]\text{Mo}(\text{CH}_2\text{CMe}_3)$. $[\text{N}_3\text{N}_F]\text{MoCl}$ (750 mg, 0.971 mmol) was added to 50 mL of toluene, and the slurry was stirred for ~ 45 min to dissolve the solid. Neopentylolithium (151 mg, 1.16 mmol, 1.2 equiv) was added as a solid to the toluene solution. The color changed instantly from orange to wine-red. After 30 min, $^{19}\text{F NMR}$ showed the reaction was complete. The toluene was removed under reduced pressure, the residue was extracted with methylene chloride, and the extract was filtered through Celite. The methylene chloride solution was reduced in volume, layered with pentane, and cooled to $-40\text{ }^{\circ}\text{C}$ to give 544 mg of product in two crops (70%): $^1\text{H NMR}$ (C_6D_6) δ 4.5 (br s, 9, $\text{C}(\text{CH}_3)_3$), -9.5 (br s, NCH_2), -66 (br s, NCH_2); $^{19}\text{F NMR}$ (C_6D_6) δ -47.3 (br s, 6, F_o), -120.7 (s, 6, F_m), -139.2 (s, 3, F_p). Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{N}_4\text{F}_{15}\text{Mo}$: C, 43.09; H, 2.87; N, 6.93. Found: C, 43.03; H, 3.16; N, 6.87.

$[\text{N}_3\text{N}_F]\text{Mo}(\text{CH}_2\text{SiMe}_3)$. $[\text{N}_3\text{N}_F]\text{MoCl}$ (153 mg, 0.198 mmol) was added to 10 mL of toluene, and the mixture was stirred for ~ 30 min. (Trimethylsilyl)methylolithium (22 mg, 0.24

mmol) was added as a solid. The color of the reaction changed instantly from orange to deep purple. The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane. The extract was filtered through Celite, and the volume was reduced in vacuo. The solution was layered with pentane and stored at $-40\text{ }^{\circ}\text{C}$ for 15 h. Red microcrystals were isolated by decantation of the mother liquor and dried under reduced pressure, yield 67 mg (41%): $^1\text{H NMR}$ (C_6D_6) δ 3.54 (s, $\text{Si}(\text{CH}_3)_3$), -11 (br s, NCH_2), -67 (br s, NCH_2); $^{19}\text{F NMR}$ (C_6D_6) δ -47.8 (br s, 6, F_o), -121.9 (s, 6, F_m), -140.1 (s, 3, F_p). Anal. Calcd for $\text{C}_{28}\text{H}_{23}\text{N}_4\text{F}_{15}\text{SiMo}$: C, 40.79; H, 2.81; N, 6.80. Found: C, 40.39; H, 2.99; N, 6.46.

$[\text{N}_3\text{N}_F]\text{Mo}\equiv\text{CCMe}_3$. A solution of $[\text{N}_3\text{N}_F]\text{Mo}(\text{CH}_2\text{CMe}_3)$ (300 mg, 0.373 mmol) in 10 mL of toluene was heated at $110\text{ }^{\circ}\text{C}$ for 24 h, at which point $^{19}\text{F NMR}$ indicated the reaction was complete. The reaction mixture was cooled to $-40\text{ }^{\circ}\text{C}$ for 15 h to yield 204 mg of product (68% yield): $^1\text{H NMR}$ (C_6D_6) δ 3.26 (t, 6, NCH_2), 2.05 (t, 6, NCH_2), 0.074 (s, 9, CMe_3); $^{19}\text{F NMR}$ (toluene) δ -150.0 (d, 6, F_o), -164.9 (t, 3, F_p), -165.2 (t, 6, F_m); $^{13}\text{C NMR}$ (CD_2Cl_2) δ 27.3 (CMe_3), 52.3 (NCH_2N), 58.0 (NCH_2N), 137, 139, 142, 144 (C_6F_5), 312.9 ($\text{Mo}\equiv\text{C}$).

$[\text{N}_3\text{N}_F]\text{W}(\mathbf{3,5}\text{-Me}_2\text{C}_6\text{H}_3)(\text{NSiMe}_3)$ (5). Trimethylsilyl azide (14 μL , 0.11 mmol) was added to a stirred solution of $[\text{N}_3\text{N}_F]\text{W}(\mathbf{3,5}\text{-Me}_2\text{C}_6\text{H}_3)$ (100 mg, 0.108 mmol) in 5 mL of THF. The color changed instantly from red to light orange. Stirring was continued for 4 h, and the THF was removed under reduced pressure. The orange residue was recrystallized from a mixture of dichloromethane and pentane at $-40\text{ }^{\circ}\text{C}$ to yield orange plates after 15 h; 75 mg was collected in two crops (69% yield): $^1\text{H NMR}$ (C_6D_6) δ 7.91 (s, 2, H_o), 6.98 (s, 1, H_p), 3.9, 3.6, 3.4, 2.8 (br s, diastereotopic NCH_2), 2.43 (s, 6, $\mathbf{3,5}\text{-Me}_2\text{C}_6\text{H}_3$), 2.34 (br s, diastereotopic NCH_2), -0.40 (s, 9, TMS); $^{19}\text{F NMR}$ (C_6D_6) δ -143.8 (s, 4, F_o), -148.4 (d, 2, F_o), -164.6 (t, 4, F_m), -165.0 (t, 2, F_p), -165.7 (t, 2, F_m), -166.5 (t, 1, F_p). Anal. Calcd for $\text{C}_{35}\text{H}_{30}\text{N}_5\text{F}_{15}\text{SiW}$: C, 41.31; H, 2.97; N, 6.88. Found: C, 41.45; H, 3.18; N, 6.56.

X-ray Structure of $[\text{N}_3\text{N}_F]\text{W}(\mathbf{O}\text{-}\mathbf{3,5}\text{-Me}_2\text{C}_6\text{H}_3)$. A purple needle was mounted in oil and placed in a cold stream of nitrogen attached to a Siemens SMART/CCD diffractometer. Unit cell dimensions were obtained from more than 25 reflections that were harvested from three sets of 5° frames scanned about ω . Integration of greater than one-half of a hemisphere of data using the SAINT program revealed monoclinic Laue symmetry consistent with the unit cell dimensions. Systematic absences indicated $P2_1/c$ as the space group. Solution (Patterson) and refinement of the structure was performed with ShelXTL set of programs. Crystallographic details are provided in Table 1, and selected interatomic distances and

angles are given in Table 2. Although the residual electron density is large, it is located in close proximity to the tungsten atom.

X-ray Structure of $[\text{N}_3\text{N}_F]\text{W}\equiv\text{CSiMe}_3$. Crystallographic data are located in Table 1, and selected bond lengths and angles are given in Table 2. Full tables of atomic coordinates and bond lengths and angles are available as Supporting Information. Suitable crystals were grown from THF layered with hexamethyldisiloxane at $-40\text{ }^{\circ}\text{C}$. A crystal was attached to a glass fiber and transferred to a Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $13.50^{\circ} < 2\theta < 21.00^{\circ}$, corresponded to a monoclinic cell with the dimensions given in Table 1. On the basis of the systematic absences of $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (No. 14).

X-ray Structure of $[\text{N}_3\text{N}_F]\text{W}(\mathbf{O})(\mathbf{3,5}\text{-Me}_2\text{C}_6\text{H}_3)$. A red prismatic crystal was mounted in oil and placed in a cold stream of nitrogen attached to a Siemens SMART/CCD diffractometer. Unit cell dimensions were obtained from more than 25 reflections that were harvested from three sets of 5° frames scanned about ω . Integration of greater than one-half of a hemisphere of data using the SAINT program revealed monoclinic Laue symmetry and a C -centered lattice consistent with the unit cell dimensions. Systematic absences indicated $C2/c$ as the space group, but upon inspection of the β angle, the nonstandard setting of $I2/a$ was chosen. Solution (Patterson) and refinement of the structure was performed with the ShelXTL set of programs. Crystallographic details are provided in Table 1, and selected interatomic distances and angles are given in Table 3.

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Supporting Information Available: Labeled ORTEP drawing and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $[\text{N}_3\text{N}_F]\text{W}(\mathbf{O}\text{-}\mathbf{3,5}\text{-Me}_2\text{C}_6\text{H}_3)$, $[\text{N}_3\text{N}_F]\text{W}\equiv\text{CSiMe}_3$, and $[\text{N}_3\text{N}_F]\text{W}(\mathbf{O})(\mathbf{3,5}\text{-Me}_2\text{C}_6\text{H}_3)$ (26 pages). Ordering information is given on any current masthead page. OM970966S