Generation and Reactivity of Cp*W(NO)(CH₂SiMe₃)H, a 16-Valence-Electron Alkyl Hydride Complex

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Treatment of solutions of $Cp^*W(NO)(CH_2SiMe_3)_2$ with H_2 generates in situ the reactive 16-valence-electron alkyl hydride $Cp^*W(NO)(CH_2SiMe_3)H$, formed by hydrogenolysis of one of the W-C σ -bonds of the dialkyl reactant. The Lewis-acidic hydride complex has not yet been isolated, but its existence has been inferred on the basis of the varied chemical reactions that it undergoes when generated in the presence of reactive substrates. PPh₃ affords the

orthometalated complex $Cp^*W(NO)(H)(PPh_2C_6H_4)$ as a yellow crystalline solid probably via the 18-electron adduct $Cp^*W(NO)(CH_2SiMe_3)(PPh_3)H$. Consistently, the same reaction effected with PPh_3-d_{15} results in complete deuteration of the hydride position in the product. Acyclic, conjugated dienes such as butadiene or 2,3-dimethyl-1,3-butadiene afford Cp^*W - $(NO)(\eta^4$ -trans-diene) complexes. The characteristic chemistry of $Cp^*W(NO)(CH_2SiMe_3)H$ is, however, dominated by the ability of its W-H link to insert unsaturated linkages, the regioselectivity of the insertions indicating that the hydride ligand is hydridic in nature. For instance, insertion of acetonitrile affords the ethylideneamido complex $Cp^*W(NO)(CH_2-SiMe_3)(N=CHMe)$, which is isolable as a diastereomeric pair. Similarly, insertions of organic reagents containing carbonyl (O=C) or imine (HN=C) functional groups produce the corresponding alkyl alkoxide or alkyl amide products, respectively, in virtually quantitative yields. Phenylacetylene affords the novel alkyl alkenyl compound $Cp^*W(NO)(CH_2SiMe_3)-(CPh=CH_2)$, which is thermally unstable and isolable in only low yields. Insertions into the W-H bond by other olefinic substrates are successful only if the unsaturated hydrocarbon also contains a Lewis-base functional group. Thus, propargylamine and allylamine

produce the related metallacyclic complexes Cp*W(NO)(CH₂SiMe₃)(NH₂CH₂CHCH) and

 $Cp*W(NO)(CH_2SiMe_3)(NH_2CH_2CH_2CH_2)$, respectively. Treatment of $Cp*W(NO)(CH_2SiMe_3)_2$ with H_2 in the presence of allyl alcohol does not produce an oxometallacycle, but rather affords the allylalkoxo complex resulting from the alcohol simply functioning as a protonic acid toward the dialkyl reactant. The solid-state molecular structures of $Cp*W(NO)(CH_2-CH_2)$

SiMe₃)(N=CHMe) and Cp*W(NO)(CH₂SiMe₃)(NH₂CH₂CH₂CH₂CH₂) have been established by single-crystal X-ray crystallographic analyses. Crystals of Cp*W(NO)(CH₂SiMe₃)(N=CHMe) are monoclinic of space group $P2_1/n$: a = 9.515(2) Å; b = 21.946(3) Å; c = 9.552(2) Å; Z = 4; V = 1946.8 Å³; T = 200 K; $R_f = 0.029$ for 2035 data ($I_0 \ge 2.5\sigma(I_0)$) and 106 variables. Crystals

of Cp* $\dot{W}(NO)(CH_2SiMe_3)(NH_2CH_2CH_2\dot{C}H_2)$ are orthorhombic of space group $P2_12_12_1$: a = 11.417(4) Å; b = 13.178(2) Å; c = 13.804(4) Å; Z = 4; V = 2076.9 Å³; T = 200 K; $R_f = 0.020$ for 2420 data $(I_0 \ge 2.5\sigma(I_0))$ and 208 variables.

Introduction

Current interest in the synthesis, characterization, and properties of organotransition-metal hydride complexes continues unabated, primarily because many important stoichiometric and catalytic chemical conversions have been demonstrated to involve metalhydrogen linkages at key stages.¹ In particular, M-H bonds play an important role in organometallic chemistry because many can insert a variety of unsaturated substrates.² In this regard, however, relatively little is known presently about the physical and chemical properties of such linkages in organometallic nitrosyl complexes.³ Consequently, we have been endeavoring for some time to develop new synthetic routes leading to such compounds.

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Our early efforts in this area involved the preparation of several hydrido nitrosyl complexes of tungsten containing the CpW(NO) [Cp = η^5 -C₅H₅] fragment by treatment of appropriate halide precursors with maingroup hydride reagents.⁴ More recently, our investigations have centered on the synthesis of hydride compounds via hydrogenation of alkyl complexes. For example, we have discovered that reaction of the dialkyl species $Cp^*W(NO)(CH_2SiMe_3)_2$ [$Cp^* = \eta^5 \cdot C_5Me_5$] with dihydrogen affords the bimetallic hydride and alkyl hydride complexes [Cp*W(NO)(H)]₂[*u*-H]₂ and [Cp*W- $(NO)(CH_2SiMe_3)](\mu-H)_2[Cp*W(NO)(H)].^5$ More importantly, however, we have found that when the hydrogenation of $Cp'W(NO)(CH_2SiMe_3)_2$ [Cp' = Cp or Cp^*] is performed in the presence of a Lewis base (L) such as a small phosphine or phosphite, the 18-valence-electron adducts, $Cp'W(NO)(CH_2SiMe_3)(L)H [L = PMe_3, P(OPh)_3,$ PMePh₂], can be isolated in good yields.⁵ These alkyl hydride adducts exhibit some interesting thermal chemistry in their own right. For example, Cp*W(NO)(CH₂-SiMe₃)(PMe₃)H undergoes reductive elimination of SiMe₄ upon heating. When this thermolysis is performed in benzene, subsequent activation of the solvent results in the formation of the aryl hydrido complex Cp*W(NO)- $(Ph)(PMe_3)H$. The phosphite analogue, $CpW(NO)(CH_2-$ SiMe₃)[P(OPh)₃]H, similarly liberates SiMe₄ when heated and then orthometalates one of the phenyl groups on the phosphite ligand to produce $CpW(NO)[P(OPh)_2-$

the phosphite ligand to produce $CpW(NO)[P(OPh)_2$

 OC_6H_4]H as the final product.

The isolation of the original Cp'W(NO)(CH₂SiMe₃)-(L)H adducts suggests that the 16-valence-electron alkyl hydride compounds, Cp'W(NO)(CH₂SiMe₃)H, are the initial species formed by treatment of the Cp'W(NO)(CH₂-SiMe₃)₂ precursors with H₂. By analogy to their dialkyl precursors, the Cp'W(NO)(CH₂SiMe₃)H compounds are expected to possess a metal-centered LUMO lying between the hydride and the alkyl ligands and trans to the nitrosyl ligand as shown below.⁶



This LUMO renders these 16-valence-electron complexes Lewis acidic and is the site of attack by Lewis bases. Consistent with this view is the fact that all of the Cp'W(NO)(CH₂SiMe₃)(L)H adducts isolated to date possess the expected four-legged piano-stool molecular structures with the L and the NO groups occupying mutually trans positions. We therefore decided to investigate the reactions of the Cp'W(NO)(CH₂SiMe₃)H intermediates with other Lewis bases, particularly those that might be capable of effecting insertion of L into W-H bonds of the Cp'W(NO)(CH₂SiMe₃)(L)H adducts since these adducts possess the requisite cis orientation of the L and H ligands. The trans orientation of the alkyl and hydride ligands in these adducts also renders them stable with respect to reductive elimination of alkane. In this paper we report the results of our detailed studies in this regard with the pentamethyl-cyclopentadienyl complex $Cp*W(NO)(CH_2SiMe_3)H$. Portions of this work have been communicated previously.^{7,8}

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions using an atmosphere of dinitrogen or argon. General procedures routinely employed in these laboratories have been described in detail previously.⁹ The requisite organometallic reagents, Cp*W-(NO)Cl2¹⁰ and Cp*W(NO)(CH2SiMe3)2,¹¹ were prepared by established procedures. Phenylacetylene (MCB) was passed through a short column of activated alumina before use, benzaldehyde (Fisher) was dried over P_2O_5 and filtered through Celite, PPh₃ (Strem) was recrystallized from hexanes, 2,3-dimethyl-1,3-butadiene (Aldrich) was dried over molecular sieves, allylamine (Aldrich) was dried over Na₂CO₃ and vacuum-transferred, and allyl alcohol (Aldrich) was likewise dried over K₂CO₃ and vacuum-transferred. Dihydrogen (Linde, extra dry), butadiene (Matheson), PPh_3-d_{15} , propargylamine, 4-phenyl-3-penten-2-one, and benzophenoneimine (Aldrich) were all used as received.

Preparation of Cp*W(NO)(PPh₂C₆H₄)H (1). Cp*W-(NO)(CH₂SiMe₃)₂ (0.48 g, 0.92 mmol) and PPh₃ (0.29 g, 1.1 mmol) were combined in a large thick-walled bomb equipped with a Kontes stopcock (500 mL capacity) and then dissolved in pentane (30 mL). The vessel was then charged with H₂ (18 psig), and the solution was stirred for 5 h, during which time the product was deposited as a yellow precipitate and the originally purple solution became red-brown in color. Approximately half of the solvent was then removed under vacuum, and the precipitate was allowed to settle to the bottom of the vessel. The supernatant solution was removed via a cannula, and the remaining solid was washed with pentane (20 mL). The powder that remained was recrystallized from Et₂O at -15 °C to obtain bright yellow crystals of the product (0.24 g from three fractions, 43% yield).

Anal. Calcd for $C_{28}H_{30}$ NOPW: C, 55.18; H, 5.02; N, 2.24. Found: C, 55.00; H, 4.95; N, 2.29. IR (Nujol) ν_{N0} 1545 cm⁻¹, ν_{WH} 1929 cm⁻¹; ¹H NMR (C_6D_6) δ 8.09 (d, ³J_{HH} = 8.0 Hz, 1 H, H_{aryl}), 7.95 (m, 2 H, H_{aryl}), 7.55 (m, 3 H, H_{aryl}), 7.20 (m, 4 H, H_{aryl}), 6.95 (m, 4 H, H_{aryl}), 3.99 (d, ²J_{PH} = 10.2 Hz, ²J_{WH} = 101 Hz, 1 H, WH), 1.79 (s, 15 H, C_5Me_5); ¹³C{¹H} NMR (C_6D_6) δ 171.75 (d, J_{CP} = 5.1 Hz, C_{ortho}), 149.23 (d, J_{CP} = 54.6 Hz, C_{ipso}), 1.44 (d, J_{CP} = 33.7 Hz, C_{ipso}), 134.3, 134.2, 133.4, 133.3, 132.2, 132.2, 130.7, 130.7, 129.9, 129.9, 128.9, 128.9, 128.8, 128.8, 128.7, 128.6, 129.5, 128.4 (C_{aryl}), 127.4 (d, J_{CP} = 9 Hz, Caryl), 105.5 (C_5Me_5), 10.8 (C_5Me_5); ³¹P{¹H} NMR (C_6D_6) δ 49.21; lowresolution mass spectrum (probe temperature 150 °C); m/z611 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO) $(\eta^4$ -diene) Complexes 2 and 3. Both of these complexes were prepared in an identical manner, except that 1 equiv of 2,3-dimethyl-1,3-butadiene was weighed into the reaction vessel during the synthesis of complex 3, whereas butadiene was condensed in excess into

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the vessel during the synthesis of 2. The preparation of the butadiene complex, 2, is described as a representative example.

Cp*W(NO)(CH₂SiMe₃)₂ (0.40 g, 0.76 mmol) was placed in a 300-mL thick-walled bomb. The vessel was evacuated and then refilled with butadiene gas (1 atm). The bomb was then cooled to -178 °C to condense the butadiene gas. Pentane (60 mL) was added slowly so that it froze on the sides of the vessel as it was added. The atmosphere was again removed under vacuum and was replaced with H₂ (15 psig). The vessel was warmed to room temperature, and the solution was stirred overnight. The solvent was removed in vacuo from the final yellow solution to obtain an orange powder which was washed with cold pentane (2 × 10 mL). The remaining powder was recrystallized from hexanes at -30 °C to obtain yellow crystals of 2 (0.17 g, 32% yield) which were isolated by removing the supernatant solution by cannulation. Complex **3** was also isolated as yellow crystals in a similar manner in 31% yield.

Anal. Calcd for $C_{14}H_{21}NOW$ (2): C, 41.70; H, 5.25; N, 3.47. Found: C, 41.73; H, 5.43; N, 3.48. IR (Nujol) ν_{NO} 1563 cm⁻¹; ¹H NMR (C_6D_6) δ 3.56 (m, 1 H, CH), 3.37 (dd, J = 5.4, 4.2 Hz, 1 H, CH), 2.95 (dd, J = 13.8, 3.6 Hz, 1 H, CH), 2.40 (dd, J = 6.3, 3.6 Hz, 1 H, CH), 1.63 (s, 15 H, C_5Me_5), 1.29 (m, 1 H, CH), 1.00 (dd, J = 12.0, 4.2 Hz, 1H, CH); ¹³C{¹H} NMR (C_6D_6) δ 104.20 (C_5Me_5), 91.8 (CH), 85.0 (CH), 54.3 (CH₂), 51.5 (CH₂), 10.4 (C_5Me_5); low-resolution mass spectrum (probe temperature 150 °C), m/z 403 [P⁺, ¹⁸⁴W].

Anal. Calcd for $C_{16}H_{25}NOW$ (3): C, 44.56; H, 5.84; N, 3.25. Found: C, 44.83; H, 5.89; N, 3.14. IR (Nujol) ν_{NO} 1574 cm⁻¹; ¹H NMR (C_6D_6) δ 3.35 (dd, J = 4.5, 0.9 Hz, 1 H, CH), 3.25 (d, J = 3.6 Hz, 1 H, CH), 2.49 (dd, J = 3.6, 1.2 Hz, 1 H, CH), 2.41 (br, 1 H, CH), 2.15 (s, 3 H, Me), 1.71 (s, 15 H, C_5Me_5), 1.20 (s, 3 H, Me); ¹³C{¹H} NMR (C_6D_6) δ 104.6 (C_5Me_5), 103.45 (=CH₂), 95.5 (=CH₂), 54.3 (CH₂), 52.3 (CH₂), 21.92 (Me), 21.7 (CH₃), 10.6 (C_5Me_5); low-resolution mass spectrum (probe temperature 180 °C), m/z 431 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO)(CH₂SiMe₃)(N=CHMe) (4). Purple Cp*W(NO)(CH₂SiMe₃)₂ (1.9 g, 3.6 mmol) was dissolved in acetonitrile (30 mL), and the solution was transferred to a 500-mL Fisher-Porter vessel. The atmosphere in the vessel was replaced with H₂ (12 psig), and the solution was stirred overnight at room temperature. The final red-orange solution was taken to dryness in vacuo, and the residue was washed with cold pentane (3 × 10 mL). The remaining yellow powder was recrystallized from hexanes at -30 °C to obtain yellow crystals (1.3 g, 78% yield) of analytically pure 4.

Anal. Calcd for $C_{16}H_{30}SiN_2OW$: C, 40.17; H, 6.32; N, 5.86. Found: C, 40.50; H, 6.34; N, 5.99. IR (Nujol) ν_{NO} 1615 cm⁻¹, ν_{CN} 1652 cm⁻¹; ¹H NMR (C_6D_6), diastereomer 1 δ 7.20 (m, 1 H, CH), 1.71 (s, 15 H, C_5Me_5), 1.45 (d, ${}^3J_{HH} = 5.4$ Hz, 3 H, N=CHMe), 0.43 (s, 9 H, SiMe_3), 0.10 (m, 2 H, CH₂), diastereomer 2 δ 6.48 (m, 1 H, CH), 1.66 (s, 15 H, C_5Me_5), 1.62 (d, ${}^3J_{HH} = 5.5$ Hz, 3 H, N=CHMe), 0.50 (s, 9 H, SiMe_3), 0.25 (m, 2 H, CH₂); ${}^{13}C{}^{1}H{}$ NMR (C_6D_6), diastereomer 1 δ 158.77 (N=CHMe), 109.55 (C_5Me_5), 21.57 (Me), 19.05 (CH₂), 10.00 (C_5Me_5), 2.85 (SiMe_3), diastereomer 2 δ 158.35 (N=CHMe), 109.00 (C_5Me_5), 20.76 (Me), 19.15 (CH₂), 9.54 (C_5Me_5), 3.10 (SiMe₃); low-resolution mass spectrum (probe temperature 150 °C), m/z 478 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO)(CH₂SiMe₃)(OCHMe₂) (5). Cp*W(NO)(CH₂SiMe₃)₂ (0.38 g, 0.72 mmol), acetone (0.5 mL, 7 mmol), and hexanes (10 mL) were placed in a thick-walled bomb (300 mL). The vessel was then charged with H₂ (~18 psig), and the reaction mixture was stirred for 5 h at ambient temperature. After this time, the solvent was removed under vacuum to leave a red powder. The powder was recrystallized from a minimum amount of pentane at -30 °C to obtain 5 as deep red crystals, which were isolated by removing the mother liquor via a cannula. A second crop of crystals was obtained from the supernatant solution by further concentration and cooling (total of 0.28 g, 79% yield).

Anal. Calcd for $C_{17}H_{33}NO_2SiW$: C, 40.58; H, 6.52; N, 2.48. Found: C, 41.21; H, 6.71; N, 2.83. IR (Nujol) 1568, 1541 cm⁻¹; ¹H NMR (C₆D₆) δ 5.22 (sept, ³J_{HH} = 6.3 Hz, 1 H, OCHMe₂), 1.61 (s, 15 H, C₅Me₅), 1.27 (d, ³J_{HH} = 6 Hz, 3 H, Me), 1.21 (d, ³J_{HH} = 6 Hz, 3 H, Me), 0.73 (d, ²J_{HH} = 12 Hz, 1 H, CH₂), 0.52 (d, ²J_{HH} = 12 Hz, 1 H, CH₂), 0.35 (s, 9 H, SiMe₃); ¹³C{¹H} NMR (C₆D₆) δ 111.8 (C₅Me₅), 82.3 (OCHMe₂), 31.9 (J_{WC} = 109 Hz, CH₂), 27.9, 26.5 (Me), 9.8 (C₅Me₅), 2.4 (SiMe₃); low-resolution mass spectrum (probe temperature 180 °C), m/z 495 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO)(CH₂SiMe₃)(OCH₂Ph) (6). Cp*W(NO)(CH₂SiMe₃)₂ (0.32 g, 0.61 mmol) was dissolved in hexanes (15 mL) in a thick-walled bomb. Benzaldehyde (0.06 g, 0.65 mmol) was added, and the atmosphere in the bomb was replaced with H₂ (~18 psig). The reaction mixture was stirred for 16 h, during which time its color changed from purple to deep orange. The solvent was removed in vacuo to leave a red-orange powder which was recrystallized in two crops from pentane at -30 °C to obtain red crystals (0.28 g total, 83% yield) of **6**.

Anal. Calcd for $C_{21}H_{33}NO_2SiW$: C, 46.38; H, 6.15; N, 2.40. Found: C, 46.41; H, 6.12; N, 2.58. IR (Nujol) $\nu_{NO} = 1545 \text{ cm}^{-1}$; ¹H NMR (C_6D_6) δ 7.41 (d, ³J_{HH} = 6.9 Hz, 2 H, H_{ortho}), 7.1 (m, 3 H, H_{aryl}), 5.97 (d, ²J_{HH} = 10.8 Hz, 1 H, OCH₂), 5.88 (d, ²J_{HH} = 10.8 Hz, 1 H, OCH₂), 1.44 (s, 15 H, C_5Me_5), 0.82 (s, 2 H, CH₂), 0.36 (s, 9 H, SiMe₃); ¹³C{¹H} NMR (C_6D_6) δ 141.7 (C_{ipso}), 129.6, 128.6, 128.0 (C_{aryl}), 111.9 (C_5Me_5), 85.5 (OCH₂), 35.1 (¹J_{WC} = 119 Hz, SiCH₂), 9.5 (C_5Me_5), 2.3 (SiMe₃); low-resolution mass spectrum (probe temperature 120 °C), m/z 543 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO)(CH₂SiMe₃)(OCHMeCH= CHPh) (7). Cp*W(NO)(CH₂SiMe₃)₂ (0.09 g, 0.17 mmol) was dissolved in hexanes (10 mL) in a small, thick-walled bomb. 4-Phenyl-3-buten-2-one (0.025 g, 0.17 mmol) was added, and the vessel was charged with H₂ (18 psig). After being stirred for 5 h, the solvent was removed in vacuo from the final reaction solution, which had developed a deep red color. The red residue was recrystallized in two crops from a minimum amount of pentane at -30 °C to obtain 7 as analytically pure red crystals (0.80 g total, 80% yield).

Anal. Calcd for C₂₄H₃₇NO₂SiW: C, 49.43; H, 6.45; N, 2.32. Found: C, 49.40; H, 6.39; N, 2.40. IR (Nujol) $\nu_{NO} = 1549 \text{ cm}^{-1}$; ¹H NMR (C₆D₆), major isomers δ 7.4 (m, 5 H, H_{aryl}), 6.68 (d, ${}^{3}J_{\rm HH} = 15.6$ Hz, 1 H, PhCHCH), 6.25 (dd, $J_{\rm HH} = 8.1$, 15.6 Hz, 1 H, PhCHCH), 5.64 (m, 1 H, OCH), 1.86 (s, 15 H, C₅Me₅), 1.44 (d, $J_{\text{HH}} = 6.3$ Hz, 3 H, Me), 0.84 (d, ${}^{2}J_{\text{HH}} = 11.7$ Hz, 1 H, CH_AH_B), 0.70 (d, ${}^2J_{HH} = 11.7$ Hz, 1 H, CH_AH_B), 0.11 (s, 9 H, Si Me_3), minor isomers 7.4 (m, 5 H, H_{aryl}), 6.48 (d, ${}^2J_{HH} = 15.6$ Hz, 1 H, PhCHCH), 6.23 (dd, $J_{\rm HH} = 6.3$, 15.6 Hz, 1 H, PhCHCH), 5.64 (m, 1 H, OCH), 1.95 (s, 15 H, C₅Me₅), 1.50 (d, ${}^{3}J_{\rm HH} = 6.3$ Hz, 3 H, Me), 0.81 (d, ${}^{2}J_{\rm HH} = 12.0$ Hz, 1 H, CH_AH_B), 0.66 (d, ${}^{2}J_{HH} = 12.0$ Hz, 1 H, CH_AH_B), 0.06 (s, 9 H, SiMe₃); ¹³C{¹H} NMR (C₆D₆) (all isomers) δ 137.0, 136.8 (PhCHCH), 134.2, 134.03 (PhCHCH), 131.2, 129.3, 128.7, 128.5, 127.7, 127.6, 126.7, 126.6 (C_{aryl}), 112.63, 112.5 (C_5Me_5), 87.9, 86.4 (OC), 35.2, 35.2 (CH₂), 26.7, 24.4 (Me), 10.1, 10.0 (C₅Me₅), 2.0, 1.91 (SiMe₃); low-resolution mass spectrum (probe temperature 150 °C), m/z 583 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO)(CH₂SiMe₃)(NHCHPh₂) (8). Cp*W(NO)(CH₂SiMe₃)₂ (0.28 g, 0.53 mmol) and benzophenoneimine (0.10 g, 0.55 mmol) were dissolved in hexanes (10 mL) contained in a thick-walled bomb which was then charged with H₂ (18 psig). After the mixture had been stirred for 8 h, the solvent was removed under vacuum to obtain a yellow solid. This solid was recrystallized from CH₂Cl₂/hexanes to obtain analytically pure product (0.16 g, 49% yield).

Anal. Calcd for $C_{27}H_{38}N_2OSiW$: C, 52.18; H, 6.24; N, 4.47. Found: C, 52.43; H, 6.19; N, 4.53. IR (Nujol) ν_{NO} 1514 cm⁻¹, ν_{NH} 3249 cm⁻¹; ¹H NMR (C₆D₆) δ 7.75 (br, 1 H, NH), 7.6 (m, 6 H, H_{aryl}), 7.4 (m, 4 H, H_{aryl}), 6.72 (d, J_{HH} = 11.4 Hz, 1 H, CPh₂H), 1.71 (s, 15 H, C₅Me₅), -0.030 (d, J_{HH} = 2.7 Hz, 2 H, CH₂), -0.085 (s, 9 H, SiMe₃); ¹³C{¹H} NMR (C₆D₆) δ 146.3, 143.3 (C_{ipso}), 128.8, 128.1, 128.0 (C_{aryl}), 126.9, 126.6, 126.5 (C_{aryl}), 78.9 ($C_{5}Me_{5}$), 24.7 (¹ J_{WC} = 104 Hz, CH₂), 9.7 (C₅Me₅), 2.0 (Si Me_3); low-resolution mass spectrum (probe temperature 120 °C), m/z 618 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO)(CH₂SiMe₃)(CPh=CH₂) (9). Cp*W(NO)(CH₂SiMe₃)₂ (0.50 g, 0.95 mmol) and phenylacetylene (0.15 g, 1.5 mmol) were dissolved in hexanes (30 mL), and the solution was transferred to a 300-mL thick-walled bomb. H₂ (18 psig) was introduced into the vessel, and the mixture was stirred for 5 h, whereupon it turned a dark brown color. The solvent was then removed under vacuum, the residue was dissolved in Et₂O (3 mL), and the solution was placed on the top of a chromatography column (Florisil, 10 × 2 cm) made up in hexanes. Elution of the column with Et₂O/ hexanes (1:2) developed first a yellow band, which was eluted, and then a red band, which was collected. The red eluate was taken to dryness in vacuo, and the residue was recrystallized from pentanes at -30 °C to obtain a small amount of complex **9** as red crystals.

Anal. Calcd for $C_{22}H_{33}$ NOSiW: C, 49.30; H, 6.29; N, 2.52. Found: C, 48.98; H, 6.17; N, 2.60. IR (Nujol) ν_{NO} 1539 cm⁻¹; ¹H NMR (C_6D_6) δ 7.87 (dd, $J_{HH} = 8.0, 1.2$ Hz, 2 H, H_{ortho}), 7.29 (t, $J_{HH} = 8.0, 2$ H, H_{meta}), 7.11 (t, $J_{HH} = 8.0, 1$ H, H_{para}), 3.88 (dd, $J_{HH} = 5.4, 1.4$ Hz, 1 H, C=CH_AH_B), 3.56 (dd, $J_{HH} = 5.4, 1.1$ Hz, 1 H, C=CH_AH_B), 1.50 (s, 15 H, C_5Me_5), 0.692 (d, $J_{HH} =$ 12.6 Hz, 1 H, CH_AH_B), 0.214 (d, $J_{HH} = 12.6$ Hz, 1 H, CH_AH_B); ¹³C{¹H} NMR (C_6D_6) δ 227.9 (WCPh=CH₂), 145.3 (C_{ipso}), 137.44 (C_{ortho}), 129.6, 128.8 (C_{aryl}), 109.6 (C_5Me_5), 83.1 (WCPh=CH₂), 35.5 (¹ $J_{WC} = 90.1$ Hz, WCH₂), 9.5 (C_5Me_5), 3.4 (SiMe₃); lowresolution mass spectrum (probe temperature 120 °C), m/z539 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO)(CH₂SiMe₃)(NH₂CH₂CH₂CH₂) (10). Cp*W(NO)(CH₂SiMe₃)₂ (0.524 g, 1.00 mmol) was placed in a 100-mL-capacity thick-walled bomb, and hexanes (20 mL) were added. An excess of allylamine was vacuum-transferred into the bomb. The bomb was then charged with H₂ (18 psig), and the reaction mixture was stirred at room temperature. After 6 h, the initially purple solution had become reddishbrown and a finely divided precipitate had appeared. The brown supernatant solution was removed by cannula, and the remaining yellow solid was washed with cold hexanes (2 × 10 mL) and dried under vacuum to obtain a yellow powder (0.231 g, 0.467 mmol). Recrystallization of this powder from CH₂-Cl₂/hexanes in two crops afforded pure crystals of 10 in the form of yellow cubes (0.18 g total, 37% yield).

Anal. Calcd for $C_{17}H_{34}N_2OSiW$: C, 41.30; H, 6.92; N, 5.67. Found: C, 41.34; H, 6.80; N, 5.54. IR (Nujol) ν_{NO} 1497 cm⁻¹; ¹H NMR (CDCl₃) δ 3.18 (br s, 2 H, NH₂CH₂CH₂CH₂W), 2.73 (m, 1 H, NH₂CH₄H_BCH₂CH₂W), 2.46 (m, 1 H, NH₂CH₄H_BCH₂-CH₂W), 1.96 (m, 1 H, NH₂CH₂CH₄H_BCH₂W), 1.83 (m, 1 H, NH₂CH₂CH₄H_BCH₂W), 1.78 (s, 15 H, C₅Me₅), 1.58 (m, 1 H, NH₂CH₂CH₄H_BW), 0.77 (m, 1 H, NH₂CH₂CH₂CH₄H_BW), 0.38 (s, 9 H, CH₂SiMe₃), -0.78 (d, ²J_{HH} = 15 Hz, 1 H, CH₄H_B-SiMe₃), -1.39 (d, ²J_{HH} = 15 Hz, 1 H, CH₄H_BSiMe₃); ¹³C{¹H} NMR (CDCl₃) δ 102.9 (C₅Me₅), 43.9, 31.4, 30.5 (NH₂CH₂-CH₂CH₂W), 10.3 (C₅Me₅), 5.9 (CH₂SiMe₃), -0.9 (CH₂SiMe₃); low-resolution mass spectrum (probe temperature 180 °C), m/z 494 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO)(CH₂SiMe₃)(NH₂CH₂CH₋CH) (11). Cp*W(NO)(CH₂SiMe₃)₂ (0.262 g, 0.500 mmol) and hexanes (30 mL) were placed in a 100-mL thick-walled bomb, an excess of propargylamine in hexanes (10 mL) was added, and the bomb was pressurized with H₂ (18 psig). After being stirred for 8 h, the reaction mixture consisted of an orange precipitate and a brown supernatant solution. The orange solid was isolated by cannulation, washed with cold hexanes (2 × 10 mL), and dried under vacuum to obtain an orange powder (0.167 g). Recrystallization of this powder from CH₂-Cl₂/hexanes afforded analytically pure crystals of 11 in the form of orange cubes (0.10 g, 42% yield).

Anal. Calcd for $C_{17}H_{32}N_2OSiW$: C, 41.47; H, 6.86; N, 5.69. Found: C, 41.51; H, 6.89; N, 5.70. IR (Nujol) $\nu_{NO} = 1501 \text{ cm}^{-1}$; ¹H NMR (CDCl₃) δ 7.23 (d, ²J_{HH} = 18 Hz, 1 H, NH_AH_B), 6.47 (d, ${}^{2}J_{\rm HH} = 18$ Hz, 1 H, NH_AH_B), 3.48 (m, 3 H, NH₂CH_A-H_BCH=CH), 2.39 (m, 1 H, NH₂CH₂CH=CH), 1.80 (s, 15 H, C₅Me₅), 0.80 (s, 9 H, CH₂SiMe₃), -0.78 (d, ${}^{2}J_{\rm HH} = 15$ Hz, 1 H, CH_AH_BSiMe₃), -1.17 (d, ${}^{2}J_{\rm HH} = 15$ Hz, 1H, CH_AH_BSiMe₃); 1³C{¹H} NMR (CDCl₃) δ 175.1 (NH₂CH₂CH=CH), 131.2 (NH₂-CH₂CH=CH), 107.2 (C₅Me₅), 53.1 (NH₂CH₂CH=CH), 14.8 (CH₂SiMe₃), 9.8 (C₅Me₅), 3.1 (CH₂SiMe₃); low-resolution mass spectrum (probe temperature 100 °C), m/z 492 [P⁺, ¹⁸⁴W].

Preparation of Cp*W(NO)(CH₂SiMe₃)(OCH₂CHCH₂) (12). Cp*W(NO)(CH₂SiMe₃)₂ (0.262 g, 0.500 mmol) and hexanes (25 mL) were placed in a small thick-walled bomb, an excess of allyl alcohol was added, and the bomb was pressurized with H₂ (18 psig). Stirring of the reaction mixture for 2 h resulted in it becoming dark red and in the deposition of an orange precipitate. The solvent was removed in vacuo, and the remaining red oil was extracted with pentane (15 mL). The red extracts were filtered through Celite (1 × 2 cm), and solvent was removed from the filtrate under vacuum to obtain a dark red oil (0.20 g). The oil was dissolved in a minimum volume of hexanes, and slow evaporation of this solution at -30 °C afforded dark red needles of 13 (0.08 g, 32% yield).

Anal. Calcd for $C_{17}H_{31}NO_2SiW$: C, 41.39; H, 6.33; N, 2.84. Found: C, 39.93; H, 6.25; N, 2.45. IR (Nujol) $\nu_{NO} = 1576 \text{ cm}^{-1}$; ¹H NMR (C_6D_6) δ 5.96 (m, ³J_{HH} = 6.0, 6.5, 10, 17 Hz, 1 H, OCH₂CH=CH₂), 5.43 (m, ²J_{HH} = 1.0 Hz, ³J_{HH} = 6.0, 6.5 Hz, ⁴J_{HH} = 0.9, 1.2, 1.5, 1.8 Hz, 2 H, OCH_AH_BCH=CH₂), 5.19 (d of m, ²J_{HH} = 0.9 Hz, ³J_{HH} = 17 Hz, ⁴J_{HH} = 0.9, 1.2 Hz, 1 H, OCH₂-CH=CH_AH_B), 5.02 (d of m, ²J_{HH} = 0.9 Hz, ³J_{HH} = 10 Hz, ⁴J_{HH} = 1.5, 1.8 Hz, 1 H, OCH₂CH=CH_AH_B), 1.60 (s, 15 H, C₅Me₅), 0.89 (d, ²J_{HH} = 12.0 Hz, 1 H, CH_AH_BSiMe₃), 0.82 (d, ²J_{HH} = 12.0 Hz, 1 H, CH_AH_BSiMe₃), 0.37 (s, 9 H, CH₂SiMe₃); ¹³C{¹H} NMR (C₆D₆) δ 138.6 (OCH₂CH=CH₂), 116.5 (OCH₂CH=CH₂), 111.8 (C₅Me₅), 83.6 (OCH₂CH=CH₂), 35.4 (CH₂SiMe₃), 9.7 (C₅Me₅), 2.2 (CH₂SiMe₃); low-resolution mass spectrum (probe temperature 120 °C), m/z 493 [P⁺, ¹⁸⁴W].

X-ray Crystallographic Analysis of $Cp^*W(NO)(CH_2-SiMe_3)(N=CHMe)$ (4). An amber-red crystal of 4 was mounted in a Lindemann capillary tube under argon. Intensity data (Mo Ka/graphite monochromator) were collected at 200 K with an Enraf Nonius CAD-4F diffractometer equipped with an extensively in-house modified low-temperature attachment. Two intensity standards were measured every hour of aquisition time and showed no significant variations during the course of data acquisition. The data were corrected for absorption by the Gaussian integration method.¹² Data reduction included intensity scaling and Lorentz and polarization corrections.

The position of the W atom was determined from a Patterson map. Subsequent Fourier synthesis revealed the nonhydrogen atoms of the NO, CH₂SiMe₃, and Cp* groups. An electron density difference map displayed peaks attributable to a disordered ligand, N=CHMe, presumably derived from acetonitrile being coordinated to the precursor tungsten hydride complex (vide infra). This disorder was modeled with two fractionally occupied isotropic sites and a single isotropic thermal parameter for each of the three non-hydrogen atoms of the ligand. A single parameter was refined for the split sites of this group such that the total N=CHMe occupancy was 1. Soft restraints were applied to the bond distances of the disordered ligand such that the lengths of the pairs of chemically equivalent bonds and the two N-C-C angles were restrained toward their respective mean values. The final fullmatrix, least-squares refinement of 1056 parameters for 2035 observed data and 8 restraints included anisotropic thermal parameters for W and Si. Hydrogen atoms were placed in calculated positions and assigned anisotropic thermal parameters initially 10% larger than those for the corresponding carbon atoms. Those of the disordered ligand were given the appropriate fractional occupancies. The calculated rotational conformation of the methyl group in either conformation of

⁽¹²⁾ Demeulenaer, J.; Tompa, H. Acta Crystallogr. 1965, 19, 1014.

Table 1. Cp*W	Crystallographic Data for ((NO)(CH ₂ SiMe ₃)(N=CHMe) (Complexes (4) and

$Cp*W(NO)(CH_2SiMe_3)(NH_2CH_2CH_2CH_2)$ (1	.0)
---	-----

	4	10
formula	WSiON ₂ C ₁₆ H ₃₀	WSiON ₂ C ₁₇ H ₃₄
fw	478.36	494.40
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_{1}2_{1}2_{1}$
$a, Å^a$	9.515(2)	11.417(4)
b, Å	21.946(3)	13.178(2)
c, Å	9.522(3)	13.804(4)
β°.	102.57(2)	
$V, Å^3$	1946.8	2076.9
Ζ	4	4
$Q_{\text{calcd}}, \text{g/cm}^3$	1.632	1.581
λ (Mo Ka), Å	0.70930 (Ka1)	0.70930 (Κα1)
μ (Mo K α), cm ⁻¹	61.22	57.4
temp, K	200	200
trans factors ^b	0.260 - 0.392	0.181 - 0.261
min–max 2θ , deg	4-48	4-54
refins with $I \geq 2.5\sigma(I)$	2035	2420
no. of variables	106	208
Rf	0.029	0.020
R_w^d	0.028	0.025
GoF^e	1.23	1.53

^a Unit cell dimensions were determined for compounds 4 and 10 from 25 reflections (34° < 2 θ < 44° and 43° < 2 θ < 50°, respectively). ^b The data were corrected for the effects of absorption by the Gaussian integration method. ^c $R = \sum |(|F_o| - |F_c|)|/\sum |F_o|$ for $I_o \ge 2.5\sigma(I_o)$. ^d For compound 4, $R_w = \sum w(|F_o| - |F_c|)/\sum wF_o^2$, where $w = [4.214t_o(x) + 4.849t_1(x) + 3.163t_2(x)]^{-1}$, $x = |F_o|/F_{max}$, and t_n are the polynomial functions of the Chebyshev series.¹⁴ For compound 10, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$, where $w = [\sigma(F_o)^2 + 0.0001(F_o)^2]^{-1}$. ^e $GoF = [\sum w(|F_o| - |F_c|)^2 / degrees of freedom]^{1/2}$.

this ligand was chosen such that a hydrogen atom eclipses the corresponding nitrogen atom when viewed along the C–C bond. While alternate conformations of these methyl groups did not significantly increase the least-squares residual, the one chosen produced a flatter electron density difference map, resulted in a slightly more stable refinement of the parameters of the ligand, and is chemically reasonable. Coordinate shifts equivalent to those of their respective carbon atoms were applied to the hydrogen atoms, and their temperature factors were refined as a single parameter. An empirical weighting scheme was applied such that $\langle w(|F_o| - |F_c|)^2 \rangle$ was near constant as a function of both $|F_o|$ and sin θ/λ .

Complex scattering factors for neutral $atoms^{13}$ were used in the calculation of structure factors. The programs used for data reduction, structure solution, and initial refinement were from the NRCVAX Crystal Structure System.¹⁴ The program suite CRYSTALS 5¹⁵was employed in the final refinement. All computations were carried out on a MicroVAX-II computer. Crystallographic data are found in Table 1. Fractional atomic coordinates are located in Table 2, and selected bond lengths and angles are provided in Table 3. A view of the solid-state molecular structure of 4 is shown in Figure 1. Tables of the coordinates for the hydrogen atoms and the anisotropic temperature factors for 4 are deposited as supplementary material.

X-ray Crystallographic Analysis of Cp*W(NO)(NH₂-

 $CH_2CH_2CH_2)(CH_2SiMe_3)$ (10). A crystal of 10 was prepared for X-ray structure determination in a manner similar to that described in the preceding section for 4. Data were also recorded at 200 K with the same instrument and were processed analogously. Two standard reflections which were

Table 2. Coordinates $(\times 10^4)$ and Isotropic or
Equivalent Isotropic Temperature Factors ($Å^2$ >
10 ³) for the Non-Hydrogen Atoms of
$Cp*W(NO)(CH_2SiMe_3)(N=CHMe)$ (4) at 200 K

- 1-				
atom	x/a	y/b	z/c	U(iso)
W	1404.6(3)	810.5(2)	2472.3(4)	30
Si	-214(3)	2110(1)	3310(3)	45
0(1)	-1343(7)	119(3)	2225(7)	56(2)
N(1)	-263(7)	443(3)	2277(7)	42(2)
C(1)	3945(8)	882(4)	3436(8)	36(2)
C(2)	3326(9)	534(4)	4463(9)	37(2)
C(3)	2724(8)	6(4)	3753(8)	33(2)
C(4)	2921(9)	13(4)	2338(9)	40(2)
C(5)	3723(9)	545(4)	2160(9)	41(3)
C(10)	4740(10)	1478(4)	3753(10)	48(3)
C(20)	3494(9)	683(4)	6031(9)	46(3)
C(30)	1988(10)	-499(5)	4416(10)	51(3)
C(40)	2541(10)	-496(5)	1260(10)	52(3)
C(50)	4307(9)	703(4)	861(9)	47(3)
C(6)	956(9)	1457(4)	4033(9)	37(2)
C(7)	898(13)	2691(6)	2619(13)	77(4)
C(8)	-1830(12)	1891(5)	1898(12)	67(3)
C(9)	-904(14)	2463(6)	4829(14)	83(4)
$N(2)^{\alpha}$	1076(13)	1134(5)	614(8)	30(3)
$C(11)^{a}$	934(14)	1244(5)	-674(10)	39(3)
$C(12)^{a}$	442(17)	1836(6)	-1395(15)	57(4)
$N(20)^{b}$	38(20)	1331(7)	828(12)	30(3)
C(110) ^b	873(22)	1622(7)	-315(13)	39(3)
C(120) ^b	1003(27)	1381(11)	-1752(16)	57(4)

^a Occupancy = 0.60(2). ^b Occupancy = 0.40.

Table 3. Selected Intramolecular Distances (Å) and Angles (deg) for Cp*W(NO)(CH₂SiMe₂)(N=CHMe) (4) at 200 K

	/(Ollyound	3)(IN CILLIE) (H) at	
W-N(1)	1.753(7)	Si-C(6)	1.853(8)
W-Cp ^a	2.03	Si-C(7)	1.87(1)
W-C(6)	2.167(8)	Si-C(8)	1.87(1)
W-N(2)	1.87^{b}	Si-C(9)	1.88(1)
W - N(20)	1.91^{b}	O(1) - N(1)	1.242(9)
N(2) - C(11)	1.23^{b}	N(20) - C(110)	1.25^{b}
C(11) - C(12)	1.50^{b}	C(110) - C(120)	1.50^{b}
N(1)-W-Cp	123.8	C(7) - Si - C(6)	108.6(5)
N(2) - W - Cp	117.3	C(8) - Si - C(6)	113.7(5)
N(20) - W - Cp	123.3	C(8) - Si - C(7)	111.1(5)
$C(6) - W - Cp^{-1}$	110.2	C(9) - Si - C(6)	108.2(5)
C(6) - W - N(1)	93.7(3)	C(9) - Si - C(7)	108.1(6)
N(2) - W - N(1)	96.5(4)	C(9) - Si - C(8)	106.9(6)
N(20) - W - N(1)	100.9(6)	Si-C(6)-W	116.3(4)
N(2) - W - C(6)	112.7(4)	C(11) - N(2) - W	168.4(9)
N(20) - W - C(6)	98.4(6)	C(12)-C(11)-N(2)	126 ^b
O(1) - N(1) - W	171.7(6)	C(110) - N(20) - W	173.0(13)
		C(120)-C(110)-N(20)	1276

 a Cp represents the center of mass of the ring carbon atoms of the pentamethylcyclopentadienyl group. b These parameters were subject to soft restraints during refinement such that the pairs of chemically equivalent values were restrained toward their respective means.

measured every hour of exposure time declined in intensity by ~8% during the course of the measurements. One complete octant of data $(+h, +k, +l; 4^{\circ} \leq 2 \theta \leq 54^{\circ})$ was measured.

Coordinates and anisotropic thermal parameters for all nonhydrogen atoms were refined. The hydrogen atoms were placed in calculated positions and were assigned isotropic temperature factors initially proportionate to the equivalent isotropic temperature factors of the corresponding C or N atom. In subsequent cycles of refinement, the coordinate shifts for the hydrogen atoms were linked with those for the atoms to which they were bound. Mean isotropic temperature factors were refined for the hydrogen atoms of each of the two chemically distinct types of methyl group and each CH_2 or NH_2 group, and the shifts were applied to the individual values.

All eight symmetry- and Friedel-related reflections were measured for each of 25 sets of indices, for which $|F_c^+| - |F_c^-|$ was calculated to be most significant in terms of $\sigma(F_o)$ (ranging

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 ⁽¹⁴⁾ Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P.
 S. NRCVAX—An Interactive Program System for Structure Analysis. J. Appl. Crystallogr. 1989, 22, 384.
 (15) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS.

⁽¹⁵⁾ Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS. Chemical Crystallography Laboratory, University of Oxford, Oxford, England, 1984.



Figure 1. Molecular structure of $Cp^*W(NO)(CH_2SiMe_3)$ -(N=CHMe) (4) at 200 K. The 50% probability displacement ellipsoids or spheres are shown for the non-hydrogen atoms. Both orientations of the disordered ethylideneamido ligand are shown with the minor orientation represented by the open spheres and unshaded bonds.

down from ~68 σ (F_o)). After absorption corrections and data reduction ($R_{merge} = 0.032$), the resultant $|F_c^+| - |F_c^-|$ values were all very small and showed only a slight preference for the polarity represented by the structural coordinates reported here. The Flack enantiopole parameter,¹⁶ included in the fullmatrix least-squares refinement of the structure against the (4-54°:2 θ) octant of data, refined to 0.50(2). This implies oriented twinning or microtwinning involving nearly equal domains of either hand within the sample.

A weighting scheme based on counting statistics was applied such that $\langle w(|F_o| - |F_c|)^2 \rangle$ was nearly constant as a function of both $|F_o|$ and sin θ/λ . Final full-matrix least-squares refinement of 208 parameters (including an extinction parameter)¹⁷ for 2420 data $(I_o \ge 2.5\sigma(I_o))$ converged at $R_f = 0.020$. As for complex 4, all computations were carried out on MicroVAX-II and 80486 computers utilizing the programs specified in the previous section. Crystallographic details are summarized in Table 1. Final fractional atomic coordinates for the nonhydrogen atoms are listed in Table 4, and selected bond lengths and angles are summarized in Table 5. A view of the solid-state molecular structure of 10 is shown in Figure 2. Tables of supplementary crystallographic data, the coordinates for the hydrogen atoms, and the anisotropic temperature factors for 10 are deposited as supplementary material.

Results and Discussion

Generation of the Transient Alkyl Hydride Complex, Cp*W(NO)(CH₂SiMe₃)H. Treatment of solutions of Cp*W(NO)(CH₂SiMe₃)₂ with molecular dihydrogen generates in situ the reactive 16-valence-electron alkyl hydride, Cp*W(NO)(CH₂SiMe₃)H, formed by hydrogenolysis of one of the W-C σ -bonds of the dialkyl reactant. The Lewis-acidic hydride complex has not yet been isolated (or spectroscopically characterized) as such, but it can be trapped by small Lewis bases, L, as

Table 4. Fractional Atomic Coordinates andEquivalent Isotropic Temperature Factors (Ų) for
the Non-Hydrogen Atoms of

Cp*V	$V(NO)(CH_2SiMe_3)(NH_2CH_2CH_2CH_2)$	(10) at 2	200
	17		

Δ						
atom	x	у	z	$U_{eq}{}^a$		
W	0.936459(16)	0.966499(14)	0.784514(14)	0.0231		
Si	1.24225(13)	1.00669(13)	0.80671(12)	0.0316		
0	1.0610(4)	0.7674(3)	0.7807(4)	0.043		
N(1)	1.0168(4)	0.8545(4)	0.7771(4)	0.032		
N(2)	0.9944(4)	1.0666(4)	0.6602(4)	0.031		
C(16)	0.8453(6)	0.9147(6)	0.6505(5)	0.038		
C(17)	0.9221(7)	0.9318(6)	0.5614(5)	0.041		
C(18)	0.9498(7)	1.0429(6)	0.5617(5)	0.043		
C(6)	1.0943(5)	1.0555(4)	0.8336(5)	0.029		
C(7)	1.2669(6)	0.9645(7)	0.6777(5)	0.048		
C(8)	1.2760(6)	0.8957(6)	0.8859(5)	0.044		
C(9)	1.3541(6)	1.1067(6)	0.8345(7)	0.053		
C(1)	0.8035(6)	0.8945(5)	0.8923(4)	0.033		
C(2)	0.7318(5)	0.9545(5)	0.8320(4)	0.029		
C(3)	0.7643(5)	1.0572(5)	0.8453(5)	0.032		
C(4)	0.8521(6)	1.0613(5)	0.9176(5)	0.036		
C(5)	0.8798(5)	0.9591(5)	0.9455(4)	0.030		
C(11)	0.7936(6)	0.7806(5)	0.9042(6)	0.042		
C(12)	0.6272(5)	0.9166(6)	0.7772(6)	0.042		
C(13)	0.7070(6)	1.1491(5)	0.7985(6)	0.043		
C(14)	0.8978(7)	1.1584(5)	0.9624(6)	0.045		
C(15)	0.9596(7)	0.9255(7)	1.0245(5)	0.048		

 a U_{eq} is the cube root of the product of the principal axes of the thermal ellipsoid.

 Table 5.
 Selected Intramolecular Distances^a (Å) and Angles (deg) for

Cp*W(NO)(CH ₂ SiMe ₃)(NH ₂ CH ₂ CH ₂ CH ₂) (10) at 200 K					
W-N(1)	1.741(5)	O-N(1)	1.255(6)		
W-N(2)	2.263(5)	N(2) - C(18)	1.485(8)		
W-C(6)	2.255(5)	C(16) - C(17)	1.528(8)		
W - C(16)	2.230(6)	C(17) - C(18)	1.497(10)		
W-C(1)	2.328(6)	C(1) - C(2)	1.410(8)		
W-C(2)	2.432(5)	C(1) - C(5)	1.423(8)		
W-C(3)	2.449(6)	C(2) - C(3)	1.415(7)		
W-C(4)	2.422(6)	C(3) - C(4)	1.416(9)		
W - C(5)	2.316(5)	C(4) - C(5)	1.436(9)		
$W-Cp^b$	2.062	C(1) - C(11)	1.513(8)		
Si-C(6)	1.845(5)	C(2) - C(12)	1.499(8)		
Si-C(7)	1.886(7)	C(3) - C(13)	1.521(8)		
Si-C(8)	1.865(7)	C(4) - C(14)	1.513(8)		
Si-C(9)	1.874(7)	C(5)-C(15)	1.488(8)		
N(1) - W - N(2)	107.2(2)	N(1) - W - C(6)	92.1(2)		
N(1) - W - C(16)	86.4(2)	N(2) - W - C(6)	72.0(2)		
N(2)-W-C(16)	71.7(2)	C(16) - W - C(6)	141.4(2)		
N(1)-W-Cp	121.5	C(16)-W-Cp	105.5		
N(2)-W-Cp	131.2	C(6)-W-Cp	108.0		
C(6) - Si - C(7)	115.4(3)	C(6) - Si - C(9)	109.7(3)		
C(6) - Si - C(8)	110.2(3)	C(7) - Si - C(9)	107.4(4)		
C(7) - Si - C(8)	106.9(3)	C(8) - Si - C(9)	106.9(3)		
W - N(2) - C(18)	118.1(4)	W-C(6)-Si	119.3(3)		
W - C(16) - C(17)	110.8(4)	W-N(1)-O	170.1(4)		
C(16)-C(17)-C(18)	105.3(5)	C(2) - C(3) - C(4)	108.3(5)		
N(2)-C(18)-C(17)	106.3(5)	C(2)-C(3)-C(13)	126.4(6)		
C(2) - C(1) - C(5)	108.9(5)	C(4) - C(3) - C(13)	125.0(5)		
C(2)-C(1)-C(11)	125.3(6)	C(3) - C(4) - C(5)	108.0(5)		
C(5)-C(1)-C(11)	125.6(6)	C(3)-C(4)-C(14)	124.4(6)		
C(1)-C(2)-C(3)	107.9(5)	C(5)-C(4)-C(14)	127.4(6)		
C(1)-C(2)-C(12)	124.9(5)	C(1) - C(5) - C(4)	106.8(5)		
C(3)-C(2)-C(12)	126.4(5)	C(1) - C(5) - C(15)	125.1(6)		

^a Distances are not corrected for thermal motion and may thus be underestimated by from 0.004 to 0.007 Å on the basis of the results of a rigid-body analysis of the thermal parameters. ^b Cp denotes the center of mass of the ring-carbon atoms of the pentamethylcyclopentadienyl group.

the $Cp*W(NO)(CH_2SiMe_3)(L)H$ adducts.⁵ More importantly, if the coordinatively unsaturated hydride is

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Figure 2. Molecular structure of $Cp^*W(NO)(CH_2SiMe_3)$ -(NH₂CH₂CH₂CH₂) (10) at 200 K. The 50% probability displacement ellipsoids are shown for the non-hydrogen

atoms.

generated in the presence of a reactive substrate, some interesting chemical transformations occur. This paper describes a series of such reactions that detail the characteristic chemical properties of the transient alkyl hydride complex. The only caveat of which one must be mindful while exploring this rich chemistry is that the reactive substrates must not react with the dialkyl starting material, a fairly potent Lewis acid in its own right,¹⁸ since Cp*W(NO)(CH₂SiMe₃)₂(substrate) adducts, once formed, are unreactive toward molecular dihydrogen. The discussion that follows is grouped in terms of the different types of substrates to which Cp*W(NO)(CH₂SiMe₃)H has been exposed.

Reaction with Triphenylphosphine. Treatment of $Cp*W(NO)(CH_2SiMe_3)_2$ with dihydrogen (1 atm) in the presence of 1 equiv of PPh₃ affords the orthometa-

lated complex $Cp^*\dot{W}(NO)(PPh_2\dot{C}_6H_4)H$ (1), which is isolable in moderate yields as a yellow crystalline solid (eq 1).



The identity of 1 has been established by standard spectroscopic methods. Its IR spectrum as a Nujol mull clearly exhibits a W-H stretching band at 1929 cm⁻¹, and its ¹H NMR spectrum in C₆D₆ displays the hydride resonance as a doublet at δ 3.99 (²J_{PH} = 10 Hz). The

latter signal is accompanied by small satellite peaks due to ¹⁸³W coupling (${}^{1}J_{WH} = 104 \text{ Hz}$), which is also indicative of a W-H linkage. The orthometalated nature of the phosphine ligand is evident from the large number of peaks in the aryl region of both the ¹H and ¹³C{¹H} NMR spectra of 1.

The first step in the formation of complex 1 is undoubtedly the trapping of the transient 16-electron alkyl hydride compound with PPh₃ to form the intermediate 18-electron species, Cp*W(NO)(CH₂SiMe₃)-(PPh₃)H. As noted above, compounds of this type have been isolated from related reactions involving smaller Lewis bases. Reductive elimination of Me₄Si from this intermediate, followed by orthometalation of one of the phenyl groups on the PPh₃ ligand, would then produce the final product. Some support for this view of the mechanism is provided by the same reaction effected with PPh_3 - d_{15} , which results in complete deuteration of the hydride position in the product. The W-D stretch in the IR spectrum expected at 1380 cm⁻¹ $(\nu_{calcd})^{19}$ for this complex is unfortunately obscured by a Nujol band. This observation indicates that the hydride ligand in 1 originates on the PPh₃ and that the reductive elimination of alkane occurs before the orthometalation step. This reductive elimination is evidently quite facile at ambient temperatures for this system. Such is not the case for other analogous complexes. For instance, $Cp^*W(NO)(CH_2SiMe_3)(PMe_3)H \ and \ CpW(NO)(CH_2-$ SiMe₃)[P(OPh)₃]H require heating to 40 and 50 °C, respectively, to induce such reactivity.²⁰ The facile reorganization of NO and triphenylphosphine from a trans to a cis orientation in Cp*W(NO)(CH₂SiMe₃)-(PPh₃)H is probably a result of the large steric interaction between the trimethylsilylmethylene ligand and the triphenylphosphine ligand, as compared to the smaller trimethylphosphine and triphenylphosphite ligands. That the NO and phosphine ligands are now cis places the alkyl ligand and hydride cis as well, affording reductive elimination, followed by orthometalation. Thus it appears that the steric bulk of the PPh₃ ligand facilitates the elimination of the bulky alkyl ligand and the replacement of a tungsten-alkyl link by a stronger tungsten-aryl bond in 1.

Reaction with Dienes. When Cp*W(NO)(CH₂-SiMe₃)₂ is reacted with dihydrogen in the presence of butadiene or 2,3-dimethyl-1,3-butadiene, η^4 -diene complexes of the type Cp*W(NO)(η^4 -trans-diene) are formed (complexes 2 and 3, respectively, eq 2). The spectro-



scopic properties of 2 resemble those exhibited by related molybdenum species whose solid-state molecular structures we have previously established.²¹ Hence, it is likely that both of these tungsten compounds are

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isostructural and contain the diene ligands attached to the metal centers in a twisted, transoidal fashion.²² Mechanistically, conversions 2 probably resemble the PPh₃ metalation reaction (vide supra). Hydrogenolysis of one of the W-C bonds of $Cp*W(NO)(CH_2SiMe_3)_2$ generates the alkyl hydride intermediate, and coordination of one double bond of the diene in an η^2 -fashion produces the 18-electron complex, $Cp*W(NO)(CH_2 SiMe_3$)(η^2 -diene)H. Elimination of Me₄Si from this intermediate with concerted coordination of the dangling double bond of the diene to the tungsten center would then produce complexes 2 and 3. Since the proposed η^2 -diene-trapped intermediate is not observable spectroscopically, the elimination of the alkane from it must be rapid once this intermediate is formed. Since Me₄Si elimination after coordination of the diene requires a cis orientation of the alkyl ligand and the hydride ligand, an insertion/de-insertion isomerization process between the coordinated diene and the hydride complex must be occurring, since the diene would coordinate initially between the alkyl and hydride ligands. We have also monitored the reaction to form $Cp*W(NO)(\eta^4$ -trans-2,3-dimethyl-1,3-butadiene) (3) by ¹H NMR spectroscopy. The spectroscopic yield of the reaction is approximately 90%, and no evidence for organic products resulting from diene hydrogenation is detectable. There is also no evidence for organometallic products resulting from insertion of one of the diene double bonds into the W-H linkage of the 16-electron alkyl hydride intermediate in the manner found for the substrates considered in the next section.

Reactions with Substrates That Insert into the W-H Bond. A number of unsaturated molecules have been reacted with the transient alkyl hydride complex to investigate the insertion chemistry of its tungstenhydrogen bond. The chemistry that we have discovered during the present study is summarized in Scheme 1. Each reaction shown in this scheme was also monitored by NMR spectroscopy to determine the spectroscopic yields of the conversions and to detect and identify any byproducts formed.

(a) Acetonitrile. When $Cp^*W(NO)(CH_2SiMe_3)_2$ is reacted with dihydrogen in the presence of acetonitrile, the ethylideneamido compound, Cp*W(NO)(CH₂SiMe₃)-(N=CHMe) (4), is formed in quantitative spectroscopic yield (Scheme 1). The product arises from insertion of the N=C bond of the acetonitrile into the W-H bond of the transient alkyl hydride.^{8a} The solid-state molecular structure of 4 reveals an ethylideneamido ligand attached via a W=N link which is disordered, as depicted in the ORTEP diagram in Figure 1. The parameters of the disordered ligand (occupancy ratio 60:40, N(2)-C(11)-C(12):N(20)-C(110)-C(120)) are consistent with its formulation as ethylideneamide (N=CHMe) doubly bonded via nitrogen to tungsten in two diastereomeric orientations. Other formulations for this group do not appear to be reasonable in terms of the observed electron density distribution and in light of the other chemical and spectroscopic evidence (vide infra). The

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weighted mean N-C bond distance for 4 (1.24 Å) compares well with that of $[Ru(tpy)(bpy)(N=CMe_2)]$ - $[ClO_4]_3$ ·H₂O (1.26(2) Å)²³ and other ethylideneamidocontaining complexes²⁴ and implies multiple-bond character of this bond comparable with or greater than that extant in the corresponding Ru-N bond distance.

The existence of two sets of signals in the ¹H and ¹³C-{¹H} NMR spectra of **4** in C_6D_6 (see Experimental Section) indicates that these isomers also persist in solution in approximately the same ratio. The presence of the two diastereomers can be attributed to the existence of a large rotational barrier about the W=N bond. This observation, along with the essentially linear W-N-C angles (168.4 and 171.7°), is consistent with the views that the ethylideneamide functions as a formal 3-electron donor and that **4** is an 18-valenceelectron complex.

(b) Organic Carbonyls. The transient alkyl hydride has also been generated in the presence of a number of organic reagents that contain a carbonyl functionality. Acetone, benzaldehyde, and 4-phenyl-3-buten-2-one all insert their carbonyl group into the W-H bond to produce an alkyl alkoxide product (complexes 5, 6, and 7, respectively, in Scheme 1) in quantitative yield, as judged by NMR spectroscopy. Interestingly, the α_{β} unsaturated ketone, 4-phenyl-3-buten-2-one, exhibits only this mode of reactivity even though, in principle, it could undergo insertion of its C=C linkage into the W-H bond or it could function like the diene reagents already discussed and coordinate to the metal center in an η^4 -fashion following alkane elimination from the transient alkyl hydride compound. We have previously obtained alkyl alkoxide complexes of the type Cp*M-(NO)(R)OR' [M = Mo, W] by treatment of the Cp*M-(NO)(R)Cl precursors with alkoxide anions.²⁵

The spectroscopic properties of complexes 5 and 6 are consistent with their possessing three-legged piano-stool molecular structures. However, the NMR data for the unsaturated ketone insertion product 7 are quite complicated and indicate the presence of two isomers that are formed in a ratio of approximately 3:2. The resonances can be attributed to the two diastereomeric pairs of enantiomers formed by addition of the racemic hydride to different faces of the ketone, i.e. (RS and SR)and (SS and RR) isomeric pairs. This mode of addition is reminiscent of the enantiofacial binding of unsaturated organic substrates to the Cp*Re(NO)(PPh₃) cation studied by Gladysz and co-workers.²⁶ Interestingly, the reaction to form 7 is slightly stereoselective and does produce one set of enantiomers in excess. Presumably the reaction proceeds through an intermediate that has the ketone coordinated to the unsaturated alkyl hydride at its Lewis-acid site between the alkyl and hydride ligands.^{6,7,27} The different product isomers would then be formed by addition of the hydride to either face of the ketone. In this case, the sterically preferred mode

of coordination of the ketone would be with the smaller substituent, the methyl group, pointing upward toward the more sterically demanding Cp* ligand. Upon insertion, these conformations would produce the SS or RR configuration, depending upon the configuration of the hydride enantiomer. Hence, the major isomers formed during the hydrogenation-insertion reaction are expected to be those displaying RR and SS configurations. The different integrations of the ¹H NMR resonances allow the signals due to each pair of enantiomers of complex 7 to be assigned, although it is not possible to assign the two sets of signals to any one absolute configuration. A ¹H NMR spectrum taken after complex 7 was recrystallized revealed that one of the enantiomer pairs had been enriched by approximately 50% from one crystallization, thereby indicating that the two sets of enantiomers are separable by fractional crystallization.

(c) Benzophenoneimine. Hydrogenation of Cp*W-(NO)(CH₂SiMe₃)₂ in the presence of benzophenoneimine demonstrates that the alkyl hydride intermediate is also able to insert imine functionalities (Scheme 1). The product of this reaction, 8, has been characterized as the alkyl amido complex Cp*W(NO)(CH₂SiMe₃)-(NHCHPh₂). The ¹H NMR spectrum of this complex contains a broad peak at δ 7.6 assignable to the NH proton, and its IR spectrum exhibits a strong $\nu_{\rm NH}$ at 3249 cm⁻¹. We have recently synthesized many alkyl and aryl amide complexes similar to 8 by metathesis reactions of appropriate alkyl chloride or amide chloride precursors.²⁸

(d) Phenylacetylene. Hydrogenation of Cp*W(NO)-(CH₂SiMe₃)₂ in the presence of phenylacetylene results in the formation of the alkyl alkenyl compound Cp*W-(NO)(CH₂SiMe₃)(CPh=CH₂) (9) via insertion of the substrate into the W-H bond of the transient alkyl hydride compound (Scheme 1). Complex 9 is only isolable in very low yield because it is prone to undergo further reactions during its synthesis. First and foremost, 9 is thermally unstable, and its thermal chemistry is dominated by its facile activation of alkane C-H bonds in a unique manner.²⁹ Second, the alkenyl product is sensitive to dihydrogen to the extent that an authentic sample of the complex decomposes slowly when exposed to the pressures of H₂ used during its synthesis.

The spectroscopic properties of 9 are consistent with its possessing the 16-valence-electron molecular structure shown in Scheme 1. The ¹H and ¹³C{¹H} NMR spectra of complex 9 also suggest the existence of a weak interaction between the Lewis-acidic tungsten center and the π -electron density of the alkenyl group, though not to the extent customarily exhibited by an authentic η^2 -alkenyl ligand (vide infra). For example, the ¹H NMR spectrum of **9** shows some unexpected coupling patterns. Both of the alkenyl protons are weakly coupled to one of the methylene protons of the trimethylsilylmethyl ligand $(J_{\rm HH} = 1.4 \text{ and } 1.1 \text{ Hz})$, a surprising coupling through five bonds and four atoms. In addition, there are tungsten satellites observable on both of the alkenyl proton signals, one coupling constant being much greater than the other $(J_{WH} = 10 \text{ and } 5.1 \text{ Hz})$. Consistently, the ${}^{13}C{}^{1}H$ NMR spectrum of **9** in C₆D₆ displays the

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alkenyl carbon resonances at 228 and 83 ppm, ^{184}W satellites being evident on both the α carbon (${}^{1}J_{WC}$ = 99 Hz) and the β carbon ($^2J_{WC} = 13$ Hz) signals. Authentic η^1 -alkenyl complexes usually display C_{α} resonances around 160 ppm and C_{β} resonances around 130 ppm,³⁰ whereas most tungsten η^2 -alkenyl compounds exhibit these signals between 230 and 270 ppm and between 20 and 40 ppm, respectively.^{31,32} Clearly, the alkenyl ligand of 9 is interacting with the tungsten center in a manner intermediate to that of the limiting η^1 and η^2 forms.

The regioselectivity of insertion, i.e. whether the unsymmetrical acetylene undergoes addition of the metal at the α or β carbon, is difficult to predict a priori for these types of insertion processes since both steric and electronic factors are operative. For example, $W(H)(CO)_2(NO)(PMe_3)_2^{32}$ and $Co(H)[N(CH_2CH_2PPh_2)_3]^{33}$ insert the activated acetylene $HC \equiv CC\{O\}OMe$ to give alkenyl complexes of the type [M]C(C{O}OMe)=CH₂, whereas $CpRe(CO)(NO)(H)^{34}$ affords the other regioisomer, namely $[M]CH=CH(C{O}OMe)$. On the other hand, the osmium complex [Os(H)(acetone)(CO)₂(PⁱPr₃)₂]-BF₄ is known to undergo both modes of insertion.³⁵ In the case of Cp*W(NO)(CH₂SiMe₃)H, its reactions with organic substrates of the type ER $[E = N \equiv, NH =, O =]$ afford complexes 4-8, which are the expected product both sterically and electronically. In other words, the evidently hydridic hydride adds to the electropositive carbon center, and the metal binds the heteroatom such that the least sterically crowded ligand results. In addition, the preferential formation of a strong W-E bond (over a W-C bond) provides a thermodynamic driving force for these processes. In contrast, the formation of complex 9 seems to be primarily under electronic control, the hydride of $Cp^*W(NO)(CH_2)$ -SiMe₃)H adding to the unsubstituted, electropositive terminus of the acetylene. Interestingly, Schwartz's reagent exhibits the opposite regiochemistry toward phenylacetylene to produce the least sterically crowded insertion product.³⁶

Hydrogenation of the dialkyl complex, Cp*W(NO)(CH₂-SiMe₃)₂, in the presence of diphenylacetylene or 1-pentyne does not yield any isolable products, and monitoring of these reactions by NMR spectroscopy gives no evidence for the formation of alkenyl products similar to 9. Insertion of symmetric acetylenes is unlikely due to the apolar nature of the unsaturation. Likewise, the products of simple alkyne insertion into the W-H bond of the transient hydride complex are presumably unstable because they contain β hydrogens and are thus prone to elimination and subsequent decomposition. Complex 9 is no exception. This alkenyl compound is, in fact, the only 16-valence-electron species of the type Cp'M(NO)(R)R' in which one of the alkyl groups contains β hydrogens that we have yet been able to isolate. Nevertheless, as noted above, it does slowly decompose in solutions at ambient temperatures, presumably via a β -H elimination pathway. The next section details our discovery of how such olefin and acetylene insertion products may be stabilized.

(e) Allylamine and Propargylamine. Allylamine and propargylamine were chosen as potentially useful olefins for the study of their insertion chemistry into the W-H link of Cp*W(NO)(CH₂SiMe₃)H on the grounds that their pendant amine functionalities would stabilize otherwise coordinatively unsaturated and highly reactive 16-valence-electron products containing β -hydrogens. Gratifyingly, this expectation has been realized. Both amines undergo insertion of their unsaturated carbon-carbon link into the W-H bond, and following insertion, the pendant amine group coordinates to the metal to stabilize the complexes toward β -hydride elimination (Scheme 1). Both reactions are quantitative by ¹H NMR spectroscopy, and the azametallacyclic products are isolable in moderate yields. Specific details of each conversion are presented in the following paragraphs.

(1) Allylamine. When $Cp^*W(NO)(CH_2SiMe_3)_2$ is reacted with dihydrogen in the presence of allylamine,

 $Cp*W(NO)(CH_2SiMe_3)(NH_2CH_2CH_2CH_2)$ (10) is the product obtained as a yellow crystalline solid. The lower yield results from the difficulty in isolating and recrystallizing this compound. The olefin insertion reaction that results in the formation of 10 is unprecedented for our tungsten hydride systems. Complex 10 was initially characterized by standard spectroscopic methods. Interestingly, the amine H signals in the ¹H NMR spectrum of the complex in CDCl₃ are observed at high field as a broad singlet at δ 3.18. The fact that only a broad singlet is observed for the two amine protons and not an AB quartet pattern as expected for diastereotopic protons is perhaps indicative of the existence of some exchange process. Regrettably, variable temperature NMR spectroscopy of complex 10 from 25 °C to the $CDCl_3$ solvent limit of -50 °C failed to bring about resolution of the individual signals. The six alkyl protons of the metallacycle give rise to multiplets integrating for one proton each, as expected for sets of diastereotopic protons. A ¹H COSY experiment revealed the three sets of diastereotopic protons, thereby allowing their assignment (see Experimental Section). The internuclear couplings between these protons are indeterminable, however, due to the broadening displayed by the signals.

Another notable spectroscopic feature of complex 10 is the nitrosyl-stretching band at 1497 cm^{-1} in its IR spectrum. This is a very low value for v_{NO} and reflects the considerable weakening of the N-O bond that results from a large degree of back-donation of electron density from the metal to the nitrosyl ligand. This increased back-donation is, in turn, a manifestation of the increased electron density at the metal center afforded by the dative bond from the amine nitrogen atom's lone pair of electrons to the tungsten center. The existence of this latter bonding interaction has been confirmed by a single-crystal X-ray crystallographic analysis of 10. The solid-state molecular structure of compound 10 is shown in Figure 2. The only significant intermolecular interaction is a hydrogen bond of 2.841-(6) Å involving O-HN(2)', where ' indicates 2 - x, -1/2+ y, 3/2 - z. The C(16)-C(17) bond length of 1.528(8)

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Å indicates the existence of a single C–C bond and confirms that the original allylic moiety of the amine has been hydrogenated. In all other aspects the intramolecular dimensions of **10** are comparable to those exhibited by related Cp*W(NO)-containing four-legged piano-stool molecules.⁵

The mechanism of formation of the azametallacycle in 10 probably proceeds via insertion of the C=C link of the allylamine into the W-H bond of Cp*W(NO)(CH₂-SiMe₃)H. The 16-valence-electron complex so formed is stabilized by the subsequent coordination of the pendant amine group to the metal center through a dative bond, thereby resulting in the stable 18-valenceelectron complex 10. That olefin insertion occurs before coordination of the pendant Lewis-base site in this system is supported by the fact that saturated amines such as tert-butylamine fail to trap the transient tungsten hydride complex as an isolable adduct. In addition, if the amine functionality were to coordinate first, then the open coordination slot of the alkyl hydride complex would be occupied, eliminating the possibility of insertion of the olefinic moiety into the W-H bond. This would lead to decomposition of the complex, as is observed for the reaction with saturated amines. If coordination of amine functionality and olefin moiety is viewed as a competitive process, then the lower yields of allylamine insertion product, as compared to the products of the reactions with the polar, unsaturated organic substrates, are rationalized. This view of the mechanism in the tungsten case contrasts with the recent findings of Hiraki and co-workers during their studies of the analogous reactions of Ru(Cl)(CO)- $(PPh_3)_3H$ with primary and secondary amines.³⁷ They find that the hydrido ligand labilizes the trans-PPh₃ ligand to substitution by allylamine. The ligand is purported to coordinate via the amine site first and then to undergo olefin insertion into the Ru-H bond.

The regioselectivity of the olefin insertion into the W-H linkage is identical to that displayed by Schwartz's reagent during the hydrozirconation of functionalized olefins.³⁶ The Cp*W(NO)(CH₂SiMe₃)H complex adds across the olefin link in such a manner that the metal ends up on the least hindered carbon center. There is no evidence for the formation of the congeneric metallacyclobutane species in this system. In contrast to phenylacetylene and the other carbonyl-, nitrile-, and imine-functionalized substrates (vide supra), polarization of the olefin moiety by the pendant amine function is probably a minor factor due to its distal relationship to the olefin link. The regioselectivity observed during the olefin insertion is thus probably determined to a greater extent by steric requirements within the olefininserted intermediate rather than by electronic factors within the substrate.

(2) **Propargylamine.** Reaction of $Cp^*W(NO)(CH_2-SiMe_3)H$ with propargylamine produces complex 11 which contains an azametallacyclopentene group (Scheme 1). The product is obtained in a yield comparable to 10, and its mechanism of formation is assumed to be similar to that proposed for 10 in the preceding paragraph. The spectroscopic properties of 11 confirm its identity. For instance, the NO stretching band in its Nujol mull IR spectrum occurs at 1501 cm⁻¹, the same

region as found for 10. The diastereotopic amine proton signals are clearly visible as doublets at δ 7.23 and 6.47 with a two-bond coupling of 18 Hz in the one-dimensional ¹H NMR spectrum of 11 in CDCl₃. These doublets also display fine structure resulting from coupling to the α -methylene protons in the ring. Likewise, the diastereotopic methylene protons in the ring give rise to signals that are evident as a virtual quartet centered about δ 3.48. This virtual guartet is superimposed on the signal of the allylic proton α to the metal center, with the entire multiplet integrating for three protons. The remaining allyl proton, which couples to both the methylene protons and the α -allyl proton. produces the broad multiplet at δ 2.39. The ¹H COSY spectrum of 11 confirms these assignments. Definitive evidence for the allylic moiety is also found in the ¹³C NMR spectrum of the complex, the allylic carbon signals at δ 175.1 and 131 being characteristic of the metalbound allylic functionality.³⁸

Closer inspection of the methyl signals in the Cp^{*} region of the one-dimensional ¹H NMR spectrum of **11** reveals the existence of a second species in the ratio of 1:5 relative to the major isomer, **11**. Downfield there also exist two broad singlets integrating as 1H each at δ 6.04 and 5.38, which exhibit fine structure and are attributable to amine protons. Slightly upfield are two broad doublets at δ 5.09 and 4.29, which also exhibit fine structure and integrate as one proton each, and these are indicative of the presence of vinyl protons.²⁰ Diastereotopic methylene signals attributable to the Me₃SiCH₂ ligand of a minor isomer are also evident in the same region as those of the major isomer, **11**.



If one acknowledges that hydrogenation of the allyl moiety can occur at either the β or γ position relative to the pendant amine functional group, then it is possible that the minor isomer is a complex containing a vinyl metallacyclobutane ligand as shown above. Indeed, this view is supported by the ¹H COSY spectrum of 11, which shows signals attributable to the vinyl protons displaying a weak mutual coupling. More importantly, partially obscured beneath the analogous methylene signal for the major isomer 11, a three-bond coupling of the vinyl protons in the vinyl metallacyclobutane to a set of diastereotopic methylene protons is evident. At the same time, a long range coupling between the amine broad singlets and the same methylene signals of the vinyl metallacyclobutane is also clearly discernible. The relative preponderance of this complex containing the five-membered azametallacycle over that with the four-membered isomer is consistent with the well-known preferential formation of a fivemembered ring over a four-membered ring. Interestingly, such a four-membered metallacyclic isomer is not observed for the saturated analogue, 10.

Allyl Alcohol. While studying the olefin insertion resulting in the formation of the amine azametallacycle

⁽³⁷⁾ Hiraki, K.; Matsunaga, T.; Kawano, H. Organometallics **1994**, *13*, 1878.

⁽³⁸⁾ Mann, B. E.; Taylor, B. F. ¹³C NMR Data for Organometallic Compounds; Academic Press: New York, 1982.

in 10, we decided to investigate whether the O analogue of 10 could be formed by utilizing allyl alcohol in place of allylamine in the hydrogenation reaction. However, instead of isolating the metallacyclic complex from the final reaction mixture, we obtained instead a red oil which was characterized as the allyl alkoxide complex, 12 (eq 3).



Characterization of 12 was made facile by the presence of the allyl signals in both the ¹H and the ¹³C NMR spectra. The allyl signals in the one-dimensional ¹H NMR spectrum are qualitatively identical to those exhibited by Cp*Mo(NO)(NHCH₂CH=CH₂)Cl, an allylamido complex studied by our group recently.³⁹ Like this molybdenum complex, the allylic protons in 12 do not show the characteristic allyl splitting pattern,⁴⁰ since incorporation of the alcohol into the complex as an alkoxide ligand renders the methylene protons diastereotopic. The most notable feature of this spectrum is the resonance of the internal allyl proton, a 10line multiplet at 5.96 ppm consisting of an overlapping doublet of doublets of doublets of doublets (${}^{3}J_{\rm HH} =$ 6.0, 6.5, 10, 17 Hz). The two largest couplings are consistent with cis and trans alkene coupling, and the two smaller couplings result from coupling to the two diastereotopic methylene protons. The nitrosyl band in the Nujol mull IR spectrum of 13 occurs at 1576 $\rm cm^{-1}$. a region characteristic of such mixed alkyl alkoxide species.²⁵ The percent carbon in the elemental analysis of 12 was lower than expected due to the impurity of the sample. These types of complexes are difficult to obtain in pure crystalline form and 12 is no exception.

The probable mechanism of formation of **12** is simple protonolysis of the dialkyl reactant by allyl alcohol resulting in loss of Me₄Si followed by coordination of the allyl alkoxide. This view is supported by the fact that complex 12 is produced by the reaction of allyl alcohol with Cp*W(NO)(CH₂SiMe₃)₂ even in the absence of H_2 . We have also shown that complex 12 can be prepared by the reaction of the lithium salt of allyl alcohol with the alkyl chloride, Cp*W(NO)(CH₂SiMe₃)-Cl,⁴¹ a methodology that has been employed to synthesize other alkyl alkoxide complexes studied by our group recently.²⁵ Unfortunately, complex 12 is inert to H_2 , and the desired metallacycle cannot be obtained in this manner. Alternate synthetic routes that will lead to such metallacyclic complexes are currently being pursued.

Stability of the Insertion Products. All of the insertion products outlined in Scheme 1 and discussed above contain one common feature that raises an important question concerning their electronic nature.

Each complex contains an alkyl ligand possessing a β -hydrogen atom and yet is an isolable species. In contrast, the isolable bis(hydrocarbyl) complexes, Cp'M-(NO)R₂ [Cp' = Cp or Cp*, M = Mo, W, R = alkyl or aryl], are devoid of β -hydrogens. The fundamental difference between the two classes of complexes is that the insertion products 4–11 attain a degree of electronic sufficiency at their metal centers, whereas the Cp'M-(NO)R₂ species remain as 16-valence-electron entities. Electronic sufficiency in 4–11 can arise in the three different ways shown below.



The first mode of electronic stabilization, namely that observed for complexes 4-8 and depicted as case I. involves dative bond formation between the heteroatom E [E = N=, O-, or HN-] and the tungsten through donation of electron density from the lone pair on E into the LUMO that lies between the alkyl ligands and trans to the nitrosyl ligand (vide supra). Case II depicts the second mode of stabilization resulting from the coordination of a pendant Lewis-base moiety, as occurs in complexes 10 and 11, and the transfer of electron density to the LUMO. Finally, as shown in case III, stabilization results from donation of electron density from the alkenyl π system of the phenyl alkenyl ligand into the LUMO of 9. As demonstrated by the work reported in this paper, the electronic stabilization is least in case III, thereby resulting in complex 9 being the most thermally sensitive and reactive insertion product.

Summary. The title compound, Cp*W(NO)(CH₂-SiMe₃)H, has not been directly observed, but its production in situ by the hydrogenation of $Cp*W(NO)(CH_2 SiMe_{3}_{2}$ has been indicated by subsequent reactivity of this putative hydride intermediate. This compound has been useful for synthesizing in high yields a number of mixed-ligand compounds such as alkyl alkoxide, alkyl amide, and alkyl alkenyl species, as well as producing trans-diene complexes that cannot be produced by other routes. As determined by the regioselectivity of its insertions of polar substrates, the hydride ligand is hydridic in nature. This feature is best demonstrated by the product of phenylacetylene insertion, during which process only one regioisomer is formed. Furthermore, this isomer is the one in which the hydride has added to the more positive end of the unsaturated linkage, even though this mode of addition forms the more sterically demanding isomer.

Reaction of the intermediate hydride complex with olefins and acetylenes leads to insertion products which are usually not thermally stable since they contain β -hydrogens. Such is the case for phenylacetylene insertion, which affords a thermally sensitive complex that has been isolated only in low yield. Interestingly, these insertion products can be stabilized by pendant Lewis-base functional groups. Thus, the hydrido intermediate combines with allylamine, and the resulting insertion product, although containing β -hydrogens, is

⁽³⁹⁾ Legzdins, P.; Rettig, S. J.; Ross, K. J. Organometallics **1993**, *12*, 2103.

⁽⁴⁰⁾ See, for example: Matta, E.; Du, Y. J. Am. Chem. Soc. 1988, 110, 8249.
(41) Lumb, S. A. Unpublished observations.

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stabilized to decomposition by coordination of the pendant amine group. Similar reactivity is observed with propargylamine, a conversion that results in the formation of a base-stabilized alkenyl complex.

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Supplementary Material Available: Tables of supplementary crystallographic data, the coordinates for the hydrogen atoms, and the anisotropic temperature factors for complexes **4** and **10** (8 pages). Ordering information is given on any current masthead page.

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