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Interligand H⋯Si interactions in tungsten silyl trihydride complexes

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ABSTRACT

The dichloride complex Cp*(Am)WCl$_2$ (**1**, Am = [(iPrN)$_2$CMe]$^-$) reacted with the primary silanes PhSiH$_3$, (*p*-tolyl)SiH$_3$, (3,5-xylyl)SiH$_3$, and (C$_6$F$_5$)SiH$_3$ to produce the W(VI) (silyl)trihydrides Cp*(Am)W(H)$_3$(SiHPhCl) (**2**), Cp*(Am)W(H)$_3$(SiHTolylCl) (**3**), Cp*(Am)W(H)$_3$(SiHXylylCl) (**4**), and Cp*(Am)W(H)$_3$[SiH(C$_6$F$_5$)Cl] (**5**). In an analogous manner, **1** reacted with PhSiH$_2$Cl to give Cp*(Am)W(H)$_3$(SiPhCl$_2$) (**6**). Complex **6** can alternatively be quantitatively produced from the reaction of **2** with Ph$_3$CCl. NMR spectroscopic studies and X-ray crystallography reveal an interligand H⋯Si interaction between one W–H and the chlorosilyl group, which is further supported by DFT calculations.

1. Introduction

In recent years the use of amidinates as ligands for early transition metal complexes has gained considerable popularity [1–3]. Amidinates are easily synthesized and can be readily modified to induce either small or drastic steric and electronic changes. Futhermore, multiple methods for installing amidinate ligands onto metal fragments have proven effective [4,5]. Amidinate-supported Group 4 complexes are active olefin polymerization catalysts, and the amidinate ligand is not directly involved in observed reactivity [6–9]. Recent work from Sita and co-workers with Group 6 complexes of the type Cp*(Am)MCl$_2$ (Am = [(iPrN)$_2$CMe]$^-$; M = Mo, W) [10] inspired the exploration of reactivity of Cp*(Am)WCl$_2$ (**1**) with organosilanes.

Research in this laboratory has focused on fundamental chemistry involving Si–H activations and the formation of silylene complexes. In particular, [(η^7-C$_5$Me$_3$(CH$_2$)$_2$)(dmpe)W(H)$_2$][B(C$_6$F$_5$)$_4$] has been shown to perform double Si–H activations to result in high oxidation state silylene complexes of the type [Cp*(dmpe)W = SiR$_2$][B(C$_6$F$_5$)$_4$] [11,12]. Similar chemistry was envisioned to occur with a Cp*(amidinate)W fragment, such as Cp*(Am)WR$_2$. Herein we present the synthesis of new tungsten complexes supported by the amidinate ligand (Am = [(iPrN)$_2$CMe]$^-$) in which a non-classical Si⋯H interaction is observed.

A number of interesting non-classical interactions have been observed in organometallic complexes containing silicon, which have been characterized as involving σ-complexes (η^2- and η^3-silane complexes), agostic interactions, and interligand hypervalent interactions [13–16], and such species have been proposed as intermediates in catalytic transformations of organosilanes [17–20]. An interligand hypervalent interaction is described as involving primarily electron donation from a metal hydride bond into an antibonding orbital of a silicon–X bond, where X is a good leaving group. This interaction results in elongation of the Si–X bond, shortening of the M–Si bond, and often but not always, increased Si–H coupling constants [15,21]. Such interactions have been well documented for Ru, Ta, and Nb complexes [22–26].

2. Results and discussion

2.1. Reactions of primary silanes with Cp*(Am)WCl$_2$

Complex **1** was found to react with a 5-fold excess of phenylsilane at 80 °C over 24 h in toluene to give Cp*(Am)W(H)$_3$(SiHRCl) (**2**) as a light brown solid in 42% yield after recrystallization from pentane at −30 °C (Eq. (1)). The yield is significantly lowered by the similar solubility properties of **2** and phenylsilane, making isolation of pure **2** difficult. In an analogous manner, **1** was found to react with *p*-tolylsilane, 3,5-xylylsilane, and (pentafluorophenyl)silane to give complexes **3**–**5**, respectively. Reactions with the bulkier silanes MesSiH$_3$, TripSiH$_3$, and DMPSiH$_3$ did not proceed, even with heating at 80 °C for one week, presumably for steric reasons.

The ^{1}H NMR spectrum of **2** contains three chemically inequivalent hydride resonances at 5.24 ppm (J_{SiH} = < 7 Hz), 0.92 ppm (J_{SiH} = 11.1 Hz), and −1.28 ppm (J_{SiH} = 24.6 Hz). The Si–H resonance at 8.41 ppm (J_{SiH} = 199.5 Hz) is shifted downfield relative to that of the free silane (4.23 ppm). The ^{29}Si NMR spectrum contains a single resonance for the silyl ligand at 43.9 ppm. The isopropyl groups of the ligand exhibit two methine resonances and four methyl

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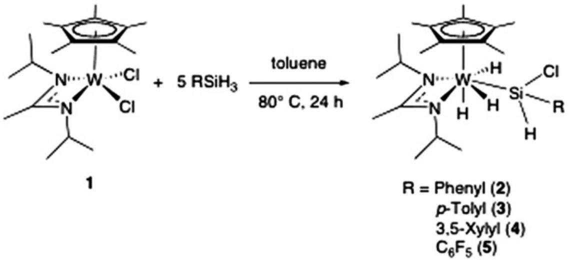
resonances, indicating C_1 symmetry for the complex. Tungsten satellites were observable for the hydride resonances, and the W–H coupling constant for all hydrides of ca. 40 Hz is similar to those reported for $[C_5Me_5(dmpe)W(H)_2]$-based compounds [11,12]. The NMR data for complexes **3**–**5** follow similar trends (Table 1). The NMR spectra were found to remain unchanged over the temperature range of −50–80 °C. Using the inversion recovery method, the minimum T_1 relaxation times were found to be 950 (H_a), 800 (H_b), and 980 ms (H_c), indicative of classical hydrides.

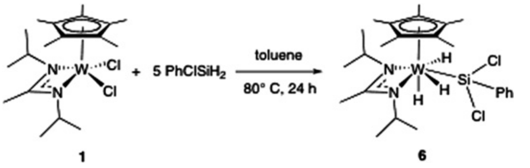


(1)

Complexes **2**–**5** appear to be quite stable and relatively unreactive. Heating at 100 °C for 24 h in C_6D_6 resulted in no detectable decomposition of **2** (by ^1H NMR spectroscopy). Addition of an excess of PMe_3 to **2** gave no reaction with heating to 100 °C for 24 h. Reactions with diphenylacetylene, benzophenone, acetophenone, norbornene, and 3,3-dimethylbut-1-ene did not proceed at room temperature but resulted in numerous unidentified organometallic species upon heating to 80 °C for 6 h.

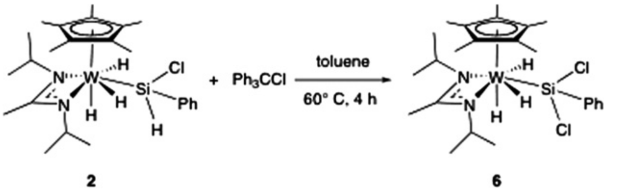
2.2. Reactions of secondary silanes with Cp*(Am)WCl$_2$

In reactions of primary silanes with complex **1**, use of less than 5 equiv of $RSiH_3$ resulted in a tertiary silyl-containing product (*vida infra*). It was therefore of interest to explore the reactivity of **1** with secondary silanes in order to isolate such species. Using the same reaction conditions employed for the synthesis of **2**–**5**, complex **1** was found to react with $H_2SiPhCl$ to afford $Cp^*(Am)W(H)_3(SiPhCl_2)$ (**6**) as a light green solid in 27% isolated yield (Eq. (2)). The ^1H NMR spectrum reveals only two inequivalent hydride resonances, integrating for three hydrides total, at 4.61 ppm (1H, $J_{SiH} = 9.9$ Hz) and 1.05 ppm (2H, $J_{SiH} = 17.8$ Hz). The ^{29}Si NMR spectrum displays a single resonance at 47.8 ppm. Interestingly, the isopropyl groups of the amidinate ligand are equivalent, indicating that the ligand lies on a plane of symmetry. Reactions of **2** with the secondary silanes Ph_2SiH_2, Et_2SiH_2, and $MesClSiH_2$ did not proceed after one week of heating at 80 °C in C_6D_6.



(2)

Complex **6** can alternatively be synthesized from reaction of **2** with one equiv of trityl chloride at 60 °C for 4 h in toluene, quantitatively by NMR spectroscopy (Eq. (3)). This method is a more convenient route to the dichlorosilyl species. Complex **6** does not react further with Ph_3CCl in C_6D_6 at 100 °C for 24 h. Thus, the Si–H bond of **2** appears to represent the most hydridic center in these type of complexes.



(3)

Comparison of the NMR spectra of complexes **2** and **6** allows for definitive assignments of the hydride resonances (Fig. 1). Thus, the resonance at ca. 5 ppm (H_a) observed in **2** and **6** corresponds to a hydride ligand that is *trans* to the Cp* ligand. The shift at ca. 1 ppm (H_b) for **2** and **6** corresponds to hydride ligands in close proximity to the Cl atom of the silyl ligand. The furthest upfield signal at ca. −1 ppm (H_c), observed only in **2**, correlates to the hydride nearest to the Si–H group. In complex **2**, H_c exhibits the largest coupling to Si ($J_{SiH} = 24.6$ ppm). This increased coupling is suggestive of a significant Si···H–W interaction (IHI). H_c is approximately *trans* to the Cl group on silicon, allowing for overlap with the Si–Cl antibonding orbital. Two such interactions are seen in complex **6** with the H_b hydrides ($J_{SiH} = 17.8$ Hz).

2.3. Solid-state structure of 2

Suitable crystals of **2** for single-crystal X-ray diffraction were grown by slow evaporation of pentane at room temperature over one week. The X-ray structure of **2** reveals a 3-legged piano stool geometry of the Cp*, amidinate ligand, and silyl ligands about W, and the W–Si bond length of 2.490(4) Å is typical for a W–Si single bond (Fig. 2). The N(1)–W(1)–N(2) angle of 63.5(4)° is as expected for an amidinate ligand, and the silyl group is canted slightly towards N(2) as seen by the N(1)–W(1)–Si(1) angle of 124.9(3)° and the N(2)–W(1)–Si(1) angle of 113.3(3)°. The elongated Si–Cl bond length of 2.138(5) Å supports the identification of an interligand H···Si interaction between a W–H and the Si–Cl antibonding orbital. Due to insufficient data, the hydrides were not located.

A similar compound, $Cp^*(CO)_2W(H)_2(SiHCl_2)$, has been reported in the literature [27]. Interestingly, this complex adopts a pseudo-octahedral structure (with the Cp* ligand considered as occupying a single site) and has a W–Si bond length of 2.4902(9) Å. This is a significantly different geometry than that observed for **2**. Additionally, both W–H bonds of $Cp^*(CO)_2W(H)_2(SiHCl_2)$ interact much more strongly with the silicon center, based on the Si···H distances of 1.91(3) and 1.90(3) Å. Coupling constants were not reported for this compound. Although two interligand hypervalent interactions have been implicated for the lengthened Si–Cl bonds (2.0981(14) and 2.1084(13) Å), the Si–Cl distance in **2** is slightly longer, indicating a stronger interaction, and this would be consistent with a more electron-rich W center in **2**.

Table 1
NMR data for complexes **2**–**5**.

Complex	δ ^1H (H_a) ($^2J_{SiH}$)	δ ^1H (H_b) ($^2J_{SiH}$)	δ ^1H (H_c) ($^2J_{SiH}$)	δ ^1H (SiH) ($^1J_{SiH}$)	δ ^{29}Si
$Cp^*(Am)WH_3(SiHPhCl)$ (**2**)	5.24 (<7)	0.92 (11.1)	−1.28 (24.6)	8.41 (199.5)	43.9
$Cp^*(Am)WH_3(SiHTolylCl)$ (**3**)	5.35 (14.4)	0.95 (9.3)	−1.15 (26.5)	8.44 (198.0)	43.2
$Cp^*(Am)WH_3(SiHXylylCl)$ (**4**)	5.39 (7.8)	0.94 (15.4)	−1.11 (31.9)	8.43 (198.1)	43.3
$Cp^*(Am)WH_3[SiH(C_6F_5)Cl]$ (**5**)	4.74 (22.7)	0.58 (10.6)	−1.61 (21.6)	8.52 (215.5)	22.1

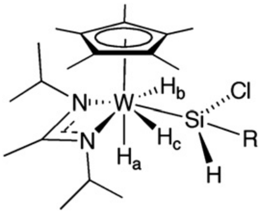


Fig. 1. Assignment of hydrides based on NMR spectroscopy.

2.4. DFT calculations of **2**

Because the hydride ligands of **2** were not located by X-ray crystallography, DFT calculations at the B3LYP/LANL2DZ level of theory were undertaken. Using the crystal structure as a starting point, several different arrangements of the hydrides were minimized, resulting in the lowest energy structure shown in Fig. 3. The bond distances and angles are in agreement with those observed by X-ray crystallography, including the elongated Si—Cl bond distance of 2.16 Å. One hydride, H_a, is located *trans* to the Cp* centroid, with a W—H bond distance of 1.69 Å. The other two hydride ligands occupy the open pockets between the amidinate and silyl ligands. The W—H group *cis* to Cl, H_b, is associated with a bond distance of 1.68 Å. The other hydride, H_c, is approximately *trans* (156°) to the Cl atom on the silyl group and is involved with a slightly longer W—H bond distance of 1.71 Å. Additionally, H_c is associated with the shortest Si—H distance (2.10 Å). These structural features correlate well with the structure hypothesized from NMR data.

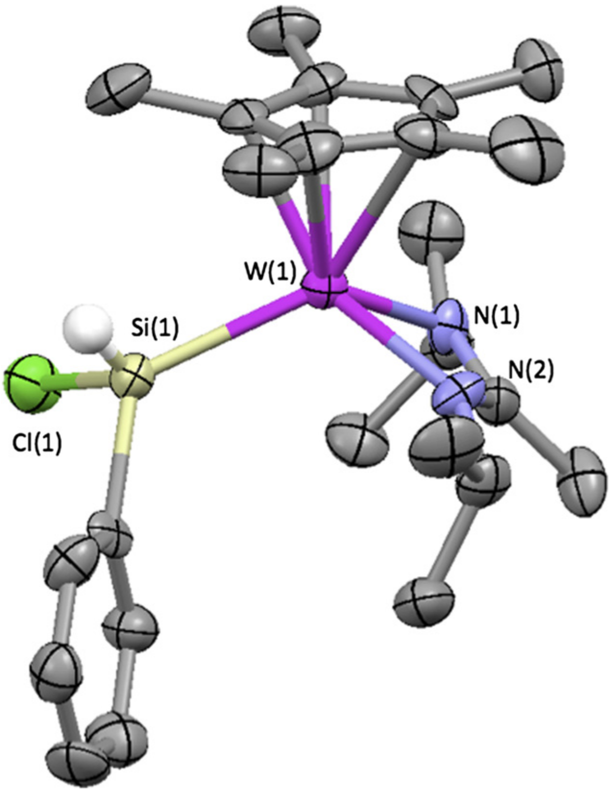


Fig. 2. Molecular structure of **2** displaying thermal ellipsoids at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): W(1)—Si(1) = 2.490(4), Si(1)—Cl(1) = 2.138(5), W(1)—N(1) = 2.138(11), W(1)—N(2) = 2.089(11). Selected angles (deg.): N(1)—W(1)—N(2) = 63.5(4), N(1)-W(1)—Si(1) = 124.9(3), N(2)—W(1)-Si(1) = 113.3(3).

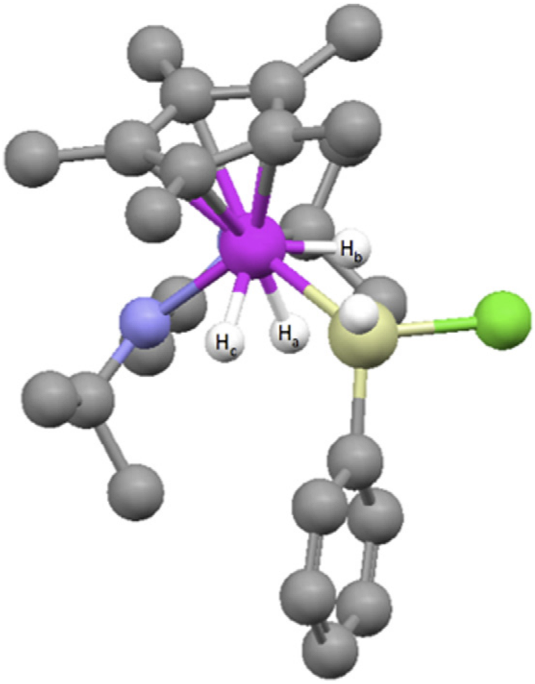


Fig. 3. Optimized geometry of Cp*(Am)W(H)$_3$(SiHPhCl).

To further probe the nature of the H···Si interactions in **2**, NMR spin—spin coupling predictions and NBO calculations were performed. The following J_{Si-H} values were found: H_a = 2 Hz, H_b = 11 Hz, and H_c = 39 Hz. These coupling constants agree very well with experimentally obtained values ($H_a \leq 7$ Hz, $H_b = 11.1$ Hz, and $H_c = 24.6$ Hz) and indicate that H_c has the strongest interaction with Si. The other two hydride ligands show little Si—H bonding. Donation from the W—H_c bonding orbital to the Si—Cl antibonding orbital was found to be present in the NBO analysis. Additional weak interactions between all W—H bonding orbitals and the W—Si antibonding orbital were identified.

2.5. Proposed mechanism

Several experiments were conducted to probe the reaction mechanism for the formation of a chlorosilyl ligand starting from a primary silane. Under the reaction conditions of Eq. (1), lower quantities of phenylsilane (2–4 equiv) resulted in unreacted **1**, complex **2**, and a side product, Cp*(Am)W(H)$_3$(SiPhCl$_2$) (**6**), as determined from an independently synthesized sample. For example, 3 equiv of phenylsilane was found to react with **1** at 80 °C for 16 h to give 10% of **1**, 20% of **6**, and 70% of **2** by NMR spectroscopy. The use of 5 equiv or more of phenylsilane cleanly yielded **2**, along with 1 equiv $H_2SiPhCl$ and 3 equiv of unreacted $PhSiH_3$. Complex **1** was heated to 80 °C for 24 h with 25 equiv of $PhSiH_3$ to give only **2** and 1 equiv of $PhSiH_2Cl$. Similarly, **1** was heated to 80 °C for 24 h with 25 equiv of $PhSiH_2Cl$ to give only **6** and 1 equiv of $PhSiHCl_2$. Thus, the complex with more chloro substituents on the silyl group appears to be the most stable product. Additionally, the formation of strong Si—Cl bonds appears to be a driving force of the reaction. For comparison, the analogous treatment of **1** with 5 equiv $PhGeH_3$ in C_6D_6 for 24 h at 80 °C results in no reaction.

The proposed mechanism, detailed in Fig. 4, involves a series of Si—H bond oxidative additions and Si—Cl bond reductive eliminations. DFT calculations were performed to determine the thermodynamic stability of each proposed intermediate, taking into account both the complexes and organosilanes. The formation of Cp*(Am)

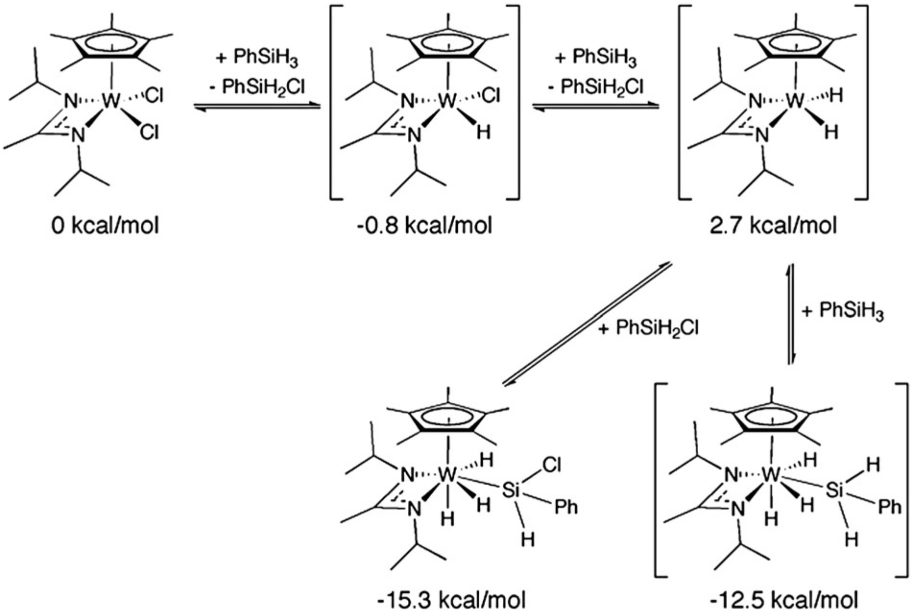


Fig. 4. Proposed mechanism for the formation of complex **2** (relative energies indicated).

WHCl from **1** and the subsequent formation of Cp*(Am)WH_2 appear to be essentially isoenergetic. Further reaction to form the isolable product **2** is downhill by 15 kcal/mol. Formation of the Cp*(Am)$H_3(SiH_2Ph)$ is calculated to be ca. 3 kcal/mol less favorable than **2**, large enough to explain the exclusive observation of **2**.

Multiple attempts to isolate or observe the Cp*(Am)WH_2 species were undertaken to gain further insight into the formation of **2**. No reaction was observed after heating **1** with an excess of Et_3SiH in C_6D_6 for 24 h at 80 °C. Complex **1** was also unreactive towards nBu_3SnH under identical conditions. Conversely, reactions with reagents such as $LiEt_3BH$, $LiAlH_4$, and $NaBH_4$ resulted in complex mixtures of products. Additionally, conversion of **1** to Cp*(Am)WR_2 complexes using MeMgCl, Bn_2Mg, nBuLi, and MeLi resulted in multiple unidentified products. In all experiments, no evidence for the targeted complex was observed.

3. Concluding remarks

In conclusion, a variety W(VI) silyl trihydride complexes are accessable starting from the W(IV) complex, Cp*(Am)WCl_2. Multiple Si–H bond activations are proposed for the formation of such complexes. Limitations of silane activations appear to be driven by steric bulk, and one driving force for the reaction seems to be the formation of Si–Cl bonds. An interligand interaction between one W–H bond and the silyl ligand is observed by NMR spectroscopy and X-ray crystallography – specifically an increased Si–H coupling constant and elongated Si–Cl bond. DFT calculations support the experimental findings. Additionally, Cp*(Am)WH_3(SiHPhCl) undergoes Si–H activation with CPh_3Cl to selectively form Cp*(Am)$WH_3(SiPhCl_2)$. All attempts to synthesize complexes of the type Cp*(Am)WR_2 (R = H, aryl, alkyl) have so far been unsuccessful. Reactions of hydrosilanes in this Cp*(Am)W system appear to be strongly driven to hexavalent hydrido silyl species such as those described above.

4. Experimental

4.1. General considerations

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and $NaHCO_3$. Pentane was then dried over $MgSO_4$ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Toluene and pentane were dried over Na and distilled under N_2. Benzene-d_6 was dried by vacuum distillation from Na/K alloy.Cp*(Am)WCl_2 (**1**) was prepared according to literature methods [10]. All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker AVB 400, AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for ^1H. $^{31}P\{^1H\}$ NMR spectra were referenced relative to 85% H_3PO_4 external standard (δ = 0). $^{13}C\{^1H\}$ NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For $^{13}C\{^1H\}$ NMR spectra, resonances obscured by the solvent signal are omitted. ^{29}Si NMR spectra were referenced relative to a tetramethylsilane standard and obtained via 2D ^1H ^{29}Si HMBC unless specified otherwise. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

4.2. Cp*(Am)W(H)$_3$(SiHPhCl) (**2**)

To a 20 mL toluene solution of Cp*(Am)WCl2 (0.100 g, 0.188 mmol) was added an excess of phenylsilane (0.108 g, 1.00 mmol). The reaction mixture was stirred at 80 °C for 24 h, after which the resulting transparent brown solution was evacuated to dryness. The remaining brown residue was then dissolved in 15 mL pentane, and the solution was filtered through Celite. The solution was then concentrated to approximately 2 mL and cooled to −35 °C. The brown precipitate was isolated by decantation and drying under vacuum to give a light tan solid in 42% yield (0.045 g, 0.079 mmol). ^1H NMR (C_6D_6, 600 MHz): δ 8.41 (1H, d, $J = 5.8$ Hz, $^1J_{SiH} = 199.5$ Hz, Si*H*), 8.16 (2H, d, $J = 7.4$ Hz, Ar*H*), 7.34 (2H, t, $J = 7.4$ Hz, Ar*H*), 7.17 (1H, t, $J = 7.4$ Hz, Ar*H*), 5.24 (1H, m, $^1J_{WH} = 34.0$ Hz, W*H*), 3.24 (1H, sept, $J = 6.5$ Hz, CH^iPr_2), 3.07 (1H, sept, $J = 6.5$ Hz, CH^iPr_2), 1.76 (15H, s, C_5Me_5), 1.26 (3H, s, C*Me*), 1.15

(3H, d, J = 6.5, CH^i*Pr*$_2$), 1.03 (3H, d, J = 6.5, CH^i*Pr*$_2$), 0.92 (1H, dd, J = 4.5 Hz, 9.5 Hz, $^1J_{\mathrm{SiH}}$ = 11.1 Hz, $^1J_{\mathrm{WH}}$ = 45.8 Hz, W*H*), 0.76 (3H, d, J = 6.5, CH^i*Pr*$_2$), 0.58 (3H, d, J = 6.5, CH^i*Pr*$_2$), −1.28 (1H, m, $^1J_{\mathrm{SiH}}$ = 24.6 Hz, $^1J_{\mathrm{WH}}$ = 47.6 Hz, W*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 173.9 (*C*Me), 151.7 (Ar*C*), 133.24 (Ar*C*), 127.9 (Ar*C*), 129.1 (Ar*C*), 103.0 (*C*$_5$Me$_5$), 49.3 (*C*H^{i}Pr$_2$), 49.0 (*C*H^{i}Pr$_2$), 25.5 (CH^i*Pr*$_2$), 24.9 (CH^i*Pr*$_2$), 23.9 (CH^i*Pr*$_2$), 23.8 (CH^i*Pr*$_2$), 15.2 (C*Me*), 10.6 (C$_5$*Me*$_5$). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 43.9. Anal. Calcd for $C_{24}H_{41}N_2ClSiW$: C, 47.65; H, 6.84; N, 4.63. Found: C, 47.54; H, 6.91; N, 4.57.

4.3. *Cp*(Am)W(H)$_3$(SiH(Tolyl)Cl) (**3**)*

By a procedure analogous to that for **2**, complex **3** was obtained as a light tan solid in 34% yield (0.040 g, 0.065 mmol). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.44 (1H, d, J = 5.9 Hz, $^1J_{\mathrm{SiH}}$ = 198.0 Hz, Si*H*), 8.14 (2H, d, J = 7.8 Hz, Ar*H*), 7.21 (2H, d, J = 7.8 Hz, Ar*H*), 5.35 (1H, m, $^1J_{\mathrm{SiH}}$ = 14.4 Hz, $^1J_{\mathrm{WH}}$ = 35.4 Hz, W*H*), 3.29 (1H, sept, J = 6.6 Hz, C*H*^{i}Pr$_2$), 3.16 (1H, sept, J = 6.6 Hz, C*H*^{i}Pr$_2$), 2.21 (3H, s, ArC*H*$_3$), 1.81 (15H, s, C$_5$*Me*$_5$), 1.32 (3H, s, C*Me*), 1.18 (3H, d, J = 6.6, CH^i*Pr*$_2$), 1.07 (3H, d, J = 6.6, CH^i*Pr*$_2$), 0.95 (1H, dd, J = 5.1 Hz, 9.5 Hz, $^1J_{\mathrm{SiH}}$ = 9.3 Hz, $^1J_{\mathrm{WH}}$ = 32.2 Hz, W*H*), 0.83 (3H, d, J = 6.6, CH^i*Pr*$_2$), 0.68 (3H, d, J = 6.6, CH^i*Pr*$_2$), −1.15 (1H, m, $^1J_{\mathrm{SiH}}$ = 26.5 Hz, $^1J_{\mathrm{WH}}$ = 47.3 Hz, W*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 173.8 (*C*Me), 148.2 (Ar*C*), 136.8 (Ar*C*), 133.5 (Ar*C*), 127.9 (Ar*C*), 102.9 (*C*$_5$Me$_5$), 49.3 (*C*H^{i}Pr$_2$), 49.0 (*C*H^{i}Pr$_2$), 25.5 (CH^i*Pr*$_2$), 25.1 (CH^i*Pr*$_2$), 24.0 (CH^i*Pr*$_2$), 23.9 (CH^i*Pr*$_2$), 21.0 (Ar*C*H$_3$), 15.2 (C*Me*), 10.7 (C$_5$*Me*$_5$). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 43.2. Anal. Calcd for $C_{26}H_{45}N_2ClSiW$: C, 48.51; H, 7.00; N, 4.53. Found: C, 49.01; H, 6.68; N, 3.94.

4.4. *Cp*(Am)W(H)$_3$(SiH(Xylyl)Cl) (**4**)*

By a procedure analogous to that for **2**, complex **4** was obtained as a light tan solid in 37% yield (0.041 g, 0.069 mmol). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.43 (1H, d, J = 6.0 Hz, $^1J_{\mathrm{SiH}}$ = 198.1 Hz, Si*H*), 7.88 (2H, s, Ar*H*), 6.67 (1H, s, Ar*H*), 5.39 (1H, m, $^1J_{\mathrm{SiH}}$ = 7.8 Hz, $^1J_{\mathrm{WH}}$ = 36.7 Hz, W*H*), 3.28 (1H, sept, J = 6.5 Hz, C*H*^{i}Pr$_2$), 3.19 (1H, sept, J = 6.5 Hz, C*H*^{i}Pr$_2$), 2.28 (6H, s, ArC*H*$_3$), 1.81 (15H, s, C$_5$*Me*$_5$), 1.34 (3H, s, C*Me*), 1.20 (3H, d, J = 6.5, CH^i*Pr*$_2$), 1.07 (3H, d, J = 6.5, CH^i*Pr*$_2$), 0.92 (1H, dd, J = 5.5 Hz, 10.4 Hz, $^1J_{\mathrm{SiH}}$ = 7.4 Hz, $^1J_{\mathrm{WH}}$ = 35.4 Hz, W*H*), 0.86 (3H, d, J = 6.5, CH^i*Pr*$_2$), 0.78 (3H, d, J = 6.5, CH^i*Pr*$_2$), −1.11 (1H, m, $^1J_{\mathrm{SiH}}$ = 31.9 Hz, $^1J_{\mathrm{WH}}$ = 46.3 Hz, W*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 173.7 (*C*Me), 151.1 (Ar*C*), 135.7 (Ar*C*), 131.4 (Ar*C*), 129.4 (Ar*C*), 102.9 (*C*$_5$Me$_5$), 49.3 (*C*H^{i}Pr$_2$), 49.1 (*C*H^{i}Pr$_2$), 25.5 (CH^i*Pr*$_2$), 25.0 (CH^i*Pr*$_2$), 24.0 (CH^i*Pr*$_2$), 22.9 (CH^i*Pr*$_2$), 21.29 (Ar*C*H$_3$), 21.27 (Ar*C*H$_3$), 15.3 (C*Me*), 10.6 (C$_5$*Me*$_5$). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 43.3. Anal. Calcd for $C_{26}H_{45}N_2ClSiW$: C, 49.33; H, 7.17; N, 4.43. Found: C, 49.37; H, 7.18; N, 4.22.

4.5. *Cp*(Am)W(H)$_3$(SiH(C$_6$F$_5$)Cl) (**5**)*

By a procedure analogous to that for **2**, complex **5** was obtained as a light tan solid in 35% yield (0.046 g, 0.0696 mmol). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.52 (1H, br s, $^1J_{\mathrm{SiH}}$ = 215.5 Hz, Si*H*), 4.74 (1H, m, $^1J_{\mathrm{SiH}}$ = 22.7 Hz, $^1J_{\mathrm{WH}}$ = 35.9 Hz, W*H*), 3.18 (1H, sept, J = 6.5 Hz, C*H*^{i}Pr$_2$), 2.99 (1H, sept, J = 6.5 Hz, C*H*^{i}Pr$_2$), 1.73 (15H, s, C$_5$*Me*$_5$), 1.23 (3H, s, C*Me*), 1.10 (3H, d, J = 6.5, CH^i*Pr*$_2$), 0.98 (3H, d, J = 6.5, CH^i*Pr*$_2$), 0.66 (3H, d, J = 6.5, CH^i*Pr*$_2$), 0.58 (1H, m, $^1J_{\mathrm{SiH}}$ = 10.6 Hz, $^1J_{\mathrm{WH}}$ = 39.9 Hz, W*H*), 0.45 (3H, d, J = 6.5, CH^i*Pr*$_2$), −1.61 (1H, m, $^1J_{\mathrm{SiH}}$ = 21.6 Hz, $^1J_{\mathrm{WH}}$ = 45.8 Hz, W*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 174.9 (*C*Me), 128.2 (Ar*C*), 127.9 (Ar*C*), 127.5 (Ar*C*), 103.6 (*C*$_5$Me$_5$), 49.4 (*C*H^{i}Pr$_2$), 48.6 (*C*H^{i}Pr$_2$), 25.1 (CH^i*Pr*$_2$), 24.4 (CH^i*Pr*$_2$), 23.6 (CH^i*Pr*$_2$), 23.5 (CH^i*Pr*$_2$), 14.9 (C*Me*), 10.5 (C$_5$*Me*$_5$). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 22.1. Anal. Calcd for $C_{24}H_{36}N_2ClFSiW$: C, 41.48; H, 5.22; N, 4.03. Found: C, 41.67; H, 5.13; N, 3.78.

4.6. *Cp*(Am)W(H)$_3$(SiPhCl$_2$) (**6**)*

By a procedure analogous to that for **2**, complex **6** was obtained as a light green solid in 27% yield (0.040 g, 0.063 mmol). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.38 (2H, d, J = 7.5 Hz, Ar*H*), 7.34 (2H, t, J = 7.5 Hz, Ar*H*), 7.09 (1H, t, J = 7.4 Hz, Ar*H*), 4.61 (1H, t, J = 8.5, $^1J_{\mathrm{SiH}}$ = 9.9 Hz, $^1J_{\mathrm{WH}}$ = 25.7 Hz, W*H*), 3.16 (2H, sept, J = 7.0 Hz, C*H*^{i}Pr$_2$), 1.87 (15H, s, C$_5$*Me*$_5$), 1.19 (3H, s, C*Me*), 1.05 (2H, d, J = 8.5, $^1J_{\mathrm{SiH}}$ = 17.8 Hz, $^1J_{\mathrm{WH}}$ = 32.8 Hz, W*H*), 0.89 (12H, ov dd, J = 7.0, CH^i*Pr*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 173.9 (*C*Me), 151.7 (Ar*C*), 133.24 (Ar*C*), 127.9 (Ar*C*), 129.1 (Ar*C*), 103.0 (*C*$_5$Me$_5$), 49.3 (*C*H^{i}Pr$_2$), 49.0 (*C*H^{i}Pr$_2$), 25.5 (CH^i*Pr*$_2$), 24.9 (CH^i*Pr*$_2$), 23.9 (CH^i*Pr*$_2$), 23.8 (CH^i*Pr*$_2$), 15.2 (C*Me*), 10.6 (C$_5$*Me*$_5$). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 47.8. Anal. Calcd for $C_{24}H_{40}N_2Cl_2SiW$: C, 45.08; H, 6.31; N, 4.38. Found: C, 45.80; H, 6.24; N, 3.98.

4.7. *X-ray crystallography*

The X-ray analysis of **2** was carried out at UC Berkeley CHEXRAY crystallographic facility. Measurements were made on an APEX CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Data was integrated and empirical absorption corrections were made using the APEX2 program package. The structure as solved by direct methods and expanded using Fourier techniques. All calculations were performed using the SHELXTL crystallographic package. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

4.8. *Computational details*

All calculations were performed in the molecular graphics and computing facility of the College of Chemistry, University of California, Berkeley (NSF grant CHE-0233882). Calculations were performed using the Gaussian '09 suite of programs [28] at the B3LYP/LANL2DZ level of theory with LANL2DZdp ECP polarization functions for W [29]. The crystal structures of **1** and **2** were used as starting geometries. Vibrational frequencies were calculated for all converged structures and confirm that these structures lie on a minimum. Graphical representations of the structures were generated using Mercury. The natural bond orbital (NBO) program in Gaussian 03 was utilized to determine the presence of a significant interaction between the W–H bonding orbital and the Si–Cl antibonding orbital.

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Appendix A. Supplementary material

CCDC 803373 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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