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# Synthons for Coordinatively Unsaturated Complexes of Tungsten, and Their Use for the Synthesis of High Oxidation-State Silylene Complexes

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***Abstract:*** Reduction of Cp*$WCl_4$ afforded the metalated complex ($\eta^6$-$C_5Me_4CH_2$)(dmpe)W(H)Cl (**1**) (Cp* = $C_5Me_5$, dmpe = 1,2-bis(dimethylphosphino)ethane). Reactions with CO and $H_2$ suggested that **1** is in equilibrium with the 16-electron species [Cp*(dmpe)WCl], and **1** was also shown to react with silanes $R_2SiH_2$ ($R_2$ = $Ph_2$ and PhMe) to give the tungsten(IV) silyl complexes Cp*(dmpe)(H)(Cl)W($SiHR_2$) (**6a**, $R_2$ = $Ph_2$; **6b**, $R_2$ = PhMe). Abstraction of the chloride ligand in **1** with $LiB(C_6F_5)_4$ gave a reactive species that features a doubly metalated Cp* ligand, [($\eta^7$-$C_5Me_3(CH_2)_2$)(dmpe)W(H)$_2$][$B(C_6F_5)_4$] (**4**). In its reaction with dinitrogen, **4** behaves as a synthon for the 14-electron fragment [Cp*(dmpe)W]$^+$, to give the dinuclear dinitrogen complex {[Cp*(dmpe)W]$_2$($\mu$-$N_2$)}{$B(C_6F_5)_4$}$_2$ (**5**). Hydrosilanes $R_2SiH_2$ ($R_2$ = $Ph_2$, PhMe, $Me_2$, Dipp(H); Dipp = 2,6-diisopropylphenyl) were shown to react with **4** in double Si−H bond activation reactions to give the silylene complexes [Cp*(dmpe)$H_2$W=$SiR_2$][$B(C_6F_5)_4$] (**8a**−**d**). Compounds **8a**,**b** ($R_2$ = $Ph_2$ and PhMe, respectively) were also synthesized by abstraction of the chloride ligands from silyl complexes **6a**,**b**. Dimethylsilylene complex **8c** was found to react with chloroalkanes RCl (R = Me, Et) to liberate trialkylchlorosilanes $RMe_2SiCl$. This reaction is discussed in the context of its relevance to the mechanism of the direct synthesis for the industrial production of alkylchlorosilanes.

## Introduction

Transition-metal silylene complexes are of interest as silicon analogues of metal carbenes, and as possible intermediates in a number of metal-catalyzed transformations involving organosilicon compounds.[1] In metal carbene chemistry, it is well established that the reactivity and electronic structure of the $CR_2$ ligand (R = H, alkyl, or aryl) is highly dependent on the nature of the metal fragment to which it is bound.[2] Late transition-metal carbene complexes are typically electrophilic at carbon, while early metal centers often give rise to nucleophilic carbene ligands. To date, a number of base-free transition-metal dialkyl and diaryl silylene complexes have been synthesized, and these feature ruthenium,[3] osmium,[4] iridium,[5] and platinum[6] in relatively high $d^n$ configurations ($n \geq 6$). In general, these silylene complexes have been shown to be very electrophilic at silicon. Thus, it is of interest to investigate silylene complexes involving early transition-metal centers with low $d^n$ configurations. Such species may exhibit novel chemical properties for the metal silylene fragment, opening pathways to new transformations for organosilicon compounds.

Our efforts to synthesize base-free silylene complexes of the more electropositive early transition elements initially focused on the group 6 metals, and herein we report the synthesis and study of silylene complexes of the type [Cp*(dmpe)$(H)_2$W=$SiR_2$][$B(C_6F_5)_4$] (Cp* = $\eta^5$-$C_5Me_5$, dmpe = $Me_2PCH_2CH_2PMe_2$, $R_2$ = $Ph_2$, $Me_2$, PhMe, Dipp(H); Dipp = 2,6-diisopropylphenyl). These compounds were prepared with the use of new, reactive tungsten complexes featuring metalated Cp* ligands, and the synthesis of this class of silylene complexes was communicated previously.[7] Ueno, Ogino, and co-workers have also recently

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reported a low-valent, base-free tungsten silylene complex, $Cp^*W(CO)_2(=SiMes_2)(SiMe_3)$.[8]

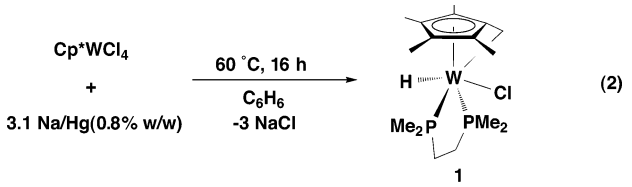
We have been interested in defining the reactivity patterns for these new high oxidation-state silylene complexes and making comparisons to those observed for their late metal counterparts. Our studies have shown that these compounds, like late metal silylenes, feature highly Lewis-acidic silicon centers. However, reactions with chloroalkanes have produced the first example of insertion of a metal-bound silylene into a C−Cl bond to liberate a trialkylchlorosilane. This homogeneous reaction demonstrates a proposed step in the direct synthesis, the metal-catalyzed heterogeneous reaction that is the primary industrial source of organosilanes.[9]

## Results and Discussion

We have previously established routes to platinum and iridium silylene complexes that involve activation of two silicon−hydrogen bonds of a hydrosilane, via oxidative addition and subsequent α-elimination.[5,6b] This route requires access to unsaturated metal centers. For example, a 14-electron metal fragment is required for formation of an 18-electron silylene dihydride complex directly from a hydrosilane (eq 1). Given the promise of this silylene-extrusion reaction as a general route to metal silylene complexes, we sought to synthesize $d^0$ examples via reactions of hydrosilanes with coordinatively unsaturated but inherently electron-rich fragments of the type $[Cp^*L_2W]^+$.[10]

$$L_nM + H_2SiR_2 \rightarrow L_n(H)_2M{=}SiR_2 \qquad (1)$$

**Tungsten Complexes Featuring Metalated Pentamethylcyclopentadienyl Ligands.** A 14-electron $[Cp^*L_2W]^+$ cation might be produced by halide ion abstraction from a formally 16-electron precursor of the type $Cp^*L_2WCl$. Complexes of this type are rare, but Baker and co-workers have prepared $Cp^*(PMe_3)(\eta^2\text{-}Me_2PCH_2)W(H)Cl$, which appears to be in equilibrium with $Cp^*(Me_3P)_2WCl$.[11] In an attempt to synthesize the related complex Cp*(dmpe)WCl as a precursor to the $[Cp^*(dmpe)W]^+$ fragment, $Cp^*WCl_4$[12] was reduced in benzene with 3.0 equiv of Na/Hg (0.8% w/w) in the presence of dmpe (eq 2). The chelating diphosphine ligand was not metalated in the reaction; however, an intramolecular C−H bond activation took place at the Cp* ligand, to produce the hydrido chloride complex $(\eta^6\text{-}C_5Me_4CH_2)(dmpe)W(H)Cl$ (**1**). This reduction proceeded over 16 h at 60 °C and resulted in isolation of **1** in 83% yield after recrystallization from pentane.




(2)

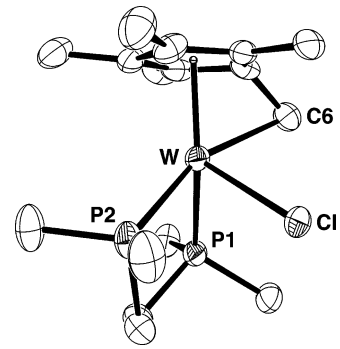



***Figure 1.*** ORTEP diagram of Cp*-metalated complex **1**.

***Table 1.*** Selected Distances (Å) and Angles (deg) for **1**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| W−P1 | 2.405(2) | W−C3 | 2.316(8) |
| W−P2 | 2.464(2) | W−C4 | 2.395(9) |
| W−Cl | 2.522(2) | W−C5 | 2.316(8) |
| W−C1 | 2.338(8) | W−C6 | 2.344(9) |
| W−C2 | 2.16(1) | | |
| Bond Angles | | | |
| P1−W−P2 | 81.38(8) | P2−W−Cl | 78.25(7) |
| P1−W−C6 | 90.6(2) | P2−W−C6 | 158.6(2) |
| P1−W−Cl | 85.74(7) | W−C6−C1 | 64.1(5) |
| Cl−W−C6 | 81.5(2) | | |

The $^1$H NMR spectrum of **1** in benzene-$d_6$ is consistent with a low-symmetry structure. Four individual doublet resonances are observed for the dmpe methyl groups at $\delta$ 0.98, 1.23, 1.29, and 1.53, and the intact ring methyl groups resonate separately at $\delta$ 2.12, 2.07, 2.06, and 1.82. The $^{31}P\{^1H\}$ NMR spectrum of **1** features two resonances at $\delta$ 10.8 ($J_{PW}$ = 233 Hz) and 18.6 ($J_{P'W}$ = 253 Hz), confirming the binding of the dmpe ligand to a low-symmetry metal center. The structure of **1** was confirmed by X-ray crystallography, and an ORTEP diagram of the molecule is shown in Figure 1. The geometry of **1** in the solid state supports the $C_1$ symmetry observed for the complex by solution NMR spectroscopy, and the binding of the $(\eta^6\text{-}C_5Me_4CH_2)$ ligand is reminiscent of that observed by Legzdins and co-workers for $(\eta^6\text{-}C_5Me_4CH_2)W(NO)(CH_2CMe_3)(PMe_3)$.[13,14] The $\pi$-bound fragment in **1** is best described as an $\eta^5$-cyclopentadienyl:$\eta^1$-alkyl ligand, although it seems to exhibit partial tetramethylfulvene character, having a shortened C1−C6 bond length of 1.41(1) Å (intermediate between single and double CC bond lengths). Selected bond distances and angles from the crystal structure of **1** are listed in Table 1, and details of the data collection are summarized in Table 2.

By analogy to $Cp^*(PMe_3)(\eta^2\text{-}Me_2PCH_2)W(H)Cl$, it seemed likely that **1** would be in equilibrium with the 16-electron intermediate Cp*(dmpe)WCl. In support of this, reaction of **1** with carbon monoxide at 70 °C over 24 h resulted in formation of the adduct Cp*(dmpe)W(CO)Cl (**2**). Compound **2** was isolated in 68% yield after recrystallization from $Et_2O$, and its

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(10) In this discussion, a $d^0$ silylene complex is one in which invocation of two metal-based electrons in bonding to the silylene ligand results in a $d^0$ electron configuration.
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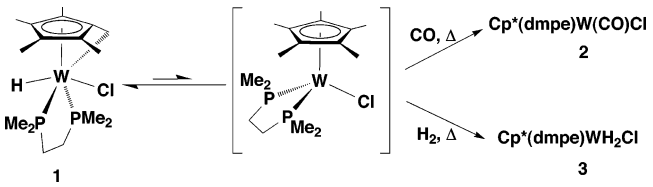
***Table 2.*** Details of Crystallographic Data Collection

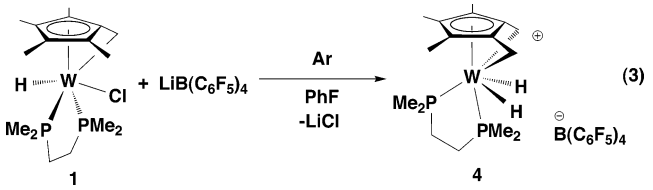
| compound | 1 | 4 | 5 | 6b | 7 | 8c |
|---|---|---|---|---|---|---|
| empirical formula | $C_{16}H_{31}ClP_2W$ | $C_{40}H_{31}BF_{20}P_2W$ | $C_{46}H_{35}BF_{21}N$ | $C_{23}H_{42}ClP_2SiW$ | $C_{35}H_{50}P_2SiW$ | $C_{42}H_{39}BF_{20}P_2SiW$ |
| FW | 504.66 | 1148.25 | 1258.36 | 626.91 | 744.66 | 1208.42 |
| crystal size (mm) | 0.18 × 0.15 × 0.13 | 0.45 × 0.25 × 0.20 | 0.17 × 0.06 × 0.04 | 0.20 × 0.13 × 0.10 | 0.21 × 0.18 × 0.15 | 0.30 × 0.15 × 0.12 |
| color | orange | orange | green | orange | yellow | orange |
| crystal system | monoclinic | monoclinic | triclinic | monoclinic | orthorhombic | orthorhombic |
| space group | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) | $P$-1 (No. 2) | $P2_1/a$ (No. 14) | $Pbca$ (No. 61) | $Pca2_1$ (No. 29) |
| $a$ (Å) | 8.7200(2) | 15.2193(2) | 12.822(1) | 17.2867(2) | 18.3293(1) | 27.4880(1) |
| $b$ (Å) | 16.6120(3) | 15.9706(2) | 14.878(1) | 9.2357(2) | 17.9586(4) | 15.5223(2) |
| $c$ (Å) | 13.9440(1) | 17.2664(3) | 15.005(1) | 17.8766(4) | 20.4990(1) | 21.3367(3) |
| α (°) | 90 | 90 | 114.902(1) | 90 | 90 | 90 |
| $\beta$ (°) | 102.536(1) | 96.322(1) | 110.473(1) | 115.65(1) | 90 | 90 |
| $\gamma$ (°) | 90 | 90 | 94.868(1) | 90 | 90 | 90 |
| $V$ (Å$^3$) | 1971.73(6) | 4171.27(9) | 2340.1(1) | 2572.83 | 6747.6(2) | 9103.9(3) |
| $Z$ | 4 | 4 | 2 | 4 | 8 | 8 |
| temp (K) | 169(1) | 153(1) | 122(1) | 142(1) | 168(1) | 155(1) |
| solution/ refinement software | TeXsan | TeXsan | SHELX-TL | TeXsan | TeXsan | TeXsan |
| $R$ | 0.033 | 0.045 | 0.046 | 0.051 | 0.023 | 0.030 |
| wR2 | | | 0.117 | | | |
| $R_W$ | 0.037 | 0.042 | | 0.069 | 0.022 | 0.037 |
| $R_{all}$ | 0.055 | 0.067 | 0.063 | 0.082 | 0.087 | 0.036 |
| GOF | 1.41 | 1.39 | 1.08 | 1.42 | 0.65 | 1.47 |

***Scheme 1***




IR spectrum exhibits a CO stretching absorbance at 1789 cm$^{-1}$, indicating that the metal center is quite electron-rich and strongly $\pi$ back-donating. This reaction suggests that the C−H bond reductive elimination/oxidative addition equilibrium shown in Scheme 1 is active for the "tucked Cp*" ligand in compound **1**. The existence of this equilibrium was further evidenced by the synthesis of the dihydride Cp*(dmpe)W(H)$_2$Cl (**3**) via reaction of **1** with excess dihydrogen at 90 °C. Reaction of **1** with deuterium gas (1 atm) at 110 °C over 10 days produced exclusively the dideuteride complex Cp*(dmpe)W(D)$_2$Cl (**3**-$d_2$), as shown by $^1$H and $^2$H NMR spectroscopy. These results indicated that this equilibrium could be utilized in activation of hydrosilanes by **1** to form tungsten−silicon bonds.

The prospect of Si−H bond activation by derivatives of compound **1** prompted us to attempt the synthesis of a more highly activated species, by abstraction of the chloride ligand in **1**. Reaction of **1** with the fluorinated borate salt Li(OEt$_2$)$_3$B(C$_6$F$_5$)$_4$ in fluorobenzene under argon resulted in a quantitative reaction within minutes and the precipitation of lithium chloride. Spectroscopic characterization of the new orange complex determined its identity to be the doubly metalated (or "doubly tucked") Cp* complex [($\eta^7$-C$_5$Me$_3$(CH$_2$)$_2$)(dmpe)W(H)$_2$][B(C$_6$F$_5$)$_4$] (**4**, eq 3). The cation **4** is an isomer of the desired 14-electron cation Cp*(dmpe)W$^+$, which was envisioned as a "synthon" or synthetic equivalent of such a species.




(3)

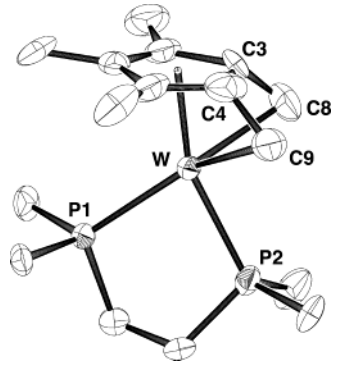



***Figure 2.*** ORTEP diagram of the cation in **4**. Hydrogen atoms are removed for clarity.

The $^1$H NMR spectrum of **4** in fluorobenzene/benzene-$d_6$ (10:1) reveals a mirror-symmetric structure for the cation. Two singlets are observed for the intact ring methyl groups at $\delta$ 1.85 (3H) and 1.68 (6H), and the diastereotopic ring methylene groups exhibit a multiplet and a singlet at $\delta$ 2.64 and 1.77, respectively. The resonance for the symmetry-equivalent tungsten hydride ligands is observed at $\delta$ −2.11, as a doublet of doublets (with $^{183}$W satellites) due to coupling to two inequivalent phosphorus nuclei ($J_{HP}$ = 58 Hz, $J_{HP'}$ = 38 Hz, $J_{HW}$ = 49 Hz). The spectroscopic properties of **4** are therefore consistent with the structure depicted in eq 3, and this was confirmed by X-ray crystallographic analysis.

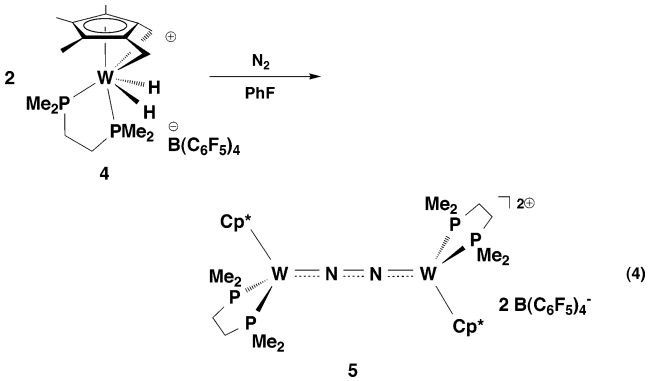
The ion pair **4** was crystallized by liquid−liquid diffusion of pentane into the product fluorobenzene solution at room temperature over 2 d. In this manner, **4** was isolated as orange crystals in 70% yield. An X-ray diffraction analysis was performed on a crystal of **4**, and an ORTEP diagram of the cation is shown in Figure 2. The C$_5$Me$_3$(CH$_2$)$_2$ ligand in this complex can be described as an $\eta^5$-cyclopentadienyl dialkyl moiety, and the binding of the C$_5$ ring is "slipped" significantly to accommodate the two W−C bonds to ring methylene carbons. This is manifested in a range of W−C$_{ring}$ distances from 2.152(9) to 2.474(9) Å. There is a slight shortening observed for the C3−C8 and C4−C9 bonds attributable to a small amount of $\eta^3$-allyl:$\eta^4$-butadiene character for the ligand. Similar geometric

***Table 3.*** Selected Distances (Å) and Angles (deg) for the Cation in **4**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| W−P1 | 2.452(2) | W−C5 | 2.35(1) |
| W−P2 | 2.450(2) | W−C8 | 2.36(1) |
| W−Cl | 2.474(9) | W−C9 | 2.34(1) |
| W−C2 | 2.338(8) | C3−C8 | 1.44(2) |
| W−C3 | 2.152(9) | C4−C9 | 1.41(2) |
| W−C4 | 2.16(1) | | |
| Bond Angles | | | |
| P1−W−P2 | 81.78(7) | W−C8−C3 | 63.9(5) |
| P1−W−C8 | 144.1(4) | W−C9−C4 | 64.7(6) |
| P1−W−C9 | 144.0(4) | P2−W−C8 | 92.3(3) |
| | | P2−W−C9 | 91.0(3) |

parameters have been observed in other doubly metalated Cp* complexes.[15,16] Selected bond distances and angles from the structure of **4** are listed in Table 3, and crystallographic details are listed in Table 2.

The cation of **4** is a synthon for the $[Cp^*(dmpe)W]^+$ fragment due to the reversibility of the Cp* methyl group activations. Evidence for this reactivity was observed in the reaction of **4** with dinitrogen. Exposure of an orange fluorobenzene solution of **4** to 1 atm of $N_2$ at room temperature caused the solution to darken within minutes. Allowing the mixture to stand at room temperature overnight resulted in the isolation of green, X-ray quality crystals of the compound $[Cp^*(dmpe)W(\mu\text{-}N_2)W(dmpe)Cp^*][B(C_6F_5)_4]_2$ (**5**, eq 4). The dicationic dinitrogen complex exhibits a symmetric structure by NMR spectroscopy in acetonitrile-$d_3$. For example, two doublet resonances (at $\delta$ 1.64 and 1.40) are observed for the dmpe methyl groups in the $^1$H NMR spectrum of **5**, and a single resonance with tungsten satellites is observed in the $^{31}P\{^1H\}$ NMR spectrum at $\delta$ 7.8.




(4)

The identity of **5** was confirmed by an X-ray crystallographic analysis, and an ORTEP diagram of the dication is shown in Figure 3. The structure of the dication has crystallographic inversion symmetry, with an inversion center located at the centroid of the N−N bond. The N−N distance of 1.22(1) Å is more than 0.1 Å longer than that in free dinitrogen, and the symmetry-related W−N bond distances are 1.888(5) Å. In comparison to other dinuclear transition-metal dinitrogen complexes, these values suggest that the bridging ligand has

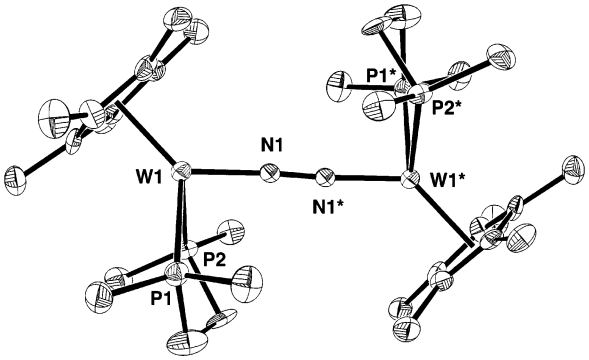



***Figure 3.*** ORTEP diagram of the dication of **5**. Hydrogen atoms are removed for clarity.

diazenido(2−) character.[17] The near linearity of the W−N−N bond angle (176.0(7)°) suggests significant $\pi$ electron delocalization across the $W_2N_2$ core. The formally tungsten(III) dinuclear complex is diamagnetic, presumably due to pairing of the odd electrons in an orbital that is delocalized over the W−N−N−W moiety. Schrock et al. have published a molecular orbital analysis for the $\pi$ bonding in the related dinuclear complexes $[W(Cp^*)Me_2X]_2(\mu\text{-}N_2)$, which is consistent with the observed diamagnetic nature of **5** as well as the observed W−N and N−N bond lengths.[18]

**Silyl and Silylene Complexes from Reactions of Hydrosilanes with ($\eta^6$-$C_5Me_4CH_2$)(dmpe)W(H)Cl.** The equilibrium shown in Scheme 1 suggested that **1** might be reactive toward hydrosilanes via oxidative addition of an Si−H bond to the intermediate 16-electron tungsten(II) complex. In fact, this process may be employed as a route to new tungsten silyl complexes. The reaction of diphenylsilane with **1** at 90 °C over 35 min resulted in formation of the new tungsten(IV) silyl(hydrido)chloride complex $Cp^*(dmpe)(H)(Cl)W(SiHPh_2)$ (**6a**, eq 5). The corresponding reaction with phenylmethylsilane proceeds similarly to give the orange phenylmethylsilyl complex Cp*(dmpe)(H)(Cl)W(SiHMePh) (**6b**). The latter complex exhibits an unsymmetrical dmpe ligand by $^{31}P\{^1H\}$ NMR spectroscopy, displaying two resonances for the phosphorus nuclei at $\delta$ 11.8 and 8.0 ($J_{PP}$ = 16 Hz), and the $^{29}Si\{^1H\}$ NMR spectrum exhibits a resonance for the silicon center as a doublet of doublets at $\delta$ 11.8 ($J_{SiP}$ = 11 Hz, $J_{SiP'}$ = 5 Hz). The $^1$H NMR spectrum of **6b** displays the appropriate ligand resonances, including a doublet of doublet resonance for its tungsten hydride ligand at $\delta$ 3.81 ($J_{HP}$ = 71 Hz, $J_{HP'}$ = 59 Hz). The spectroscopic properties of **6a** are very similar to those of **6b**, including a downfield-shifted $^1$H NMR resonance for its hydride ligand at $\delta$ 4.62 ($J_{HP}$ = 59 Hz, $J_{HP'}$ = 46 Hz). These unusual $^1$H NMR chemical shifts appear related to the fact that the hydride ligands are located in positions trans to the centroids of the Cp* ligands. Schrock and coworkers have reported anomalously downfield-shifted methyl resonances in the $^1$H NMR spectra of $[Cp^*WMe_4]^+$ and $Cp^*WMe_5$, and these signals were attributed to the methyl

(15) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc., Chem. Commun.* **1985**, *14*, 945.
(16) (a) Carter, S. T.; Clegg, W.; Gibson, V. C.; Kee, T. P.; Sanner, R. D. *Organometallics* **1989**, *8*, 253. (b) Gibson, V. C.; Kee, T. P.; Carter, S. T.; Sanner, R. D.; Clegg, W. *J. Organomet. Chem.* **1991**, *418*, 197.
(17) See, for example: (a) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115. (b) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200−202*, 379. (c) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804.
(18) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331.

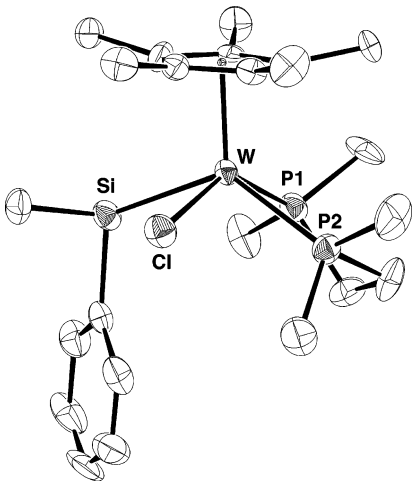
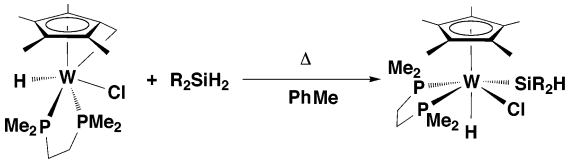



***Figure 4.*** ORTEP diagram of the silyl complex **6b**. Hydrogen atoms are omitted for clarity.

groups that are trans to the Cp* ligand centroids in these compounds.[19]




(5)

**1** **6**

The connectivity of compound **6b** was confirmed by an X-ray diffraction study, and an ORTEP diagram of the molecular structure is shown in Figure 4. Details of the data collection are listed in Table 2. This structure features a tungsten−silicon bond distance of 2.549(3) Å, which is in the range of W−Si bond distances observed in reported tungsten silyl complexes. The hydride ligand in **6b** was not located in the electron density map, although it is almost certainly in a position trans to the Cp* centroid, as the remaining ligands form a four-legged piano stool type structure.

Compounds **6a** and **6b** were synthesized as precursors to tungsten silylene complexes, and their reactivities were explored in this regard. Reactions of compound **6a** or **6b** with an alkylating agent such as benzyl Grignard were examined as routes to silylene hydride complexes via reductive elimination of alkane from an intermediate alkyl(silyl)hydride complex according to Scheme 2. Alkylation of **6a** with $BnMgCl(OEt_2)$ ($Bn = -CH_2Ph$) in benzene proceeded quantitatively to produce a new yellow species that was isolated in good yield by crystallization from pentane. However, no toluene was observed in the reaction mixture, and the isolated product features a benzyl group (by $^1H$ NMR spectroscopy), observed as a singlet resonance for the $PhCH_2$ group at $\delta$ 2.93. Characterization of the product from this reaction revealed its identity as the tungsten silyl complex $Cp^*(dmpe)(H)_2W(SiPh_2Bn)$ (**7**), isolated as yellow crystals in 67% yield.

The structure of complex **7** was confirmed by X-ray diffraction analysis, and an ORTEP diagram of the molecule is shown in Figure 5. The structure can be described as a pseudo eight-coordinate tungsten(IV) silyl dihydride complex, and the hydride ligands were located and their coordinates were refined. The Cp*, dmpe, silyl, and a single hydride form the basis of a four-legged piano stool type structure, and the second hydride ligand caps the $P_2SiH$ face (in a position trans to the Cp* centroid). The details of the data collection for the structure of **7** are listed in Table 2. The W−Si bond distance in this structure is 2.576(3) Å and is in the expected range for W−Si single bonds. It is noteworthy that the complex has apparent mirror-symmetry by $^1H$ NMR spectroscopy and therefore is not stereochemically rigid in solution. That is, the hydride ligands appear as one resonance in the $^1H$ NMR spectrum, and no single hydride is fixed in a position trans to the Cp* centroid.

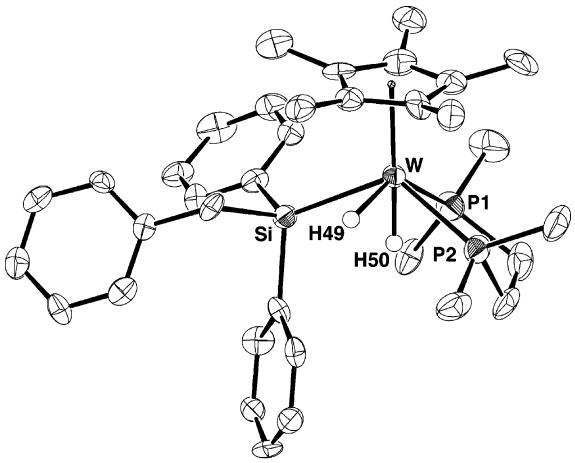
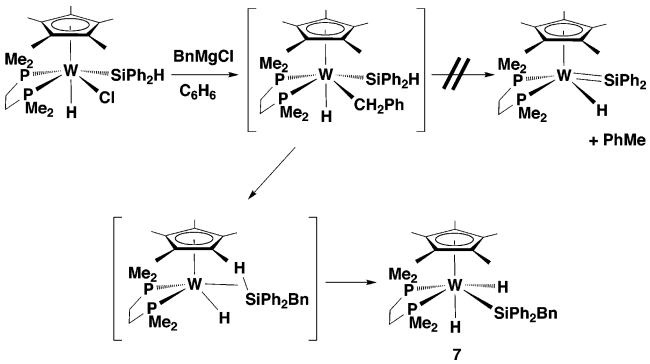



***Figure 5.*** ORTEP diagram of the silyl complex **7**. Hydrogen atoms (except hydrides) are omitted for clarity.

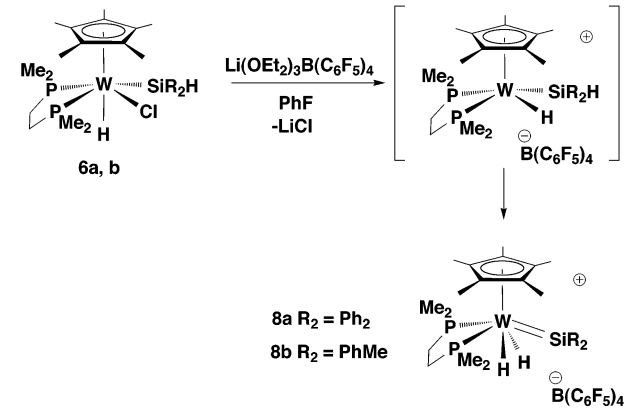
***Scheme 2***




The mechanism for the formation of **7** probably involves an inner-sphere redistribution of substituents at silicon. Reductive elimination of a silicon−carbon bond in the silyl-benzyl intermediate could form an intermediate Si−H complex $[Cp^*(dmpe)(H)W(\eta^2\text{-}H-SiPh_2Bn)]$, which would decompose to **7** via Si−H oxidative addition. If silane were completely eliminated from the coordination sphere of the metal, one would expect other (sterically accessible) silanes present to scramble into the product that is formed. However, when this reaction occurred in the presence of 10 equiv of $PhSiH_3$, the diphenylbenzylsilyl product formed quantitatively. This suggests that complete elimination of $Ph_2BnSiH$ from the coordination sphere of the metal does not occur. As this alkylation reaction did not produce a silylene complex, we pursued alternate methods for converting **6a** to such a species. Abstraction of the chloride ligand in these tungsten silyls proved successful in this regard.

(19) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.

*Scheme 3*




Exchange of the chloride ligand in complex **6a** for the noncoordinating anion $B(C_6F_5)_4^-$ was achieved by reaction of the silyl complex with 1 equiv of $Li(OEt_2)_3B(C_6F_5)_4$. Upon mixing fluorobenzene solutions of the two reagents, a reaction immediately occurred, as evidenced by formation of the white LiCl precipitate and a color change to slightly darker orange. The $^{29}Si\{^1H\}$ NMR spectrum of the new product showed a single broad resonance at $\delta$ 277, and this downfield chemical shift suggests that this product is the 18-electron silylene dihydride complex $[Cp^*(dmpe)(H)_2W{=}SiPh_2][B(C_6F_5)_4]$ (**8a**, Scheme 3). The $^1H$ NMR spectrum of the new complex features a multiplet resonance at $\delta$ −3.97 for the two symmetry equivalent hydride ligands. As shown in Scheme 3, this reaction also proceeds cleanly for phenylmethyl silyl complex **6b**, to produce the phenylmethylsilylene complex **8b** ($^{29}Si\{^1H\}$ NMR in PhF: $\delta$ 297). These reactions likely proceed via unobserved intermediate 16-electron silyl hydride cations. A 1,2-hydride migration from silicon to the metal would then give the observed silylene dihydride product (Scheme 3).

Although the spectroscopic evidence supported the description of **8a** and **8b** as silylene complexes, a confirmation of their structures by X-ray crystallography was desired. Unfortunately, the complexes were isolated as microcrystalline solids that are not suitable for single-crystal diffraction studies. Furthermore, attempted syntheses of silyl derivatives analogous to **6**, which might serve as precursors to silylene complexes, were unsuccessful with $Me_2SiH_2$ and $^iPr_2SiH_2$. For example, $Me_2SiH_2$ reacted with **1** in benzene at 60 °C to give an inseparable mixture of products, and $^iPr_2SiH_2$ does not react with **1** at 60 °C. Decomposition of the reagents was observed at temperatures above 80 °C. An alternate route to silylene complexes related to **8a**−**b** was therefore desired. Such a method was discovered, involving reactions of hydrosilanes with the reactive complex **4**.

**Silylene Complexes by Direct, Double Si−H Bond Activation Reactions.** At 60 °C in fluorobenzene, **4** reacts with dimethylsilane over 1 h under argon to form the silylene complex $[Cp^*(dmpe)(H)_2W{=}SiMe_2][B(C_6F_5)_4]$ (**8c**), isolated in 65% yield after crystallization from fluorobenzene/pentane (eq 6). The $^1H$ NMR spectrum of the dimethylsilylene complex in PhF exhibits a single resonance for two equivalent, silicon-bound methyl groups at $\delta$ 0.89, and there are two doublets for the equivalent pairs of dmpe methyl groups at $\delta$ 1.42 and 1.12. The dmpe ligand is also symmetric by $^{31}P\{^1H\}$ NMR spectroscopy, featuring only one singlet resonance with $^{183}W$ satellites at $\delta$ 13.4 ($J_{PW}$ = 221 Hz). The characterization of **8c** as a silylene complex was confirmed by its downfield-shifted peak at $\delta$ 314 in the $^{29}Si\{^1H\}$ NMR spectrum.

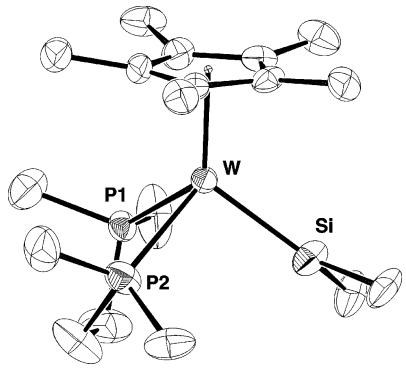
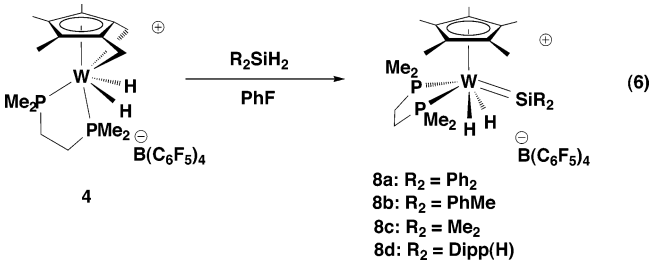



***Figure 6.*** ORTEP diagram of one of the cations in the structure of silylene complex **8c**. The counterion and hydrogen atoms are omitted for clarity.

***Table 4.*** Selected Distances (Å) and Angles (deg) for the Cations in **8c**

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| W1−P1 | 2.475(2) | W2−P3 | 2.487(2) |
| W1−P2 | 2.476(2) | W2−P4 | 2.431(3) |
| W1−Si1 | 2.358(2) | W2−Si2 | 2.354(3) |
| Bond Angles | | | |
| P1−W1−P2 | 75.23(7) | P3−W2−P4 | 76.08(8) |
| P1−W1−Si1 | 97.77(7) | P3−W2−Si2 | 97.37(9) |
| P2−W1−Si1 | 97.00(8) | P4−W2−Si2 | 108.6(1) |

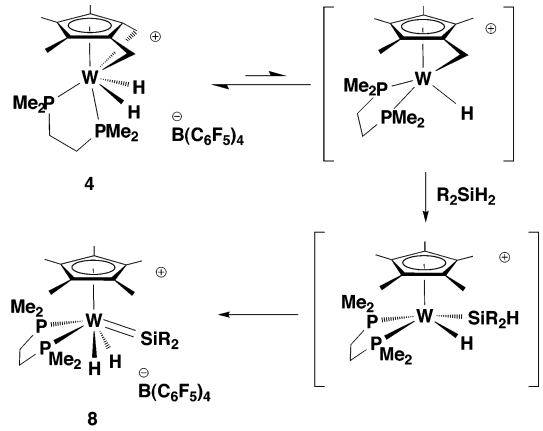



(6)

To establish the geometry for these tungsten silylenes, complex **8c** was studied by X-ray diffraction techniques. Slow liquid−liquid diffusion of pentane into a fluorobenzene solution of **8c** produced orange, X-ray quality crystals of the dimethylsilylene complex. The solid-state structure has two cation/anion pairs in its asymmetric unit, and an ORTEP diagram of one of the cations is shown in Figure 6. In each cation, the silylene ligand is planar with the sum of the angles around silicon center being essentially 360° (359.4(6)° and 359.5(8)°). The two independent cations possess very short tungsten−silicon bond distances (2.358(2) and 2.354(3) Å). For comparison, a range of 2.389−2.708 Å for W−Si bond lengths was determined by a search of the Cambridge structural database. The structural parameters observed here (Table 4) are in keeping with those observed for reported transition-metal silylene complexes.[3−6,8]

Tungsten silylenes **8a** and **8b** were also synthesized by reactions of **4** with $Ph_2SiH_2$ and $PhMeSiH_2$, respectively, and this method is the more convenient route for their preparation. In each case, the reaction is complete in 1 h at 60 °C in fluorobenzene. These reactions likely proceed via the unobserved 16-electron cation $[\eta^6\text{-}(C_5Me_4CH_2)(dmpe)W(H)]^+$, which is likely in equilibrium with **4** (Scheme 4). The proposed

***Scheme 4***




mechanism of Scheme 4 is supported by the observation that diphenylsilane-$d_2$ reacted with **4** to form [Cp*(dmpe)(D)$_2$W=SiPh$_2$][B(C$_6$F$_5$)$_4$], having greater than 90% deuterium incorporation at the tungsten hydride positions (by $^1$H and $^2$H NMR spectroscopy). Given the utility of this hydrosilane activation reaction, we pursued the synthesis of silylene complexes from primary (monosubstituted) silanes.

Nearly all known examples of metal silylene complexes lacking donor stabilization feature silicon centers with alkyl or aryl substituents at silicon. Recently, Tessier and co-workers reported the generation in solution of a metal silylene complex with a hydride substituent at silicon, [(Et$_3$P)$_3$(H)$_2$Ir=Si(H)(C$_6$H$_3$-Mes$_2$-2,6)][B(C$_6$F$_5$)$_4$].[20] It is of interest to synthesize more examples of hydrosilylene complexes and to probe the chemistry and spectroscopic properties of Si−H groups on sp$^2$-hybridized silicon centers.

Reactions of **4** with the monosubstituted silanes PhSiH$_3$ and MesSiH$_3$ (Mes = 2,4,6-trimethylphenyl) resulted in complex mixtures of products from which no clean compounds could be isolated. However, reaction of **4** with DippSiH$_3$ (Dipp = 2,6-diisopropylphenyl) proceeded cleanly over 1 h at 60 °C in fluorobenzene to give the silylene complex [Cp*(dmpe)(H)$_2$W=Si(H)Dipp] (**8d**). It seems likely that the steric bulk of the isopropyl groups of the Dipp ligand is necessary to stabilize this type of complex. The $^1$H NMR spectrum of **8d** features a uniquely downfield-shifted Si−H resonance at $\delta$ 10.83 ($J_{HSi}$ = 167 Hz, $J_{HW}$ = 17 Hz), as well as a multiplet for its dihydride ligands at $\delta$ −4.01. Analogously to complexes **8a**−**c**, the $^{31}$P-{$^1$H} NMR spectrum of **8d** features a single resonance with a chemical shift of $\delta$ 12.3 ($J_{PW}$ = 209 Hz). The $^1$H, $^{29}$Si HMQC 2D NMR spectrum of **8d** revealed a resonance at $\delta$ 286 that is coupled strongly to the Si−H proton ($J_{HSi}$ = 167 Hz). Complex **8d** was isolated as an analytically pure orange solid by removing the volatiles under reduced pressure.

To investigate possible H−H and Si−H interligand bonding interactions in complexes **8a**−**d**, various spectroscopic methods were employed. On the basis of $^1$H NMR $T_1$ relaxation experiments, the hydride ligands in these complexes appear to be classical in nature. Using the null method, the $T_1$(min) values for the dhydride ligands in **8a**, **b**, **c**, and **d** were determined to be in the range of 600−800 ms. Such $T_1$ values suggest classical dihydride character, rather than the presence of a dihydrogen ligand.[21] To investigate the possibility of WH···Si interactions in these compounds, the $^2J_{HSi}$ coupling constants were determined from $^1$H-detected, 1D $^{29}$Si HMQC BIRD filtered NMR experiments. Because these coupling constants (7, 17, 17, and 15 Hz for **8a**, **b**, **c**, and **d**, respectively) are less than 20 Hz, it would appear that there is little or no interaction between the hydride and silylene ligands in these compounds.

**Reactivity of the Tungsten Silylene Complexes.** In light of the electrophilicity of the silicon centers in late metal silylene complexes,[2−6] it was of interest to probe the Lewis-acidity of the silicon centers in these new tungsten compounds. Reaction of dimethylsilylene complex **8c** with 1 equiv of pyridine in fluorobenzene resulted in an immediate color change of the solution to red. The new product was isolated by crystallization from fluorobenzene/pentane, and its spectroscopic characterization is consistent with its identity as the pyridine adduct [Cp*-(dmpe)(H)$_2$WSiMe$_2$(py)][B(C$_6$F$_5$)$_4$] (**9**). Complex **9** has a $^{29}$Si-{$^1$H} NMR resonance at $\delta$ 85, signifying that the silicon center is four coordinate.[8,22] The pyridine ligand appears to be strongly bound to a Lewis-acidic silicon center, and drying the crystals of **9** under vacuum overnight did not result in removal of the coordinated pyridine. From this result, it appears that silylene complexes **8** behave similarly to late transition-metal silylenes with respect to Lewis-acidic behavior at silicon.

Additional studies with these complexes were designed to discover chemical reactivities that differ from those of the known silylene complexes, and this was achieved in reactions of **8c** with chloroalkanes. Recently, we reported the reaction of an osmium silylene complex with benzyl chloride, which proceeds by chlorine atom transfer to silicon and a net oxidation of the osmium center.[4] Interest in the reactions of silylene complexes with chloroalkanes is derived from the fact that surface-bound copper silylenes are postulated as intermediates in the direct synthesis of alkylhalosilanes.[9] Studies on this heterogeneous process suggest that, in the course of the reaction, surface-bound silylenes insert into the C−Cl bonds of chloroalkanes to give the observed products. We were interested in the reactions of these new tungsten silylene complexes with chloroalkanes and have observed a related reaction in which a tungsten-bound silylene inserts into a C−Cl bond.

Heating a fluorobenzene solution of **8c** and excess (approximately 5 equiv) MeCl to 70 °C for 30 min in a sealed NMR tube resulted in a red solution. The $^1$H NMR spectrum of this mixture displayed a resonance for Me$_3$SiCl (78% yield by internal cyclooctane standard), the product of insertion of dimethylsilylene into the C−Cl bond of MeCl. It seemed that the reaction formed paramagnetic tungsten products, as only trace diamagnetic impurities are observed spectroscopically.

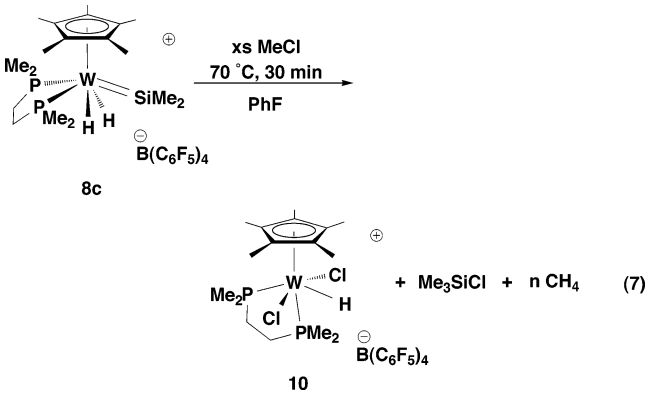
Isolation of the major metal-containing product (**10**) was achieved by crystallization, and the red crystals were analyzed by X-ray diffraction. The solid-state structure of this new complex identified it as the tungsten(V) dichlorohydride complex [Cp*(dmpe)W(H)Cl$_2$][B(C$_6$F$_5$)$_4$] (**10**, eq 7). The structure is of sufficient quality to conclusively determine connectivity; however, disorder of the Cp* and dmpe ligands in the cation prevented refinement of accurate metric parameters. The hydride

(20) Simons, R. S.; Gallucci, J. C.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2002**, *654*, 224.

(21) Crabtree, R. H.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

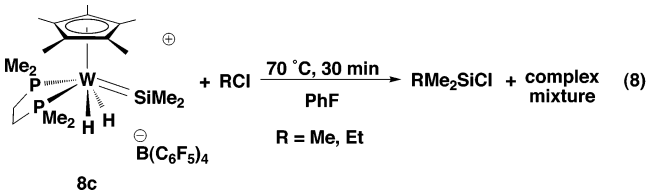
(22) For examples of donor-stabilized tungsten silylene complexes: (a) Ueno, K.; Sakai, M.; Ogino, H. *Organometallics* **1998**, *17*, 2138. (b) Sakaba, H.; Tsukamoto, M.; Hirata, T.; Kabuto, C.; Horino, H. *J. Am. Chem. Soc.* **2000**, *122*, 11511.

ligand was not located in the structure; however, its location was inferred to be in the open coordination site at the tungsten center of the cation. Further confirmation of the presence of a hydride ligand in **10** was obtained by IR spectroscopy, which revealed a W−H stretching absorbance at 1879 $cm^{-1}$. In the course of reaction, the tungsten is oxidized from tungsten(IV) to tungsten(V), and more than 1 equiv of MeCl is involved in this transformation. It was therefore of interest to explore the reactions of **8c** with a stoichiometric quantity of chloroalkane.




(7)

Using a glass bulb of known volume, 1 equiv of MeCl was introduced to a sample of **8c**, and the NMR tube was sealed and heated at 70 °C for 30 min (eq 8). A $^1$H NMR spectrum of the resulting orange/brown solution revealed the presence of $Me_3SiCl$ in 82% yield and a mixture of diamagnetic metal-containing products. Under the same conditions, EtCl reacted with **8c** to produce an orange/brown solution and $EtMe_2SiCl$ (76% yield) by $^1$H and $^{29}$Si{$^1$H} NMR spectroscopy. The tungsten complexes formed in these reactions have not been identified, and these may include paramagnetic species.




(8)

## Concluding Remarks

The metalated Cp* complexes **1** and **4** are sources of the reactive fragments Cp*(dmpe)WCl and [Cp*(dmpe)W]$^+$, respectively. Reactions of these species with small molecules suggested that they might be useful in Si−H bond activations toward the syntheses of silyl and silylene complexes of tungsten. Both **1** and **4** react with hydrosilanes, and this reactivity has provided a route to a new class of formally $d^0$ silylene complexes of the type $[Cp^*(dmpe)(H)_2W{=}SiR_2][B(C_6F_5)_4]$ (**8**).

Spectroscopic studies indicate that these complexes are accurately described as silylene dihydrides, and a reaction with pyridine has shown them to be electrophilic at silicon. This electrophilicity suggests that the silylene ligands in these complexes may be described as neutral, two-electron donor ligands that receive stabilization by $\pi$ back-bonding from the tungsten center. By this description of the bonding, the tungsten centers are $d^2$ and in the +4 oxidation state. Silylene complexes **8** represent the first instances of donor-free silylene ligands coordinated to transition metals that have only two d-electrons. This is a significant advancement toward a more diverse collection of silylene complexes and the beginning of the study of the chemistry of these new species.

It seems that the reactivity of early metal silylenes is distinct from that of their late metal analogues. The dimethylsilylene complex **8c** was shown to react with chloroalkanes in a fashion that parallels the proposed mechanism for the direct synthesis. This is an unprecedented example of silylene insertion into a C−Cl bond by a discrete molecular silylene complex, and it provides support for the proposed intermediacy of metal silylenes in that process. In contrast, the osmium silylene complex $[Cp^*(Me_3P)_2Os{=}SiMe_2]^+$ acquires a chlorine radical from $PhCH_2Cl$ to form the osmium(III) cation $[Cp^*(Me_3P)_2(SiMe_2Cl)]^+$,[4] and there is no Si−C bond formation observed. These reactions highlight the potential for early metal silylene complexes to exhibit new and potentially useful reactivities.

The electrophilicity observed for the silicon centers in these compounds inspires interest in synthesizing analogues with more strongly $\pi$-donating metal centers. Therefore, the possibility of silylene chemistry with more electropositive early transition metals such as tantalum and zirconium is a subject of continuing exploration.

## Experimental Section

**General.** All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques or in a drybox under nitrogen. Fluorobenzene was distilled from $P_2O_5$, and pentane was distilled from sodium/benzophenone. To remove olefin impurities, pentane was pretreated with concentrated $H_2SO_4$, 0.5 N $KMnO_4$ in 3 M $H_2SO_4$, $NaHCO_3$, and then anhydrous $MgSO_4$. Benzene-$d_6$ was distilled from Na/K alloy. *m*-Fluorotoluene was vacuum transferred from $CaH_2$ and degassed prior to use. The reagents $Li(Et_2O)_{2.5}B(C_6F_5)_4$,[23] $Cp^*WCl_4$,[12] and 1,2-bis(dimethylphosphino)ethane[24] were synthesized according to published procedures. Other chemicals were obtained from commercial suppliers and used as received. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. FT-infrared spectra were recorded as KBr pellets or Nujol mulls on a Mattson FTIR 3000 instrument.

**NMR Measurements.** Routine $^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H}, and $^{29}$Si{$^1$H} NMR spectra were recorded at 298 K on either a Bruker DRX-500 instrument equipped with a 5 mm broad band probe and operating at 500.1 MHz ($^1$H), 125.8 MHz ($^{13}$C), 202.5 MHz ($^{31}$P), and 99.4 MHz ($^{29}$Si) or a Bruker AMX-400 instrument operating at 400.1 MHz ($^1$H), 100.6 MHz ($^{13}$C), or 61.4 MHz ($^2$H). Chemical shifts are reported in ppm downfield from internal $SiMe_4$ ($^1$H, $^{13}$C, $^{29}$Si), and external 85% $H_3PO_4$ ($^{31}$P); coupling constants are given in hertz. Samples of **2**, **3a**−**c**, and **4** were prepared as 0.4 mL solutions in a 10:1 mixture of fluorobenzene/benzene-$d_6$ to obtain a deuterium lock signal. Bruker XWINNMR software (ver. 2.1) was used for all data processing. $T_1$(min) measurements were made for dihydride protons in **3a**−**c** using *m*-fluorotoluene as the solvent.

**X-ray Crystallography.** The single-crystal X-ray analysis of compound **1** was carried out by Dr. Fred Hollander and Dr. Dana Caulder at the UC Berkeley CHEXRAY crystallographic facility. Structural analyses of compounds **4**, **5**, **6b**, **7**, **8c**, and **10** were carried out by the authors using the same facility. Measurements were made on a Bruker SMART CCD area detector with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å). Data were integrated by the program SAINT and were analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. Structures were

(23) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.
(24) Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.

solved by direct methods and expanded using Fourier techniques. Calculations for the structures of complex **5** was performed using the SHELX-TL software package. For the remainder of the structures, all calculations were performed using the teXsan crystallographic software package. Details of data collections and refinements are in Table 2 and in the Supporting Information CIF files.

**($\eta^6$-$C_5Me_4CH_2$)(dmpe)W(H)Cl (1).** A round-bottomed Schlenk flask was charged with 70.1 g of Na/Hg amalgam (0.8% w/w, 24.4 mmol), 1.36 mL of dmpe (8.14 mmol), 50 mL of benzene, and a magnetic stirbar. In a separate 100 mL Schlenk tube was agitated Cp*$WCl_4$ (3.75 g, 8.14 mmol) to a slurry in 75 mL of benzene. With continued agitation, the orange slurry was quickly added via cannula to the amalgam and dmpe with vigorous stirring. Immediately upon addition, the reaction became dark green, and a mild exotherm occurred. Within 5 min of rapid stirring, the slurry had changed color to brown/red, and it was allowed to stir for 1 h at ambient temperature. The mixture was heated to 60 °C, was stirred for 16 h, and then was allowed to cool to room temperature. The supernatant was filtered away from the salts and mercury to give a dark red solution. Removal of benzene in vacuo yielded a dark red waxy solid. Pentane (25 mL) was added and removed under reduced pressure to aid in removal of benzene from the product. Further drying under vacuum yielded 3.40 g (83%) of **1** as a red/brown solid. The product is of sufficient purity to be used in subsequent reactions. Orange/red X-ray quality crystals of **1** were obtained by recrystallization from pentane. $^1$H NMR (benzene-$d_6$): $\delta$ 3.82 (d, 1H, $\eta^6$-$C_5Me_4CH_2$, $J_{HP}$ = 9 Hz), 2.69 (s, 1H, $\eta^6$-$C_5Me_4CH_2$), 2.12 (s, 3H, $\eta^6$-$C_5Me_4CH_2$), 2.07 (s, 3H, $\eta^6$-$C_5Me_4CH_2$), 2.06 (s, 3H, $\eta^6$-$C_5Me_4CH_2$), 1.82 (s, 3H, $\eta^6$-$C_5Me_4CH_2$), 1.70 (m, 1H, $PCH_2$), 1.54 (m, 1H, $PCH_2$), 1.53 (d, 3H, P*Me*, $J_{HP}$ = 8 Hz), 1.35 (m, 1H, $PCH_2$), 1.29 (d, 3H, P*Me*, $J_{HP}$ = 9 Hz), 1.23 (d, 3H, P*Me*, $J_{HP}$ = 9 Hz), 1.03 (m, 1H, $PCH_2$), 0.98 (d, 3H, P*Me*, $J_{HP}$ = 7 Hz), −8.25 (dd, 1H, W−*H*, $J_{HP}$ = 42 Hz, $J_{HP'}$ = 73 Hz, $J_{HW}$ = 42 Hz). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 110.5 (s, $\eta^6$-$C_5Me_4CH_2$), 109.4 (s, $\eta^6$-$C_5Me_4CH_2$), 102.4 (s, $\eta^6$-$C_5Me_4CH_2$), 87.2 (s, $\eta^6$-$C_5Me_4CH_2$), 86.3 (s, $\eta^6$-$C_5Me_4CH_2$), 60.2 (t, $\eta^6$-$C_5Me_4CH_2$, $J_{CP}$ = 8 Hz), 34.6 (dd, $PCH_2$, $J_{CP}$ = 11 Hz, $J_{CP'}$ = 28 Hz), 32.4 (dd, $PCH_2$, $J_{CP}$ = 28 Hz, $J_{CP'}$ = 12 Hz), 24.3 (dd, P*Me*, $J_{CP}$ = 3 Hz, $J_{CP'}$ = 40 Hz), 18.5 (dd, P*Me*, $J_{CP}$ = 3 Hz, $J_{CP'}$ = 26 Hz), 16.7 (s, $\eta^6$-$C_5Me_4CH_2$), 15.2 (d, P*Me*, $J_{CP}$ = 20 Hz), 13.0 (s, $\eta^6$-$C_5Me_4CH_2$), 12.9 (s, $\eta^6$-$C_5Me_4CH_2$), 12.6 (s, $\eta^6$-$C_5Me_4CH_2$), 11.3 (d, P*Me*, $J_{CP}$ = 25 Hz). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 18.6 (s, $J_{PW}$ = 253 Hz), 10.8 (s, $J_{PW}$ = 233 Hz). IR (KBr, $cm^{-1}$): 1896 m ($\nu_{WH}$). Anal. Calcd for $C_{16}H_{31}P_2ClW$: C, 38.08; H, 6.19. Found: C, 38.36; H, 6.49.

**Cp*(dmpe)W(CO)Cl (2).** A solution of 0.100 g (0.198 mmol) of compound **1** in 3 mL of toluene was added to a sealable flask. This solution was placed under vacuum for 15 s, and the flask was then backfilled with 1 atm of carbon monoxide. Heating the sealed reaction vessel for 24 h at 70 °C resulted in a red solution. Removal of the volatiles under reduced pressure and recrystallization from 3 mL of ether at −30 °C over 12 h resulted in isolation of 0.072 g of orange/red microcrystalline **3** (68% yield). $^1$H NMR (benzene-$d_6$): $\delta$ 1.78 (s, 15H, $C_5Me_5$), 1.58 (d, 3H, P*Me*, $J_{HP}$ = 9 Hz), 1.46 (d, 3H, P*Me*, $J_{HP}$ = 9 Hz), 1.3 (m, 2H, $2PCH_2$), 1.2 (m, 1H, $PCH_2$), 1.12 (d, 3H, P*Me*, $J_{HP}$ = 8 Hz), 0.76 (d, 3H, P*Me*, $J_{HP}$ = 7 Hz), 0.73 (m, 1H, $PCH_2$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 244.4 (dd, W*C*O, $J_{CP}$ = 18 Hz, $J_{CP'}$ = 4 Hz), 100.7 (d, $C_5Me_5$, $J_{CP}$ = 2 Hz), 35.8 (dd, P*Me*, $J_{CP}$ = 33 Hz, $J_{CP'}$ = 16 Hz), 28.7 (dd, P*Me*, $J_{CP}$ = 29 Hz, $J_{CP'}$ = 13 Hz), 21.3 (dd, *P*$CH_2$, $J_{CP}$ = 40 Hz, $J_{CP'}$ = 2 Hz), 20.5 (d, $PCH_2$, $J_{CP}$ = 32 Hz), 19.2 (dd, P*Me*, $J_{CP}$ = 16 Hz, $J_{CP'}$ = 3 Hz), 14.5 (dd, P*Me*, $J_{CP}$ = 25 Hz, $J_{CP'}$ = 3 Hz), 12.0 (d, $C_5Me_5$, $J_{CP}$ = 1 Hz). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 23.8 (s, $J_{PW}$ = 266 Hz), 19.2 (s, $J_{PW}$ = 297 Hz). IR (Nujol, $cm^{-1}$): 1789 m ($\nu_{CO}$). Anal. Calcd for $C_{17}H_{31}ClOP_2W$: C, 38.33; H, 5.87. Found: C, 38.58; H, 5.92.

**Cp*(dmpe)W(H)$_2$Cl (3).** A solution of 0.148 g (0.293 mmol) of compound **1** in 3 mL of toluene was added to a 10 mL sealable flask. The mixture was placed under vacuum for 15 s, and the flask was then backfilled with 1 atm of hydrogen. Heating the sealed reaction vessel for 18 h at 90 °C resulted in a red solution. Removal of the volatiles under reduced pressure and recrystallization from 4 mL of ether at −30 °C over 12 h resulted in isolation of 0.120 g of orange/red crystals of **2** (81% yield). $^1$H NMR (benzene-$d_6$): $\delta$ 2.17 (s, 15H, $C_5Me_5$), 1.49 (m, 2H, $2PCH_2$), 1.36 (m, 12H, 4P*Me*), 1.40 (m, 2H, $2PCH_2$), −6.17 (m, 2H, W$H_2$, $J_{HP}$ = 65 Hz, $J_{HW}$ = 60 Hz). $^{13}$C NMR (benzene-$d_6$): $\delta$ 92.8 (s, $C_5Me_5$), 31.8 (t, $2PCH_2$, $J_{CP}$ = 21 Hz), 24.4 (virtual t, 2P*Me*, $J_{CP}$ = 21 Hz), 13.9 (s, $C_5Me_5$), 11.3 (virtual t, 2P*Me*, $J_{CP}$ = 13 Hz). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 23.1 (s, $J_{PW}$ = 156 Hz). IR (KBr, $cm^{-1}$): 1841 m ($\nu_{WH}$), 1827 m ($\nu_{WH}$). Anal. Calcd for $C_{16}H_{33}ClP_2W$: C, 37.93; H, 6.56. Found: C, 38.00; H, 6.69.

**Cp*(dmpe)W(D)$_2$Cl (3-*d*$_2$).** A sealable NMR tube was charged with 0.013 g (26 $\mu$mol) of **1** and 0.4 mL of benzene-$d_6$. The solution was degassed with three freeze−pump−thaw cycles, and then the tube was backfilled with 1 atm of deuterium gas. Heating the tube at 110 °C in an oil bath for 10 d resulted in quantitative conversion of **1** to the dideuteride complex **3**-$d_2$. The complex's NMR spectra are identical to those of dihydride **3**, except that there is no hydride resonance in the $^1$H NMR spectrum, and the $^{31}P\{^1H\}$NMR spectrum shows coupling to the two deuterium nuclei. $^2$H NMR (benzene-$d_6$): $\delta$ −6.10 (t, W$D_2$, $J_{DP}$ = 8 Hz). $^{31}P\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 23.0 (quintet, $^{183}$W satellites, $J_{PW}$ = 156 Hz, $J_{PD}$ = 8 Hz).

**[($\eta^7$-$C_5Me_3(CH_2)_2$)(dmpe)W(H)$_2$][B($C_6F_5$)$_4$] (4).** To a sealable reaction flask was added 0.100 g (0.198 mmol) of **1** and 0.173 g (0.198 mmol) of $Li(Et_2O)_{2.5}B(C_6F_5)_4$. The sealed flask was fitted to a vacuum transfer apparatus on a Schlenk line, and 3 mL of fluorobenzene was vacuum transferred onto the solids at −78 °C. The flask was backfilled with argon and warmed to room temperature, and the orange solution was allowed to stir for 1 h. The mixture was filtered into another Schlenk flask under argon, and 4 mL of pentane was layered upon the fluorobenzene solution. After the mixture was left standing for 1 d, orange crystals had precipitated. The supernatant was decanted via cannula, and the crystals were dried under vacuum to give 0.159 g of **2** in 70% yield. $^1$H NMR (fluorobenzene): $\delta$ 2.64 (s, 2H, $\eta^7$-$C_5Me_3(CH_2)_2$), 1.85 (s, 3H, $\eta^7$-$C_5Me_3(CH_2)_2$), 1.77 (m, 2H, $\eta^7$-$C_5Me_3(CH_2)_2$), 1.71 (m, 2H, $PCH_2$), 1.68 (s, 6H, $\eta^7$-$C_5Me_3(CH_2)_2$), 1.60 (m, 2H, $PCH_2$), 1.28 (d, 6H, P$Me_2$, $J_{HP}$ = 10 Hz), 1.07 (d, 6H, P$Me_2$, $J_{HP}$ = 9 Hz), −2.11 (dd, 2H, W(*H*)$_2$, $J_{HP}$ = 38 Hz, $J_{HP'}$ = 58 Hz, $J_{HW}$ = 49 Hz). $^{31}P\{^1H\}$ NMR (fluorobenzene): $\delta$ 14.7 (s, $J_{PW}$ = 142 Hz), 11.3 (s, $J_{PW}$ = 207 Hz). $^{13}C\{^1H\}$ NMR (fluorobenzene): $\delta$ 150.4, 148.5, 138.2, 136.4 (m, B($C_6F_5$)$_4$), 109.7 (s, $\eta^7$-$C_5Me_3(CH_2)_2$), 108.9 (d, $\eta^7$-$C_5Me_3(CH_2)_2$), $J_{CP}$ = 21 Hz), 106.4 (s, $\eta^7$-$C_5Me_3(CH_2)_2$), 51.0 (dd, $\eta^7$-$C_5Me_3(CH_2)_2$), $J_{CP}$ = 2 Hz, $J_{CP'}$ = 6 Hz), 32.2 (dd, $PCH_2$, $J_{CP}$ = 9 Hz, $J_{CP'}$ = 38 Hz), 30.4 (dd, $PCH_2$, $J_{CP}$ = 7 Hz, $J_{CP'}$ = 34 Hz), 20.0 (d, P$Me_2$, $J_{CP}$ = 35 Hz), 17.3 (d, P$Me_2$, $J_{CP}$ = 33 Hz), 11.3 (s, $\eta^7$-$C_5Me_3(CH_2)_2$), 10.2 (s, $\eta^7$-$C_5Me_3(CH_2)_2$). IR (Nujol, $cm^{-1}$): 1861 w ($\nu_{WH}$), 1843 w ($\nu_{WH}$). Anal. Calcd for $C_{40}H_{31}BF_{20}P_2W$: C, 41.84; H, 2.72. Found: C, 41.90; H, 2.90.

**{[Cp*(dmpe)W]$_2$($\mu$-N$_2$)}{B($C_6F_5$)$_4$}$_2$ (5).** To 0.200 g (0.396 mmol) of **1** and 0.360 g (0.396 mmol) of $Li(OEt_2)_3B(C_6F_5)_4$ was added 10 mL of fluorobenzene under nitrogen. The mixture changed color from orange to dark orange/brown within minutes and was allowed to stand. After 24 h, green crystals had formed on the sides of the flask, and there was a fine white precipitate of LiCl present. The supernatant was decanted via cannula, and the green crystals were washed three times with 5 mL of pentane. With each wash, the mixture was slurried and the fine LiCl was removed as a suspension with the wash pentane. Drying the crystals under vacuum for 8 h gave 0.238 g of **5** (59% yield). $^1$H NMR (acetonitrile-$d_3$): $\delta$ 2.08 (s, 15H, $C_5Me_5$), 1.8 (m, 4H, $2PCH_2$), 1.64 (d, 6H, 2P*Me*, $J_{HP}$ = 10 Hz), 1.40 (d, 6H, 2P*Me*, $J_{HP}$ = 10 Hz). $^{31}P\{^1H\}$ NMR (acetonitrile-$d_3$): $\delta$ 7.8 (s, tungsten satellites, $J_{PW}$ = 374 Hz). $^{13}C\{^1H\}$ NMR (acetonitrile-$d_3$): $\delta$ 149.9 (br, B($C_6F_5$)$_4$), 147.9 (br, B($C_6F_5$)$_4$), 138.2 (br, B($C_6F_5$)$_4$), 136.2 (br, B($C_6F_5$)$_4$), 107.3 (s, $C_5Me_5$), 37.1 (m, $2PCH_2$), 21.5 (m, 2P*Me*), 14.4 (m, 2P*Me*), 12.7 (s, $C_5Me_5$). Anal. Calcd for $C_{40}H_{31}NBF_{20}P_2W$: C, 41.34; H, 2.69; N, 1.21. Found: C, 41.49; H, 2.73; N, 1.09.

**Cp*(dmpe)(H)W(SiPh$_2$H)Cl (6a).** Diphenylsilane (0.401 g, 2.18 mmol) was dissolved in 10 mL of toluene, and the resulting solution was added via cannula to a solution of **1** (1.00 g, 1.98 mmol) in 20 mL of toluene. The orange mixture was heated for 35 min at 90 °C, resulting in precipitation of some of the product as an orange microcrystalline solid. Toluene was then removed under reduced pressure, and the orange product was washed with 3 × 15 mL pentane. Compound **6a** was isolated as 0.837 g of a light orange solid (61% yield). $^1$H NMR (methylene chloride-$d_2$): $\delta$ 7.98 (m, 2H, *o-Ph*), 7.82 (m, 2H, *o-Ph*), 7.12 (m, 2H, *p-Ph*), 7.05 (m, 4H, *m-Ph*), 5.44 (s, 1H, Si*H*), 4.62 (dd, 1H, W*H*, $J_{HP}$ = 59 Hz, $J_{HP'}$ = 46 Hz), 1.82 (s, 15H, C$_5$*Me*$_5$), 1.70 (d, 3H, P*Me*, $J_{HP}$ = 9 Hz), 1.63 (m, 1H, PC*H*$_2$), 1.55 (m, 1H, PC*H*$_2$), 1.45 (d, 3H, P*Me*, $J_{HP}$ = 8 Hz), 1.40 (d, 3H, P*Me*, $J_{HP}$ = 9 Hz), 1.30 (m, 2H, 2PC*H*$_2$), 1.16 (d, 3H, P*Me*, $J_{HP}$ = 7 Hz). $^{13}$C{$^1$H} NMR (methylene chloride-$d_2$): $\delta$ 151.8, 149.8 (*i-Ph*), 137.4, 135.6 (*o-Ph*), 126.8, 126.1 (*m-Ph*), 126.0, 125.9 (*p-Ph*), 95.5 (*C*$_5$Me$_5$), 38.5 (m, P*C*H$_2$), 30.4 (m, P*C*H$_2$), 18.5 (m, P*Me*), 18.4 (m, P*Me*), 18.3 (m, P*Me*), 13.7 (d, P*Me*, $J_{CP}$ = 17 Hz), 11.4 (s, C$_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (methylene chloride-$d_2$): $\delta$ 8.6 (d, $^{183}$W satellites, $J_{PP}$ = 15 Hz, $J_{PW}$ = 205 Hz), 7.9 (d, $^{183}$W satellites, $J_{PP}$ = 15 Hz, $J_{PW}$ = 240 Hz). $^1$H, $^{29}$Si HMQC (benzene-$d_6$): $\delta$ 9.3 (*Si*−H, $J_{HSi}$ = 157 Hz). IR (Nujol, cm$^{-1}$): 2026 m ($\nu_{SiH}$), 1910 w ($\nu_{WH}$). Anal. Calcd for $C_{28}H_{43}ClP_2SiW$: C, 48.41; H, 6.29. Found: C, 48.45; H, 6.44.

**Cp*(dmpe)(H)W(SiHPhMe)Cl (6b).** Phenylmethylsilane (0.280 g, 2.29 mmol) was dissolved in 10 mL of toluene, and the resulting solution was added via cannula to a solution of **1** (1.00 g, 1.98 mmol) in 20 mL of toluene. The orange solution was heated at 100 °C for 30 min and then allowed to cool to room temperature. The volatile material was removed under reduced pressure, and the orange solid was washed twice with 10 mL of cold pentane. Drying the product under vacuum gave **6b** as 0.630 g of a light orange solid (51% yield). $^1$H NMR (benzene-$d_6$): $\delta$ 8.28 (m, 2H, *o-Ph*), 7.35 (m, 2H, *m-Ph*), 7.20 (m, 1H, *p-Ph*), 5.28 (m, 1H, Si−*H*), 3.81 (dd, 1H, W−*H*, $J_{HP}$ = 71 Hz, $J_{HP'}$ = 59 Hz), 1.79 (s, 15H, C$_5$*Me*$_5$), 1.64 (d, 3H, P*Me*, $J_{HP}$ = 11 Hz), 1.26 (d, 3H, P*Me*, $J_{HP}$ = 12 Hz), 1.2 (m, 1H, PC*H*$_2$), 1.1 (m, 1H, PC*H*$_2$), 0.95 (d, 3H, P*Me*, $J_{HP}$ = 9 Hz), 0.9 (m, 1H, PC*H*$_2$), 0.89 (d, 3H, Si*Me*, $J_{HH}$ = 5 Hz), 0.5 (m, 1H, PC*H*$_2$), 0.44 (d, 3H, P*Me*, $J_{HP}$ = 9 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 154.3, 135.8, 127.6, 126.8 (s, *Ph*), 95.5 (s, *C*$_5$Me$_5$), 38.7 (dd, P*Me*, $J_{CP}$ = 40 Hz, $J_{CP'}$ = 8 Hz), 30.7 (dd, P*Me*, $J_{CP}$ = 34 Hz, $J_{CP'}$ = 8 Hz), 18.9 (m, P*C*H$_2$), 18.7 (m, P*C*H$_2$), 17.7 (m, P*Me*), 14.3 (m, P*Me*), 11.6 (s, C$_5$*Me*$_5$), 2.5 (s, Si*Me*). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 11.8 (d, $J_{PP}$ = 16 Hz, $J_{PW}$ = 207 Hz), 8.0 (d, $J_{PP}$ = 16 Hz, $J_{PW}$ = 254 Hz). $^{29}$Si{$^1$H} NMR (benzene-$d_6$): $\delta$ 11.8 (dd, $J_{SiP}$ = 11 Hz, $J_{SiP'}$ = 5 Hz). IR (KBr, cm$^{-1}$): 1900 w ($\nu_{WH}$). Anal. Calcd for $C_{23}H_{41}ClP_2SiW$: C, 44.06; H, 6.59. Found: C, 43.79; H, 6.49.

**Cp*(dmpe)(H)$_2$W(SiPh$_2$Bn) (7).** To a slurry of 0.150 g (0.217 mmol) of **6a** in 10 mL of C$_6$H$_6$ was added 2.2 mL (0.22 mmol) of a 1.0 M solution of BnMgCl in Et$_2$O. Immediately upon addition, the solution changed color from orange to yellow, and a white precipitate of MgCl$_2$ was formed. The volatile material was removed in vacuo, and the yellow product was extracted into 6 mL of toluene. The solution was filtered and concentrated to 1 mL and was cooled to −30 °C overnight. Yellow crystals of the product **7** were isolated in 67% yield (0.162 g) by decanting the supernatant via cannula and drying under vacuum. $^1$H NMR (benzene-$d_6$): $\delta$ 7.78 (d, 4H, *o-Ph*), 7.28 (t, 4H, *m-Ph*), 7.22 (m, 2H, Ar−*H*), 7.01 (m, 2H, Ar−*H*), 6.95 (m, 1H, Ar−*H*), 6.91 (m, 2H, Ar−*H*), 2.93 (s, 2H, SiC*H*$_2$Ph), 1.77 (s, 15H, C$_5$*Me*$_5$), 1.31 (d, 6H, 2P*Me*, $J_{HP}$ = 8 Hz), 1.04 (d, 6H, 2P*Me*, $J_{HP}$ = 7 Hz), 0.9 (m, 2H, 2PC*H*$_2$), 0.8 (m, 2H, 2PC*H*$_2$), −6.16 (t, 2H, W(*H*)$_2$, $J_{HP}$ = 35 Hz, $J_{HW}$ = 31 Hz, $J_{HSi}$ = 12 Hz). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 148.0, 145.8, 138.1, 129.1, 127.2, 126.4, 126.0, 125.7 (s, *Ar*), 91.1 (s, *C*$_5$Me$_5$), 41.7 (s, Si*C*H$_2$Ph), 35.6 (m, *2P*Me*), 26.6 (m, 2P*Me*), 16.7 (m, 2P*C*H$_2$), 12.1 (s, C$_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (benzene-$d_6$): $\delta$ 14.33 (s, $^{183}$W satellites, $J_{PW}$ = 244 Hz). $^{29}$Si{$^1$H} NMR (benzene-$d_6$): $\delta$ 28.6 (s). IR (KBr, cm$^{-1}$): 1932 w ($\nu_{WH}$), 1861 m ($\nu_{WH}$). Anal. Calcd for $C_{35}H_{50}P_2SiW$: C, 56.45; H, 6.77. Found: C, 56.56; H, 7.01.

**[Cp*(dmpe)(H)$_2$W=SiPh$_2$][B(C$_6$F$_5$)$_4$] (8a).** A sealable reaction flask was charged with 0.100 g (0.198 mmol) of **1**, 0.173 g (0.198 mmol) of Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$, and 0.040 g (0.217 mmol) of Ph$_2$SiH$_2$ and sealed in a drybox. On a Schlenk line, 3 mL of fluorobenzene was added to the flask via cannula, and the orange solution was heated at 70 °C for 1 h. The solution was then filtered into a 10 mL Schlenk tube to remove LiCl, and 5 mL of pentane was layered onto the product solution via cannula. Overnight, the product precipitated as the liquids diffused together. The supernatant was filtered away, and the product was dried under reduced pressure for 6 h, yielding 0.192 g of **8a** as an orange/yellow solid (73% yield). $^1$H NMR (fluorobenzene): $\delta$ 7.63 (d, 4H, *o-Ph*, $J_{HH}$ = 7 Hz), 7.34 (t, 4H, *m-Ph*, $J_{HH}$ = 7 Hz), 7.28 (m, 2H, *p-Ph*), 1.86 (s, 15H, C$_5$*Me*$_5$), 1.36 (m, 2H, 2PC*H*$_2$), 1.34 (d, 6H, 2P*Me*, $J_{HP}$ = 8 Hz), 1.19 (d, 6H, 2P*Me*, $J_{HP}$ = 7 Hz), 1.15 (m, 2H, 2PC*H*$_2$, $J_{HP}$ = 8 Hz), −3.97 (m, 2H, W(*H*)$_2$, $J_{HW}$ = 47 Hz). $^{13}$C{$^1$H} NMR (fluorobenzene): $\delta$ 150.9 (s, Si*Ph*), 150.4, 148.6, 138.3, 136.3 (m, B(*C*$_6$F$_5$)$_4$), 134.6, 130.9, 128.7 (s, Si*Ph*), 100.3 (s, *C*$_5$Me$_5$), 32.3 (m, 2P*C*H$_2$), 27.5 (m, 2P*Me*), 17.1 (m, 2P*Me*), 12.5 (s, C$_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (fluorobenzene): $\delta$ 13.5 (s, $J_{PW}$ = 204 Hz). $^{29}$Si{$^1$H} NMR (fluorobenzene): $\delta$ 277 (br). IR (KBr, cm$^{-1}$) 1900 w br ($\nu_{WH}$). Anal. Calcd for $C_{52}H_{43}BF_{20}P_2SiW$: C, 46.94; H, 3.26. Found: C, 47.33; H, 3.44.

**[Cp*(dmpe)(D)$_2$W=SiPh$_2$][B(C$_6$F$_5$)$_4$] (8a-*d*$_2$).** A sealable NMR tube was charged with 0.020 g (40 $\mu$mol) of **1**, 0.0074 g (0.040 $\mu$mol) of Ph$_2$SiD$_2$, and 0.036 g (40 $\mu$mol) of Li(Et$_2$O)$_3$B(C$_6$F$_5$)$_4$ in 0.4 mL of fluorobenzene. The tube was then heated at 70 °C for 1 h, resulting in a yellow/orange solution of **8a**-$d_2$ and a small amount of precipitated LiCl. The complex's NMR spectra are identical to those of the silylene dihydride **8a**, except that there is only a trace hydride resonance in the $^1$H NMR spectrum, and the $^{31}$P{$^1$H}NMR spectrum shows coupling to the two deuterium nuclei. $^2$H NMR (fluorobenzene): $\delta$ 1.87 (t, integrates to 0.18D, $J_{DH}$ = 1.8 Hz), −3.65 (m, 2D, W*D*$_2$). $^{31}$P{$^1$H} NMR (fluorobenzene): $\delta$ 13.7 (quintet, $^{183}$W satellites, $J_{PW}$ = 200 Hz, $J_{PD}$ = 5 Hz).

**[Cp*(dmpe)(H)$_2$W=SiPhMe][B(C$_6$F$_5$)$_4$] (8b).** A sealable reaction flask was charged with 0.100 g (0.198 mmol) of **1**, 0.173 g (0.198 mmol) of Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$, and 0.027 g (0.217 mmol) of PhMeSiH$_2$ and sealed in a drybox. On a Schlenk line, 3 mL of fluorobenzene was added to the flask via cannula, and the orange solution was heated at 70 °C for 1 h. The solution was then filtered into a 10 mL Schlenk tube to remove LiCl, and 5 mL of pentane was layered onto the product solution via cannula. Overnight, the product precipitated as the liquids diffused together. The supernatant was filtered away, and the product was dried under reduced pressure for 6 h, yielding 0.178 g of **8b** as an orange/yellow solid (70% yield). $^1$H NMR (fluorobenzene): $\delta$ 7.76 (d, 2H, *o-Ph*, $J_{HH}$ = 7 Hz), 7.40 (t, 2H, *m-Ph*, $J_{HH}$ = 7 Hz), 7.33 (m, 1H, *p-Ph*), 1.87 (s, 15H, C$_5$*Me*$_5$), 1.47 (d, 6H, 2P*Me*, $J_{HP}$ = 9 Hz), 1.35 (m, 2H, 2PC*H*$_2$), 1.30 (s, 3H, Si*Me*), 1.18 (d, 6H, 2P*Me*, $J_{HP}$ = 8 Hz), 1.08 (m, 2H, 2PC*H*$_2$), −4.02 (m, 2H, W(*H*)$_2$, $J_{HW}$ = 48 Hz). $^{13}$C{$^1$H} NMR (fluorobenzene): $\delta$ 150.7 (s, Si*Ph*), 150.4, 148.5, 138.3, 136.3 (m, B(*C*$_6$F$_5$)$_4$), 133.9, 131.6, 128.9 (s, Si*Ph*), 100.6 (s, *C*$_5$Me$_5$), 32.1 (m, 2P*C*H$_2$), 28.4 (m, 2P*Me*), 25.3 (s, Si*Me*), 16.8 (m, 2P*Me*), 12.5 (s, C$_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (fluorobenzene): $\delta$ 13.3 (s, $J_{PW}$ = 201 Hz). $^{29}$Si{$^1$H} NMR (fluorobenzene): $\delta$ 297 (m). IR (KBr, cm$^{-1}$): 1900 w br ($\nu_{WH}$). Anal. Calcd for $C_{47}H_{41}BF_{20}P_2SiW$: C, 44.43; H, 3.25. Found: C, 45.59; H, 3.00. Repeated attempts to obtain satisfactory elemental analysis on compound **8b** were unsuccessful, possibly due to residual fluorobenzene in the sample that could not be removed under vacuum (Anal. Calcd for **8b**·(PhF)$_{0.5}$: C, 45.54; H, 3.32).

**[Cp*(dmpe)(H)$_2$W=SiMe$_2$][B(C$_6$F$_5$)$_4$] (8c).** A sealable reaction flask was charged with 0.100 g (0.198 mmol) of **1** and 0.173 g (0.198 mmol) of Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$. On a Schlenk line, 3 mL of fluorobenzene was vacuum transferred onto the solids at −20 °C. The headspace of the flask was then backfilled with an excess of dimethylsilane (approximately 20 mL at 1 atm, 0.9 mmol) and sealed. The mixture was allowed to stir for 1 h at 70 °C, and the orange solution was filtered

into a 10 mL Schlenk flask to remove LiCl. Pentane (5 mL) was carefully layered onto the product solution, and the flask was stoppered. Over 7 d at room temperature, the pentane diffused into the fluorobenzene solution, precipitating 0.156 g (65% yield) of **8c** as orange crystals. $^1$H NMR (fluorobenzene): $\delta$ 1.83 (s, 15H, $C_5$*Me*$_5$), 1.42 (d, 6H, 2P*Me*, $J_{HP}$ = 8 Hz), 1.40 (m, 2H, 2PC*H*$_2$), 1.20 (m, 2H, 2PC*H*$_2$), 1.12 (d, 6H, 2P*Me*, $J_{HP}$ = 7 Hz), 0.89 (s, 6H, Si*Me*$_2$), −5.90 (m, 2H, W(*H*)$_2$, $J_{HW}$ = 48 Hz). $^{13}$C{$^1$H} NMR (fluorobenzene): $\delta$ 150.4, 148.6, 138.7, 136.3 (m, B($C_6$F$_5$)$_4$), 100.3 (s, $C_5$Me$_5$), 32.7 (m, 2P*C*H$_2$), 29.7 (m, 2P*Me*), 27.1 (s, Si*Me*$_2$), 17.2 (m, 2P*Me*), 12.5 (s, $C_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (fluorobenzene): $\delta$ 13.4 (s, $J_{PW}$ = 221 Hz). $^{29}$Si{$^1$H} NMR (fluorobenzene): $\delta$ 314 (t, $J_{SiP}$ = 11 Hz). IR (KBr, cm$^{-1}$): 1949 vw br ($\nu_{WH}$), 1868 vw br ($\nu_{WH}$). Anal. Calcd for $C_{42}H_{39}BF_{20}P_2SiW$: C, 41.74; H, 3.25. Found: C, 42.02; H, 3.53.

**[Cp*(dmpe)(H$_2$)W=Si(H)Dipp][B(C$_6$F$_5$)$_4$] (8d).** A Schlenk flask was charged with 0.100 g (0.198 mmol) of **1**, 0.173 g (0.198 mmol) of Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$, and 0.038 g (0.198 mmol) of DippSiH$_3$, and 4 mL of fluorobenzene was added to the flask via cannula. The orange solution was heated at 70 °C for 1 h. The solution was then filtered to remove LiCl, and the volatile materials were removed under reduced pressure, giving **8d** as an orange oily solid. The flask was then cooled to −196 °C to solidify the oil. With a bar magnet, the stirbar was employed to scrape the solid from the walls of the flask. Drying this material under vacuum at low temperature for 5 min and at room temperature for 1 h yielded 0.151 g of **8d** (57% yield) as an orange powder. $^1$H NMR (fluorobenzene): $\delta$ 10.83 (s, 1H, Si*H*, $J_{HSi}$ = 167 Hz, $J_{HW}$ = 17 Hz), 3.09 (septet, 2H, 2C*H*Me$_2$, $J_{HH}$ = 7 Hz), 1.98 (s, 15H, $C_5$*Me*$_5$), 1.50 (d, 2P*Me*, $J_{HP}$ = 8 Hz), 1.5 (m, 2H, 2PC*H*$_2$), 1.4 (m, 2H, 2PC*H*$_2$), 1.25 (d, 12H, 2CH*Me*$_2$, $J_{HH}$ = 7 Hz), 1.21 (d, 6H, 2P*Me*, $J_{HP}$ = 8 Hz), −4.1 (m, 2H, W(*H*)$_2$, $J_{HW}$ = 39 Hz). $^{13}$C{$^1$H} NMR (fluorobenzene): $\delta$ 151.4 (*Ar*−*Dipp*), 150.4, 148.6 (br, B($C_6$F$_5$)$_4$), 145.0 (*Ar*−*Dipp*), 138.3, 136.5 (br, B($C_6$F$_5$)$_4$), 132.0, 123.6 (*Ar*−*Dipp*), 101.0 ($C_5$Me$_5$), 36.0 (2*C*HMe$_2$), 32.5 (m, 2P*C*H$_2$), 28.1 (m, 2P*Me*), 24.4 (2CH*Me*$_2$), 16.2 (m, 2P*Me*), 12.1 ($C_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (fluorobenzene): $\delta$ 12.3 (s, $J_{PW}$ = 209 Hz). $^1$H, $^{29}$Si HMQC (fluorobenzene): $\delta$ 286 (*Si*H, $J_{SiH}$ = 167 Hz). IR (KBr, cm$^{-1}$): 2118 w ($\nu_{SiH}$), 1864 w ($\nu_{WH}$). Anal. Calcd for $C_{52}H_{51}BF_{20}P_2SiW$: C, 46.58; H, 3.83. Found: C, 46.96; H, 4.00.

**[Cp*(dmpe)(H)$_2$W=SiMe$_2$(py)][B(C$_6$F$_5$)$_4$] (9).** To a solution of 0.150 g (0.124 mmol) of **8c** in 4 mL of fluorobenzene was added 12 $\mu$L (0.15 mmol) of pyridine, and the solution immediately changed color from orange to dark red. Pentane (6 mL) was carefully layered on top of the red solution, and the flask was sealed and allowed to stand at room temperature. Red crystals formed overnight, and the supernatant was decanted via cannula. The crystals were dried under reduced pressure to give 0.109 g of **9** (68% yield). $^1$H NMR (fluorobenzene): $\delta$ 8.38 (m, 2H, *o-py*), 7.35 (m, 1H, *p-py*), 7.21 (m, 2H, *m-py*), 1.69 (s, 15H, $C_5$*Me*$_5$), 1.44 (m, 2H, 2PC*H*$_2$), 1.23 (d, 6H, 2P*Me*, $J_{HP}$ = 8 Hz), 1.18 (m, 2H, 2PC*H*$_2$), 1.08 (d, 6H, 2P*Me*, $J_{HP}$ = 7 Hz), 0.54 (s, 6H, Si*Me*$_2$), −8.25 (dd, 2H, W(*H*)$_2$, $J_{HP}$ = 21 Hz, $J_{HP'}$ = 36 Hz, $J_{HW}$ = 47 Hz). $^{13}$C{$^1$H} NMR (fluorobenzene): $\delta$ 150.4, 148.5, 138.2, 136.3 (m, B($C_6$F$_5$)$_4$), 149.9, 145.5, 137.2 (s, *py*), 95.5 (s, $C_5$Me$_5$), 34.0 (dd, 2P*C*H$_2$, $J_{HP}$ = 12 Hz, $J_{HP'}$ = 21 Hz), 26.1 (dd, 2P*Me*, $J_{HP}$ = 6 Hz, $J_{HP'}$ = 33 Hz), 20.1 (d, 2P*Me*, $J_{HP}$ = 22 Hz), 17.5 (s, Si*Me*$_2$), 13.3 (s, $C_5$*Me*$_5$). $^{31}$P{$^1$H} NMR (fluorobenzene): $\delta$ 15.5 (s, $J_{PW}$ = 245 Hz). $^{29}$Si{$^1$H} NMR (fluorobenzene): $\delta$ 85 (m). IR (KBr, cm$^{-1}$): 1870 w ($\nu_{WH}$), 1844 w ($\nu_{WH}$). Anal. Calcd for $C_{47}H_{44}BF_{20}NP_2SiW$: C, 43.85; H, 3.44. Found: C, 44.10; H, 3.31.

**[Cp*(dmpe)W(H)Cl$_2$][B(C$_6$F$_5$)$_4$] (10).** A sealable flask was charged with 0.060 g (0.050 mmol) of **8c** in 0.8 mL of fluorobenzene. The solution was degassed, and the headspace was backfilled with 1 atm of MeCl. Heating the flask in an oil bath at 70 °C for 30 min gave a red-colored solution. The product solution was layered with 2 mL of pentane and allowed to stand overnight, resulting in formation of red crystals of **10**. The product was isolated by decanting the supernatant and drying under vacuum to give 0.024 g (44% yield) of **10** as red crystals. Compound **10** exhibits no $^1$H or $^{31}$P{$^1$H} NMR resonances due to its paramagnetism. EPR (fluorobenzene): $g$ = 1.97 (complex multiline pattern observed due to hyperfine coupling to $^{35}$Cl, $^{37}$Cl, $^{31}$P, and $^1$H ligands). IR (Nujol, cm$^{-1}$): 1879 vw ($\nu_{WH}$). Anal. Calcd for $C_{40}H_{32}BCl_2F_{20}P_2W$: C, 39.37; H, 2.64. Found: C, 39.76; H, 2.63.

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**Supporting Information Available:** Infrared spectral data for the reported complexes (PDF), and crystallographic information files (CIF) for **1**, **4**, **5**, **6b**, **7**, **8c**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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