*J. Am. Chem. Soc.* **2001,** *123,* 9702−9703

# High Oxidation-State (Formally d$^0$) Tungsten Silylene Complexes via Double Si−H Bond Activation

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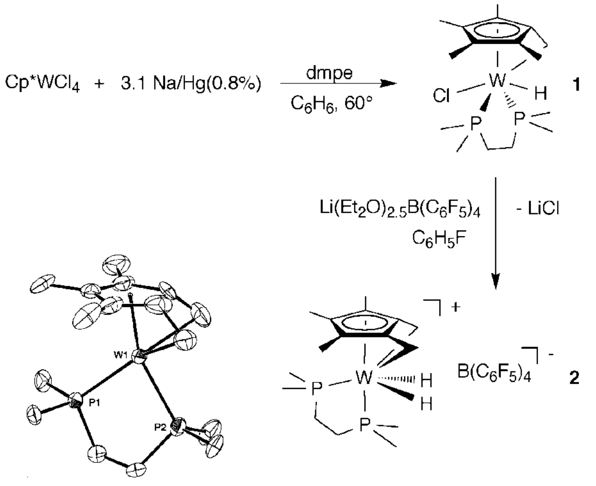
*Received July 3, 2001*

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) are 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,[5,6] and platinum[7,8] in relatively high d$^n$ configurations ($n \geq 6$). In general, these late metal silylene complexes have been shown to be very electrophilic at silicon. Thus, it is of interest to investigate silylene complexes involving strongly $\pi$-donating 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 metals initially focused on the group 6 metals, and herein we report base-free tungsten silylene complexes of the type $[Cp^*(dmpe)(H)_2W{=}SiR_2][B(C_6F_5)_4]$, ($Cp^* = \eta^5$-$C_5Me_5$, dmpe = $Me_2PCH_2CH_2PMe_2$). These compounds were prepared with use of a new, reactive tungsten-based synthon featuring a doubly metalated Cp* ligand. Previously, base-stabilized silylene complexes of the $Cp'W(CO)_2$ fragment ($Cp' = C_5H_5$, $C_5Me_5$) have been reported.[9,10]

We have established routes to platinum and iridium silylene complexes involving activation of two silicon−hydrogen bonds of a hydrosilane, via oxidative addition and subsequent α-elimination.[5,8] Significantly, this route requires access to coordinatively unsaturated metal centers (eq 1).

$$L_nM + R_2SiH_2 \rightarrow L_n(H)_2M{=}SiR_2 \qquad (1)$$

**Scheme 1.** Syntheses of Tucked Cp* Complex **1** and Doubly Tucked Cation **2**



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 $[Cp^*L_2W]^+$.[11] A possible precursor to such a fragment is $Cp^*(Me_3P)(\eta^2$-$Me_2PCH_2)W(H)Cl$, which appears to be in equilibrium with $Cp^*(Me_3P)_2WCl$.[12] In an attempt to develop a route to the $[Cp^*(dmpe)W]^+$ fragment, $Cp^*WCl_4$[13] was reduced with 3.0 equiv of Na/Hg (0.8% w/w) in the presence of dmpe. This procedure afforded crystalline orange-red $(\eta^6$-$C_5Me_4CH_2)(dmpe)W(H)Cl$ (**1**) in 75% yield after recrystallization from pentane (Scheme 1). Thus, unlike $Cp^*(Me_3P)_2WCl$, which undergoes intramolecular C−H activation of a phosphine ligand, 16-electron $Cp^*(dmpe)WCl$ degrades via metalation of the Cp* ligand.[14,16] The NMR spectra of **1** reflect the absence of mirror or rotational symmetry. For example, the four methyl groups of the dmpe ligand give rise to individual doublet resonances at $\delta$ 0.98, 1.23, 1.29, and 1.53 in the $^1H$ NMR spectrum. Compound **1** was also characterized by X-ray crystallography.[15]

Reaction of **1** with $[Li(OEt_2)_{2.5}][B(C_6F_5)_4]$ in fluorobenzene under argon gives $[(\eta^7$-$C_5Me_3(CH_2)_2)(dmpe)W(H)_2][B(C_6F_5)_4]$, **2**, (Scheme 1), a rare example of a “doubly tucked” Cp* metal

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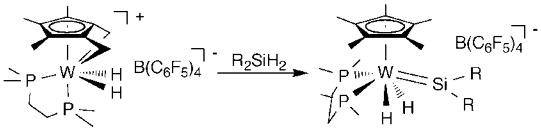
10.1021/ja0165436 CCC: $20.00

dihydride complex.[16,17] Compound **2** can be generated and used in situ or isolated as an orange crystalline solid in 70% yield by crystallization from fluorobenzene/pentane. Consistent with the structure shown in Scheme 1, the $^1$H NMR spectrum of **2** contains two resonances assigned to the Cp* methyl groups, at $\delta$ 1.68 and 1.85. Two singlets are observed for the diastereotopic hydrogens of the two equivalent methylene groups at $\delta$ 2.64 and 1.77, and tungsten hydride ligands are observed as a doublet of doublets at $\delta$ −2.11 ($J_{HP} = 38$ Hz, $J_{HP'} = 58$ Hz, $J_{HW} = 49$ Hz). Complex **2** was also characterized crystallographically, and an ORTEP diagram of the cation is displayed in Scheme 1. This species appeared to be a potential source of the [Cp*(dmpe)W]$^+$ fragment, providing the facile reductive elimination of two C−H bonds.

At room temperature in fluorobenzene, **2** reacts with dimethylsilane over 3 days under argon to form the silylene complex [Cp*(dmpe)(H)$_2$W═SiMe$_2$][B(C$_6$F$_5$)$_4$] (**3a**), isolated in 65% yield after crystallization from fluorobenzene/pentane (eq 2). The analogous diphenyl- and phenylmethylsilylene complexes (**3b** and **3c**, respectively) were synthesized in the same fashion from the corresponding silanes. In preparations of **3a**, **b**, and **c** it is most convenient to use a one-pot synthesis in which the chloride is abstracted from **1** in the presence of the silane. These reactions likely proceed via Si−H oxidative addition to a 16-electron "mono-tucked" cation, which appears to be thermally accessible at room temperature but was not observed spectroscopically.



(2)

**2**

**3a:** $R_2 = Me_2$
**3b**: $R_2 = PhMe$
**3c**: $R_2 = Ph_2$

The characterization of **3a** as a silylene complex was confirmed by a downfield resonance in the $^{29}$Si{$^1$H} NMR spectrum at $\delta$ 314. Silylene complexes **3b** and **3c** exhibit similarly downfield-shifted $^{29}$Si{$^1$H} NMR resonances at $\delta$ 297 and 277, respectively. X-ray quality crystals of the orange dimethylsilylene dihydride complex **3a** were obtained from a fluorobenzene/pentane solution of the complex. The structure contains two independent cation−anion pairs in the asymmetric unit, and one of the cations is shown in Figure 1. In each cation, the silylene ligand is planar with the sum of the angles around the silicon center being within error of 360° (359.4(6)° and 359.5(8)°). The two crystallographically independent cations possess very short tungsten−silicon bond distances (2.358(2) and 2.354(3) Å). A search of the Cambridge structural database revealed a range of 2.389−2.708 Å for W−Si bond lengths.

To investigate possible H−H and Si−H interligand bonding interactions in complexes **3a**−**c,** various spectroscopic methods were employed. On the basis of $^1$H NMR $T_1$ relaxation experiments, the hydride ligands in the silylene dihydride complexes appear to be classical in nature. Using the null method, the $T_1$(min) values for the dihydride ligands in **3a**, **b**, and **c** 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 in these complexes.[18] To investigate the possibility of W(H)···Si interactions in these compounds, the $^2J_{HSi}$ coupling constants were determined from $^1$H-detected, 1D $^{29}$Si HMQC BIRD filtered NMR experiments.[19] Since these coupling constants (7, 17, and 17 Hz for **3a**, **b**, and **c**, respectively) are less than 20 Hz, it appears that there is little or no interaction between the hydride and silylene ligands in these complexes.

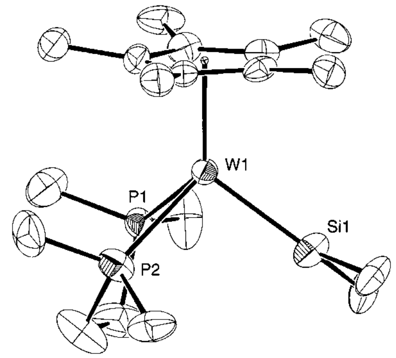


**Figure 1.** ORTEP diagram of one of the crystallographically independent cations in the X-ray structure of dimethylsilylene complex **3a**. Hydrogen atoms were omitted for clarity.

The new compounds reported here represent high oxidation-state silylene complexes in a formally d$^0$ electron configuration. Alternatively, these complexes may be viewed as d$^2$ in character, if tungsten-based electrons are not invoked in bonding to the silylene ligand. In preliminary reactivity studies, we have found that **3a** reacts with 1 equiv of pyridine to form an isolable adduct, the dark red complex [Cp*(dmpe)(H)$_2$WSiMe$_2$(py)][B(C$_6$F$_5$)$_4$] (**4**). Whereas this behavior is similar to what is expected for a late metal silylene complex, the reaction of **3a** with MeCl in fluorobenzene at 90 °C for 20 min produces Me$_3$SiCl, formally by insertion of dimethylsilylene into the C−Cl bond. This latter reaction contrasts with what has been found for the late metal complex [Cp*(Me$_3$P)$_2$Os═SiMe$_2$][B(C$_6$F$_5$)$_4$], which reacts with alkyl chlorides to form [Cp*(Me$_3$P)$_2$OsSiMe$_2$Cl][B(C$_6$F$_5$)$_4$]. Future work will explore further concepts of the reactivity of these new tungsten silylene complexes.

**Acknowledgment** is made to the National Science Foundation for their generous support of this work, and to Dr. Rudy Nunlist for valuable discussions. The authors would also like to thank Drs. Fred Hollander and Dana Caulder of the CHEXRAY X-ray crystallography facility at U.C. Berkeley for obtaining the crystal structure of compound **1**.

**Supporting Information Available:** Procedures for the synthesis and characterization of **1**, **2**, **3a**−**c**, and **4** (PDF) and X-ray crystallographic information for **1**, **2**, and **3a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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