Novel η^3-1-Silaallyl Tungsten Complexes via Si−H Bond Activation of Hydrovinylsilanes: Structure and Reactivity toward Methanol

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η^3-1-Silaallyl complexes, silicon analogues of η^3-allyl complexes, have been postulated as intermediates in several reactions of vinyl-substituted organosilicon compounds with transition metal complexes. However, their isolation and characterization have not been reported so far.[1,2] In an extension of our recent reactivity studies on the labile tungsten complexes cis-Cp*(CO)$_2$W(L)Me (L = MeCN, pyridine) toward Si−H bonds,[3] the reactions of cis-Cp*(CO)$_2$W(MeCN)Me (**1**) with hydrovinylsilanes were studied to reveal for the first time the formation of η^3-1-silaallyl complexes via thermal Si−H bond activation. We describe here their synthesis, structure, and reactivity toward methanol.

The reaction of **1** with HSiMe$_2$(CH=CH$_2$) in C$_6$D$_6$ resulted in the rapid formation of Cp*(CO)$_2$W(η^3-Me$_2$SiCHCH$_2$) (**2**) in 80% NMR yield accompanied by liberation of MeCN (δ 0.65) and methane (δ 0.15) (Scheme 1). Although it was not possible to isolate **2** in a pure state, Cp*(CO)$_2$W(η^3-Me$_2$SiCHCMe$_2$) (**3**) was successfully isolated as a pure, air-sensitive yellow solid in 54% yield in the reaction of **1** with HSiMe$_2$(CH=CMe$_2$).[4]

Scheme 1
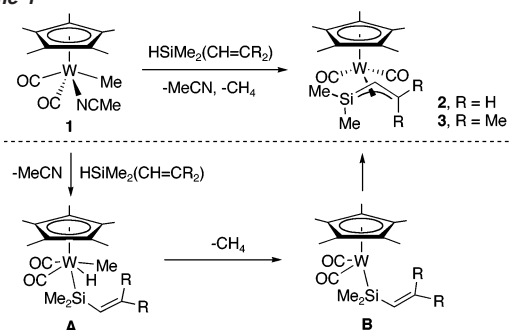
In the ^{1}H NMR spectrum of **2** in C$_6$D$_6$, the 1-silaallyl ligand shows three vinyl proton signals assigned to the central methine proton (δ 1.05) and the terminal methylene protons (δ 1.45 and 1.89) in addition to two SiMe signals (δ 0.14 and 0.46), and the assignments of the vinyl proton signals are based on the HETCOR spectrum.[4] The exo conformation of the silaallyl ligand is derived from an NOE experiment causing an intensity enhancement for the central methine proton upon irradiating the Cp* signal (δ 1.64). In the case of **3**, the methine proton signal resonated at δ 1.16 as a singlet together with SiMe$_2$ (δ 0.38 and 0.43) and CMe$_2$ (δ 1.54 and 1.90) signals, and its intensity is increased by irradiation of the Cp* signal (δ 1.68), similarly indicating the exo conformation.

A plausible mechanism for the formation of **2** and **3** is shown in Scheme 1, where the hydrido(methyl)silyl intermediate **A** is formed by oxidative addition of the hydrovinylsilane to coordinatively unsaturated Cp*W(CO)$_2$Me generated by dissociation of the acetonitrile ligand from **1**. Reductive elimination of methane in **A** affords the intermediate **B**, which can be viewed as a coordinatively unsaturated η^1-1-silaallyl species, and the vinyl moiety ligates to the metal center to afford the η^3-1-silaallyl complex. Prototypical
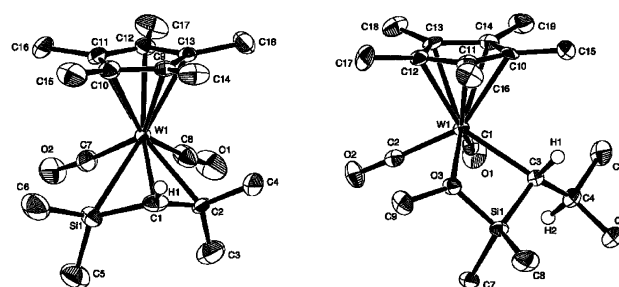
Figure 1. ORTEP diagrams of **3** (left) and **6** (right), showing 50% thermal ellipsoids. Methyl hydrogen atoms are omitted for clarity.

η^1-allyl to η^3-allyl conversion is well known in the formation of η^3-allyl complexes.[5]

The η^3-coordination of the Me$_2$SiCHCMe$_2$ moiety in **3** is shown by the X-ray crystal analysis, and the ORTEP diagram is depicted in Figure 1. The 1-silaallyl ligand coordinates to the metal center in an exo fashion in accordance with the NOE experiment. The most characteristic is the short Si1−C1 bond length of 1.800(4) Å, which is essentially equal to the Si−C bond lengths of known η^2-silene complexes,[6] coordination compounds of silenes R$_2$Si=CR$_2$[7] to transition metal fragments: 1.78(2) Å for Cp*(P^{i}Pr$_3$)HRu(η^2-SiPh$_2$CH$_2$),[6a,d] 1.800(8) Å for Cp$_2$W(η^2-SiMe$_2$CH$_2$),[6b] and 1.810-(6) Å for Cp*(PMe$_3$)Ir(η^2-SiPh$_2$CH$_2$).[6c] These Si−C bond lengths lie between typical Si−C single bond lengths (1.86−1.91 Å)[8] and double bond lengths (1.70−1.76 Å) in silenes[7,8] and have been recognized as a reflection of the partial double bond character of the Si−C bonds,[6] indicating that the Si1−C1 bond in **3** has a partial multiple bond character quite similar to that of the Si−C bonds in the η^2-silene complexes.[9] The C1−C2 length (1.411(5) Å) is comparable to the average (1.40 Å) of two C−C bond lengths (1.37(2) and 1.43(2) Å) of the allyl ligand in the η^3-allyl complex Cp*(CO)$_2$W(η^3-CH$_2$CHCH$_2$).[10]

Another noticeable feature is the sum of three C−X−C (X = Si1, C2) angles about Si1 and C2 atoms: 346.3° about Si1 and 350.9° about C2. These similar values are in the intermediate range between expected values for sp^2 (360°) and sp^3 (328.5°) hybridization and suggest that the Si1 and C2 atoms take similar types of hybridization. The corresponding sums about silicon atoms in η^2-silene complexes are in the range of 341−353°.[6] The above characteristics of the bond lengths and angles for **3** would allow us to describe its coordination mode as the η^3-1-silaallyl coordination rather than another possible η^1,η^2-1-silaallyl coordination extreme, Cp*(CO)$_2$W($\eta^1:\eta^2$-Me$_2$Si−CH=CMe$_2$), for which a longer Si1−C1 bond length and a more sp^3-like hybridization of Si1 atom should be expected. The ^{29}Si resonances for **2** (δ 13.8) and **3** (δ 8.8) are close to the lower-field end of those for the silene complexes (δ 6 to −21).[6]

η^3-Allyl complexes have been shown to generally exhibit high reactivity toward nucleophiles, typically at terminal carbon atoms.[5] As an initial reactivity study of the silaallyl complexes, we chose

to examine the weak nucleophile, methanol, considering also the fact that the Si−M bonds of the closely related η^2-silene complexes are cleaved by methanol to form hydrido-(methoxysilyl)alkyl complexes.[6b,c]

Addition of MeOH (ca. 1 equiv) to a C_6D_6 solution of **2** led to the formation of hydrido-(methoxysilyl)alkene complex, *trans*-Cp*(CO)$_2$WH(η^2-MeOMe$_2$SiCH=CH$_2$) (**4**, 92% by ^{1}H NMR), which was isolated as a red oil in 38% yield in the preparative reaction (eq 1). In the room-temperature ^{1}H NMR spectrum, very broad signals due to WH (δ −4.71) and SiMe$_2$ (around δ 0.19 and 0.43) were observed, but vinyl proton signals were indistinguishable. When the sample was cooled to −40 °C in toluene-d_8, the WH (δ −4.69) and SiMe$_2$ (δ 0.23 and 0.59) signals became sharp, and three vinyl proton signals were clearly detected at δ 0.15, 1.36, and 1.97 in addition to Cp* (δ 1.54) and OMe (δ 3.54) signals. These spectral changes are ascribed to rotation of the alkene ligand and site exchanges between the hydride and vinyl protons.[11] The trans configuration of the CO ligands is supported by the relative intensity of two CO stretching vibrations (1957 (m) and 1879 (s) cm^{-1}) in the IR spectrum. The formation of **4** is reasonably explained by nucleophilic attack of MeOH to the silicon atom of **2** to cleave the Si−W bond followed by protonation at the resulting anionic tungsten center, showing reactivity similar to that of the Si−M bonds in the η^2-silene complexes toward MeOH described above.

(1)
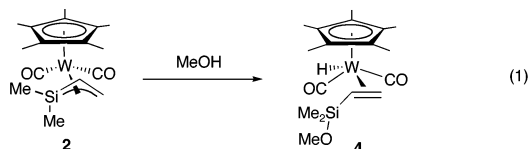
On treating a C_6D_6 solution of **3** with MeOH at room temperature, a single diastereomer of unexpected four-membered metallacycle **6** was obtained as a red solid in 56% yield (eq 2). The structure was fully characterized including X-ray analysis,[4] which showed anti configuration of the isopropyl group at the chiral α-carbon to the Cp* ligand as depicted in Figure 1 and the relatively short Si1−C3 bond length of 1.833(5) Å. Similar and slightly increased shortening of a Si−C bond (1.820(5) Å) in a four-membered silametallacycle has been observed for [*rac*-C$_2$H$_4$(indenyl)$_2$ZrCH(SiMe$_3$)SiMe$_2$Cl]$^+$.[12]

(2)
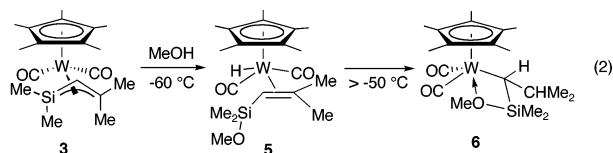
To gain insight into the formation mechanism of **6**, the reaction of **3** with MeOH was monitored by low-temperature ^{1}H NMR spectroscopy. A mixture of **3** and MeOH in toluene-d_8 was allowed to react at −78 °C, and the spectrum was recorded at −60 °C. Interestingly, it showed the complete conversion of **3** to two hydride species in an ca. 1:0.9 ratio, revealing extremely high reactivity toward the nucleophile, and they are tentatively assigned to an isomeric mixture of hydrido-(methoxysilyl)alkene complexes **5**.[13] The major component gives a doublet hydride signal at δ −6.12

(J = 7.2 Hz) coupled to a doublet at δ 0.20 (J = 7.2 Hz), which is attributable to the methine proton of the alkene ligand, while the minor affords a broad hydride signal at δ −8.94 and a broad singlet assignable to the methine proton at δ −0.34.[4,14] With an increase in temperature, the signals of the isomers became broader, and their conversion to **6** was observed. At −20 °C, **5** disappeared, and **6** was solely detected. These observations suggest that several dynamic processes such as interconversion between the isomers, exchange between the hydride and vinyl proton, and alkene rotation may be operative in the isomeric hydrides **5**, and that **6** may be derived from insertion of the (methoxysilyl)alkene ligand into the W−H bond in **5**, probably in a cis isomer, to form the sterically least hindered α-carbon followed by intramolecular trapping of the resulting coordinatively unsaturated species or its agostic form by the methoxy group. The remarkable difference in the stabilities of **4** and **5** is quite interesting and would be ascribed to at least the steric congestion of the alkene ligands; the more highly substituted alkene ligand such as that in **5** would destabilize the alkene complex to favor the formation of the metallacycle. We are currently making efforts to get more detailed information about the insertion processes and explore the reactivity of the η^3-1-silaallyl complexes.

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(13) One trans and two cis isomers are conceivable for a single rotamer of the alkene complex **5**.
(14) The signal at δ 0.15 observed for **4** is assigned to the methine proton adjacent to the silicon atom.[4] The values of δ 0.20 and −0.34 are close to this chemical shift, suggesting their assignments to the corresponding methine protons of the isomeric **5**.