Synthesis of a Silylene- and Hydride-bridged Re-W Heterobimetallic Complex and Its Photolysis to Form Novel Silenyl-bridged Heterobimetallic Complexes

Hiroyuki Sakaba,* Kazushige Ishida, and Hiroshi Horino*

Department of Chemistry, Graduate School of Science, Tohoku University, Kawauchi, Sendai 980-77

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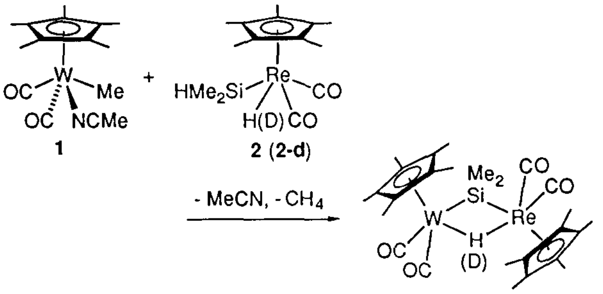
The reaction of *cis*-$Cp^*W(CO)_2(MeCN)Me$ (**1**) with $Cp^*(CO)_2Re(H)SiMe_2H$ (**2**) gave the silylene- and hydride-bridged heterobimetallic complex $Cp^*(CO)_2W(\mu\text{-}SiMe_2)(\mu\text{-}H)Re(CO)_2Cp^*$ (**3**). Photolysis of **3** produced an isomeric mixture of novel silenyl-bridged heterobimetallic complexes $Cp^*(CO)_2HW(\mu\text{-}\eta^1,\eta^2\text{-}SiMeCH_2)ReH(CO)_2Cp^*$ (**4**).

We have recently reported the synthesis of *cis*-$Cp^*W(CO)_2(MeCN)Me$ (**1**) and the stereospecific substitution of the labile acetonitrile ligand by phosphines.[1] One of fundamental reactions of such a labile complex is oxidative addition to a coordinatively unsaturated species generated from the complex. An intriguing example is the formation of $(CO)_4Mn(\mu\text{-}SiR_2)(\mu\text{-}H)Pt(PPh_3)_2$ from $Mn(CO)_5SiR_2H$ and $Pt(C_2H_4)(PPh_3)_2$ *via* oxidative addition of the Si-H bond of the Mn complex to unsaturated $Pt(PPh_3)_2$.[2] This Mn-Pt complex is a rare example of silylene- and hydride-bridged heterobimetallic complexes. Here we report a new entry to this class of complexes, a silylene- and hydride-bridged Re-W bimetallic complex using oxidative addition reaction of **1** and the photolysis of the heterobimetallic complex to produce novel silenyl-bridged Re-W bimetallic complexes.

The reaction of **1** with $Cp^*(CO)_2Re(H)SiMe_2H$ (**2**)[3] in toluene took place at room temperature to give $Cp^*(CO)_2W(\mu\text{-}SiMe_2)(\mu\text{-}H)Re(CO)_2Cp^*$ (**3**) in 72% isolated yield with evolution of methane.[6] The formation of **3** can be rationalized by oxidative addition of the Si-H bond of **2** to coordinatively unsaturated $Cp^*(CO)_2WMe$ generated from **1** to give a transient intermediate $Cp^*(CO)_2W(H)(Me)(\mu\text{-}SiMe_2)Re(H)(CO)_2Cp^*$. Reductive elimination of methane from the intermediate generates a vacant site at the tungsten center, to which the neighboring rhenium hydride coordinates to produce **3**.

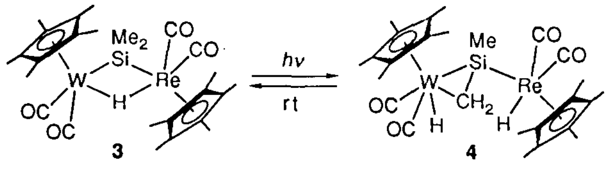


A single stereoisomer was produced in the reaction. We tentatively assign it to the *trans* isomer considering the bulkiness of Cp* ligands. The IR spectrum of **3** in KBr showed a very weak broad absorption centered around 940 cm^{-1} over the range of ca. 800 - 1100 cm^{-1}. This absorption may be assigned to $\nu_{W\text{-}H\text{-}Re}$, since an absorption due to $\nu_{M\text{-}H\text{-}M}$ generally appears very broad at ca. 1100 ± 300 cm^{-1}.[7] To confirm the assignment, the IR spectrum was compared with that of the deuterated complex $Cp^*(CO)_2W(\mu\text{-}SiMe_2)(\mu\text{-}D)Re(CO)_2Cp^*$ (**3-d**, 97% D)[8] synthesized by the reaction of **1** with $Cp^*(CO)_2Re(D)SiMe_2H$ (**2-d**, 97% D).[9] In the spectrum of **3-d**, no very broad absorption was observed in the range of 800 - 1100 cm^{-1} and a new relatively broad absorption was found at 698 cm^{-1}. The ratio of the absorption frequencies observed for **3** and **3-d** is close to the calculated value and hence we assigned the very broad absorption for **3** to $\nu_{W\text{-}H\text{-}Re}$. No loss of deuteride was observed in the reaction of **1** with **2-d** and this observation supports the mechanism described above.

In accord with the assignment of the bridging hydride, the ^1H NMR spectrum of **3** shows a characteristic hydride signal with W-satellites of 37.5 Hz at δ -11.19 along with a very broad SiMe signal at δ 1.05 at room temperature. As expected from the observation of the broad SiMe signal, **3** shows temperature-dependent spectral change. On cooling, the SiMe signal was sharpened and split into two signals (δ 1.35 and 0.91 at -50 °C). The ^{13}C NMR spectrum at -50 °C showed the expected four sharp CO resonances at δ 232.1 (J_{WC} = 151 Hz), 232.0 (J_{WC} = 164 Hz), 213.8 and 200.5, while the spectrum at room temperature showed a single sharp resonance at δ 231.2 (J_{WC} = 157 Hz) and two weak broad resonances at δ 213.1 and 200.3. These phenomena denote that two dynamic processes, the site exchange of SiMe groups and that of CO ligands, exist in the complex.[10]

Another spectral characteristic for **3** is the ^{29}Si resonance observed at δ 168.3. Similar low-field ^{29}Si resonances have been observed for silylene-bridged bimetallic complexes. For example, the ^{29}Si resonance of $Cp(CO)Fe(\mu\text{-}SiH^tBu)(\mu\text{-}CO)Fe(CO)Cp$ is observed at δ 254.4.[11] Lesser extent of downfield shift observed for **3** seems to reflect the weaker 3-center 2-electron interaction in the W-H-Re moiety compared to the direct metal-metal interaction in the diiron complex and the strong electron-donation to the silylene moiety from two electron rich third raw transition metal fragments.

When a toluene-d_8 solution of **3** in a sealed NMR tube was irradiated with a 100 W medium pressure Hg lamp at 5 °C for 30 min and its ^1H NMR spectrum was observed at -60 °C, two products were observed in a ratio of 3 : 2 (total ca. 50%) along with unreacted **3** (ca. 50%). The reaction mixture had reached to a photostationary state under the conditions and further irradiation did not increase the conversion. The products are characterized as a mixture of two isomers of $\mu\text{-}\eta^1,\eta^2$-silenyl-bridged Re-W bimetallic complex **4** by low-temperature NMR spectra, but it is difficult to assign their definite structures



among several possible isomeric structures at present. At room temperature the isomers show coalesced ^{1}H NMR signals and reverts to **3** with $t_{1/2} \approx 40$ min at 25 °C, indicating that they are interconvertible and thermally unstable.

For the major isomer, two hydride signals are observed at δ -9.27 and -9.33 at -60 °C, and the latter signal accompanying W-satellites of 52 Hz is assigned to the WH and the former without satellites to the ReH. The J_{WH} (52 Hz) is considerably larger than that (37.5 Hz) of the bridging hydride in **3**. The inequivalent CH_2 protons are resonated at δ 1.39 (dd, J = 9.5, 3.5 Hz) and -0.17 (d, J = 9.5 Hz) in addition to the SiMe (δ 0.92, d, J = 1.8 Hz) and Cp* (δ 1.84 and 1.70) signals. The small couplings of 3.5 and 1.8 Hz observed for the respective signals at δ 1.39 and 0.92 are due to the couplings to the WH.[12] This is evidenced by a decoupling experiment; irradiation of the WH signal changed the doublet of doublets at δ 1.39 and the doublet at δ 0.92 to a doublet (J = 9.5 Hz) and a singlet, respectively.[13]

For the minor isomer, two hydride signals are resonated at δ -8.69 and -11.43 at -60 °C, but they are too broad to observe W-satellites. When the temperature was lowered to -80 °C, the signals became sharp enough to see the satellites and could be assigned to the WH (δ -8.62, J_{WH} = 51 Hz) and ReH (δ -11.46). These behaviors suggest the existence of the relatively fast exchange process for the hydrides. Although a doublet due to one of the inequivalent CH_2 protons was observed at δ -0.65 (J = 9.1 Hz, -80 °C) in addition to the SiMe (δ 1.15) and Cp* (δ 1.88 and 1.62) signals, the expected counterpart doublet of doublets was not found. To search for it, the ^{1}H,^{1}H COSY spectrum was observed at -80 °C. A cross peak correlated to the doublet at δ -0.65 was found around δ 1.6, in which a very intense Cp* signal (δ 1.59) of unreacted **3** was resonated. Furthermore, a cross peak correlated to the WH signal at δ -8.62 was also observed around δ 1.6. From these observations, we conclude that the minor product also has a hydrido-silene-tungsten skeleton similar to the major product and that the signal due to one of the CH_2 protons is probably obscured by the Cp* signal of unreacted **3**.

In the ^{13}C DEPT 135 spectrum at -50 °C, the expected negative signals assigned to the WCH_2 carbons were observed at δ -14.7 (major) and -12.6 (minor) along with positive signals at δ 5.95 (major) and 5.99 (minor) due to the $SiCH_3$ carbons. Two sets of CO signals were observed at δ 246.3, 236.2, 204.1, and 202.5 (major), and 244.5, 235.0, 205.5, and 202.7 (minor) in the $^{13}C\{^1H\}$ NMR spectrum at -80 °C. These spectral data for the $WH(\mu\text{-}\eta^1,\eta^2\text{-}SiMeCH_2)$ moieties, especially the coupling constants, are very similar to those of the closely related η^2-silene-tungsten complex $Cp^*(CO)_2WH(\eta^2\text{-}SiMe_2CH_2)$ synthesized by Wrighton; δ_{1H} 1.03 (WC*H*H, dd, J = 10, 4 Hz), -0.87 (WCH*H*, d, J = 10 Hz), -10.78 (WH, J_{WH} = 54 Hz), and δ_{13C} -27.6 (WCH_2) at -73 °C.[14] The small coupling constant (4 Hz) observed for the signal at δ 1.03 has been assigned to the coupling between the WCH and WH protons. Upfield shift of a ^{13}C signal of a coordinated-silene carbon has been observed for isolated silene-transition-metal complexes.[15] Attempts to observe ^{29}Si NMR and J_{CH} for the WCH_2 carbon were unsuccessful because of the low solubility of **3** and the low conversion of **3** to **4**.

Although several η^2-silene complexes have been characterized so far, their synthetic methods are limited to two types of reactions, the intramolecular activation of a Si-H bond of $L_nMCH_2SiR_2H$ complexes and the reductive dechlorination of $L_nClMCH_2SiR_2Cl$ complexes using magnesium.[16] Recently intermediacy of a silene complex formed by the intramolecular oxidative addition of a C-H bond (β-H elimination of a alkylsilyl group) has been postulated in several reactions,[17] but there is no report on the characterization of a silene complex *via* such a process. To our knowledge, this is the first spectroscopic characterization of a silene complex resulting from the intramolecular oxidative addition of a C-H bond.

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References and Notes

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3 Complex **2** was synthesized by the reaction of $K[Cp^*(CO)_2ReH]$[4] with Me_2HSiCl. Although only a single CO resonance was observed in the ^{13}C NMR spectrum of **2**, a relative intensity ratio (1.0) of ν_{CO} absorptions at 1972 and 1898 cm^{-1} suggests a *cis* configuration. It has been reported that the *cis* isomer is thermodynamically more stable than the *trans* isomer for $Cp(CO)_2Re(H)SiPh_3$.[5]
Selected data for **2**: ^{1}H NMR (500 MHz, $C_6D_5CD_3$) δ 4.62 (septet of doublets, $^3J_{HSiCH}$ = 3.7 Hz, $^3J_{HSiReH}$ = 0.6 Hz, 1H, SiH), 1.74 (s, 15H, Cp*), 0.74 (dd, $^3J_{HCSiH}$ = 3.7 Hz, $^4J_{HCSiReH}$ = 0.7 Hz, 6H, SiMe), -9.79 (br, 1H, ReH). $^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_5CD_3$) δ 203.5 (CO), 98.3 (C_5Me_5), 10.2 (C_5Me_5) 4.1 (SiMe). ^{29}Si NMR (99 MHz, $C_6D_5CD_3$) δ -14.3. IR (C_6H_6) ν_{CO}= 1972 (s), 1898 (s) cm^{-1}. MS (EI, ^{187}Re) m/z (relative intensity) 438 (M^+, 65). HRMS found 438.1028; calcd for $C_{14}H_{23}O_2ReSi$ 438.1025.

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6 Selected data for **3**: ^{1}H NMR (400 MHz, $C_6D_5CD_3$, -50 °C) δ 1.95 (s, 15H, Cp*), 1.59 (s, 15H, Cp*), 1.35 (s, 3H, SiMe), 0.91 (s, 3H, SiMe), -11.37 (s, J_{WH} = 37 Hz, 1H, μ-H). $^{13}C\{^1H\}$ NMR (150 MHz, $C_6D_5CD_3$ -50 °C) δ 232.1 (J_{WC} = 151 Hz, WCO), 232.0 (J_{WC} = 164 Hz, WCO), 213.8 (ReCO), 200.5 (ReCO), 101.3 (C_5Me_5), 99.5 (C_5Me_5), 13.0 (SiMe), 12.7 (SiMe), 11.3 (C_5Me_5), 9.9 (C_5Me_5). IR ($C_6D_5CD_3$) ν_{CO}= 1937 (m), 1891 (vs), 1873 (s), 1817 (s) cm^{-1}. MS (FAB, ^{184}W, ^{187}Re): m/z (relative intensity) 812 (M^+, 10). Anal. Found: C, 38.24; H, 4.29%. Calcd for $C_{26}H_{37}O_4ReSiW$: C, 38.47; H, 4.59%.

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8 The D content was calculated from the relative intensity of the remaining ReHW signal to the Cp* signal.
Selected data for **3-d**: MS (FAB, ^{184}W, ^{187}Re) m/z (relative intensity) 813 (M^+, 5).

9 Selected data for **2-d**: MS (EI, ^{187}Re) m/z 439 (relative intensity) (M^+, 88). HRMS found 439.1078; calcd for $C_{14}H_{22}DO_2ReSi$ 439.1087.

10 $\Delta G^{\ddagger}_{297}$ for the SiMe exchange was calculated to be 58.0 kJ mol^{-1}.

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12 The WH signal ($\Delta\nu_{1/2}$ = 9 Hz) was observed relatively broader compared to the ReH signal ($\Delta\nu_{1/2}$ = 5 Hz), but the small couplings were not seen for the WH signal.

13 These spin-spin interactions were confirmed by the observation of three cross peaks in the ^{1}H,^{1}H COSY spectrum at -60 °C: δ -9.33 ↔ 0.92, -9.33 ↔ 1.39, -0.17 ↔ 1.39.

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