Protonation of Bis-μ-diethylsilyl Complex $\{(C_5Me_5)Ru(\mu\text{-}\eta^2\text{-}HSiEt_2)\}_2(\mu\text{-}H)(H)$: Enhancement of Bonding Interaction between Bridging Silicon and Hydride Ligands

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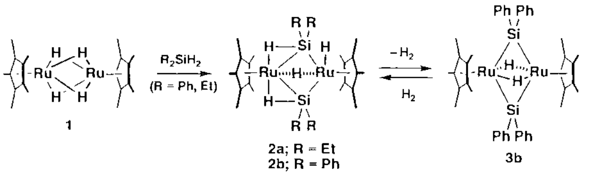
A bis-μ-diethylsilyl complex $\{Cp^*Ru(\mu\text{-}\eta^2\text{-}HSiEt_2)\}_2(\mu\text{-}H)(H)$ (**2a**; Cp* = $\eta^5\text{-}C_5Me_5$) reacted with CF_3SO_3H to afford a cationic bis-μ-diethylsilane complex $[\{Cp^*Ru(\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2SiEt_2)\}_2(\mu\text{-}H)][X]$ (**4a**, X = CF_3SO_3, BPh_4). An X-ray diffraction study of **4a-BPh$_4$** revealed its pseudo C_2 symmetric structure and $\mu\text{-}\eta^2\text{:}\eta^2$-coordination of the bridging silicon.

Complexes having many metal centers in appropriate arrangement facilitate bond activation via co-operative interaction of neighboring metal centers. We have demonstrated notable reactivities of multimetallic polyhydride clusters towards hydrocarbons,[1a,b] phosphines,[1c] and hydrosilanes.[2] The reaction of a multimetallic cluster with a dihydrosilane often resulted in the formation of a complex having a bridging silicon ligand. Reactivity of an M–Si bond has been widely investigated in relation to a wide variety of catalytic reactions, such as silane polymerization, hydrosilylation, and disproportionation.[3] Most of these studies, however, have been limited to mononuclear complexes. Although numerous transition metal complexes containing a bridging silicon ligand have been synthesized, little was known about their reactivities.[4]

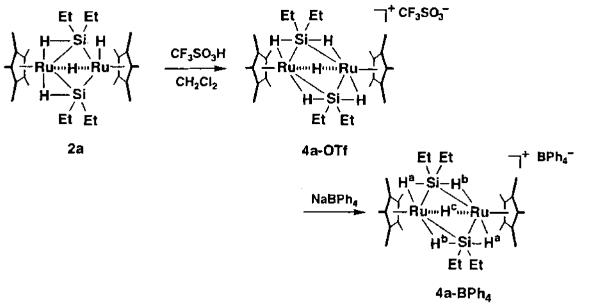


(1)

We have reported the synthesis of bis-μ-silyl complexes **2** by the reaction of $Cp^*Ru(\mu\text{-}H)_4RuCp^*$ (**1**) with secondary silanes (eq 1).[2a] Complex **2** has a pseudo-symmetry plane passing through the two ruthenium atoms. Since the 2e–3c (2-electron 3-center) Ru–H–Si bonds were formed on one Ru center, the environment of two metal centers was inequivalent. The η^2-Si–H bonds of **2b** were cleaved upon heating to yield a bis-μ-silylene complex **3b** which has σ-Ru–Si bonds. This reaction clearly showed that one ruthenium center acted as a coordination site and the other was an activation site together with reactivity of a coordinated Si–H bond toward oxidative addition reaction.

Oxidation of a metal center weakens metal-ligand interaction due to reduction of d-electron density, thereby promotes bond formation between ligands. A cationic metal center can be formed by protonation as well as oxidation. Thus, protonation of a bis-μ-silyl complex was investigated in relation to bond formation at the bridging silicon ligands. We report herein the reaction of **2a** with CF_3SO_3H to yield a cationic bis-μ-diethylsilane complex $[\{Cp^*Ru(\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2SiEt_2)\}_2(\mu\text{-}H)](BPh_4)$ (**4a-BPh$_4$**). This is the first reported example of formation of a bis-μ-silane complex from a μ-silyl complex induced by protonation.

Treatment of bis-μ-diethylsilyl complex **2a** with CF_3SO_3H at –78 ºC in CH_2Cl_2 led to the formation of a cationic bis-μ-silane complex **4a-OTf**. While complex **4a-OTf** was very sensitive to air and moisture, complex **4a-BPh$_4$**, which was obtained by exchanging the counter anion to BPh_4^-, was stable enough to be isolated in analytically pure form. Complex **4a-BPh$_4$** was characterized by means of ^1H, ^{13}C, and ^{29}Si NMR spectroscopies, FD–MS, and elemental analysis (eq 2).[5]



(2)

In the ^1H NMR spectrum of **4a-BPh$_4$** measured at 297.6 K, a singlet assignable to hydride resonance was observed at δ –13.45. The intensity ratio between the signal of Cp* ligands and that of the hydrides was estimated at 30:5. This indicates the occurrence of protonation. At 173 K, the resonance for hydrides split into two peaks with intensity ratio of 1:4 (Figure 1). This result clearly showed that the site-exchange process of the hydrides took place in **4a**. The resonance appeared at δ –13.40 (1H) was assignable to the hydride ligand, H^c, bridging between the two ruthenium atoms. Slight broadening of the signal at δ –13.64 at 173 K showed that the site-exchange between H^a and H^b still occurred.

The $J_{Si\text{–}H}$ value of 18 Hz measured at room temperature was the average of those among magnetically inequivalent silicons (Si, Si') and the magnetically inequivalent five protons (H^a, H^b, H^c). The sum of $J_{Si\text{–}Ha}$ and $J_{Si\text{–}Hb}$ was, therefore, estimated at 90 Hz.

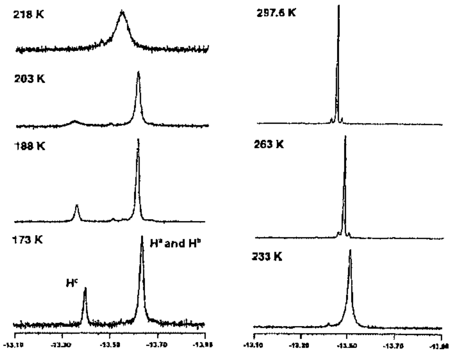


Figure 1. Variable temperature ^1H NMR spectra showing hydride region of **4a-BPh$_4$** (CD_2Cl_2, 400 MHz).

We assigned $J_{Si–Hb}$ to be ca. 70 Hz and $J_{Si–Ha}$ to be ca. 20 Hz , respectively, based on the line shape analysis using gNMR® programs. The presence of such two kinds of Si–H interaction was confirmed by the X-ray diffraction study.

The ^{1}H signal of the Cp* ligands did not show any temperature dependence. This fact was fully consistent with the pseudo C_2 symmetrical structure of **4a-BPh$_4$** as shown in Figure 2. The shape of the signals for the ethyl groups on the bridging silicon also did not change over the wide range of temperature. This implies that the Ru_2Si_2 moiety was rigid.

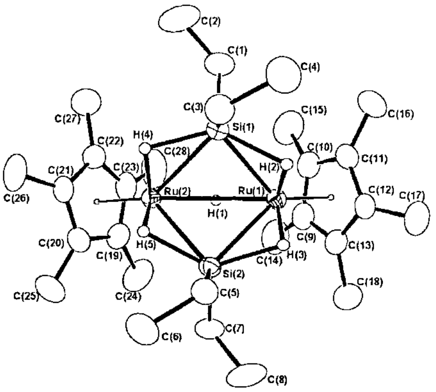


Figure 2. Molecular structure and labeling scheme of a cationic part of **4a-BPh$_4$**. Selected bond lengths (Å) and angles (deg). Anion and THF atoms are neglected for clarity: Ru(1)-Ru(2), 3.023(2); Ru(1)-Si(1), 2.4348(9); Ru(1)-Si(2), 2.497(1); Ru(2)-Si(1), 2.517(1), Ru(2)-Si(2), 2.439(1); Si(1)-H(2), 1.81(4); Si(1)-H(4), 1.73(3); Si(2)-H(3), 1.77(3); Si(2)-H(5), 1.78(3); Ru(1)-Si(1)-Ru(2), 75.23(3); Ru(1)-Si(2)-Ru(2), 75.53(3); Si(1)-Ru(1)-Si(2), 85.43(4); Si(1)-Ru(2)-Si(2), 84.88(4)

Although significant down-field shift of the ^{29}Si resonance is anticipated for the cationic complex, the ^{29}Si signal of **4a-BPh$_4$** appeared at δ 108.3, which was almost the same as that of bis-μ-diethylsilyl complex **2a** (δ 111.7). Coordination of a secondary silane to a diruthenium complex in a μ-η^2:η^2-fashion resulted in up-field shift of the ^{29}Si resonance. The ^{29}Si signal of the μ-silane complex $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si^tBu_2)$ appeared at δ 75.5, which was considerably higher magnetic field than that of **2a**.[2b] It was, thus, considered that the ^{29}Si resonance of **4a** was observed in a similar region to **2a** as a result of offset between the up-field shift due to weak H–Si–H interaction and the down-field shift derived from the cationic metal center.

The structure of **4a-BPh$_4$** was determined by X-ray crystallography using a single crystal obtained from THF at –20 ºC. An ORTEP diagram of **4a-BPh$_4$** is depicted in Figure 2.[6] The pseudo C_2 symmetrical Ru_2Si_2 core of **4a-BPh$_4$** adopted a folded-parallelogram structure. It is contrasted to the C_s symmetrical structure of **2a**, in which the Ru_2Si_2 core formed a folded-kite structure. The Ru(1)–Ru(2) distance of 3.023(2) Å implies bonding interaction between the two ruthenium atoms. Complex **4a-BPh$_4$** has two long Ru–Si bonds and two short ones; Ru(1)–Si(2) (2.497(1) Å) and Ru(2)–Si(1) (2.517(1) Å) are slightly longer than Ru(1)–Si(1) (2.4348(9) Å) and Ru(2)–Si(2) (2.439(1) Å). The difference in the two Ru–Si distances in the Ru_2Si_2 core in **4a-BPh$_4$** is much smaller than that observed in **2a**; the σ-Ru–Si bond distance of **2a** was 2.33 Å (av) and the Ru–Si bond distance in the 2e-3c Ru–H–Si interaction was 2.57 Å (av).[2a]

Five hydride ligands of **4a-BPh$_4$** were located during difference Fourier synthesis. One of them, H(1), bridges the two ruthenium atoms. The other hydrogen atoms, H(2)–H(5), were located between the ruthenium and silicon atoms. These hydrides formed 2e-3c Ru–H–Si bonds. Although it is difficult to determine the accurate position of the hydrogen atom attached to a heavy atom by an X-ray diffraction study, the significant difference in the Ru–Si distances shows that there were two kinds of Ru–H–Si interaction.

In the IR spectrum of **4a-BPh$_4$**, absorption assigned to the stretching vibration of the 2e-3c Ru–H–Si bond was not observed. This is probably due to obstruction by the strong absorption of the BPh_4 anion.

Increase in the positive charge at the ruthenium centers upon protonation would result in weakening of Ru–Si and Ru–H interaction. As a result of protonation, bonding interaction between the μ-silyl and the terminal hydride ligand was produced. Although reductive elimination of secondary silanes from cationic bis-μ-silane complex **4a** has not yet been observed upon heating, reactivity of the cationic complex **4** was significantly different from that of **2**. We are now investigating reactivities of **4** with several nucleophiles, especially nucleophilic displacement reaction at the bridging silicon.

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Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday

References and Notes

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3. See for example; *The Chemistry of Organic Silicon Compounds*; S. Patai, Z. Rappoport, Eds.; Wiley: New York, 1989.
4. a) J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, **99**, 175 (1999). b) H. Ogino and H. Tobita, *Adv. Organomet. Chem.* **42**, 223 (1998).
5. Preparation of **4a-BPh$_4$**: Treatment of **2a** (37.0 mg, 0.057 mmol) with CF_3SO_3H (4 μL, 0.061 mmol) in CH_2Cl_2 (10 mL) at –78 ºC under argon atmosphere resulted in color change of the solution from yellow to dark-green. The solution was then slowly warmed up to room temperature. After stirring for 5 min at room temperature, large excess amount of $NaBPh_4$ was added. The product was extracted with three portions of 10 mL of CH_2Cl_2 and the combined extracts was passed through Celite on a glass filter. After the solvent was removed in vacuo, the residual solid was rinsed 5 times with 5 mL of pentane. Removal of pentane in vacuo afforded 46 mg of **4a-BPh$_4$** as a yellow solid (Yield 83%). ^{1}H NMR (23ºC, CD_2Cl_2): δ –13.45 (s, 5H, $J_{Si–H}$ = 18 Hz, Ru*H*), 0.79 (m, 8H, $–CH_2CH_3$), 0.99 (m, 12H, $–CH_2CH_3$), 2.05 (s, 30H, Cp*), 6.8–7.4 (m, 20H, Ph). (–100 ºC): –13.64 (br, 4H, Ru–*H*–Si), –13.40 (s, 1H, Ru–*H*–Ru), 0.64 (m, 8H, $–CH_2CH_3$), 0.86 (m, 12H, $–CH_2CH_3$), 1.97 (s, 30H, Cp*), 6.8–7.3 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (23 ºC, CD_2Cl_2): δ 9.3 ($–CH_2CH_3$), 11.2 ($–CH_2CH_3$), 12.5 (C_5Me_5), 15.3 ($–CH_2CH_3$), 16.2 ($–CH_2CH_3$), 100.9 (C_5Me_5), 122.2 (Ph), 126.1 (Ph), 136.5 (Ph), 164.6 (Ph). $^{29}Si\{^1H\}$ NMR (23 ºC, CD_2Cl_2): δ 108.3. FD–MS: *m/z* = 651; Anal. Calcd for $C_{52}H_{75}BRu_2Si_2$: C, 64.44; H, 7.80. Found: C, 63.91; H, 7.80.
6. Crystal data for $[\{Cp^*Ru(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2SiEt_2)\}_2(\mu\text{-}H)][BPh_4]\cdot THF$: $C_{56}H_{83}BORu_2Si_2$ (fw = 1041.52), triclinic, space group *P*-1(#2), a = 14.343(9) Å , b = 15.675(5) Å, c = 12.838(2) Å, α = 109.40(1°, β = 90.81(3)°, γ = 92.32(4)°, V = 2719(2)Å^3, Z = 2, D_{calcd} = 1.284 g/cm^3, μ(Mo Kα) = 6.35 cm^{-1}, R = 0.029 (R_w = 0.039) on reflection 8293 (I > 3.00σ(*I*)).