Iridium-Catalyzed Redistribution of Hydrodisilanes *via* a Silyl(silylene)iridium(III) Complex: Synthesis of a Donor-Stabilized Silyl(silylene)iridium(III) Complex

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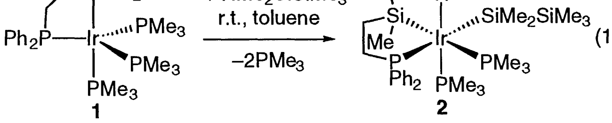
Thermolysis of $HMePhSiSiMe_3$ in the presence of a catalytic amount of $Ir\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_3$ resulted in the redistribution of substituents to give its isomer $HMe_2SiSiMe_2Ph$. We propose the mechanism involving the 1,3-Me-shift on a silyl(silylene) complex, which was trapped as a donor-stabilized silyl(silylene)iridium(III) complex.

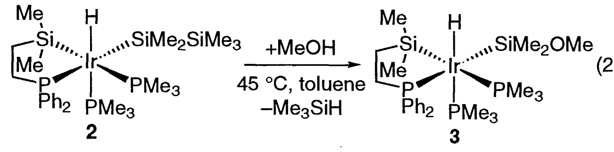
A silyl(silylene) complex has been considered as a key intermediate in transition-metal-mediated redistribution reactions of organosilicon compounds.[1] It was found that photo-chemical conversion of $CpFe(CO)_2SiMe_2SiMeR_2$ (R = Ph, Et, CD_3) to $CpFe(CO)_2SiMe_{3-n}R_n$ (n = 0, 1, 2) is accompanied by the scrambling of substituents on silicon atoms, and Pannell et al. and we proposed a mechanism involving the 1,3-migration of substituents on silyl(silylene) intermediates.[2] Recently, Pannell et al. reported that thermolysis of hydrodisilanes with a catalytic amount of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(SiMe_3)$ caused isomerization of disilanes, where they proposed a mechanism involving a silyl(silylene)iron intermediate.[3] Tamao et al. described a Pd(0)-catalyzed skeletal rearrangement of alkoxytrisilanes, and they proposed the mechanism involving a silyl(silylene)palladium(II) intermediate, which is stabilized by an intramolecular donor.[4] In these catalytic reactions, however, nothing has been explored on the isolation of the intermediate, i.e., the silyl(silylene) complex or its stabilized form. We report here an Ir(I) complex $Ir\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_3$ (**1**)[5] not only catalyzes the redistribution of hydrodisilanes but also forms a donor-stabilized bis(silylene)iridium complex, i.e., the stabilized form of the silyl(silylene) complex.

Treatment of **1** with 1 equiv. $HSiMe_2SiMe_3$ at room temperature gave a hydrido(disilanyl)iridium(III) complex $Ir(H)(SiMe_2SiMe_3)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2$ (**2**) (eq 1).[6] Recrystallization of **2** from toluene-hexane afforded colorless crystals of **2** in 89% yield. The ^1H, ^{29}Si, and ^{31}P NMR data established that **2** possesses three phosphorous atoms in a *fac*-configuration as in eq 1.



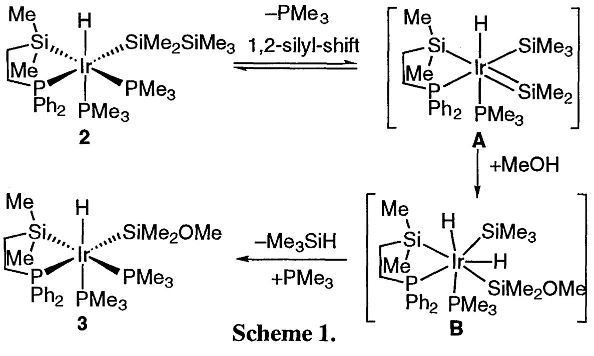
(1)

In the presence of MeOH, **2** was converted, on heating to 45 °C for 2 h, to $Ir(H)(SiMe_2OMe)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2$ (**3**)[7] in 73% isolated yield (eq 2),[8] although **2** was thermally stable at this temperature in the absence of MeOH. In the ^1H NMR spectrum, a signal of SiOMe appears as a singlet at 3.45 ppm.



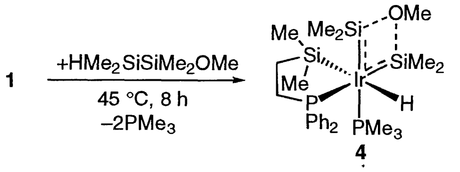
(2)

A plausible mechanism is illustrated in Scheme 1: The dissociation of a PMe_3 ligand followed by the reversible 1,2-silyl-shift gives a silyl(silylene) intermediate **A**. MeOH is known to work as an efficient trapping agent of silylene complex to give a hydrido(methoxysilyl) complex.[9] Therefore, MeOH adds to the Ir=Si double bond to give a seven-coordinate iridium(V) intermediate **B**, which then undergoes the reductive elimination of Me_3SiH[10] and ligation of PMe_3 to give **3**.



Scheme 1.

To confirm the existence of a silyl-silylene intermediate **A**, complex **1** was allowed to react with $HMe_2SiSiMe_2OMe$. The reaction proceeded cleanly at 45 °C for 8 h to give hydridobis(silylene) complex **4** (eq 3).[11,12] The geometry of **4** can be uniquely determined by the NMR data. The ^{31}P NMR spectrum shows an AX pattern at -60.6 ppm and 32.0 ppm (J(PP*cis*) = 28.9 Hz), which is consistent with the geometry as shown in eq 3. In the ^{29}Si NMR spectrum, the signals of two silylene ligands appeared inequivalently at 62.8 ppm (dd, J(SiP*trans*) = 135.9 Hz, J(SiP*cis*) = 11.8 Hz) and 63.1 ppm (dd, J(SiP*trans*) = 136.9 Hz, J(SiP*cis*) = 13.0 Hz), which are shifted to significantly downfield from those of previously reported silyliridium compounds.[5,9b,13] Moreover, the upfield shift of the ^1H NMR signal for the SiOMe group (2.77 ppm) is characteristic of methoxy-bridged bis(silylene) complexes.[14]



(3)

The formation of **4** can be also explained by the mechanism involving the 1,2-silyl-shift to the iridium center as shown in Scheme 1. In the case of $HMe_2SiSiMe_2OMe$, a silyl(silylene) intermediate corresponding to **A** can be stabilized by the bridging methoxy group to give a bis(silylene) complex **4**.

Reaction of **1** with 5 equiv. $HPhMeSiSiMe_3$ was carried out at room temperature for 2 h. Complex **1** reacted with 1 equiv. $HPhMeSiSiMe_3$ to give **5** via the rearrangement of substituents on a disilanyl ligand (eq 4).[15] A small amount of $HMe_2SiSiMe_2Ph$ was also detected spectroscopically. The formation of **6**, a simple oxidative addition product, was

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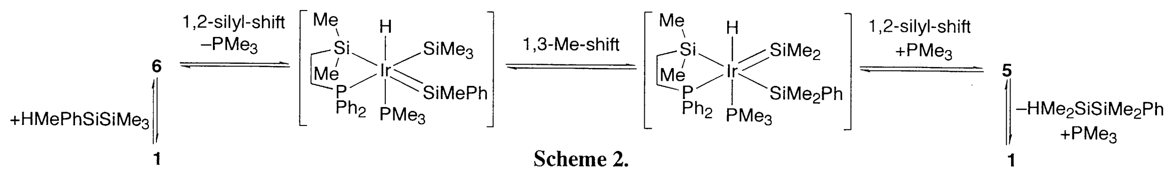
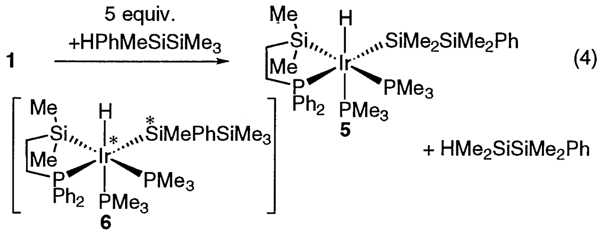


Scheme 2.

confirmed in the course of the reaction, but **6** finally disappeared.[16] Furthermore, thermolysis of this solution at 45 °C underwent the rearrangement of hydrodisilane to give an isomeric mixture of $HPhMeSiSiMe_3$ and $HMe_2SiSiMe_2Ph$. After 5 days, the molar ratio of $HPhMeSiSiMe_3$ to $HMe_2SiSiMe_2Ph$ became 2 : 3, and **5** finally decomposed.[17] We treated $HMe_2SiSiMe_2Ph$ under the same conditions in the presence of **1**, which resulted in the formation of a mixture of $HPhMeSiSiMe_3$ and $HMe_2SiSiMe_2Ph$ in the ratio of 2 : 5. The decomposition of **5** formed in the reaction was also confirmed spectroscopically.[17] Each reaction led to the isomeric mixture of hydrodisilane in the different ratio. This means that an active catalyst **5**[18] decomposed before achieving the equilibrium.[17] This isomerization reactions can be explained by the mechanism shown in Scheme 2. This mechanism also involves the generation of a silyl(silylene) intermediate, which causes a 1,3-Me-shift and 1,2-silyl-shift. The resulting disilanyl complex eliminates an isomeric hydrodisilane.



(4)

To detect the silyl-silylene intermediate in Scheme 2, we employed $HMe(MeO)SiSiMe_3$ instead of $HPhMeSiSiMe_3$. Thermolysis of **1** in the presence of $HMe(MeO)SiSiMe_3$ led to the clean formation of **4**. This apparently demonstrates that the skeletal rearrangement of hydrodisilanes take place *via* the silyl(silylene) intermediate, which causes the 1,3-Me-shift as shown in Scheme 2.

In this paper, we firstly succeeded in the isolation of a donor-stabilized silyl(silylene) species, which is a stabilized form of a key intermediate formed in the transition-metal-mediated redistribution of substituents of silicon atoms.

References and Notes

1 H. K. Sharma and K. H. Pannell, *Chem. Rev.*, **95**, 1351 (1995).

2 K. H. Pannell, J. Cervantes, C. Hernandez, J. Cassias, and S. Vincenti, *Organometallics*, **5**, 1056 (1986). H. Tobita, K. Ueno, and H. Ogino, *Bull. Chem. Soc. Jpn.*, **61**, 2979 (1988).

3 K. H. Pannell, M. Brun, H. Sharma, K. Jones, and S. Sharma, *Organometallics*, **13**, 1075 (1994).

4 K. Tamao, G. Sun, and A. Kawachi, *J. Am. Chem. Soc.*, **117**, 8043 (1995).

5 M Okazaki, H. Tobita, and H. Ogino, *Organometallics*, **15**, 2790 (1996).

6 Selected data for **2**: ^1H NMR (300 MHz, C_6D_6) δ -12.78 (dt, J(HP*trans*) = 105.1 Hz, J(HP*cis*) = 17.1 Hz, 1H, IrH). ^{29}Si NMR (59.6 MHz, C_6D_6) δ -51.3 (ddd, J(SiP*trans*) = 115.6 Hz, J(SiP*cis*) = 11.4, 12.7 Hz, Ir<u>Si</u>Me2SiMe3), -13.6 (t, J(SiP*cis*) = 11.4 Hz, SiMe3), 10.5 (ddd, J(S<u>i</u>P*trans*) = 116.2 Hz, J(SiP*cis*) = 11.5, 7.7 Hz, $IrSiMe_2CH_2$). ^{31}P NMR (121.5 MHz, C_6D_6) δ -69.4 (t, J(PP*cis*) = 23.7 Hz, PMe3), -61.4 (dd, J(PP*cis*) = 23.7, 17.3 Hz, PMe3), 27.6 (dd, J(PP*cis*) = 17.3, 23.7 Hz, PPh_2). Anal. Found: C, 43.29; H, 7.00%. Calcd for $C_{27}H_{54}IrP_3Si_3$: C, 43.35; H, 7.28%.

7 Selected data for **3**: ^1H NMR (300 MHz, C_6D_6) δ -12.82 (dt, J(HP*trans*) = 99.0 Hz, J(HP*cis*) = 18.0 Hz, 1H, IrH), 3.45 (s, 3H, OMe). ^{31}P NMR (121.5 MHz, C_6D_6) δ -65.5 (dd, J(PP*cis*) = 23.1, 25.5 Hz, PMe3), -59.9 (dd, J(PP*cis*) = 20.2, 25.5 Hz, PMe3), 25.6 (dd, J(PP*cis*) = 20.2, 23.1 Hz, PPh_2). Anal. Found: C, 42.94; H, 7.01%. Calcd for $C_{25}H_{48}IrOP_3Si_2$: C, 42.53; H, 6.85%.

8 Formation of Me_3SiH was confirmed by ^1H NMR spectroscopy. ^1H NMR data of Me_3SiH (300 MHz, C_6D_6) δ 4.16 (sep., J(HH) = 3.6 Hz, 1H, SiH), 0.00 (d, 9H, SiMe3).

9 a) K. Ueno, H. Tobita, S. Seki, and H. Ogino, *Chem. Lett.*, **1993**, 1723. b) M. Okazaki, H. Tobita, and H. Ogino, *Chem. Lett.*, **1996**, 477.

10 There is another possibility that **B** eliminates $HSiMe_2OMe$ instead of $HSiMe_3$, although the formation of $HSiMe_2OMe$ was not observed in the ^1H NMR spectrum. This is attributable to the existence of the electron-withdrawing methoxy group on the silicon atom. An electron-withdrawing group on a silicon atom is known to strengthen a M–Si bond by increasing M-Si π-bonding involving Si d or σ* orbital.

11 Selected data for **4**: ^1H NMR (300 MHz, C_6D_6) δ -9.88 (dd, J(HP*cis*) = 14.3, 19.7 Hz, 1H, IrH), 2.77 (s, 3H, SiOMe). ^{29}Si NMR (59.6 MHz, C_6D_6) δ 12.5 (dd, J(SiP*cis*) = 9.2, 11.7 Hz, silyl), 62.8 (dd, J(SiP*trans*) = 135.9 Hz, J(SiP*cis*) = 11.8 Hz, silylene), 63.1 (dd, J(SiP*trans*) = 136.9 Hz, J(SiP*cis*) = 13.0 Hz, silylene). ^{31}P NMR (121.5 MHz, C_6D_6) δ -60.6 (d, J(PP*cis*) = 28.9 Hz, PMe3), 32.0 (d, PPh_2). Exact mass (70 eV, DEI) *m/z* Calcd for $C_{24}H_{45}IrOP_2Si_3$: 688.1883. Found: 688.1889.

12 At room temperature, the reaction of **1** and $HMe_2SiSiMe_2OMe$ gave $Ir(H)(SiMe_2SiMe_2OMe)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_3$ corresponding to **2**. Spectroscopic data are similar to those for **2**.

13 M. Okazaki, Y. Kawano, H. Tobita, S. Inomata, and H. Ogino, *Chem. Lett.*, **1995**, 1005.

14 a) H. Tobita, K. Ueno, M. Shimoi, and H. Ogino, *J. Am. Chem. Soc.*, **112**, 3415 (1990). b) H. Tobita, H. Wada, K. Ueno, and H. Ogino, *Organometallics*, **13**, 2545 (1994). c) T. Takeuchi, H. Tobita, and H. Ogino, *Organometallics*, **10**, 835 (1991).

15 Selected data for **5**: ^1H NMR (300 MHz, C_6D_6) δ -12.79 (dt, J(HP*trans*) = 104.4 Hz, J(HP*cis*) = 16.7 Hz, 1H, IrH). ^{29}Si NMR (59.6 MHz, C_6D_6) δ -51.2 (ddd, J(SiP*trans*) = 119.0 Hz, J(SiP*cis*) = 11.3, 12.8 Hz, Ir<u>Si</u>Me2SiMe2Ph), -16.0 (t, J(SiP*cis*) = 11.8 Hz, SiMe2Ph), 10.3 (ddd, J(SiP*trans*) = 115.6 Hz, J(SiP*cis*) = 7.5, 11.4 Hz, $IrSiMe_2CH_2$). ^{31}P NMR (121.5 MHz, C_6D_6) δ -69.6 (t, J(PP*cis*) = 23.8 Hz, PMe3), -61.9 (dd, J(PP*cis*) = 17.1, 23.8 Hz, PMe3), 27.5 (dd, J(PP*cis*) = 17.1, 23.8 Hz, PPh_2). Anal. Found: C, 47.20; H, 6.93%. Calcd for $C_{32}H_{56}IrP_3Si_3$: C, 47.44; H, 6.97%.

16 Complex **6** is a mixture of diastereomers **6a** and **6b**. ^{31}P NMR (121.5 MHz, C_6D_6) data for **6a**: δ 28.1 (dd, J(PP*cis*) = 16.3 Hz, 24.2 Hz, PPh_2), -63.5 (dd, J(PP*cis*) = 16.3, 24.2 Hz, PMe3), -72.6 (t, J(PP*cis*) = 24.2 Hz, PMe3). **6b**: 29.4 (dd, J(PP*cis*) = 17.1, 23.2 Hz, PPh_2), -62.5 (dd, J(PP*cis*) = 17.1, 23.2 Hz, PMe3), -71.8 (t, J(PP*cis*) = 23.2 Hz, PMe3).

17 Decomposition of **5** may be attributable to the reaction with a small amount of H_2O or thermal evolution of the SiR_2 moiety. The decomposition resulted in the formation of *fac*-$[Ir(H)(SiMe_3)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$, *fac*-$[Ir(H)(SiMe_2Ph)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2]$, and some unidentified products.

18 In the presence of an isolated **5**, the catalytic isomerization of the hydrodisilane, $HPhMeSiSiMe_3$ or $HMe_2SiSiMe_2Ph$, also took place in a similar manner. This means that **5** is one of active catalytic species.

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