Generation of Hydrido(silylene)iridium(I) Complex *via* [1,2] H Shift from the Silicon Atom to the Iridium(I) Metal Center

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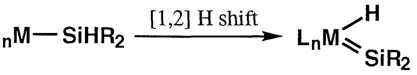
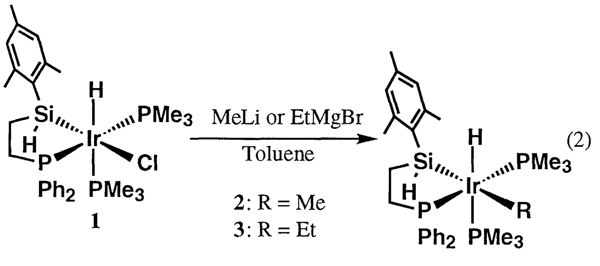
Thermolysis of alkyl-hydrido complexes, $L_nIr(R)(H)$ [L_n = {$MesHSi(CH_2)_2PPh_2$}$(PMe_3)_2$, R = Me, Et], caused the reductive elimination of alkane to generate a 16e iridium(I) species L_nIr (**A**). Intermediate **A** underwent the intramolecular C-H bond activation. Reactivity of **A** with MeOH revealed that **A** underwent a [1,2] H shift from the silicon atom to the iridium center to give hydrido(silylene) complex $Ir(H)\{\eta^2\text{-}MesSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**B**) reversibly.

Transition metal hydrosilyl complexes can be regarded as a key intermediate in catalytic reactions such as transition metal catalyzed silane oligomerization[1] and redistribution of substituents on silicon atoms.[2] In many of these reactions, hydrosilyl complexes are assumed to undergo [1,2] H shift from a silicon atom to a metal center to generate hydrido(silylene) complexes (eq 1).[3] Nevertheless, there is little evidence for a generation of a silylene complex by the [1,2] H shift,[4,5] although silylene complexes have been studied for a long time.[6] We describe here the generation of a hydrido(silylene)iridium(I) complex from a 16e (hydrosilyl)iridium(I) complex via [1,2] H shift and also the intramolecular C-H bond activation of the latter complex.



$$L_nM\text{—}SiHR_2 \xrightarrow{[1,2]\ \text{H shift}} L_nM\overset{H}{\underset{SiR_2}{\lessgtr}} \qquad (1)$$

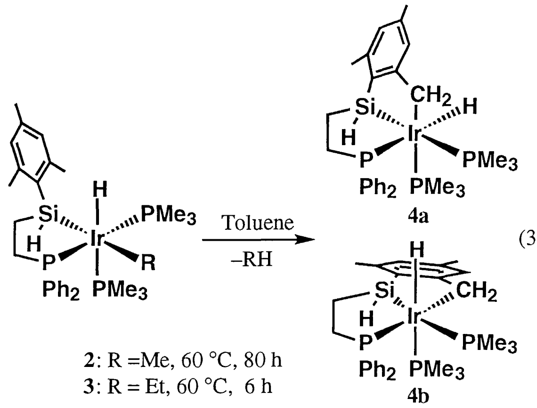
The alkyl-hydrido complexes **2**[7] and **3**[8] can be readily prepared by adding the corresponding alkyl sources (MeLi and EtMgBr) to a toluene solution of chloro complex **1**[9] as colorless crystals in 57 and 62% yields, respectively (eq 2).



(2)

The ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra of **2** and **3** show that complexes **2** and **3** possess alkyl, hydrido, and silyl ligands in a *mer* position. These complexes **2** and **3** can be regarded as models for hydrosilation formed in the intermediates.

Thermolysis of **3** at 60 °C for 6 h led to the clean formation of **4** via the reductive elimination of ethane, which was observed by ^1H NMR spectrum (eq 3). Thermolysis of **2** proceeded more slowly (60 °C, 80 h) than that of **3** to give the same product **4** quantitatively via reductive elimination of methane (eq 3). The product **4** was a mixture of two isomers **4a** and **4b** in the ratio of 5 : 3, but its recrystallization from toluene-haxane afforded colorless crystals of only **4a**.[10] These isomers **4a** and **4b** have been uniquely characterized by NMR spectroscopy. The arrangement of three coordinating atoms C, Si, and P of the tridentate ligand are facial for **4a** and meridional for **4b**. In the ^{13}C DEPT135 NMR spectrum of **4a**, the signal of $IrCH_2$ was observed as a doublet of triplets at δ 3.3 ppm {$^2J(CP\mathit{trans})$ = 61.4 Hz, $^2J(CP\mathit{cis})$ = 4.7 Hz), the chemical shift characteristic of the carbon directly bound to a transition metal. Furthermore, the negative phase of this signal indicates that an even number of hydrogen is attached to the carbon. In the ^{13}C-^1H HETCOR spectrum, the ^{13}C signal of $IrCH_2$ at 3.30 ppm correlates with the ^1H signals appeared at 2.66 and 3.28 ppm, indicating that these signals are assigned to the nonequivalent methylene protons.

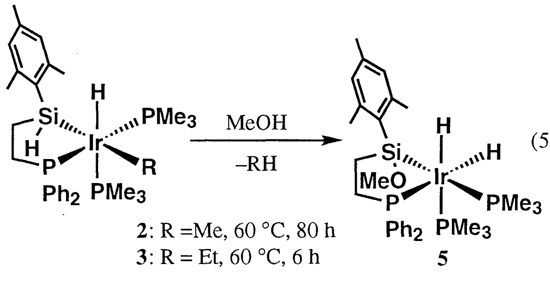


(3)

Heating of **4a** in C_6D_6 at 60 °C caused partial geometric isomerization to **4b** which reached to an equilibrium with the ratio of **4a** : **4b** = 5 : 3 (eq 4).

$$\mathbf{4a} \xrightleftharpoons{C_6D_6,\ 60\ °C} \mathbf{4b} \qquad (4)$$

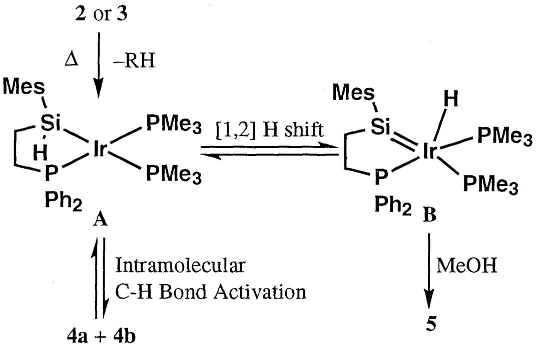
Thermolysis of **2** or **3** in the presence of MeOH afforded Dihydrido(methoxysilyl)iridium(III) complex **5**[11] via the reductive elimination of alkane quantitatively (eq 5). The reaction of **3** with MeOH was monitored by ^1H NMR spectroscopy. The ^1H NMR signals of **4** were observed in



(5)

the course of the reaction, though these signals finally disappeared. The ^{1}H, ^{31}P, and ^{29}Si NMR spectra of **5** show that complex **5** possesses two hydrido ligands and a silyl ligand in a *fac* position. The ^{1}H NMR signal of SiOMe appears as a singlet at 3.40 ppm. The IR spectrum of **5** shows an absorption at 1066 cm^{-1} assigned to the ν(Si-O) vibration. The NOESY spectrum of **5** shows a cross peak between the ^{1}H NMR signals of a SiOMe moiety and a PMe$_3$ ligand (*trans* to IrH), which is consistent with the geometry as shown in eq 5.

A possible mechanism which explain the formation of complexes **4** and **5** is shown in Scheme 1. This mechanism involves the first generation of a 16e hydrosilyliridium(I) intermediate **A**, which is not detected by NMR spectroscopy, through the reductive elimination of alkane. Recently, Tilley et al. observed a highly reactive 16e silyliridium(I) complex, Ir{Si(SiMe$_3$)$_3$}(PMe$_3$)$_3$, in solution at -80 °C by ^{31}P NMR spectroscopy.[12] In the absence of any trapping agent, **A** activates an intramolecular C-H bond in an *o*-methyl group of the Mes group to give **4** reversibly. Perhaps complex **4** is stabilized by the chelate effect of two fused five-membered rings. To our knowledge, **4** is one of few examples of the silametallacycle formed by the *sp*^{3}-C-H bond activation. Apart from **4**, other examples are Ir(H)-{(CH$_2$)$_2$OSi(OEt)$_2$}(PMe$_3$)$_3$[13] and Ir(H)-{SiMe$_2$SiMe(SiMe$_3$)SiMe$_2$CH$_2$}(PMe$_3$)$_3$.[12] Intermediate **A** undergoes [1,2] H shift to give a hydrido(silylene) intermediate **B** reversibly. In the presence of MeOH, MeOH traps **B** via nucleophilic attack to the silylene ligand to afford a hydrido(methoxysilyl) complex **5**. MeOH is known to work as a good trapping agent for silylene complexes,[14] since M=Si bond is fairly polarized in the M$^{\delta-}$-Si$^{\delta+}$ fashion.[15] Introduction of a methoxyl group at the silicon atom seems to demonstrate the facile migration of a hydrogen atom from the silicon atom to the iridium center.



Scheme 1. A possible mechanism for the formation of **4** and **5**.

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7 Selected data for **2**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ -12.00 (dt, *J*(HP*trans*) = 122.7 Hz, *J*(HP*cis*) = 19.1 Hz, 1H, IrH), 0.43 (q, *J*(HP*cis*) = 6.2 Hz, 3H, IrMe). ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ -37.2 (ddd, *J*(CP*cis*) = 6.2, 8.8, 14.5 Hz, IrMe). ^{31}P NMR (121.5 MHz, C$_6$D$_6$) δ 31.3 (dd, *J*(PP*trans*) = 344.2 Hz, *J*(PP*cis*) = 15.8 Hz, PPh$_2$), -49.4 (dd, *J*(PP*trans*) = 344.2 Hz, *J*(PP*cis*) = 22.4 Hz, PMe$_3$ (*trans* to PPh$_2$)), -62.0 (dd, PMe$_3$ (*trans* to IrH)). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ -14.3 (dt, *J*(SiP*cis*) = 7.2, 10.6 Hz). MS (70 eV, DEI) *m/z* 722 (3, M^{+}), 706 (100, M^{+}-CH$_4$). Anal. Found: C 52.78, H 7.18%. Calcd for C$_{30}$H$_{48}$IrP$_3$Si · 1/2 (C$_6$H$_5$CH$_3$): C 52.39, H 6.82%.

8 Spectroscopic data for **3** are similar to those for **2**.

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10 Selected data for **4a**: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ -11.59 (dt, *J*(HP*trans*) = 132.2 Hz, *J*(HP*cis*) = 17.8, 1H, IrH), 2.66, 3.28 (m, 2H, IrCH$_2$). ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 3.3 (dt, *J*(CP*trans*) = 61.4 Hz, *J*(CP*cis*) = 4.7 Hz, IrCH$_2$). ^{31}P NMR (121.5 MHz, C$_6$D$_6$) δ -60.9 (t, *J*(PP*cis*) = 20.1 Hz, PMe$_3$), -59.6 (dd, *J*(PP*cis*) = 13.7, 20.1 Hz, PMe$_3$), 24.0 (dd, PPh$_2$). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ 21.7 (ddd, *J*(SiP*trans*) = 131.1 Hz, *J*(SiP*cis*) = 10.7, 7.9 Hz). MS (70 eV, DEI) *m/z* 706 (100, M^{+}). Anal. Found: C 48.55, H 6.41%. Calcd for C$_{29}$H$_{44}$IrP$_3$Si: C 49.34, H 6.28%. Spectroscopic data for **4b** are omitted because of its similarity to those for **4a**.

11 Selected data for **5**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ −12.79 (dt, *J*(HP*trans*) = 100.2 Hz, *J*(HP*cis*) = 18.0 Hz, 1H, IrH), -11.46 (dt, *J*(HP*trans*) = 112.7 Hz, *J*(HP*cis*) = 21.0 Hz, 1H, IrH), 2.24 (s, 3H, SiOMe). ^{31}P NMR (121.5 MHz, C$_6$D$_6$) δ -63.0 (t, *J*(PP*cis*) = 19Hz, PMe$_3$), -55.3 (t, PMe$_3$), 33.3 (t, PPh$_2$). ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 49.5 (d, *J*(CP) = 5.0 Hz, SiOMe). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ 46.2 (ddd, *J*(SiP*trans*) = 146.2 Hz, *J*(SiP*cis*) = 9.6, 6.5 Hz). IR (KBr) 1066 cm^{-1} (ν(Si-O)). MS (70 eV, DEI) *m/z* 738 (21, M^{+}). Anal. Found: C 50.07, H 6.63%. Calcd for C$_{30}$H$_{48}$IrOP$_3$Si · 1/4 (C$_6$H$_5$CH$_3$): C 50.11, H 6.62%.

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