Light- and Heat-Induced Geometric Isomerization of Chloro(hydrido)iridium(III) Complex Containing a (2-Phosphinoethyl)silyl Chelate Ligand

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Photolysis of chloro(hydrido)(silyl)iridium complex [Ir(Cl)(H){HMesSi(CH_2)$_2$$PPh_2$}($PMe_3$)$_2$] (**1**) caused the geometric isomerization to **2** which reached to a photostationary state with the ratio of **1** : **2** = 29 :71. Both **1** and **2** take *mer* configuration, but **1** has a hydrido ligand opposite to one of PMe_3's while **2** has that opposite to the PPh_2. On thermolysis, **2** reverted to **1** quantitatively.

Several octahedral, tertiary phosphine complexes are known to undergo geometric isomerization on photolysis.[1] For most of these complexes, the reverse isomerization occurs on thermolysis. However, these studies have been limited to the types of complexes, [RuX_2L_4],[2] [IrX_3L_3],[3] and [$M(H)(X)_2L_3$][3,4] ; (M = Rh, Ir; X = halide; L = π-acidic two-electron-donor ligand). Recently, interest in transition metal catalyzed hydrosilylation,[5] silane oligomerization,[6] and redistribution of substituents on silicon[7] has promoted studies of silyl-transition metal complexes.[8] But the photochemical behavior of hydrido(silyl) complexes has not been investigated in detail. We report here the first reversible thermal and photochemical geometric isomerization of the octahedral hydrido(silyl)iridium(III) complex, which was observed for a complex containing a new (2-phosphinoethyl)silyl chelate ligand, *mer*-[Ir(Cl)(H)-{HMesSi(CH_2)$_2$$PPh_2$}($PMe_3$)$_2$] (Mes = 2,4,6-$C_6H_2Me_3$).

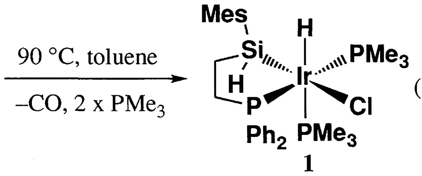
A chelate ligand precursor, $MesH_2Si(CH_2)_2PPh_2$,[9] has been prepared as a colorless microcrystalline solid in 93% yield by applying the preparative method of (2-phosphinoethyl)silanes reported by Stobart et al. (eq 1).[10]

$$MesH_2Si(CH{=}CH_2) + PHPh_2 \xrightarrow[\text{toluene}]{h\nu,\ 12\ h} MesH_2Si(CH_2)_2PPh_2 \qquad (1)$$

The ^{29}Si NMR spectrum shows a doublet at -43.4 ppm (^3J(SiP) = 23 Hz), which is a value characteristic of (2-phosphinoethyl)silanes.

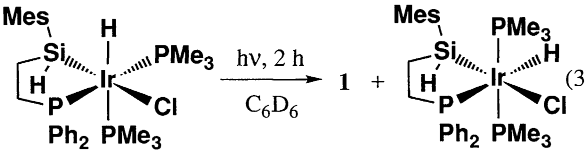
On heating the toluene solution of the ligand precursor $MesH_2Si(CH_2)_2PPh_2$ and the cationic iridium(I) complex [$Ir(CO)(PMe_3)_4$]Cl in a sealed tube at 90 °C for 36 h, chloro(hydrido)iridium(III) complex **1**[11] was formed in 80% yield (eq 2). The geometry of **1** can be uniquely determined by the ^{31}P, ^1H, and ^{29}Si NMR spectra. The ^{31}P signal of Ir-PPh_2 appears at δ 19.7 ppm as a doublet of doublets with one large coupling with a *trans* PMe_3 and one small coupling with a *cis* PMe_3. In the ^1H NMR spectrum, a hydrido signal appears as a doublet of triplets at -9.41 ppm due to one large *trans* coupling and two nearly identical small *cis* couplings with ^{31}P's, which indicates that a PMe_3 ligand is located at the position opposite to the hydrido ligand. These assignments are confirmed by the $^{29}Si\{^1H\}$ NMR spectrum that shows a ddd signal with three nearly identical small *cis* coupling constants (J_{SiP} = 5.8, 6.7, 7.4 Hz). In the geometry of complex **1**, the strongly *trans*-influencing silyl ligand[12] is located at the position opposite to the least *trans*-influencing chloro ligand.

$MesH_2Si(CH_2)_2PPh_2$ + [$Ir(CO)(PMe_3)_4$]Cl



1 (2)

Irradiation of complex **1** in C_6D_6 with a 450 W medium-pressure mercury lamp caused the geometric isomerization to complex **2**[13] (eq 3). This reaction reached to a photostationary state within 2 h to give a mixture of **1** and **2** in the ratio of 29 : 71. Only **2** crystallized out on cooling the C_6D_6 solution of the mixture of **1** and **2**.



1 **2** (3)

29 : 71

In the ^{31}P NMR spectrum of **2**, two nearly chemically equivalent PMe_3 ligands show only one doublet due to the coupling with a *cis* PPh_2 at -48.9 ppm. In the ^1H NMR spectrum, an Ir-H resonance appears at -10.27 ppm as a doublet of triplets due to one large *trans* coupling and two identical small *cis* couplings with ^{31}P's, which suggests that the hydrido ligand is located at the position opposite to a phosphine ligand. Moreover, the signal of ^{29}Si appears as a ddd at -19.8 ppm due to three small couplings with ^{31}P's, implying that the silyl ligand is located at the *cis* position of all three phosphine ligands.

The geometry of **2** was unequivocally determined by the X-ray crystal structure analysis.[14] The molecular structure, selected bond lengths, and angles are shown in Figure 1. Although the hydrido ligand could not be located crystallographically, the arrangement of other ligands and the above-mentioned spectroscopic data plainly indicate that the hydrido ligand occupies the position opposite to PPh_2. Therefore, complex **2** takes a slightly distorted octahedral geometry.

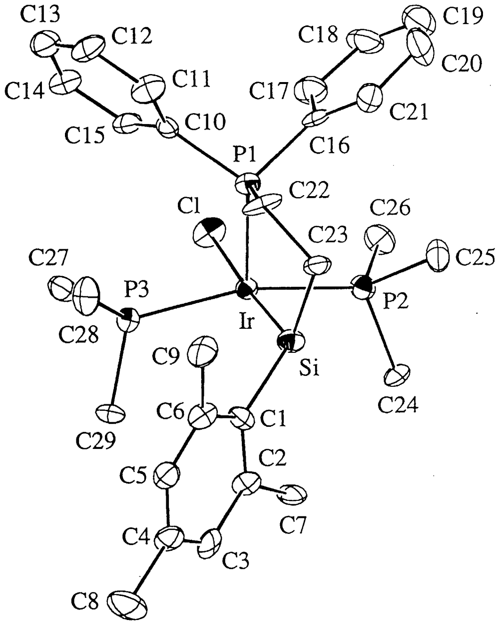


Figure 1. ORTEP drawing of complex **2**.
Selected bond lengths (Å) and bond angles (deg); Ir-Si 2.352(5), Ir-P1 2.349(3), Ir-P2 2.331(4), Ir-P3 2.336(4), Ir-Cl 2.542 (4); Cl-Ir-P1 95.4(1), Cl-Ir-P2 87.8(2), Cl-Ir-P3 88.9(1), Cl-Ir-Si 175.2(2), P1-Ir-P2 99.3(1), P1-Ir-P3 98.5(1), P1-Ir-Si 85.8(1), P2-Ir-P3 162.1(2), P2-Ir-Si 87.5(2), P3-Ir-Si 95.5(2).

Thermolysis of **2** at 80 °C gave **1** quantitatively (eq 4). The isomerization proceeded to completion within 12 h. Thus, **1** is thermodynamically more stable than the isomer **2** probably due to a steric reason: In **2**, two PMe$_3$ ligands are both at *cis* positions of the bulky PPh$_2$, whereas in **1**, one is at *cis* and the other at *trans* positions of the PPh$_2$.

$$\mathbf{2} \xrightarrow{80\ ^\circ\mathrm{C}} \mathbf{1} \qquad (4)$$

The mechanism of isomerization may involve the initial photo-dissociation of PMe$_3$ like most of other octahedral phosphine complexes,[2-4] but the reductive elimination of the Si-H cannot be ruled out. The mechanistic study is now in progress.

References and Notes

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9 ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 7.43-7.31, 7.10-6.99 (m, 10H, PPh$_2$), 6.69 (s, 2H, *m*-Mes), 4.61 (t, $^{3}J_{\mathrm{HH}}$ = 3.7 Hz, 2H, SiH$_2$), 2.31 (s, 6H, *o*-Mes*Me*$_2$), 2.11 (m, 2H, PCH$_2$), 2.08 (s, 3H, *p*-Mes*Me*), 0.99 (m, 2H, SiCH$_2$). ^{31}P NMR (36.3 MHz, C$_6$D$_6$) δ -11.3. ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ -43.4 (d, $^{3}J_{\mathrm{SiP}}$ = 23 Hz). IR (Toluene) 2150 cm^{-1} (ν_{SiH}). MS (70 eV, EI) *m/z* 362 (7, M$^+$), 243 (68, M$^+$-Mes), 183 (100, PPh$_2$-2H). Exact MS(70 eV, EI) *m/z* Calcd for C$_{23}$H$_{27}$PSi : 362.1620. Found : 362.1621.

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11 ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 8.36 (m, 4H, *o*-PPh$_2$), 7.16-6.90 (m, 6H, *m,p*-PPh$_2$), 6.83, 6.72 (s, 2H, *m*-Mes), 4.77 (dd, $^{3}J_{\mathrm{HH}}$ = 6.4, 20.1 Hz, 2H, SiH$_2$), 2.68, 2.64 (s, 6H, *o*-Mes*Me*$_2$), 2.13 (s, 3H, *p*-Mes*Me*), 2.62, 1.84 (m, 2H, PCH$_2$), 1.34 (dd, J_{HP} = 9.7, 2.3 Hz, 9H, PMe$_3$ (*trans* to PPh$_2$)), 1.09 (d, J_{HP} = 7.9 Hz, 9H, PMe$_3$ (*trans* to IrH)), 1.29, 1.06 (m, 2H, SiCH$_2$), -9.41 (dt, J(HP$_{trans}$) = 130 Hz, J(HP$_{cis}$) = 17 Hz, 1H, IrH). ^{31}P NMR (36.3 MHz, C$_6$D$_6$) δ 19.7 (dd, J(PP$_{trans}$) = 329.0 Hz, J(PP$_{cis}$) = 11.1 Hz, PPh$_2$), -43.5 (dd, J(PP$_{trans}$) = 329.0 Hz, J(PP$_{cis}$) = 22.2 Hz, PMe$_3$ (*trans* to PPh$_2$), -49.4 (dd, J(PP$_{cis}$) = 11.1, 22.2 Hz, PMe$_3$ (*trans* to IrH). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ -19.8 (ddd, J_{SiP} = 5.8, 6.7, 7.4 Hz). IR (KBr) 2129, 2058 cm^{-1} (ν_{SiH}, ν_{IrH}). MS (70 eV, EI) *m/z* 742 (18, M$^+$), 662 (100, M$^+$-(C$_6$H$_5$ + 3H)). Anal. Calcd for C$_{29}$H$_{45}$ClIrP$_3$Si : C 46.92, H 6.11, Cl 4.78%. Found : C 47.29, H 5.85, Cl 4.57%.

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13 ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) 8.32, 7.90 (m, 4H, *o*-PPh$_2$), 7.42-7.24 (m, 6H, *m,p*-PPh$_2$), 6.75 (s, 2H, *m*-Mes), 4.04 (t, $^{3}J_{\mathrm{HH}}$ = 13.4 Hz, 1H, SiH), 3.13, 2.16 (m, 2H, PCH$_2$), 2.54 (s, 6H, *o*-Mes*Me*$_2$), 2.21 (s, 3H, *p*-Mes*Me*), 1.27 (dd, J_{HP} = 1.7, 5.7 Hz, PMe$_3$ (*syn* to Mes)), 0.98 (dd, J_{HP} = 1.6, 5.8 Hz, PMe$_3$ (*anti* to SiH)), -10.27 (dt, J(HP$_{trans}$) = 134 Hz, J(HP$_{cis}$) = 21 Hz). ^{31}P NMR (36.3 MHz, C$_6$D$_6$) δ -1.9 (t, J(PP$_{cis}$) = 19.5 Hz, PPh$_2$), -48.9 (d, J(PP$_{cis}$) = 19.5 Hz, PMe$_3$ x 2). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$) δ -16.2 (dt, J_{SiP} = 1.7, 12.1 Hz). IR (KBr) 2065, 2054 cm^{-1} (ν_{SiH}, ν_{IrH}). MS (70 eV, EI) *m/z* 742 (19, M$^+$), 662 (100, M$^+$-(C$_6$H$_5$ + 3H)). Anal. Calcd for C$_{29}$H$_{45}$ClIrP$_3$Si : C 46.92, H 6.11, Cl 4.78%. Found : C 47.68, H 6.07, Cl 4.52%.

14 Crystallographic data for **2**; C$_{29}$H$_{45}$ClIrP$_3$Si, M = 742.36, *orthorhombic*, space group *Pnca* (variant No.60), a = 14.279(2) Å, b = 31.943(5) Å, c = 13.951(2) Å, V = 6363(2) Å^3, Z = 8, D_{C} = 1.55 gcm^{-3}, μ(Mo-Kα) = 47.2 cm^{-1}. The structure was solved by direct methods and refined anisotropically using UNICS-III. 12569 unique reflections were collected by ω scan in the range 3° <2θ< 55°, with 3836 ($|F_{\mathrm{o}}| > 3\sigma(F_{\mathrm{o}})$) used in calculations. The final reliability factors converged R = 0.072 and R_{w} = 0.078.