Synthesis and Structure of the {(2-Phosphinoethyl)silyl}-tris(tertiary phosphine)iridium(I) Complex $Ir\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_3$

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The hydridomethyl(silyl)iridium(III) complex $Ir(H)(Me)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2$ (**2**) reacted quantitatively with PMe_3 at 60 °C to give the {(2-phosphinoethyl)silyl}tris(tertiary phosphine)iridium(I) complex $Ir\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_3$ (**3**) as reddish orange crystals through the reductive elimination of methane. X-ray crystal structure analysis revealed that **3** adopts a slightly distorted five-coordinate, trigonal-bipyramidal geometry with the silyl ligand occupying an axial site. Complex **3** generates the 16e silyliridium(I) complex $Ir\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2$ (**A**) easily at room temperature.

Introduction

Interest in transition-metal-catalyzed hydrosilation,[1] silane oligomerization,[2] and redistribution of substituents on silicon atoms[3] has promoted the studies on transition-metal silyl complexes. Silyliridium and -rhodium complexes make one of the most important classes of compounds among them, because many iridium and rhodium complexes are known to become active catalysts for these reactions,[4] and silyliridium and -rhodium complexes are assumed to play important roles in the catalytic cycles. However, stable silyliridium(I) or -rhodium(I) complexes have been rare. The first structurally characterized silylrhodium(I) complex was Rh(tripsi)(CO) (tripsi = $Si(CH_2CH_2PPh_2)_3$).[5] In 1990, Thorn and Harlow reported the first synthesis of a 16e silylrhodium(I) complex, $Rh(SiPh_3)(PMe_3)_3$.[6] As for 16e silyliridium(I) complexes, the 16e species $L_3Ir(SiR_3)$ (L = π-acidic two-electron-donor ligand) are attracting increasing attention as key intermediates in some stoichiometric reactions.[7−9] However, only very recently has a 16e silyliridium(I) complex, $Ir\{Si(SiMe_3)_3\}(PMe_3)_3$, been detected in solution at −80 °C by ^{31}P NMR spectrocopy.[9] Several 18e five-coordinate silyliridium(I) complexes have been reported, but all of them are stabilized by the coordination of strongly π-acidic carbonyl ligands.[8,10] We report here the synthesis and crystal structure of the first silyliridium(I) complex containing no strongly π-acidic ligands, $Ir\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_3$. Moreover, this paper describes that $Ir\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_3$ liberates one molecule of PMe_3 under very mild conditions to generate the 16e silyliridium(I) complex $Ir\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2$.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere. Reagent-grade toluene and hexane were distilled from sodium−benzophenone ketyl immediately before use. Benzene-d_6 and toluene-d_8 were dried over a potassium mirror and transferred into NMR tubes under vacuum. $HMe_2Si(CH_2)_2PPh_2$,[11] PMe_3,[12] $[Ir(CO)(PMe_3)_4]Cl$,[13] and $P(CD_3)_3$[14] were prepared according to literature methods. Other chemicals were purchased from Wako Pure Chemical Industries, Ltd., and used as received. All NMR spectra were recorded on a Bruker ARX-300 spectrometer. ^{29}Si NMR spectra were obtained by the DEPT pulse sequence. IR spectra were recorded on a Bruker IFS66v spectrometer.

$Ir(Cl)(H)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2$ (1). A Pyrex tube (20 mm o.d.) was charged with $[Ir(CO)(PMe_3)_4]Cl$ (1.03 g, 1.84 mmol) and $HMe_2Si(CH_2)_2PPh_2$ (0.503 g, 1.85 mmol), and toluene (10 mL) was introduced into this tube under high vacuum by the trap-to-trap-transfer technique. The Pyrex tube was flame-sealed. The sealed tube was placed in an oil bath, where the sample was kept at 80 °C. After 36 h, the tube was unsealed in a N_2 glovebox. Removal of the volatiles under reduced pressure resulted in a pale yellow oily residue, which was extracted by toluene and hexane (2:1), and the extract was filtered through a Celite pad. The solvent was removed from the filtrate under reduced pressure. Recrystallization of the residue from toluene−hexane yielded $Ir(Cl)(H)\{\eta^2\text{-}Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2$ (**1**; 0.88 g, 1.35 mmol, 73%) as colorless crystals. ^1H NMR (300 MHz, C_6D_6): δ 8.28−8.22, 8.09−8.03 (m, 4H, *o*-PPh_2), 7.14−7.07, 7.04−6.92 (m, 6H, *m*- and *p*-PPh_2), 2.27, 1.98 (m, 1H × 2, PCH_2), 1.58 (dd, $J(HP)$ = 2.3, 9.4 Hz, 9H, PMe_3 (*trans* to PPh_2)), 0.90 (d, $J(HP)$ = 7.8 Hz, 9H, PMe_3 (*trans* to IrH)), 0.83, 0.71 (m, 1H × 2, $SiCH_2$),

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

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(14) Our method of preparation is essentially the same as that previously reported by Green et al.,[12] except that we use CD_3I instead of CH_3I.

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0.50, 0.33 (s, 3H × 2, SiMe$_2$), −10.04 (dt, J(HP*trans*) = 126.7, J(HP*cis*) = 17.5 Hz, 1H, IrH). ^{13}C NMR (75.5 Hz, C$_6$D$_6$): δ 139.7, 137.6, 134.7, 132.1, 129.5, 128.7, 128.4, 127.9 (Ar), 30.0 (d, J(CP) = 38.9 Hz, PCH$_2$), 20.0 (dd, J(CP) = 3.4, 22.2 Hz, SiCH$_2$), 19.8 (dt, J(CP) = 34.8, 3.5 Hz, PMe$_3$), 17.7 (dt, J(CP) = 27.5, 2.5 Hz, PMe$_3$), 10.0 (dd, J(CP) = 5.4, 2.1 Hz, SiMe), 4.9 (d, J(CP) = 4.2 Hz, SiMe). ^{31}P NMR (121.5 Hz, C$_6$D$_6$): δ 26.6 (dd, J(PP*trans*) = 334.6 Hz, J(PP*cis*) = 18.2 Hz, PPh$_2$), −42.1 (dd, J(PP*trans*) = 334.6 Hz, J(PP*cis*) = 20.9 Hz, PMe$_3$ (*trans* to PPh$_2$)), −49.9 (dd, PMe$_3$ (*trans* to IrH)). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ 5.8 (ddd, J(SiP*cis*) = 8.7, 5.7, 2.8 Hz). IR (KBr): 2048 cm^{-1} (ν(IrH)). MS (70 eV, DEI): *m/z* 652 (80, M$^+$), 650 (100, M$^+$ − 2H), 616 (11, M$^+$ − HCl). Anal. Calcd for C$_{22}$H$_{39}$ClIrP$_3$Si·$^1/_2$(C$_6$H$_5$CH$_3$): C, 43.86; H, 6.21; Cl, 5.08. Found: C, 44.01; H, 6.05; Cl, 4.64.

Ir(H)(Me){η^2-Me$_2$Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (2). A diethyl ether solution (2.7 mL) of MeLi (0.75 M, 2.0 mmol) was added to the toluene (20 mL) solution of **1** (0.44 g, 0.67 mmol) at −48 °C, and the mixture was warmed to room temperature. The reaction mixture was stirred at room temperature for 2 h. Volatile material was removed under reduced pressure, and the residue was extracted with a mixture of toluene and hexane (2:1). The extract was filtered through an alumina column. The solvent was removed from the filtrate under reduced pressure. Recrystallization of the residue from toluene−hexane gave Ir(H)(Me){η^2-Me$_2$Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (**2**; 0.29 g, 0.46 mmol, 69%) as colorless crystals. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.90−7.84, 7.59−7.52 (m, 4H, *o*-PPh$_2$), 7.13−7.07, 7.04−6.96 (m, 6H, *m*- and *p*-PPh$_2$), 2.68, 1.63 (m, 1H × 2, PCH$_2$), 1.46 (dd, J(HP) = 2.3, 8.8 Hz, 9H, PMe$_3$ (*trans* to PPh$_2$)), 0.82 (d, J(HP) = 7.5 Hz, 9H, PMe$_3$ (*trans* to IrH)), 1.08, 0.61 (m, 1H × 2, SiCH$_2$), 0.72, 0.58 (s, 3H × 2, SiMe$_2$), 0.27 (q, J(HP) = 4.4 Hz, 3H, IrMe), −12.60 (ddd, J(HP*trans*) = 120.6, J(HP*cis*) = 23.4, 17.7 Hz, 1H, IrH). ^{13}C NMR (75.5 Hz, C$_6$D$_6$): δ 140.6, 137.8, 134.2, 131.8, 129.2, 128.4, 127.9, 127.5 (Ar), 36.3 (dd, J(CP) = 39.5, 1.9 Hz, PCH$_2$), 21.6 (dd, J(CP) = 20.5, 4.1 Hz, SiCH$_2$), 21.2 (dt, J(CP) = 33.4, 4.0 Hz, PMe$_3$), 18.7 (dt, J(CP) = 27.3, 2.4 Hz, PMe$_3$), 11.8 (d, J(CP) = 6.0 Hz, SiMe), 6.6 (d, J(CP) = 2.2 Hz, SiMe), −38.3 (ddd, J(CP) = 14.8, 8.2, 6.5 Hz, IrMe). ^{31}P NMR (121.5 Hz, C$_6$D$_6$): δ 35.2 (dd, J(PP*trans*) = 349.7 Hz, J(PP*cis*) = 19.2 Hz, PPh$_2$), −48.4 (dd, J(PP*trans*) = 349.7 Hz, J(PP*cis*) = 20.7 Hz, PMe$_3$ (*trans* to PPh$_2$)), −61.2 (dd, PMe$_3$ (*trans* to IrH)). ^{29}Si NMR (59.6 MHz, C$_6$D$_6$): δ 10.5 (ddd, J(SiP*cis*) = 17.7, 9.6, 8.1 Hz). IR (KBr): 2044 cm^{-1} (ν(IrH)). MS (70 eV, DEI): *m/z* 632 (1, M$^+$), 617 (100, M$^+$ − CH$_3$), 616 (71, M$^+$ − CH$_4$). Anal. Calcd for C$_{23}$H$_{42}$IrP$_3$Si·$^1/_8$(C$_6$H$_5$CH$_3$): C, 44.57; H, 6.74. Found: C, 44.69; H, 6.54.

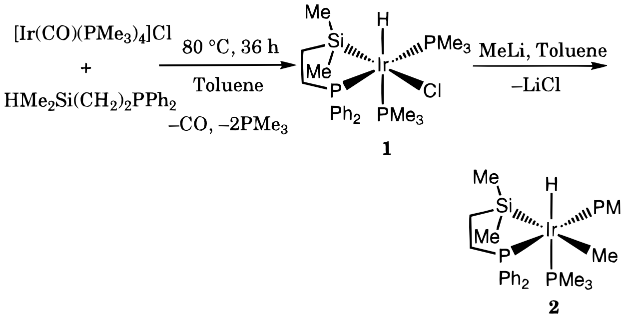
Ir{η^2-Me$_2$Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_3$ (3). A Pyrex tube (12 mm o.d.) was charged with **2** (0.20 g, 0.32 mmol) and PMe$_3$ (163 μL, 1.58 mmol), and toluene (2 mL) was introduced into this tube under high vacuum by the trap-to-trap-transfer technique. The Pyrex tube was flame-sealed. The sealed tube was placed in the oil bath, where it was kept at 60 °C for 8 h. The sample was cooled to −30 °C to allow the growing of red-orange crystals, which were collected by filtration to give Ir{η^2-Me$_2$Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_3$ (**3**; 0.17 g, 0.25 mmol, 78%). ^{1}H NMR (300 MHz, C$_6$D$_6$, T = −60 °C) δ 7.80−7.74 (m, 4H, *o*-PPh$_2$), 7.26−6.94 (m, 6H, *m*- and *p*-PPh$_2$), 2.59 (q, J = 5.8 Hz, 2H, PCH$_2$), 1.49 (br s, 9H × 2, PMe$_3$ × 2 (equatorial)), 0.91 (s, 6H, SiMe$_2$), 0.80 (d, 9H, J = 6.3 Hz, PMe$_3$ (axial)), 0.68 (dt, J = 34.1, 6.9 Hz, 2H, SiCH$_2$). ^{1}H NMR (300 MHz, C$_6$D$_6$, T = 50 °C): δ 7.70−7.64 (m, 4H, *o*-PPh$_2$), 7.13−7.00 (m, 6H, *m*- and *p*-PPh$_2$), 2.38 (q, J = 7.6 Hz, 2H, PCH$_2$), 1.33 (br, 9H × 3, PMe$_3$ × 3), 0.57 (dt, J = 32.0, 7.6 Hz, 2H, SiCH$_2$), 0.56 (s, 6H, SiMe$_2$). ^{13}C NMR (75.5 Hz, C$_6$D$_6$, T = −60 °C): δ 143.4, 134.7, 127.7, 127.4 (Ar), 36.9 (d, J(CP) = 25.8 Hz, PCH$_2$), 27.8 (br, PMe$_3$ × 2 (equatorial)), 24.5 (br, PMe$_3$ (axial)), 22.0 (d, J(CP) = 29.4, SiCH$_2$), 9.4 (q, J(CP) = 6.7 Hz, SiMe$_2$). ^{13}C NMR (75.5 Hz, C$_6$D$_6$, T = 50 °C): δ 144.6, 134.2, 128.1, 127.2 (Ar), 37.4 (dd, J(CP) = 33.5, 3.5 Hz, PCH$_2$), 27.7 (br s, PMe$_3$ × 3), 22.2 (dd, J(CP) = 34.4, 3.3 Hz, SiCH$_2$), 9.6 (q, J(CP) = 6.2 Hz, SiMe$_2$). ^{31}P NMR (121.5 MHz, C$_6$D$_6$, T = −60 °C): δ 43.6 (m, PPh$_2$), −55, −56 (m, PMe$_3$). ^{31}P NMR (121.5 MHz, C$_6$D$_6$, T = 80 °C): δ 44.3 (br q, J(PP) = 79 Hz, PPh$_2$), −57.0 (br, d, J(PP) = 79 Hz, PMe$_3$). MS (70 eV, DEI): *m/z* 692 (0.3, M$^+$), 616 (100, M$^+$ − PMe$_3$). Anal. Calcd for C$_{25}$H$_{47}$IrP$_4$Si: C, 43.40; H, 6.85. Found: C, 43.66; H, 6.58.

Table 1. Crystallographic Data for Ir{η^2-Me$_2$Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_3$ (3)

formula	C$_{25}$H$_{47}$IrP$_4$Si
fw	691.85
cryst syst	orthorhombic
space group	*Pnaa* (variant of No. 56)
a/Å	14.176(2)
b/Å	36.042(5)
c/Å	11.884(3)
V/Å^3	6072(2)
Z	8
d_{calcd}/g cm^{-3}	1.51
μ(Mo Kα)/cm^{-1}	49.1
cryst size/mm	0.30 × 0.25 × 0.20
T/°C	20
reflns measd	$\pm h,k,l$
2θ range/deg	3−50
no. of unique data	9708
no. of data used with $\|F_o\| > 3\sigma(F_o)$	3182
no. of params refined	281
R^a	0.071
$R_w{}^b$	0.083

[a] $R = \sum||F_o| - F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F_o|) + aF_o{}^2]^{-1}$, where a = 0.001.

Scheme 1



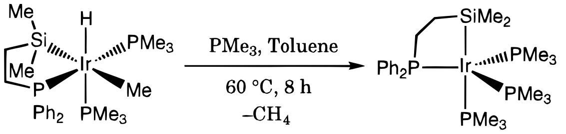
X-ray Crystal Structural Determination of 3. Intensity data for X-ray crystal structure analysis were collected at 20 °C on a Rigaku AFC-6A diffractometer with graphite-monochromated Mo Kα radiation. A single crystal of **3** was sealed in a glass capillary under a N$_2$ atmosphere. The crystal structure was solved by direct methods and refined anisotropically using UNICS-III. A total of 9708 unique reflections were collected by ω-scan in the range 3° < 2θ < 50°, with 3182 ($|F_o| > 3\sigma(F_o)$) used in calculations. None of the hydrogen atoms were found. Crystallographic data for **3** are listed in Table 1.

Reaction of 3 with P(CD$_3$)$_3$. A Pyrex NMR tube (5 mm o.d.) was charged with **3** (15 mg, 0.022 mmol) and P(CD$_3$)$_3$ (11 μL, 0.11 mmol), and benzene-d_6 (0.7 mL) was introduced into this tube under high vacuum by the trap-to-trap-transfer technique. The NMR tube was flame-sealed. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy.

Results and Discussion

Synthesis of Ir(H)(Me){η^2-Me$_2$Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (2). The hydrido methyl complex Ir(H)(Me){η^2-Me$_2$Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (**2**) can be readily prepared by the reactions shown in Scheme 1. Thermolysis of the toluene solution of the ligand precursor HMe$_2$Si(CH$_2$)$_2$PPh$_2$ and the cationic iridium(I) complex [Ir(CO)(PMe$_3$)$_4$]Cl in a sealed tube at 80 °C for 36 h gave the chlorohydridoiridium(III) complex Ir(Cl)(H){η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_2$ (**1**) as colorless crystals in 73% yield. The geometry of **1** can be uniquely determined by the ^1H, ^{31}P, and ^{29}Si NMR spectra. Addition of MeLi to **1** in toluene at −48 °C resulted in the formation of complex **2**. Workup and recrystallization from toluene−hexane afforded colorless crystals of **2** in 69% yield. The ^1H, ^{31}P, ^{13}C, and ^{29}Si NMR spectral data establish that **2** possesses hydrido, methyl, and silyl ligands in a *mer* relationship. The ^{13}C resonance of Ir−Me appears at −38.3 ppm as a ddd coupled with three *cis*-^{31}P (J(CP*cis*) = 6.5, 8.2, 14.8 Hz). This chemical shift is characteristic of the carbon directly bound to a transition metal through a σ bond. In the complex *fac*-Ir(H)(Me)(SiR_3)$(PMe_3)_3$ previously reported by Aizenberg and Milstein,[7] a strongly *trans*-influencing silyl ligand[15] is located *trans* to the PMe_3 ligand. In contrast, surprisingly the silyl ligand in **3** is located *trans* to the strongly *trans*-influencing methyl ligand.

Synthesis of Ir{η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_3$ (3). Reaction of **2** with 5 equiv of PMe_3 in toluene at 60 °C for 8 h resulted in an orange solution, from which reddish orange crystals of Ir{η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_3$ (**3**) were obtained in 78% yield (eq 1). The



2 **3** (1)

structure of **3** has been determined by spectroscopic and analytical methods and by X-ray crystal structure analysis.

The five-coordinate complex **3** is fluxional in C_6D_5-CD_3 at room temperature. In the ^1H NMR spectrum at 50 °C, the three (one axial and two equatorial) PMe_3 ligands appear equivalently at δ 1.33 ppm as a very broad singlet. At −60 °C, the signals of one axial and two equatorial PMe_3 ligands appear nonequivalently at δ 0.80 ppm as a doublet (J = 6.3 Hz) and at 1.49 ppm as a slightly broad singlet in the intensity ratio of 1:2, respectively. At 80 °C, the ^{31}P resonance of the PPh_2 moiety appears at 44.3 ppm as a broad quartet coupled with the ^{31}P nuclei of three PMe_3 ligands (J(PP) = 79 Hz), which is consistent with the intramolecular exchange of three PMe_3 ligands.[16] It is known that the analogous iridium(I) complex Ir(Me)$(PMe_3)_4$ exhibits an intramolecular exchange process of PMe_3 ligands.[17]

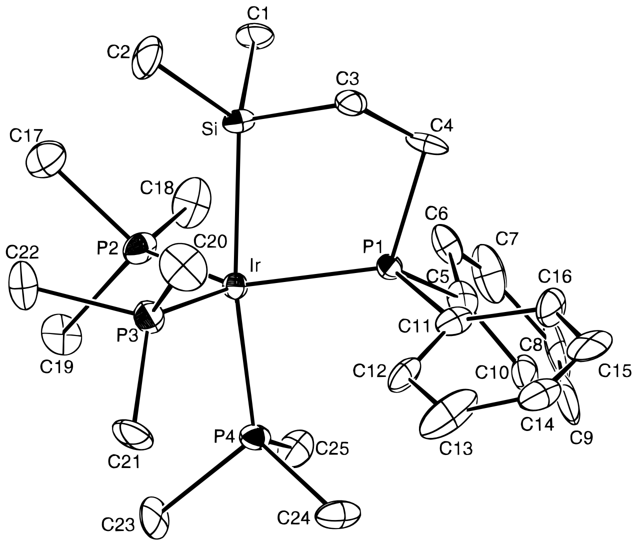


Figure 1. ORTEP drawing of Ir{η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_3$ (**3**).

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Ir{η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_3$ (3)

	Distances		
Ir−P1	2.279(5)	Ir−P2	2.289(5)
Ir−P3	2.290(5)	Ir−P4	2.347(4)
Ir−Si	2.447(5)		
	Angles		
P1−Ir−P2	130.4(2)	P1−Ir−P3	118.5(2)
P1−Ir−P4	91.4(2)	P1−Ir−Si	80.6(2)
P2−Ir−P3	109.5(2)	P2−Ir−P4	92.7(2)
P2−Ir−Si	87.1(2)	P3−Ir−P4	98.8(2)
P3−Ir−Si	91.4(2)	P4−Ir−Si	169.2(2)

Structure of 3. The ORTEP drawing for **3** is shown in Figure 1. Selected bond distances and angles of **3** are listed in Table 2. The complex **3** takes a five-coordinate, slightly distorted trigonal-bipyramidal arrangement in which the silicon atom and a PMe_3 ligand occupy axial positions while the PPh_2 moiety and two PMe_3 ligands are located in equatorial sites. The Ir−Si bond length lies in the normal range (2.447(5) Å)[18] and is close to that of the previously reported silyliridium(I) complex Ir($PPh_2CH_2CH_2SiMe_2$)(PPh_3)$(CO)_2$ (2.454(6) Å).[10] The Ir−P(PPh_2) bond length (2.279(5) Å) of **3** is shorter than that of Ir($PPh_2CH_2CH_2SiMe_2$)(PPh_3)$(CO)_2$ (2.342(5) Å).[10] This indicates that back-donation of d electrons from the iridium center to the phosphorus atom in the former is more effective than that in the latter because of the more electron-rich metal center in the former. The overall structural features of **3** are similar to those of structurally determined Ir(I) complexes: Ir($PPh_2CH_2CH_2SiMe_2$)(PPh_3)$(CO)_2$,[10] Ir(H)$(CO)_2$$(PPh_3)_2$,[19] and Ir(COEt)$(CO)_2$(dppe).[20] All of these complexes adopt distorted-trigonal-bipyramidal geometry with a σ-donor ligand occupying an axial position. There is only one 18e silylrhodium(I) complex that has been structurally characterized by an X-ray diffraction study, Rh(tripsi)(CO) (tripsi = Si$(CH_2CH_2PPh_2)_3$), reported by Joslin and Stobart, which also takes a distorted-trigonal-bipyramidal geometry with the silyl fragment and carbonyl ligand occupying the axial sites.[5] We should mention that only two types of silyliridium(I) compounds have been synthesized previously. One is Ir($PPh_2CH_2CH_2SiMe_2$)(PPh_3)$(CO)_2$,[10] with two carbonyl ligands in the equatorial plane. The other is Ir(SiR_3)$(PCy_3)(CO)_3$ (R = Et, Ph),[8] with three carbonyl ligands all in the equatorial plane according to the IR and NMR spectroscopic data. Therefore, complex **3** is the first example of a silyliridium(I) complex with no carbonyl ligands. Complex **3** is expected to be more electron-rich than other silyliridium(I) complexes previously reported

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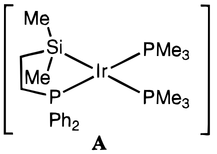
(20) Deutsch, P. P.; Eisenberg, R. *Organometallics* **1990**, *9*, 709.

due to the coordination of four electron-releasing phosphine ligands and thus to be more reactive.

Lability of PMe_3 Ligands in 3. To investigate the lability of PMe_3 ligands in complex **3**, 5 equiv of $P(CD_3)_3$ was vacuum-transferred into the C_6D_6 solution of **3**. Instantly, the intensity of the ^1H NMR signal of PMe_3 ligands in **3** decreased at room temperature and the signal of free PMe_3 with the corresponding intensity appeared. The intensity ratio of the ^{31}P NMR resonances of free PMe_3 to free $P(CD_3)_3$ after 10 min was 5:4. After 30 min, the ^{31}P NMR intensity ratio reached ca. 3:5 and no further change of the ratio was observed after this. This apparently means that a statistical fraction, i.e. $^5/_8$, of the PMe_3 ligands in **3** was replaced by $P(CD_3)_3$ at room temperature to give a mixture of $L'Ir(PMe_3)_{3-m}(P(CD_3)_3)_m$ (**3**-*d'*: $L' = SiMe_2(CH_2)_2PPh_2$, $m = 1-3$) with the same geometry as that of **3** (eq 2).

$$\underset{\mathbf{3}}{L'Ir(PMe_3)_3} \xrightarrow[C_6D_6,\ r.t.]{P(CD_3)_3} \underset{\mathbf{3\text{-}d'}}{L'Ir(PMe_3)_{3-m}(P(CD_3)_3)_m} + PMe_3 \quad (2)$$

$m = 1, 2, 3$



A

These observations are consistent with the facile generation of the 16e silyliridium(I) complex $Ir\{\eta^2-Me_2Si(CH_2)_2PPh_2\}(PMe_3)_2$ (**A**) from complex **3** even at room temperature. The analogous Rh complex $Rh(SiPh_3)(PMe_3)_3$ was isolated by the reaction of $Rh(Me)(PMe_3)_3$ with $HSiPh_3$ at room temperature.[6] They proposed the silylrhodium(III) complex $Rh(H)(Me)(SiPh_3)(PMe_3)_3$ as an intermediate, which eliminated methane to give $Rh(SiPh_3)(PMe_3)_3$. Recently, Aisenberg and Milstein reported that thermolysis of *fac*-$(Me_3P)_3Ir(Me)(H)(SiPh_3)$ in C_6D_6 under relatively severe conditions (100 °C for 24 h) led to the formation of *ortho*-metalated product $(Me_3P)_3Ir\{(C_6H_4)SiPh_2\}(H)$, and they assumed the generation of the 16e silyliridium(I) complex $(Me_3P)_3Ir(SiPh_3)$ as a key intermediate by methane reductive elimination from the hydrido methyl complex.[7] Owing to the unprecedentedly mild conditions for the dissociation of PMe_3 from **3**, the complex **3** could be a convenient precursor for generating a highly reactive 16e silyliridium(I) species.

Conclusions

We have prepared the novel silyliridium(I) complex **3** with no carbonyl ligand. X-ray crystal structure analysis revealed that **3** takes a slightly distorted trigonal bipyramidal geometry with the silyl and a PMe_3 ligand occupying the axial positions. Complex **3** undergoes an intramolecular fluxional process of PMe_3 ligands and also dissociates a PMe_3 ligand under mild conditions to generate a reactive 16e silyliridium(I) species.

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Supporting Information Available: Text giving details of the X-ray structure determination and tables of crystal data, atomic positional and thermal parameters, and bond distances and angles for **3** (6 pages). Ordering information is given on any current masthead page.

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