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Thermal reactions of alkyl(hydrido)(hydrosilyl)iridium(III) complexes: generation of a hydrido(silylene)iridium(I) species via the reductive elimination of alkane and 1,2-H-shift from the silicon atom to the Ir(I) metal center

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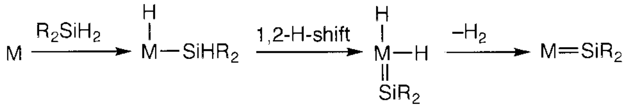
Abstract

Heating of alkyl(hydrido)(hydrosilyl)iridium(III) complexes $L_nIr(R)(H)$ [$L_n = \{\eta^2\text{-MesHSi}(CH_2)_2PPh_2\}(PMe_3)_2$, Mes = 2,4,6-$C_6H_2Me_3$, R = Me, Et] led to the reductive elimination of alkane. Subsequently, the resulting hydrosilyliridium(I) intermediate L_nIr (**A**) activated the intramolecular carbon–hydrogen bond to give $Ir(H)\{\eta^3\text{-}CH_2C_6H_2(CH_3)_2SiH(CH_2)_2PPh_2\}(PMe_3)_2$. In the presence of MeOH, **A** was quickly trapped with MeOH to give a methoxysilyliridium(III) complex $Ir(H)_2\{\eta^2\text{-Mes(MeO)Si}(CH_2)_2PPh_2\}(PMe_3)_2$. This reactivity of **A** with MeOH clearly supports the occurrence of a 1,2-H-shift from the silyl silicon atom to the iridium center to generate a hydrido(silylene)iridium(I) species $Ir(H)[\eta^2\text{-}\{=SiMes(CH_2)_2PPh_2\}](PMe_3)_2$. © 1998 Elsevier Science S.A.

Keywords: Silyliridium; Silylene complex; 1,2-migration; Carbon–hydrogen bond activation

1. Introduction

Transition-metal silyl complexes have attracted much attention as intermediates in the catalytic transformation of hydrosilanes [1,2]. In particular, hydrosilyl complexes $M–SiHR_2$ have been assumed to be key intermediates formed in transition-metal-catalyzed dehydrogenative condensation of hydrosilanes and redistribution of substituents on silicon atoms [1–4]. In many of these catalytic reactions, hydrosilyl(hydrido) complexes, resulting from oxidative addition of dihydrosilanes to transition-metals, undergo dissociation of dihydrogen to give a silylene intermediate [5–8].[2] 1,2-Migration of hydrogen on a hydrosilyl silicon atom to a transition-metal and subsequent dissociation of dihydrogen can be assumed to be a possible route for dehydrogenation (Eq. (1), [9,10].[3] Nevertheless, the most intense studies have been focused on silyl complexes with no Si–H bond, and the reactivities of hydrosilyl complexes are relatively unexplored. This paper describes the thermal reactivities of $Ir(R)(H)\{\eta^2\text{-MesHSi}(CH_2)_2PPh_2\}(PMe_3)_2$ (R = Me, Et, H). In these systems (R = Me, Et), we revealed that a 16e-hydrosilyliridium(I) complex $Ir(\eta^2\text{-MesHSi}(CH_2)_2PPh_2\}(PMe_3)_2$ resulting from reductive elimination of alkane undergoes a 1,2-H-shift to give a hydrido(silylene) species $Ir(H)[\eta^2\text{-}\{=SiMes(CH_2)_2PPh_2\}](PMe_3)_2$ under relatively mild conditions. In the presence of MeOH, $Ir(H)[\eta^2\text{-}\{=SiMes(CH_2)_2PPh_2\}](PMe_3)_2$ reacts quickly with MeOH to give $Ir(H)_2\{\eta^2\text{-Mes(MeO)Si}(CH_2)_2PPh_2\}(PMe_3)_2$. In contrast, dihydrido complex $Ir(H)_2\{\eta^2\text{-MesHSi}(CH_2)_2PPh_2\}(PMe_3)_2$ is inert to the thermal reductive elimination of dihydrogen. A part of this work has been published as a preliminary communication ([11,12]).



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[2] The formation of silylene complexes via dehydrogenation has been reported in Refs. [5,6].

[3] The generation of a hydrido–silylene complex via the 1,2-H-shift from the silyl silicon atom to the metal center is reported in Refs. [9,10].

2. Experimental

All manipulations were carried out under a dry nitrogen atmosphere. Reagent-grade toluene, hexane, diethyl ether, and THF were distilled from sodium–benzophenone ketyl immediately before use. Benzene-d_6 was dried over a potassium mirror and transferred into an NMR tube under vacuum. MesLi [13] and $[Ir(CO)(PMe_3)_4]Cl$ [14] were prepared according to literature methods. Other chemicals were purchased from Wako Pure Chemical Industries and used as received. NMR spectra were recorded on a Bruker ARX-300 spectrometer. ^{29}Si NMR spectra were obtained using the DEPT pulse sequence. IR spectra were recorded on a Bruker IFS66v spectrometer.

2.1. *$MesSiCl_2(CH=CH_2)$*

To a toluene solution (120 ml) of $SiCl_3(CH=CH_2)$ (22 ml, 0.17 mol) was added a suspension (150 ml) of MesLi (22 g, 0.17 mol) in toluene (150 ml) at room temperature. After stirring for 12 h, the resulting mixture was filtered through a Celite pad. The solvent was removed from the filtrate under reduced pressure. Molecular distillation of the residue (120°C, 2 mm Hg) gave $MesSiCl_2(CH=CH_2)$ as a colorless oil. Yield 10.0 g (21%). ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H, *p*-ArMe), 2.56 (s, 6H, *o*-$ArMe_2$), 6.18–6.48 (m, 3H, $CH=CH_2$), 6.87 (s, 2H, ArH). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 21.1 (*p*-ArMe), 24.8 (*o*-$ArMe_2$), 126.8 (*ipso*-Ar), 129.8 (*m*-Ar), 134.9 ($CH=\mathit{C}H_2$), 136.1 ($\mathit{C}H=CH_2$), 141.8 (*p*-Ar), 144.6 (*o*-Ar). $^{29}Si\{^1H\}$ NMR (59.6 MHz, $CDCl_3$) δ 2.3. IR (KBr) 854 cm^{-1} ($\omega(CH_2)$). Exact mass found: 244.0240. $C_{11}H_{14}Cl_2Si$. Calc.: 244.0242.

2.2. *$MesSiH_2(CH=CH_2)$*

$MesSiCl_2(CH=CH_2)$ (10.0 g, 0.040 mol) in THF (30 ml) was added dropwise to a suspension of $LiAlH_4$ (3.0 g, 0.079 mol) in THF (80 ml) over a period of 30 min. After addition was complete, the mixture was refluxed for 2 h. The flask was then cooled in an ice bath and 5% sulfuric acid solution (100 ml) was carefully added to the reaction mixture. The resulting precipitate was filtered, and the filtrate was placed in a separatory funnel and washed with a saturated $NaHCO_3$ solution, a dilute NaCl solution, and water, respectively. The organic layer was dried over anhydrous $MgSO_4$. Molecular distillation (130°C, 15 mm Hg) afforded $MesSiH_2(CH=CH_2)$ as a colorless oil. Yield 6.0 g (85%). ^1H NMR (300 MHz, C_6D_6) δ 2.09 (s, 3H, *p*-ArMe), 2.38 (s, 6H, *o*-$ArMe_2$), 4.83 (d, $J(HH)=2.3$ Hz, 2H, SiH_2), 5.74–6.07 (m, 3H, $CH=CH_2$), 6.72 (s, 2H, ArH). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 21.1 (*p*-ArMe), 23.4 (*o*-$ArMe_2$), 125.7 (*ipso*-Ar), 128.1 (*m*-Ar), 130.9 ($\mathit{C}H=CH_2$), 135.6 ($CH=\mathit{C}H_2$), 139.7 (*p*-Ar), 144.7 (*o*-Ar). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6) δ -52.0. IR (KBr) 2150 cm^{-1} ($\nu(SiH)$), 855 cm^{-1} ($\omega(CH_2)$). Anal. found: C, 74.36; H, 9.34. $C_{11}H_{16}Si$. Calc.: C, 74.93; H, 9.15%. Exact mass found: 176.1025. $C_{11}H_{16}Si$. Calc.: 176.1021.

2.3. *$MesH_2Si(CH_2)_2PPh_2$*

A deoxygenated solution of $MesSiH_2(CH=CH_2)$ (1.08 g, 6.12 mmol) and $HPPh_2$ (1.14 g, 6.12 mmol) in toluene (5 ml) was irradiated with a 450 W medium pressure Hg lamp through a Pyrex sleeve at 0°C for 12 h with stirring. Removal of solvent from the reaction mixture under reduced pressure followed by crystallization from toluene–hexane at -30°C gave colorless needles of $MesH_2Si(CH_2)_2PPh_2$. Yield 2.06 g (93%). ^1H NMR (300 MHz, C_6D_6) δ 0.80–0.91 (m, 2H, $SiCH_2$), 2.08 (s, 3H, *p*-ArMe), 1.99–2.20 (m, 2H, PCH_2), 2.31 (s, 6H, *o*-$ArMe_2$), 4.34 (t, $J=2.7$ Hz, 2H, SiH_2), 6.76 (s, 2H, $C_6\mathit{H}_2Me_3$), 7.00–7.41 (m, 10H, PPh_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6) δ 6.5 (d, $J(CP)=13$ Hz, $SiCH_2$), 21.3 (*p*-ArMe), 23.9 (*o*-$ArMe_2$), 24.0 (d, $J(CP)=16$ Hz, PCH_2), 126.9, 128.6, 128.7, 133.1, 139.3, 139.6, 144.6 (Ar). $^{31}P\{^1H\}$ NMR (36.3 MHz, C_6D_6) δ -11.3. $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6) δ -43.4 (d, $J(SiP)=23$ Hz). IR (toluene) 2150 cm^{-1} ($\nu(SiH)$). Exact mass found: 362.1621. $C_{13}H_{27}PSi$. Calc.: 362.1620.

2.4. *$Ir(Cl)(H)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**1**)*

To $[Ir(CO)(PMe_3)_4]Cl$ (0.71 g, 1.27 mmol) and $MesH_2Si(CH_2)_2PPh_2$ (0.46 g, 1.27 mmol) in a Pyrex tube (20 mm o.d.) connected to a vacuum line was introduced toluene (3 ml) by the trap-to-trap-transfer technique. The tube was flame-sealed under vacuum and then heated to 80°C for 24 h. The tube was opened in an N_2 glove bag. Removal of the volatiles under reduced pressure resulted in a pale yellow oily residue, which was extracted using a toluene–hexane (2:1) mixture. The solvent was removed under reduced pressure. Recrystallization from toluene–hexane gave a white powder of $Ir(Cl)(H)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**1**). Yield 0.76 g (80%). ^1H NMR (300 MHz, C_6D_6) δ -9.41 (dt, $J(HP_{trans})=130$ Hz, $J(HP_{cis})$ 17 Hz, 1H, IrH), 1.06, 1.29 (m, 2H, $SiCH_2$), 1.09 (d, $J(HP)=7.9$ Hz, 9H, PMe_3 (*trans* to IrH)), 1.34 (dd, $J(HP)=9.7$, 2.3 Hz, 9H, PMe_3 (*trans* to PPh_2)), 1.84, 2.62 (m, 2H, PCH_2), 2.13 (s, 3H, *p*-ArMe), 2.64, 2.68 (s, 6H, *o*-$ArMe_2$), 4.77 (dd, $^3J(HH)=6.4$, 20.1 Hz, 2H, SiH_2), 6.72, 6.83 (s, 2H, *m*-Mes), 6.90–7.16 (m, 6H, *m*, *p*-PPh_2), 8.36 (m, 4H, *o*-PPh_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 12.5 (d, $J(CP)=20.1$ Hz, $SiCH_2$), 16.1

(dt, J(CP) = 27.9, 2.4 Hz, PMe_3), 18.7 (dt, J(CP) = 35.6, 3.3 Hz, PMe_3), 21.1 (*p*-ArMe), 23.5 (d, J(CP) = 3.2 Hz, *o*-ArMe), 26.2 (*o*-ArMe), 28.0 (d, J(CP) 37.4 Hz, PCH_2), 128.1, 128.5, 128.6, 128.9, 129.6, 129.6, 131.2, 132.6, 134.1, 134.7, 135.8, 136.5, 137.7, 139.8, 143.6, 145.1 (Ar). $^{31}P\{^1H\}$ NMR (36.3 MHz, C_6D_6) δ −49.4 (dd, $J(PP_{cis})$ = 11. 1, 22.2 Hz, PMe_3 (*trans* to IrH)), −43.5 (dd, $J(PP_{trans})$ = 329.0 Hz, $J(PP_{cis})$ = 22.2 Hz, PMe_3 ($_{trans}$ to PPh_2)), 19.7 (dd, $J(PP_{trans})$ 329.0 Hz, $J(PP_{cis})$ 11.1 Hz, PPh_2). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6) δ −19.8 (ddd, $J(SiP_{cis})$ 5.8, 6.7, 7.4 Hz). IR (KBr) 2058, 2129 cm^{-1} (ν(SiH), ν(IrH)). MS (70 eV, EI) m/z 742(18, M^+), 662 (100, M^+–(C_6H_5 + 3H)). Anal. found: C, 47.29; H, 5.85; Cl, 4.57. $C_{29}H_{45}ClIrP_3Si$. Calc.: C, 46.92; H, 6.11; Cl, 4.78%.

2.5. Photolysis of Ir(Cl)(H){η^2-MesHSi(CH_2)$_2$ PPh_2}(PMe_3)$_2$ (1)

To Ir(Cl)(H){η^2-MesHSi(CH_2)$_2$$PPh_2$}($PMe_3$)$_2$ (**1**) (30 mg, 0.040 mmol) in a Pyrex NMR tube (5 mm o.d.) connected to a vacuum line was added benzene-d_6 (0.7 ml) by the trap-to-trap-transfer technique. The tube was flame-sealed under vacuum and irradiated. The reaction was monitored by ^{1}H NMR spectroscopy. The photostationary state of the geometric isomerization was attained between **1** and its geometric isomer **2**, after irradiation for 1 h with the ratio of **1**:**2** = 5:3. The resulting solution was concentrated under reduced pressure. Careful crystallization from benzene-d_6 at room temperature gave colorless crystals of **2**, which were suitable for X-ray crystal structure analysis. Yield 11 mg (37%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ −10.27 (dt, $J(HP_{trans})$ = 134.0 Hz, $J(HP_{cis})$ 21.3 Hz, 1H, IrH), 0.97, 1.75 (m, 1H × 2, $SiCH_2$), 0.98 (dd, J(HP) 1.6, 5.8 Hz, 9H, PMe_3 (*syn* to Mes)), 1.27 (dd, J(HP) = 1.7, 5.7 Hz, 9H, PMe_3 (*anti* to Mes)), 2.16, 3.13 (m, 1H × 2, PCH_2), 2.21 (s, 3H, *p*-ArMe), 2.54 (s, 6H, *o*-ArMe$_2$), 3.13, 2.16 (m, 2H, PCH_2), 4.04 (t, J(HH) = 13.4 Hz, 1H, SiH), 6.75 (s, 2H, *m*-Mes), 7.42–7.24 (m, 6H, *m*, *p*-PPh_2), 8.32, 7.90 (m, 4H, *o*-PPh_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 13.7 (d, J(CP) = 23.9 Hz, $SiCH_2$), 16.0 (ddd, J(CP) = 25.0, 14.1, 3.1 Hz, PMe_3), 18.0 (ddd, J(CP) = 25.3, 14.2, 3.5 Hz, PMe_3), 19.7 (*p*-ArMe), 23.1 (*o*-ArMe$_2$), 25.6 (d, J(CP) = 35.3 Hz, PCH_2), 127.4, 127.5, 127.6, 127.8, 128.2, 128.6, 129.0, 129.4, 130.8, 133.9, 136.7, 139.1, 139.5, 140.0 (Ar). $^{31}P\{^1H\}$ NMR (36.3 MHz, C_6D_6) δ −48.9 (d, $J(PP_{cis})$ 19.5 Hz, PMe_3 × 2), −1.9 (t, $J(PP_{cis})$ = 19.5 Hz, PPh_2). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6) δ −16.2 (dt, $J(SiP_{cis})$ = 1.7, 12.1 Hz). IR (KBr) 2054, 2065 cm^{-1} (ν(SiH), ν(IrH)). MS (70 eV, EI) m/z 742 (19, M^+), 662 (100, M^+–(C_6H_5 + 3H)). Anal. found: C, 47.68; H, 6.07; Cl, 4.52. $C_{29}H_{45}ClIrP_3Si$. Calc.: C, 46.92; H, 6.11; Cl, 4.78%.

Table 1
Crystallographic Data for Ir(H)(Cl){η^2-MesHSi(CH_2)$_2$$PPh_2$}($PMe_3$)$_2$ (**2**)

Formula	$C_{29}H_{45}ClIrP_3Si$
fw	742.36
Crystal system	Orthorhombic
Space group	*Pnca*
a (Å)	14.279(2)
b (Å)	31.943(5)
c (Å)	13.951(2)
V (Å^3)	6363(2)
Z	8
$d_{calc.}$ (g cm^{-3})	1.55
μ(Mo Kα) (cm^{-1})	47.2
Crystal size (mm)	0.20 × 0.20 × 0.10
T (°C)	20
2θ range (°)	3–55
No. of unique data	12569
No. of data used with $\|F_o\| > 3\sigma(F_o)$	3836
No. of params refined	317
R^a	0.072
R_w^b	0.078

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

2.6. X-ray crystal structure determination of 2

Intensity data from the X-ray crystal structure analysis were collected at 20°C on a Rigaku AFC-6A diffractometer with graphite-monochromated Mo–Kα radiation. The crystal structure was solved by direct methods and refined anisotropically using UNICS-III. 12569 unique reflections were collected by ω scan in the range $3° < 2\theta < 55°$, with 3836 ($|F_o| > 3\sigma(F_o)$) used in calculations. None of the hydrogen atoms was found. Crystallographic data for **2** are listed in Table 1. The final atomic coordinates and temperature factors of non-hydrogen atoms are listed in Table 2.

2.7. Ir(H)(Me){η^2-MesHSi(CH_2)$_2$$PPh_2$}($PMe_3$)$_2$ (3)

To a solution of Ir(Cl)(H){η^2-MesHSi(CH_2)$_2$$PPh_2$}($PMe_3$)$_2$ (**1**) (0.21 g, 0.28 mmol) in 10 ml of toluene was added MeLi (0.6 M, 0.75 ml, 1.6 equiv.) via syringe at −48°C. The reaction mixture was slowly warmed up to room temperature and stirred for 1 h. The volatiles were removed under reduced pressure. The residue was extracted using toluene–hexane (2:1, 40 ml). The extract was filtered through an alumina column. After removal of solvent, recrystallization from toluene–hexane afforded Ir(H)(Me){η^2-MesHSi(CH_2)$_2$$PPh_2$}($PMe_3$)$_2$ (**3**) as colorless crystals. Yield 115 mg (57%). ^{1}H NMR (300 MHz, C_6D_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), 1.01

Table 2
Final atomic coordinates and temperature factors of the non-hydrogen atoms of $Ir(H)(Cl)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$(**2**)

Atom	x	y	z	B_{eq}
Ir	3597.0(4)	1567.2(1)	2816.0(4)	2.4
Cl	4795(3)	1820(1)	4034(3)	4.1
P(1)	3991(3)	855(1)	2946(3)	2.8
P(2)	4647(3)	1764(1)	1618(3)	3.2
P(3)	2454(3)	1594(1)	4012(3)	3.1
Si	2572(3)	1355(1)	1589(3)	3.1
C(1)	1247(9)	1477(4)	1654(11)	3.1
C(2)	991(9)	1892(4)	1473(11)	3.0
C(3)	39(11)	2024(5)	1545(11)	3.9
C(4)	−655(10)	1736(5)	1764(12)	3.9
C(5)	−406(10)	1327(5)	1901(11)	3.6
C(6)	502(11)	1182(4)	1821(11)	3.5
C(7)	1707(10)	2233(4)	1190(13)	4.1
C(8)	−1707(12)	1883(6)	1861(16)	6.5
C(9)	655(13)	704(4)	1865(12)	4.6
C(10)	3979(9)	598(4)	4137(11)	2.8
C(11)	3697(12)	175(4)	4241(13)	4.3
C(12)	3705(12)	5(5)	5137(13)	4.8
C(13)	3967(11)	231(5)	5944(14)	4.7
C(14)	4257(13)	653(5)	5832(13)	4.9
C(15)	4271(11)	833(4)	4916(12)	3.7
C(16)	5172(11)	700(4)	2521(11)	3.5
C(17)	5943(11)	880(5)	3019(13)	4.7
C(18)	6871(11)	787(5)	2672(16)	6.0
C(19)	7010(14)	528(6)	1912(16)	6.3
C(20)	6227(15)	334(6)	1464(17)	7.3
C(21)	5307(12)	435(5)	1755(13)	4.4
C(22)	3117(11)	536(4)	2243(12)	4.2
C(23)	2876(10)	780(4)	1301(11)	3.3
C(24)	4310(11)	2251(4)	967(12)	4.1
C(25)	4921(12)	1413(4)	601(12)	4.4
C(26)	5838(10)	1925(5)	2003(14)	4.9
C(27)	2840(11)	1717(5)	5217(12)	4.2
C(28)	1732(11)	1130(5)	4224(13)	4.8
C(29)	1565(10)	1996(5)	3845(13)	4.4

[a] Atomic coordinates are multiplied by 10^4. Thermal parameters are given by the equivalent temperature factors (Å^2).

(d, J(HP) = 7.6 Hz, 9H, PMe_3 (*trans* to IrH)), 1.02, 1.39 (m, 1H × 2, $SiCH_2$), 1.21 (dd, J(HP) = 9.0, 2.2 Hz, 9H, PMe_3 (*trans* to PPh_2), 2.22 (s, 3H, *p*-ArMe), 2.31 (m, 1H × 2, PCH_2), 2.81, 2.82 (s, 3H × 2, *o*-$ArMe_2$), 5.19 (dt, J(HP) = 16.6, 4.1 Hz, 1H, SiH), 6.85, 6.94 (s, 1H × 2, *m*-Mes), 6.85–7.15 (m, 6H, *m*, *p*-PPh_2), 7.60–7.66, 7.95–8.01 (m, 4H, *o*-PPh_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ −37.2 (ddd, $J(CP_{cis})$ = 6.2, 8.8, 14.5 Hz, IrMe), 12.2 (ddd, J(CP) = 19.4, 3.1, 1.2 Hz, $SiCH_2$), 17.3 (ddd, J(CP) = 27.3, 3.0, 2.3 Hz, PMe_3), 20.1 (ddd, J(CP) = 34.3, 4.1, 3.5 Hz, PMe_3), 21.2 (*p*-ArMe), 24.0 (d, J(CP) = 2.8 Hz, *o*-ArMe), 26.5 (*o*-ArMe), 35.5 (dd, J(CP) = 37.7, 2.2 Hz, PCH_2), 128.2, 128.8, 129.1, 129.3, 132.1, 134.1, 136.2, 137.5, 140.4, 140.9, 143.3, 144.8 Ar). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ −62.0 (dd, $J(PP_{cis})$ = 15.8, 22.4 Hz, PMe_3 (*trans* to IrH)), −49.4 (dd, $J(PP_{trans})$ = 344.2 Hz, $J(PP_{cis})$ = 22.4 Hz, PMe_3 (*trans* to PPh_2)), 31.3 (dd, $J(PP_{trans})$ = 344.2 Hz, $J(PP_{cis})$ = 15.8 Hz, PPh_2). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6) δ −14.3 (dt, $J(SiP_{cis})$ = 7.2, 10.6 Hz). IR (KBr) 2004, 2087 cm^{-1} (ν(SiH), ν(IrH)). MS (70 eV, DEI) m/z 722 (3, M^+), 706 (100, $M^+–CH_4$). Anal. found: C, 52.78; H, 7.18. $C_{30}H_{48}IrP_3Si \cdot 1/2\ (C_6H_5CH_3)$. Calc.: C, 52.39; H, 6.82%.

2.8. *$Ir(H)(Et)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$* (**4**)

A diethyl ether solution of EtMgBr (2.0 M, 0.24 ml, 2.0 equiv.) was added to a toluene solution (10 ml) of $Ir(Cl)(H)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**1**) (0.18 g, 0.24 mmol) at −48°C, and the mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure. The residue was extracted with toluene–hexane (2:1). The extract was filtered through an alumina column and concentrated. Recrystallization of the residue from toluene–hexane afforded $Ir(H)(Et)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**4**) as colorless crystals. Yield 110 mg (62%). ^1H NMR (300 MHz, C_6D_6) δ −12.23 (ddd, $J(HP_{trans})$ = 120.0 Hz, $J(HP_{cis})$ 22.4, 14.9 Hz, 1H, IrH), 0.95 (d, J(HP) = 7.6 Hz, 9H, PMe_3 (*trans* to IrH)), 0.95, 1.35 (m, 1H × 2, $SiCH_2$), 1.03, 1.49 (m, 1H × 2, $IrCH_2CH_3$), 1.30 (dd, J(HP) = 8.9, 1.6 Hz, 9H, PMe_3 (*trans* to PPh_2), 2.00 (t, J(HH) 7.6 Hz, 3H, $IrCH_2CH_3$), 2.03, 2.53 (m, 1H × 2, PCH_2), 2.23 (s, 3H, *p*-ArMe), 2.81, 2.87 (s, 3H × 2, *o*-$ArMe_2$), 5.06 (dd, J(HH) = 17.7, 5.0 Hz, 1H, SiH), 6.88, 6.96 (s, 1H × 2, *m*-Mes), 6.99–7.11 (*m*, 6H, *m*, *p*-PPh_2), 7.52–7.57, 8.05–8.11 (m, 4H, *o*-PPh_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ −18.3 (q, $J(CP_{cis})$ = 7.1 Hz, $IrCH_2CH_3$), 9.3 (dd, J(CP) = 19.6, 2.1 Hz, $SiCH_2$), 16.7 (dt, J(CP) = 26.9, 2.4 Hz, PMe_3), 21.0 (dt, J(CP) 33.0, 4.0 Hz, PMe_3), 21.3 (*p*-ArMe), 24.5 (d, J(CP) = 2.3 Hz, *o*-ArMe), 26.3 (d, J(CP) = 9.7 Hz, *o*-ArMe), 26.6 ($IrCH_2CH_3$) 35.4 (dd, J(CP) = 37.0, 2.3 Hz, PCH_2), 127.6, 127.7, 128.1, 128.8, 129.0, 129.2, 129.4, 132.5, 134.6, 136.2, 136.3, 138.5, 140.2, 143.4, 145.0 (Ar). $^{31}P\{^1H\}$ NMR (36.3 MHz, C_6D_6) δ −64.3 (dd, $J(PP_{cis})$ = 22.2, 29.0 Hz, PMe_3 (*trans* to IrH)), −51.9 (dd, $J(PP_{trans})$ 340.3 Hz, $J(PP_{cis})$ = 22.2 Hz, PMe_3 (*trans* to PPh_2)), 29.0 (dd, $J(PP_{trans})$ = 340.3 Hz, $J(PP_{cis})$ = 11.1 Hz, PPh_2). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6) δ −20.0 (dt, $J(SiP_{cis})$ = 9.3, 11.8 Hz). IR (KBr) 2031, 2125 cm^{-1} (v(SiH), v(IrH)). MS (DEI, 70 eV) m/z 736 (4, M^+), 706 (100, $M^+–C_2H_6$). Anal. found: C, 53.05; H, 6.93. $C_{30}H_{48}IrP_3Si \cdot 1/2\ (C_6H_5CH_3)$. Calc.: C, 52.99; H, 6.96%.

2.9. *$Ir(H)_2\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$* (**5**)

To a THF suspension (25 ml) of $LiAlH_4$ (160 mg, 4.21 mmol) was added a THF solution (25 ml) of $Ir(Cl)(H)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**1**) (0.26 g, 0.35 mmol). The reaction mixture was stirred at room temperature for 5 h, and then refluxed for 2 h. Volatiles were evaporated under reduced pressure, and the residue was extracted with toluene–hexane (2:1). The extract was filtered through an alumina column and concentrated under reduced pressure. Crystallization from toluene–hexane afforded $\mathrm{Ir(H)_2\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2}$ (**5**) as a white powder. Yield 156 mg (63%). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$) δ -12.51 (dt, $J(\mathrm{HP}_{trans}) = 106.2$ Hz, $J(\mathrm{HP}_{cis}) = 15.6$ Hz, 1H, IrH), -11.93 (dt, J(HP*trans*) = 113.4 Hz, $J(\mathrm{HP}_{cis}) = 20.7$ Hz, 1H, IrH), 1.11 (d, $J(\mathrm{HP}) = 8.0$ Hz, 9H, $\mathrm{PMe_3}$ (*trans* to IrH)), 1.15, 1.42 (m, 1H × 2, $\mathrm{SiCH_2}$), 1.23 (d, $J(\mathrm{HP}) = 7.7$ Hz, 9H, $\mathrm{PMe_3}$ (*trans* to Si)), 2.22, 2.54 (m, 1H × 2, $\mathrm{PCH_2}$), 2.26 (s, 3H, *p*-ArMe), 2.88 (s, 6H, *o*-$\mathrm{ArMe_2}$), 5.24 (dd, $J(\mathrm{HH}) = 17.3$, 7.8 Hz, 1H, SiH), 6.92 (s, 2H, *m*-Mes), 7.01–7.13 (m, 6H, *m*, *p*-$\mathrm{PPh_2}$), 7.45, 7.82 (m, 4H, *o*-$\mathrm{PPh_2}$). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{C_6D_6}$) δ 15.0 (dd, $J(\mathrm{CP}) = 23.7$, 3.1 Hz, $\mathrm{SiCH_2}$), 21.1 (*p*-ArMe), 21.4 (dt, $J(\mathrm{CP}) = 29.3$, 4.6 Hz, $\mathrm{PMe_3}$), 26.0 (dt, $J(\mathrm{CP}) = 25.8$, 3.6 Hz, $\mathrm{PMe_3}$), 24.4 (*o*-$\mathrm{ArMe_2}$), 37.6 (dd, $J(\mathrm{CP}) = 37.0$, 11.4 Hz, $\mathrm{PCH_2}$), 127.9, 128.2, 128.5, 128.8, 129.2, 132.0, 133.3, 135.9, 140.5, 143.1 (Ar). ^{31}P{^{1}H} NMR (36.3 MHz, $\mathrm{C_6D_6}$) δ -61.4 (dd, $J(\mathrm{PP}_{cis}) = 16.2$, 20.3 Hz, $\mathrm{PMe_3}$), -59.0 (dd, $J(\mathrm{PP}_{cis}) = 16.2$, 20.3 Hz, $\mathrm{PMe_3}$), 35.2 (t, $J(\mathrm{PP}_{cis}) = 16.2$ Hz, $\mathrm{PPh_2}$). ^{29}Si{^{1}H} NMR (59.6 MHz, $\mathrm{C_6D_6}$) δ -4.4 (ddd, $J(\mathrm{SiP}_{trans})$ 123.8 Hz, $J(\mathrm{SiP}_{cis}) =$ 10.6, 5.5 Hz). IR (KBr) 2007, 2029, 2042 cm^{-1} (ν(IrH), ν(SiH)). MS (DEI, 70 eV) m/z 708 (37, $\mathrm{M^+}$), 706 (100, $\mathrm{M^+ – H_2}$). Anal. found: C, 43.78; H, 6.26. $\mathrm{C_{22}H_{40}IrP_3Si \cdot 1/8\ (C_6H_5CH_3)}$. Calc.: C, 43.66; H, 6.57%.

2.10. Thermolysis of *Ir(H)(Me)*{η^2-*MesHSi(CH$_2$)$_2$PPh$_2$*}*(PMe$_3$)$_2$* (**3**)

A Pyrex sample tube (15 mm o.d.) with a greaseless vacuum valve was charged with $\mathrm{Ir(H)(Me)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2}$ (**3**) (0.25 g, 0.35 mmol) and toluene (5.0 ml). The solution was degassed on a vacuum line by the conventional freeze–pump–thaw method. The tube was flame-sealed under vacuum and then heated at 60°C for 80 h. It was then opened in an $\mathrm{N_2}$ glove box. Volatiles were removed under reduced pressure to give a mixture of an isomeric pair of $\mathrm{Ir(H)\{\eta^3\text{-}CH_2C_6H_2(CH_3)_2SiH(CH_2)_2PPh_2\}(PMe_3)_2}$ (**6a** and **6b**). Crystallization from toluene–hexane at -30°C gave colorless crystals of **6a**. Yield 0.13 g (53%). Data for **6a**: ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$) δ -11.59 (dt, $J(\mathrm{HP}_{trans}) = 132.2$ Hz, $J(\mathrm{HP}_{cis}) = 17.8$ Hz, 1H, IrH), 0.88, 1.50 (m, 1H × 2, $\mathrm{SiCH_2}$), 1.23 (d, $J(\mathrm{HP}) = 7.8$ Hz, 9H, $\mathrm{PMe_3}$), 1.23 (d, $J(\mathrm{HP}) = 7.3$ Hz, 9H, $\mathrm{PMe_3}$), 1.66, 2.56 (m, 1H × 2, $\mathrm{PCH_2}$), 2.66, 3.28 (m, 1H × 2, $\mathrm{IrCH_2}$), 2.35, 2.85 (s, 6H, *o*-$\mathrm{ArMe_2}$), 5.58 (m, 1H, SiH), 6.90–7.55 (m, 12H, ArH). ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{C_6D_6}$) δ 3.3 (dt, $J(\mathrm{CP}_{trans}) = 61.4$ Hz, $J(\mathrm{CP}_{cis}) = 4.7$ Hz, $\mathrm{IrCH_2}$), 14.0 (dd, $J(\mathrm{CP}) = 25.5$, 3.8 Hz, $\mathrm{SiCH_2}$), 21.1 (dt, $J(\mathrm{CP}) = 23.6$, 1.9 Hz, $\mathrm{PMe_3}$), 21.5, 22.9 (s, ArMe), 23.5 (dt, $J(\mathrm{CP}) = 30.2$, 3.8 Hz, $\mathrm{PMe_3}$), 29.4 (dd, $J(\mathrm{CP}) = 36.9$, 11.3 Hz, $\mathrm{PCH_2}$), 125.8, 126.8, 129.2, 129.6, 131.7, 132.1, 132.6, 137.9, 139.7, 141.7, 142.3 (Ar). ^{31}P{^{1}H} NMR (121.5 MHz, $\mathrm{C_6D_6}$) δ -60.9 (t, $J(\mathrm{PP}_{cis}) = 20.1$ Hz, $\mathrm{PMe_3}$), -59.6 (dd, $J(\mathrm{PP}_{cis}) = 13.7$, 20.1 Hz, $\mathrm{PMe_3}$), 24.0 (dd, $J(\mathrm{PP}_{cis}) =$ 13.7, 20.1 Hz, $\mathrm{PPh_2}$). ^{29}Si{^{1}H} NMR (59.6 MHz, $\mathrm{C_6D_6}$) δ 21.7 (ddd, $J(\mathrm{SiP}_{trans}) = 131.1$ Hz, $J(\mathrm{SiP}_{cis}) = 7.9$, 10.7 Hz), IR (KBr) 2023, 2054 cm^{-1} (v(IrH), v(SiH)). Exact mass found: 706.2057. $\mathrm{C_{29}H_{44}P_3Si}$. Calc.: 706.2055. Anal. found: C, 48.55; H, 6.41. $\mathrm{C_{29}H_{44}IrP_3Si}$. Calc.: C, 49.34; H, 6.28%. Data for **6b**: ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$) δ -12.09 (*d*t, $J(\mathrm{HP}_{trans}) = 105$ Hz, $J(\mathrm{HP}_{cis}) = 18$ Hz, 1H, IrH), 1.03 (*d*, $J(\mathrm{HP}) = 7.3$ Hz, 9H, $\mathrm{PMe_3}$), 1.11 (d, $J(\mathrm{HP}) = 6.8$ Hz, 9H, $\mathrm{PMe_3}$), 2.39, 2.81 (s, 3H × 2, $\mathrm{ArMe_2}$), 5.23 (m, 1H, SiH). ^{13}C NMR (75.5 MHz, $\mathrm{C_6D_6}$) δ 2.8 (dt, $J(\mathrm{CP}_{trans}) = 62.8$ Hz, $J(\mathrm{CP}_{cis}) = 5.1$ Hz, $\mathrm{IrCH_2}$). ^{29}Si NMR (59.6 MHz, $\mathrm{C_6D_6}$) δ 18.9 (ddd, $J(\mathrm{SiP}_{trans}) = 134.0$ Hz, $J(\mathrm{SiP}_{cis})$ 18.0, 4.4 Hz). ^{31}P NMR (121.5 MHz, $\mathrm{C_6D_6}$) δ -59.6 (dd, $J(\mathrm{PP}_{cis}) = 6.9$, 13.7 Hz, $\mathrm{PMe_3}$ (*trans* to Si)), -59.4 (dd, $J(\mathrm{PP}_{cis}) = 6.9$, 8.4 Hz, $\mathrm{PMe_3}$ (*trans* to IrH)), 25.8 (dd, $J(\mathrm{PP}_{cis}) = 8.4$, 13.7 Hz, $\mathrm{PPh_2}$).

2.11. Thermolysis of *Ir(H)(Et)*{η^2-*MesHSi(CH$_2$)$_2$PPh$_2$*}*(PMe$_3$)$_2$* (**4**)

A Pyrex sample tube (15 mm o.d.) with a greaseless vacuum valve was charged with $\mathrm{Ir(H)(Et)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2}$ (**4**) (0.30 g, 0.40 mmol) and toluene (5.0 ml). The solution was degassed on a vacuum line by the conventional freeze–pump–thaw method. The tube was flame-sealed under vacuum and then heated at 60°C for 6 h. The procedure gave **6**. The isolation of the product **6a** was the same as the method described above. Yield 0.15 g (55%).

2.12. Attempted thermal reaction of *Ir(H)$_2$*{η^2-*MesHSi(CH$_2$)$_2$PPh$_2$*}*(PMe$_3$)$_2$* (**5**)

A Pyrex NMR tube (5 mm o.d.) was charged with $\mathrm{Ir(H)_2\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2}$ (**5**) (8 mg), 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 the ^{1}H and ^{31}P{^{1}H} NMR spectroscopy (r.t. to 80°C). No change was observed on the ^{1}H and ^{31}P{^{1}H} NMR spectra at 80°C for 12 h.

2.13. Photolysis of *Ir(H)$_2$*{η^2-*MesHSi(CH$_2$)$_2$PPh$_2$*}*(PMe$_3$)$_2$* (**5**)

A Pyrex NMR tube (5 mm o.d.) was charged with $\mathrm{Ir(H)_2(\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2}$ (**5**) (8 mg), 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 photo reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy.

*2.14. Thermolysis of Ir(H)(R){η^2-MesHSi(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (R = Me (**3**), Et (**4**)) in the presence of PMe$_3$*

A Pyrex NMR tube (5 mm o.d.) was charged with **3** or **4** and PMe$_3$ (5 equiv.) via syringe, and benzene-d_6 (0.7 ml) was introduced into the tube under high vacuum by the trap-to-trap-transfer technique. The NMR tube was flame-sealed. The tube was heated to 60°C and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. The clean formation of **6** was observed.

*2.15. Thermal reaction of Ir(H)(R){η^2-MesHSi(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$(R = Me (**3**), Et (**4**)) with CO*

A solution of **3** or **4** in C$_6$D$_6$ (0.7 ml) was placed in a 5 mm o.d. NMR tube which was sealed by a septum. Carbon monoxide was bubbled through the solution via a needle at room temperature. The sealed NMR tube was heated to 60°C and the reaction was monitored by NMR spectroscopy. The formation of Ir{η^2-MesHSi(CH$_2$)$_2$PPh$_2$}(PMe$_3$)(CO)$_2$ (**7**) was confirmed at 60°C (for 80 h (**3**), 6 h (**4**)). The isolation of **7** was carried out as follows: A solution of Ir(H)(Et){η^2-MesHSi(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (**4**) (0.15 g, 0.20 mmol) in toluene was stirred under CO at 60°C for 6 h, and the resulting colorless solution was concentrated in vacuo. Crystallization from toluene–hexane gave a white powder of Ir(η^2-MesHSi(CH$_2$)$_2$PPh$_2$}(PMe$_3$)(CO)$_2$ (**7**). Yield 0.11 g (80%). ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 0.89 (d, J(HP) = 9.4 Hz, 9H, PMe$_3$), 0.98, 1.15 (m, 1H × 2, SiCH$_2$), 2.17 (s, 3H, p-ArMe), 2.18, 2.66 (m, 1H × 2, PCH$_2$), 2.70 (s, 6H, o-ArMe$_2$), 5.38 (m, 1H, SiH), 6.85 (s, 2H, m-Mes), 6.97–7.61 (m, 10H, ArH). ^{13}C{1H} NMR (75.5 MHz, C$_6$D$_6$) δ 11.9 (dd, J(CP) = 27.0, 2.5 Hz, SiCH$_2$), 21.1 (dt, J(CP) = 31.5, 4.3 Hz, PMe$_3$), 21.5 (p-ArMe), 24.5 (o-ArMe$_2$), 37.7 (dd, J(CP) = 35.3, 8.8 Hz, PCH$_2$), 128.4, 128.5, 128.9, 129.3, 129.5, 130.2, 132.1, 134.2, 137.5, 143.8 (Ar), 185.3 (dd, J(CP) = 27.5, 11.7 Hz, CO), 186.0 (dd, J(CP) = 31.1, 11.4 Hz, CO). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$) δ −60.8 (d, J(PP$_{cis}$) = 27.1 Hz, PMe$_3$), 31.6 (d, J(PP$_{cis}$) = 27.1 Hz, PPh$_2$). ^{29}Si{^{1}H} NMR (59.6 MHz, C$_6$D$_6$) δ 13.1 (dd, J(SiP$_{trans}$) = 74.4 Hz, J(SiP$_{cis}$) = 9.6 Hz). IR (KBr) 2079 cm^{-1} (ν(SiH)), 1903, 1959 (ν(CO)). Mass (DEI, 70 Ev) m/z 686 (11, M$^+$), 658 (100, M$^+$–CO), 630 (54, M$^+$–2CO). Anal. found: C, 49.41; H, 5.38. C$_{28}$H$_{35}$IrO$_2$P$_2$Si. Calc.: C, 49.04; H, 5.14%.

*2.16. Thermal geometric isomerization of **6***

A Pyrex NMR tube was charged with **6a** (8 mg), and benzene-d_6 (0.7 ml) was introduced into the tube under vacuum by the trap-to-trap-transfer technique. The NMR tube was flame-sealed under vacuum. The thermal geometric isomerization at 60°C was monitored periodically by ^{1}H NMR spectroscopy. After 3 h, the geometric isomerization reached to an equilibrium with a ratio of **6a**: **6b** = 5:3.

*2.17. Thermal reaction of **6a** with CO*

A C$_6$D$_6$ solution (0.7 ml) of **6a** (8 mg) was placed in a 5 mm o.d. NMR tube, and CO was bubbled through the solution via a needle. This sample was kept at 60°C in an oil bath, and the reaction was monitored periodically by ^{1}H NMR spectroscopy. The clean formation of **7** was observed.

*2.18. Thermal reaction of Ir(H)(R){η^2-MesHSi(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (**3**: R = Me, **4**: R = Et) with MeOH*

A Pyrex NMR tube (5 mm o.d.) was charged with **3** or **4** and MeOH (5 equiv.) via syringe, and benzene-d_6 (0.7 ml) was introduced into the 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{^{1}H} NMR spectroscopy. The formation of Ir(H)$_2${η^2-Mes(MeO)Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (**8**) at 60°C (for 80 h (**3**), 6 h (**4**)) was confirmed. The isolation of the product **8** was carried out as follows: A Pyrex tube (20 mm o.d.) was charged with Ir(H)(Et){η^2-MesHSi(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (**4**) (0.29 g, 0.40 mmol) and MeOH (8.1 μl, 5 equiv.) via syringe, and benzene-d_6 was introduced into the tube under high vacuum by the trap-to-trap-transfer technique. The tube was flame-sealed. The sample was placed in an oil-bath at 60°C for 6 h. The tube was opened in the glove bag, and volatiles were removed under reduced pressure. Crystallization of the residue from toluene–hexane gave colorless crystals of Ir(H)$_2${η^2-Mes(MeO)Si(CH$_2$)$_2$PPh$_2$}(PMe$_3$)$_2$ (**8**). Yield 0.23 g (78%). ^{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), 1.20 (d, J(HP) = 7.5 Hz, 9H, PMe$_3$), 1.22 (d, J(HP) = 8.3 Hz, 9H, PMe$_3$), 1.42, 1.52 (m, 1H × 2, SiCH$_2$), 2.10, 2.52 (m, 1H × 2, PCH$_2$), 2.24 (s, 3H, p-ArMe), 2.92 (br. s, 6H, o-ArMe$_2$), 3.40 (s, 3H, SiOMe), 6.91 (s, 2H, m-Mes), 6.98–7.14, 7.50–7.57, 7.77–7.83 (m, 10H, PPh$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$) δ 21.0 (p-ArMe), 21.4 (dd, J(CP) = 24.0, 7.9 Hz, SiCH$_2$), 22.7 (ddd, J(CP) = 29.2, 5.1, 3.3 Hz,

PMe_3), 24.6 (br. s, o-$ArMe_2$), 25.4 (dt, J(CP) = 25.1, 3.5 Hz, PMe_3), 34.1 (dd, J(CP) = 36.4, 10.2 Hz, PCH_2), 49.5 (d, J(CP) = 5.0 Hz, SiOMe), 127.8, 128.4, 128.5, 129.0, 129.5, 132.1, 132.5, 133.4, 140.3, 140.4, 142.8, 143.6 (Ar). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) δ −63.0 (t, $J(PP_{cis})$ = 19 Hz, PMe_3), −55.3 (t, $J(PP_{cis})$ = 19 Hz, PMe_3), 33.3 (t, $J(PP_{cis})$ = 19 Hz, PPh_2). $^{29}Si\{^1H\}$ NMR (59.6 MHz, C_6D_6) δ 46.2 (ddd, $J(SiP_{trans})$ = 146.2 Hz, $J(SiP_{cis})$ = 9.6, 6.5 Hz). IR (KBr) 2013 cm^{-1} (ν(IrH)), 1066 cm^{-1} (ν(Si–O)). MS (70 eV, DEI) m/z 738 (21, M^+). Anal. found: C, 50.07; H, 6.63. $C_{30}H_{48}IrOP_3Si \cdot 1/4$ ($C_6H_5CH_3$). Calc.: C, 50.11; H, 6.62%.

2.19. Reaction of Ir(H)(Cl){η^2-MesHSi(CH_2)$_2$$PPh_2$}($PMe_3$)$_2$ (1) with NaOMe

Ir(H)(Cl){η^2-MesHSi$(CH_2)_2PPh_2$}$(PMe_3)_2$ (**1**) (15 mg, 0.020 mmol) and a MeOH solution of NaOMe (1.5 M, 40 μl, 3 equiv.) was placed in a Pyrex NMR tube (5 mm o.d.) connected to a vacuum line. Benzene-d_6 (0.7 ml) was transferred into the NMR tube by the trap-to-trap-transfer technique. The sample was flame-sealed under vacuum. The clean formation of $Ir(H)_2$\{η^2-MesHSi$(CH_2)_2PPh_2$\}$(PMe_3)_2$ (**5**) was confirmed by NMR spectroscopy.

3. Results and discussion

3.1. Preparation of chelate ligand precursor

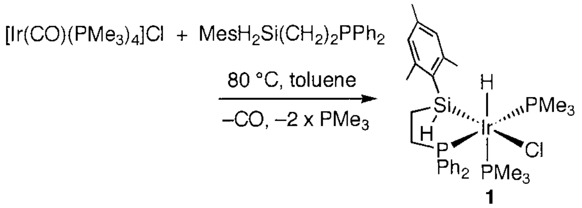
$MesH_2Si(CH_2)_2PPh_2$ can be prepared as colorless crystals according to the preparative method reported by Holmes-Smith et al. ([15], Eq. (2)). In the $^{31}P\{^1H\}$ NMR spectrum, the signal of PPh_2 appears at −11.3 ppm as a singlet. The $^{29}Si\{^1H\}$ NMR spectrum shows a doublet at −43.4 ppm (J(SiP) = 23 Hz). These chemical shifts are characteristic of $RPPh_2$ and R_2SiH_2, respectively.

$$\mathrm{MesLi} + \mathrm{Cl_3Si(CH{=}CH_2)} \xrightarrow{-\mathrm{LiCl}} \mathrm{MesSiCl_2(CH{=}CH_2)} \xrightarrow[\mathrm{THF}]{\mathrm{LiAlH_4}} \mathrm{MesH_2Si(CH{=}CH_2)} \xrightarrow[\mathrm{PPh_2H}]{h\nu} \mathrm{MesH_2Si(CH_2)_2PPh_2} \qquad (2)$$

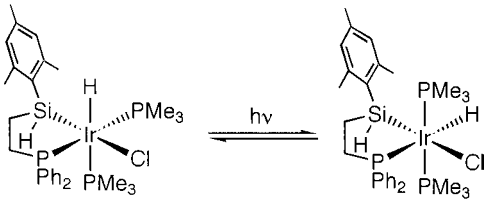
3.2. Preparation of chloro(hydrido)(hydrosilyl) complex 1

Heating the toluene solution of the cationic iridium(I) complex $[Ir(CO)(PMe_3)_4]Cl$ with $MesH_2Si(CH_2)_2PPh_2$ at 80°C for 36 h in a sealed-tube resulted in the formation of the relatively air-stable complex Ir(Cl)(H)\{η^2-MesSiH$(CH_2)_2PPh_2$\}$(PMe_3)_2$ (**1**) in 80% yield as a white powder (Eq. (3)). The IR and NMR spectra of **1** strongly support the structure as shown in Eq. (3). The IR spectrum shows a ν(IrH) absorption in the usual metal–hydrido region. The IrH resonance appears in the ^1H NMR spectrum as a doublet of triplets at −9.41 ppm with one large *trans* and two identical *cis* P–H coupling constants ($J(HP_{trans})$ = 130 Hz, $J(HP_{cis})$ = 17 Hz). The ^1H NMR spectrum also contains a doublet of doub1et signal at 4.77 ppm (J(HH) = 1.9, 6.8 Hz) assigned to that of SiH. The $^{31}P\{^1H\}$ NMR spectrum established that **1** possesses three phosphoros atoms in a *mer*-geometry. The resonance of the PPh_2 moiety in the $^{31}P\{^1H\}$ NMR spectrum appears at 19.7 ppm as a doublet of doublets with one typical large *trans* and one *cis* P–P coupling constants ($J(PP_{trans})$ = 329.0 Hz, $J(PP_{cis})$ = 11.1 Hz). In the ^{29}Si NMR spectrum, the ^{29}Si resonance appears at −19.8 ppm as a ddd with three nearly identical *cis* Si–P coupling constants ($J(SiP_{cis})$ = 5.8, 6.7, 7.4 Hz). The structure of **1** was also confirmed by the elemental analysis and mass spectral data.

A single crystal of a geometric isomer of **1** suitable for X-ray crystal structure analysis was obtained. Complex **1** underwent geometric isomerization on photolysis to give **2** (Eq. (4)). This photoreaction reached a photostationary state within 2 h. The molar ratio of **1** to **2** is 29:71. Careful crystallization of the resulting solution afforded colorless crystals of **2**. The ^{31}P resonances for the two nearly chemically equivalent PMe_3 ligands overlap each other and appear as a doublet at −48.9 ppm with a *cis* P–P coupling constant ($J(PP_{cis})$ = 19.5 Hz). Other spectroscopic data for **2** are similar to those for **1**.



1 (3)



1 **2** (4)

3.3. X-ray structure of complex 2

The geometry of **2** was unequivocally determined by X-ray crystal structure analysis (Fig. 1). Selected bond distances and angles are listed in Tables 3 and 4. Although the hydrido ligand could not be located crys-

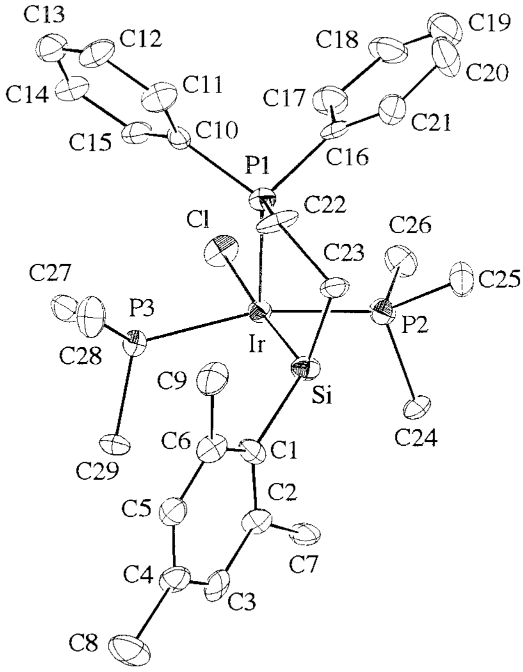


Fig. 1. ORTEP drawing of $Ir(H)(Cl)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**2**).

tallographically, NMR data clearly indicate that the hydrido ligand occupies the position opposite to the PPh_2 moiety. Therefore, one can easily see that the coordination geometry around iridium is a slightly distorted six-coordinate octahedron. The Ir–Si bond length is relatively short compared to that of previously reported silyl–iridium compounds [1,2,16,17]. This may be due to the coordination of a weakly *trans*-influencing chloro ligand opposite the silyl ligand.

3.4. *Synthesis of* $Ir(H)(R)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ *(R = Me* (**3**)*, Et* (**4**)*, H* (**5**)*)*

Methyl–hydrido complex **3** was prepared as colorless crystals in 57% isolated yield by the reaction of **1** with MeLi in toluene at −48°C (Eq. (5)). The NMR and IR data are in good agreement with the structure shown in Eq. (5). The IR spectrum shows a v(IrH) band in the usual metal–hydride region. The ^1H NMR spectrum shows pseudo quartets at 0.43 ppm ($J(HP_{cis}) = 6.2$ Hz, 3H), which is assigned to the signal of IrMe. The IrMe resonance in the $^{13}C\{^1H\}$ NMR spectrum appears as a ddd at −37.2 ppm with three nearly identical C–P *cis* coupling constants ($J(CP_{cis}) = 6.2$, 8.8, 14.5 Hz). The chemical shift is characteristic of carbon directly bound to a transition-metal through a σ-bond. The ^{31}P resonance of the PPh_2 moiety appears as a doublet of doublets at 31.3 ppm with one large *trans* and small *cis* P–P coupling constants ($J(PP_{trans}) = 344.2$ Hz, $J(PP_{cis}) = 15.8$ Hz), which indicates that the three phosphorus atoms in **3** are located in a *mer*-geometry. Recently, Aizenberg and Milstein reported the synthesis of methyl(hydrido)(silyl)iridium(III) complexes *fac*-$Ir(Me)(H)(SiR_3)(PMe_3)_3$ by the thermal reaction of $MeIr(PMe_3)_4$ with $HSiR_3$ [17]. In these complexes, a strongly *trans*-influencing silyl ligand is located at the position *trans* to the PMe_3 ligand [17,18]. In contrast, surprisingly, the silyl ligand in **3** is located *trans* to the strongly *trans*-influencing methyl ligand.

Table 3
Selected bond distances (Å) for $Ir(H)(Cl)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**2**)

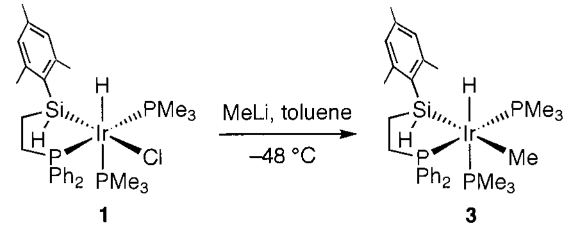
Ir–Cl	2.542(4)	Ir–P(1)	2.349(3)
Ir–P(2)	2.331(4)	Ir–P(3)	2.336(4)
Ir–Si	2.352(5)	–	–
P(1)–C(10)	1.86(2)	P(1)–C(16)	1.85(2)
P(1)–C(22)	1.89(2)	P(2)–C(24)	1.87(2)
P(2)–C(25)	1.85(2)	P(2)–C(26)	1.86(2)
P(3)–C(27)	1.81(2)	P(3)–C(28)	1.83(2)
P(3)–C(29)	1.82(2)	–	–
Si–C(1)	1.93(1)	Si–C(23)	1.93(1)

Table 4
Selected bond angles (°) for $Ir(H)(Cl)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**2**)

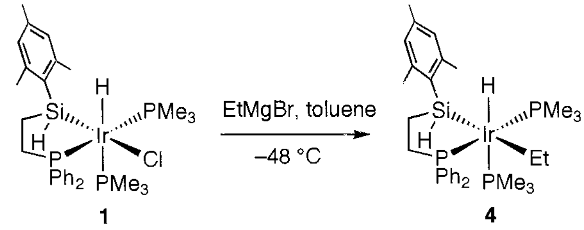
Cl–Ir–P(1)	95.4(1)	Cl–Ir–P(2)	87.8(2)
Cl–Ir–P(3)	88.9(1)	Cl–Ir–Si	175.2(2)
P(1)–Ir–P(2)	99.3(I)	P(1)–Ir–P(3)	98.5(1)
P(1)–Ir–Si	85.8(1)	P(2)–Ir–P(3)	162.1(2)
P(2)–Ir–Si	87.5(2)	P(3)–Ir–Si	95.5(2)

Ethyl–hydrido complex **4** was also prepared as colorless crystals in 62% isolated yield by adding EtMgBr to **1** in toluene at 48°C (Eq. (6)). The spectroscopic data support the geometry shown in Eq. (6). The resonance of $IrCH_2$ in the $^{13}C\{^1H\}$ NMR spectrum appears as a pseudo quartet at −18.3 ppm with three identical *cis* C–P coupling constants ($J(CP_{cis}) = 7.1$ Hz). In the ^{13}C–^1H HETCOR spectrum, the ^{13}C signal of $IrCH_2$ at −18.3 ppm correlates with the ^1H signals at 1.03 and 1.49 ppm. In the ^1H–^1H COSY spectrum, the signals of $IrCH_2$ at 1.03 and 1.49 ppm correlate with the signal at 2.00 ppm (t, $J(HH) = 7.6$ Hz, 3H), which is assigned to $IrCH_2C\mathit{H}_3$.

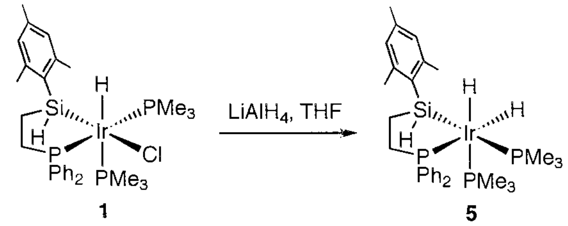
Complex **1** reacted with $LiAlH_4$ in THF to give a dihydridoiridium(III) complex **5** (Eq. (7)). Crystallization of **5** from toluene–hexane afforded a white powder in 63% isolated yield. The spectroscopic data are consistent with the geometry shown in Eq. (7). The IrH signals appear in the ^1H NMR spectrum as two doublets of triplets at −12.51 ($J(HP_{trans}) = 106.2$ Hz, $J(HP_{cis}) = 15.6$ Hz) and −11.93 ppm ($J(HP_{trans}) = 113.4$ Hz, $J(HP_{cis}) = 20.7$ Hz) splitted by P–H couplings. The $^{31}P\{^1H\}$ NMR spectrum exhibits signals of three inequivalent mutually coupled phosphorus atoms with nearly identical *cis* P–P coupling constants, which establishes that **5** possesses three phosphorus atoms in a *fac*-relationship as shown in Eq. (7).



(5)



(6)



(7)

3.5. Thermal reactions of $Ir(H)(R)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (R = Me (**3**), Et (**4**), H(**5**))

Thermolysis of **3** at 60°C for 80 h resulted in the clean formation of **6** via reductive elimination of methane and the intramolecular carbon–hydrogen bond activation (Eq. (8)). The ^{1}H NMR spectrum contains a very sharp singlet at 0.15 ppm, which is assigned to free CH_4 in C_6D_6. The thermal reaction of **4** proceeded more quickly (60°C, 6 h) to give the same product **6**. The evolution of ethane was also confirmed by ^{1}H NMR spectroscopy (0.79 ppm in C_6D_6). Interestingly, complex **4** is inert to β-hydrogen elimination under these conditions, although many transition-metal ethyl complexes are known to undergo β-hydrogen elimination even at room temperature [19]. Product **6** was a mixture of the geometric isomers **6a** and **6b** in the ratio of 5:3. Recrystallization of **6** from toluene–hexane at -30°C gave colorless crystals of only **6a**. The spectroscopic data clearly support the geometries of **6a** and **6b** shown in Eq. (8). The arrangement of three coordinating atoms C, Si, and P of the tridentate ligand around Ir(III) are facial for **6a** and meridional for **6b**. The $^{13}C\{^1H\}$ spectrum of **6a** contains a doublet of triplets at δ 3.3 ppm ($J(CP_{trans}) = 61.4$ Hz, $J(CP_{cis}) = 4.7$ Hz), which can be assigned to the methylene carbon directly bound to the iridium center. In the $^{13}C-^1H$ HETCOR spectrum, the ^{13}C signal of $IrCH_2$ at 3.3 ppm correlates with two ^{1}H signals at 2.66 and 3.28 ppm. Furthermore, the resonance of $IrCH_2$ in the $^1H\{^{31}P\}$ NMR spectrum appears as an AB splitting pattern as shown in Fig. 2. The $^{29}Si\{^1H\}$ NMR spectrum shows a ddd signal at 21.7 ppm with one large *trans* and two nearly identical *cis* coupling constants ($J(SiP_{trans}) = 131.1$ Hz, $J(SiP_{cis}) =$ 10.7, 7.9 Hz). The NMR data for **6b** are similar to those for **6a**.

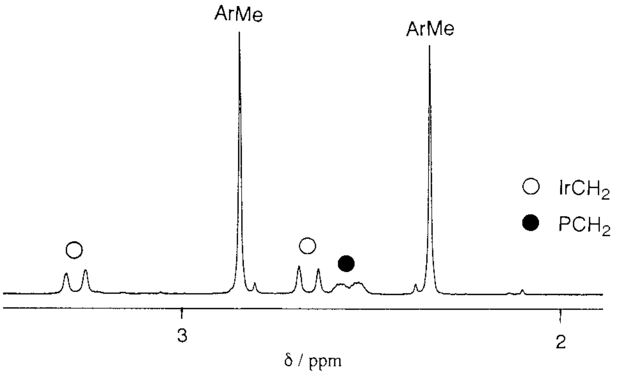
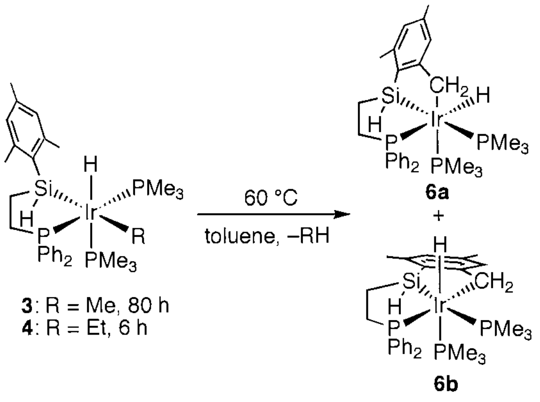
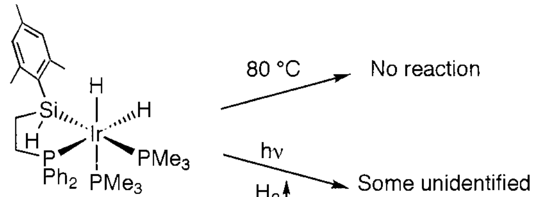


Fig. 2. $^1H\{^{31}P\}$ NMR spectrum of **6a**.

In contrast to complexes **3** and **4**, complex **5** is thermally stable at 80°C for 12 h (Eq. (9)). This order of thermal stability is in accordance with that of the typical bond strength of $L_nM\text{-}X$ (X = H > Me > Et) [20]. We carried out the photolysis of **5** in C_6D_6 (Eq. (9)). The reaction proceeded with the evolution of H_2 to give several unidentified products. The formation of H_2 was confirmed by ^{1}H NMR spectroscopy (4.46 ppm in C_6D_6).



(8)



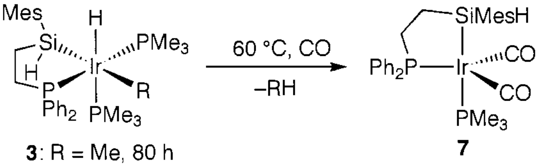
(9)

3.6. Attempted reaction of **3** or **4** with PMe_3

In a previous paper, we described the generation of a 16e-Ir{η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_2$ from Ir(H)(R){η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_2$ (R = Me, Et) via reductive elimination of alkane [21]. We succeeded in trapping the 16e-Ir{η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_2$ by adding PMe_3 as Ir{η^2-$Me_2Si(CH_2)_2PPh_2$}$(PMe_3)_3$. Therefore, we also carried out the thermal reactions of **3** and **4** with excess PMe_3 at 60°C. Even in the presence of PMe_3, intramolecular carbon–hydrogen bond activation took place in both reactions to give **6** quantitatively. The formation of a PMe_3 adduct Ir{η^2-$MesHSi(CH_2)_2PPh_2$}$(PMe_3)_3$ was not observed, because **6** is thermodynamically more stable than the PMe_3 adduct due to the chelate effect.

3.7. Thermal reaction of **3** or **4** with CO

The reactions of **3** and **4** were carried out in the presence of more sterically favorable carbon monoxide. The reaction proceeded at 60°C cleanly to give a dicarbonyliridium(I) complex Ir{η^2-$MesHSi(CH_2)_2PPh_2$}$(CO)_2(PMe_3)$ (**7**) (Eq. (10)). [4] The formation of a monocarbonyl compound Ir{η^2-$MesHSi(CH_2)_2PPh_2$}$(CO)(PMe_3)_2$ was not observed. Assignment of the coordination geometry of **7** is based on the NMR and IR spectroscopic data. The IR spectrum shows two ν(CO) bands in the terminal carbonyl region (1959, 1903 cm^{-1}). In the $^{13}C\{^1H\}$ NMR spectrum, the signals of two carbonyl ligands appear inequivalently at 185.3 ppm (J(HP) = 27.5, 11.7 Hz) and 186.0 ppm (J(HP) = 31.1, 11.4 Hz) as two doublets of doublets. In agreement with the *cis* geometry of two phosphorus atoms, the signal of a PMe_3 ligand in the $^{31}P\{^1H\}$ NMR spectrum appears at −60.8 ppm as a doublet with a P–P*cis* coupling constant ($J(PP_{cis})$ = 27.1 Hz). The ^{29}Si resonance shows a doublet of doublets at 13.1 ppm coupled with one *trans* and one *cis*-^{31}P nuclei ($J(SiP_{trans})$ = 74.4, $J(SiP_{cis})$ = 9.6 Hz).



3: R = Me, 80 h
4: R = Et, 6 h

7

(10)

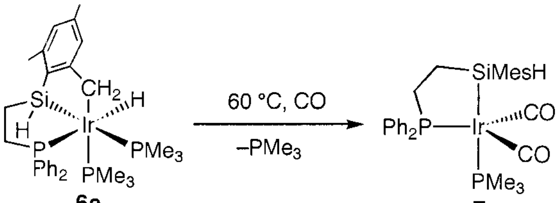
3.8. Thermal geometric isomerization of **6**

Thermolysis of isolated complex **6a** at 60°C resulted in geometric isomerization to **6b** which reached to an equilibrium with the ratio of **6a** and **6b** = 5:3 (Eq. (11)). Several octahedral, tertiary phosphine complexes are known to undergo geometric isomerization on photolysis or thermolysis. In most cases, the mechanism involves the dissociation of a phosphine ligand, and the addition of tertiary phosphine retards the isomerization [24]. Interestingly, addition of 5 equiv. of trimethylphosphine did not retard the isomerization of **6a**.

$$\mathbf{6a} \xrightleftharpoons{C_6D_6,\ 60\ °C} \mathbf{6b} \qquad (11)$$

3.9. Thermal reaction of **6a** with CO

The thermal reaction of **6a** with CO proceeded at 60°C to give a dicarbonyliridium(I) complex **7** (Eq. (12)). The observation is consistent with the hypothesis that the C–H bond oxidative addition is reversible at 60°C between Ir{η^2-$MesHSi(CH_2)_2PPh_2$}$(PMe_3)_2$ (**A**) and **6** (see Scheme 1). Recently, Aizenberg and Milstein reported the reversible *ortho*-metalation of the transient $(Me_3P)_3Ir(SiMe_2Ph)$ to give *fac*-$(Me_3P)_3Ir$\{η^2-(*o*-$C_6H_4SiMe_2$)\}(H) [23]. Importantly, in the course of the reaction, the isomerization to **6b** was completely inhibited, which seems to demonstrate that the geometric isomerization between **6a** and **6b** takes place via the intermediate **A**.



6a

7

(12)

3.10. A possible formation mechanism of **6** and **7**

Scheme 1 shows one possible mechanism that allows the formation of **6** and **7**. Complex **3** or complex **4** eliminates the corresponding alkane via reductive elimination to give a 16e-silyliridium(I) complex **A**. In the absence of any trapping agent, **A** activates an intramolecular C–H bond to give **6** reversibly. In the presence of carbon monoxide, CO traps the intermediate **A** to give a dicarbonyliridium(I) complex **7**. Aizenberg and Milstein [17] and also Mitchell et al. [25] independently described the generation of unsaturated silyliridium(I) complexes that undergo intramolecular carbon–hydrogen bond activation to give silyliridium(III) complexes. These results suggest that unsaturated silyliridium(I) species should be quite reactive compared with other four-coordinate complexes of d^8 metals.

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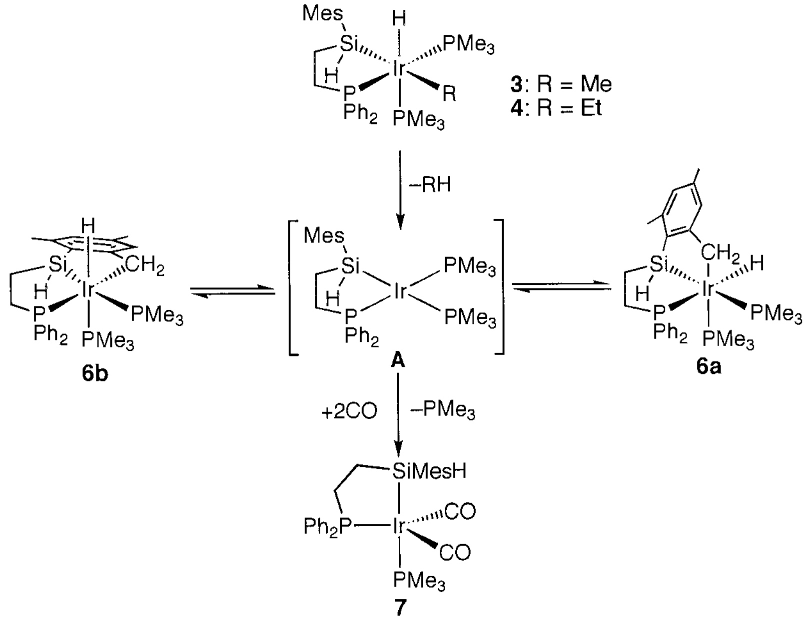
[4] The synthesis of silyldicarbonylbis(tertiary phosphine)iridium(I) complexes is reported in Refs. [22,23].



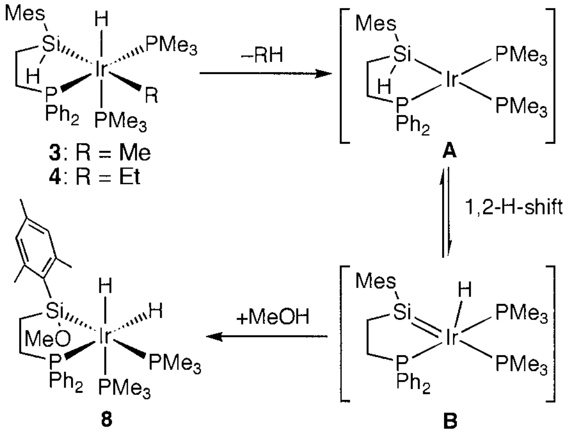
Scheme 1.

3.11. Thermal reactions of **3** or **4** with MeOH

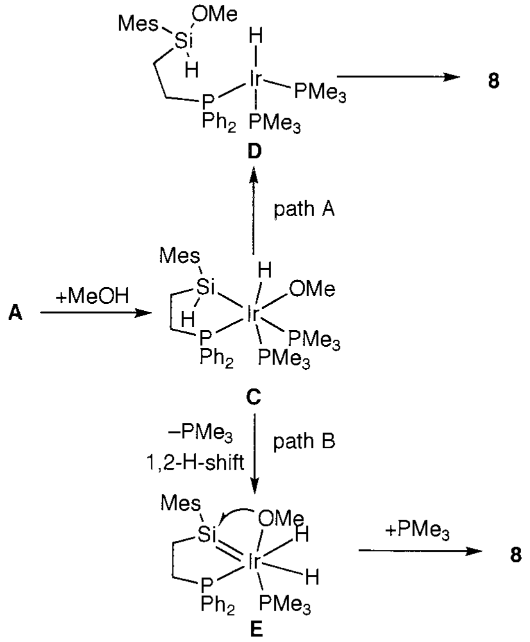
Complexes **3** and **4** reacted with MeOH at 60°C to give a dihydrido(methoxysilyl)iridium(III) complex $\mathrm{Ir(H)_2\{\eta^2\text{-}Mes(MeO)Si(CH_2)_2PPh_2\}(PMe_3)_2}$ (**8**) (Eq. (13)). The formation of the corresponding alkane was confirmed by ^{1}H NMR spectroscopy. The IR and NMR data clearly support the geometry depicted in Eq. (13). The IR spectrum shows a ν(Si–O) absorption at 1066 cm^{-1}. The ^{1}H NMR spectrum exhibits a singlet at 3.40 ppm assigned to SiOMe. The ^{31}P{^{1}H} NMR spectrum established that **8** has three phosphorus atoms in a *fac*-relationship. The ^{31}P resonance of the $\mathrm{PMe_3}$ ligand *trans* to the silyl moiety appears as a pseudo-triplet at -63.0 ppm coupled with two *cis* ^{31}P nuclei. The ^{29}Si{^{1}H} NMR spectrum contains a ddd at 46.2 ppm coupled with one *trans* ($J(\mathrm{SiP}_{trans}) = 146.2$ Hz) and two *cis* ^{31}P nuclei ($J(\mathrm{SiP}_{cis}) = 9.6$, 6.5 Hz). In the NOESY spectrum, the ^{1}H NMR signal of a SiOMe moiety correlates with the signal of a $\mathrm{PMe_3}$ ligand *trans* to IrH, which is consistent with the geometry in Eq. (13).

One possible mechanism for the formation of **8** is illustrated in Scheme 2. In this mechanism, it is assumed that the intermediate **A** is in quick equilibrium with a hydrido(silylene) complex **B** through the reversible 1,2-H-shift from the silyl silicon atom to the unsaturated iridium center of **A**. In the presence of MeOH, MeOH attacks the silylene silicon atom of **B** nucleophilically to afford a methoxysilyl iridium(III) complex **8**. MeOH is known to be an effective trapping agent for silylene complexes [26], since the M=Si bond is fairly polarized in the $\mathrm{M^{\delta-}Si^{\delta+}}$ fashion ([27,28]). Introduction of a methoxyl group to the silicon atom is likely to demonstrate the facile migration of a hydrogen from the silyl silicon atom to the iridium center.

An alternative mechanism involving the generation of a hydrido(methoxy)iridium(III) complex **C** could be considered as shown in Scheme 3. According to path A, intermediate **C** undergoes reductive elimination of the Si–OMe bond to give the chelate-ring-opened iridium(I) intermediate **D**. Subsequently, intramolecular Si–H oxidative addition takes place to give **8**. By path B, the intermediate **C** loses a $\mathrm{PMe_3}$ ligand and then undergoes a 1,2-H-shift to give a silylene species **E**. The intermediate **E** causes the migration of the methoxy ligand on the silylene silicon atom and the ligation of $\mathrm{PMe_3}$ to give **8**. Esteruelas et al. described the reaction of $\mathrm{Ir(H)(SiHPh_2)_2(CO)_2(PCy_3)}$ with ROH. They proposed a mechanism comprising the initial generation of $\mathrm{Ir(H)(OR)(SiHPh_2)(CO)_2}$ followed by the 1,2-H-shift to



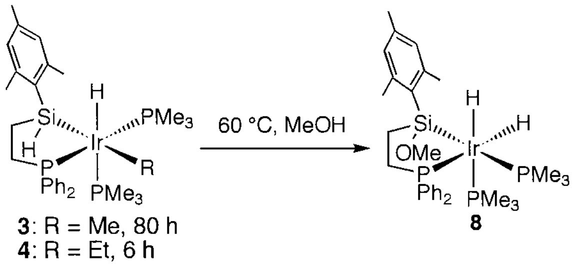
Scheme 2.



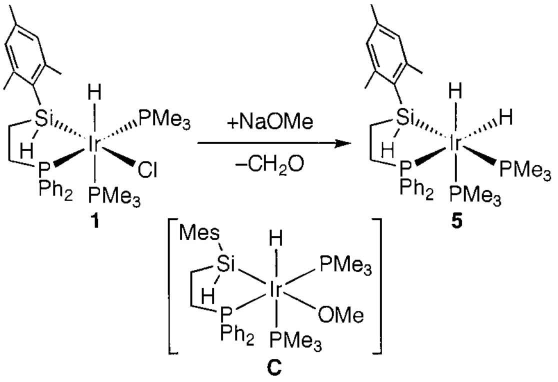
Scheme 3.

give a silylene intermediate $Ir(H)_2(OR)(=SiPh_2)(CO)_2$ as in path B [10].

To get information about the possibility of Scheme 3, we carried out the reaction of **1** with NaOMe. Transition-metal chloro complexes are known to give alkoxy complexes on addition of NaOR [29]. The reaction proceeded at room temperature to give a dihydrido iridium(III) complex **5** quantitatively (Eq. 14). Formaldehyde was detected by ^1H NMR spectroscopy. Hydrido–methoxy complexes are known to cause β-hydrogen elimination to give a dihydrido complex and formaldehyde [30]. In this reaction, the formation of **8** was not observed at all. Based on these observations we could rule out the mechanism involving the generation of a hydrido–methoxy iridium(III) complex.



(13)



(14)

A listing of additional bond distances, bond angles, thermal parameters, and tables of observed and calculated structure factors is available from the authors.

4. Conclusion

Thermolysis of alkyl(hydrido)(hydrosilyl)iridium(III) complexes $Ir(R)(H)\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ [R=Me (**3**), Et (**4**)] proceeded by reductive elimination of alkane to give the transient unsaturated silyliridium(I) complex $Ir\{\eta^2\text{-}MesHSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**A**). Reactive intermediate **A** activated the intramolecular carbon–hydrogen bond to give $Ir(H)(\eta^3\text{-}CH_2C_6H_2(CH_3)_2SiH(CH_2)_2PPh_2\}(PMe_3)_2$ (**6**). In the presence of MeOH, **A** reacted with MeOH to give a dihydrido(methoxysilyl)iridium(III) complex $Ir(H)_2\{\eta^2\text{-}Mes(MeO)Si(CH_2)_2PPh_2\}(PMe_3)_2$ (**8**). The latter observation clearly supports facile and reversible 1,2-migration of hydrogen on **A** from the silyl silicon atom to the unsaturated iridium center to give the hydrido(silylene) complex $Ir(H)\{\eta^2\text{-}MesSi(CH_2)_2PPh_2\}(PMe_3)_2$ (**B**) under relatively mild conditions.

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