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Synthesis and Characterization of *fac*-Tris(trimethylphosphino)iridium(III) Silane Complexes[†]

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The synthesis and characterization of iridium(III) silyl complexes of the form $IrHX(PMe_3)_3SiRR'_2$ (X = H or D; R = H, D, Cl, or Ph; R′ = Ph or *t*-Bu) are described. The complexes are prepared by the oxidative addition of $SiXRR'_2$ to $IrH(PMe_3)_4$ with the loss of PMe_3. Three of the complexes have been characterized by single-crystal X-ray diffraction techniques: $IrH_2(PMe_3)_3(SiHPh_2)$, triclinic, space group $P\bar{1}$, $a = 9.793(2)$ Å, $b = 16.385(2)$ Å, $c = 16.807(4)$ Å, $\alpha = 88.32(2)^\circ$, $\beta = 99.70(2)^\circ$, $\gamma = 94.72(2)^\circ$, $V = 2649.0(10)$ Å^3, $Z = 4$; $IrH_2(PMe_3)_3(SiCl(t\text{-}Bu)_2)$, orthorhombic, space group $Pbca$, $a = 18.519(3)$ Å, $b = 15.264(2)$ Å, $c = 18.982(3)$ Å, $V = 5635.6(15)$ Å^3, $Z = 8$; and $IrH_2(PMe_3)_3(SiPh_3)$, $C2/c$, $a = 34.011(7)$ Å, $b = 9.779(2)$ Å, $c = 18.733(4)$ Å, $\beta = 105.46(3)^\circ$, $V = 5998(2)$ Å^3, $Z = 8$. Refinement to convergence gave the conventional and weighted agreement factors $R = 0.038$ and $R_w = 0.042$, $R = 0.037$ and $R_w = 0.040$, and $R = 0.061$ and $R_w = 0.075$ for each structure, respectively.

Introduction

The oxidative addition of silyl hydrides to transition-metal centers is a step in catalytic cycles such as hydrosilylation,[1] dehydrogenative coupling of silanes,[2] alkyl redistribution reactions of silanes,[3] and silylene transfer reactions[4] by the late transition metals and is a major route for the formation of metal–silicon bonds.[5] Iridium silyl complexes of general formula $IrX(Y)(SiR_3)(PMe_3)_3$ are of recent interest because they can be formed by the oxidative addition of a silyl chloride[6] or can oxidatively add to carbon hydrogen bonds.[7] As part of an ongoing study of the interaction of transition metals with silanes, we report the reactions of silanes, most of which contain two reactive substituents, with $IrH(PMe_3)_4$ to form iridium–silyl complexes.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques[8] with greaseless glassware. $IrCl_3{\cdot}3H_2O$ was purchased from Johnson Matthey. Trichlorosilane, triphenylchlorosilane, diphenyldichlorosilane, and di-*tert*-butyldichlorosilane were obtained from Hüls America and were degassed before using. Di-*tert*-butylchlorosilane was synthesized from trichlorosilane and *tert*-butyllithium (Aldrich).[9] The dihydridosilanes di-*tert*-butylsilane and diphenylsilane or the corresponding deuterides were produced by treating the dichlorosilanes with a slight excess of either lithium aluminum hydride or lithium aluminum deuteride.[9,10] The silyl hydrides were characterized by the Si–H stretches in their IR spectra, and the silyl deuterides were characterized by the absence of the Si–H stretch and the presence of an Si–D stretch at 1548 cm^{-1} for Ph_2SiD_2 ($\bar{\nu}$(Si–H)/$\bar{\nu}$(Si–D) = 1.382) and 1532 cm^{-1} for $(t\text{-}Bu)_2SiD_2$ ($\bar{\nu}$(Si–H)/$\bar{\nu}$(Si–D) = 1.380). (See Table 2.) All solvents were freshly distilled under nitrogen from sodium and benzophenone. The NMR samples were dissolved in deuterated solvents under inert atmosphere conditions. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 200 MHz. The ^1H spectra were referenced to the residual proton resonance of the solvent; the ^{13}C spectra were referenced to the ^{13}C resonance of the solvent; and the ^{31}P spectra were referenced to external 85% H_3PO_4, such that shifts to higher frequencies relative to the reference are taken as positive. The ^{29}Si NMR spectra were obtained at 300 MHz using the DEPT pulse sequence[11] and were referenced to external TMS. The mass spectra were obtained from B.F. Goodrich using the field desorption (FD-MS) mode. Elemental

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Table 1. ^{1}H NMR Resonance Frequencies for Complexes 1–4[a]

compd	δ(Ir–H)	δ(Si–H)	δ(*cis*-P(CH$_3$)$_3$)[b]	δ(*trans*-P(CH$_3$)$_3$)[c]	δ(C$_6$H$_5$)	δ(C(CH$_3$)$_3$)
1	−12.12 (dd, 92.6 Hz, 17.6 Hz)	5.51 (q, 8.5 Hz)	1.19 (d, 7.1 Hz)	1.29 (d, 7.2 Hz)	8.29 (d, 7.9 Hz), 7.29 (t, 7.2 Hz), 7.12 (d, 7.4 Hz)	
1(D)	−12.10 (dt, 111.6 Hz, 19.5 Hz)		1.17 (d, 7.2 Hz)	1.28 (d, 7.4 Hz)	8.29 (d, 8.0 Hz), 7.29 (t, 7.2 Hz), 7.13 (d, 7.4 Hz)	
2	−13.06 (dd, 92.6 Hz, 16.4 Hz)	4.50 (q, 9.0 Hz)	1.37 (d, 6.9 Hz)	1.24 (d, 7.2 Hz)		1.53 (s)
2(D)	−13.03 (dt, 116.3 Hz, 21.1 Hz)		1.33 (d, 7.0 Hz)	1.25 (d, 7.3 Hz)		1.53 (s)
3	−13.16 (dd, 89.6 Hz, 16.2 Hz)		1.33 (d, 7.3 Hz)	1.15 (d, 7.7 Hz)		1.50 (s)
4	−12.16 (dd, 91.6 Hz, 18.7 Hz)		1.04 (d, 7.3 Hz)	1.32 (d, 7.6 Hz)	8.10 (d, 7.6 Hz), 7.28 (t, 7.2 Hz), 7.19 (d)[d]	

[a] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets. All spectra were run in C$_6$D$_6$. [b] Signal for the protons bound to the two trimethylphosphine ligands *cis* to the silyl ligand. [c] Signal for the protons bound to the trimethylphosphine ligand *trans* to the silyl ligand. [d] Coupling constant unavailable due to interference from the solvent.

Table 2. IR Data for Complexes 1–4

compd	$\bar{\nu}$(Ir–H) (cm^{-1})	$\bar{\nu}$(Si–H) (cm^{-1})	$\bar{\nu}$(Ir–D) or $\bar{\nu}$(Si–D) (cm^{-1})
1	2002 (s) 2042 (s)	2018 (s)	
1(D)	2000 (m) 2042 (m)		1439 (m)
2	2006 (s) 2172 (w, br)	1952 (s)	
2(D)	2005 (m) 2170 (w, br)		1420 (s)
3	2031 (s) 2105 (s)		
4	2055 (m) 2065 (m)		
SiH$_2$(Ph)$_2$		2139 (vs)	
SiD$_2$(Ph)$_2$			1548 (vs)
SiH$_2$(*t*-Bu)$_2$		2114 (vs)	
SiD$_2$(*t*-Bu)$_2$			1532 (s), 1545 (s)[a]
SiH(Ph)$_3$		2110 (s)	
SiHCl(*t*-Bu)$_2$		2136 (s)	

[a] The peaks are nearly indistinguishable.

analyses were performed by either Schwarzkopf Microanalytical Laboratory or Oneida Research Services, Inc., with the aid of a combustion catalyst. Uncorrected melting points were recorded in capillaries sealed under argon unless otherwise stated.

Synthesis of the Iridium Complexes. The complex IrH(PMe$_3$)$_4$ was synthesized from IrCl(PMe$_3$)$_4$.[12] The complex IrCl(PMe$_3$)$_4$ was prepared[13] from [Ir(C$_8$H$_{14}$)Cl]$_2$, which in turn was prepared[14] from IrCl$_3$·3H$_2$O. The products **1–4** were moderately air-stable in the solid state, but were unstable as solutions in air. The ^{1}H NMR and infrared data for compounds **1–4** are given in Tables 1 and 2, respectively.

Synthesis of IrH$_2$(PMe$_3$)$_3$SiHPh$_2$, 1. To a stirred solution of IrH(PMe$_3$)$_4$ (0.41 g, 0.82 mmol) in toluene (12 mL) was added SiH$_2$Ph$_2$ (0.25 mL, 1.35 mmol), dropwise via syringe. A vigorous reaction immediately took place. The reaction was stirred at room temperature for 48 h, during which the original brown solution lightened to a yellow orange color. The solvent was removed under vacuum, and the resulting solid was washed with 2 mL of hexane. The yield was 87%. Colorless crystals suitable for X-ray analysis were obtained upon recrystallization from benzene. Anal. Calcd for IrP$_3$SiC$_{21}$H$_{40}$: C, 41.64; H, 6.66. Found: C, 41.79; H, 6.56. ^{13}C[^{1}H] (C$_6$D$_6$): 137.4, 128.8, 127.8, 127.2 (s, SiPh); 27.5 (d of t, 26 Hz, 4 Hz, 1P(CH$_3$)$_3$); 23.8 (t of d, 16 Hz, 5 Hz, 2P(CH$_3$)$_3$). ^{31}P[^{1}H] (C$_6$D$_6$): −60.9 (d, 21 Hz, 2P); −62.3 (t, 22 Hz, 1P). ^{29}Si (DEPT, C$_6$D$_6$): −0.323 (d of t, 128 Hz, 10 Hz).

Synthesis of IrHD(PMe$_3$)$_3$SiDPh$_2$, 1(D). To a stirred solution of IrH(PMe$_3$)$_4$ (0.33g, 0.67 mmol) in toluene (10 mL) was added SiD$_2$Ph$_2$ (0.13 mL, 0.70 mmol), dropwise via syringe. A vigorous reaction immediately took place, and the solution lightened to a yellow color. The reaction was stirred at room temperature for 5 days. The solution was then reduced to half its original volume under vacuum, causing the precipitation of the colorless crystals of **1(D)**. The solution was filtered, and the solid **1(D)** was washed with 2 mL of hexane: mp (in air) 178–180 °C. Anal. Calcd for IrP$_3$SiC$_{21}$H$_{38}$D$_2$: C, 41.50; H, 6.96; P, 15.29. Found: C, 42.00; H, 6.64; P, 15.69 (where D = H for anal. calcd). ^{13}C[^{1}H] (C$_6$D$_6$) d 137.4 (one obscured), 127.7, 127.2 (s, SiPh); 27.5 (pseudo d of t, 26 Hz, 4 Hz, 1P(CH$_3$)$_3$); 23.7 (pseudo t of d, 14 Hz, 4 Hz, 2P(CH$_3$)$_3$). ^{31}P[^{1}H] (C$_6$H$_6$ with 15% C$_6$D$_6$): −60.4 (pseudo d, 21 Hz, 2P); −61.5 (pseudo t, 22 Hz, 1P).

Synthesis of IrH$_2$(PMe$_3$)$_3$SiH(*t*-Bu)$_2$, 2. To a stirred solution of IrH(PMe$_3$)$_4$ (0.51 g, 1.02 mmol) in toluene (12 mL) was added SiH$_2$(*t*-Bu)$_2$ (0.25 mL, 1.26 mmol), dropwise via syringe. After 48 h, half of the solvent was removed under vacuum and the flask immersed in a −78 °C bath for 24 h. The resulting colorless solid **2** was filtered from the solution and was washed with hexanes (2 mL). The yield was 71%. ^{13}C[^{1}H] (C$_6$H$_6$): 34.0 (s, *C*(CH$_3$)$_3$); 29.5 (C(*C*H$_3$)$_3$); 27.5 (d of t, 26 Hz, 4 Hz, 1P(CH$_3$)$_3$); 23.8 (t of d, 16 Hz, 6 Hz, 2P(CH$_3$)$_3$). ^{29}Si (DEPT, C$_6$D$_6$): 23.7 (d of t, 126 Hz, 9 Hz).

Synthesis of IrHD(PMe$_3$)$_3$SiD(*t*-Bu)$_2$, 2(D). This complex was prepared from SiD$_2$(*t*-Bu)$_2$ (0.07 mL, 0.33 mmol) and IrH(PMe$_3$)$_4$ (0.16 g, 0.32 mmol) in toluene (5 mL) using the same procedure as for **2**, except for a reaction time of 3 days. The yield was 44%; mp 163–164 °C. Anal. Calcd for IrP$_3$SiC$_{17}$H$_{46}$D$_2$: C, 35.96; H, 8.87; P, 16.37 (where D = H for anal. calcd). Found: C, 35.86; H, 8.25; P, 17.88. ^{13}C[^{1}H] (C$_6$D$_6$): 33.4 (pseudo s that contains both *C*(CH$_3$)$_3$ and C(*C*H$_3$)$_3$); 27.2 (pseudo d, 24 Hz, 1P(CH$_3$)$_3$); 24.7 (pseudo d, 28 Hz, 2P(CH$_3$)$_3$). ^{31}P[^{1}H] (C$_6$D$_6$): −62.0 (pseudo d (shows minor additional splittings), 18 Hz, 2P); −63.3 (pseudo t, 16 Hz, 1P). FD-MS: calcd *m/z* for (^{193}IrP$_3$SiC$_{17}$H$_{46}$D$_2$)(M$^+$) 568, found 568; calcd *m/z* for (^{191}IrP$_3$SiC$_{17}$H$_{46}$D$_2$)(M$^+$) 566, found 566.

Synthesis of IrH$_2$(PMe$_3$)$_3$SiCl(*t*-Bu)$_2$, 3. The dropwise addition of SiHCl(*t*-Bu)$_2$ (0.09 mL, 0.45 mmol) to a stirred solution of IrH(PMe$_3$)$_4$ (0.22 g, 0.45 mmol) in toluene (2 mL) caused the precipitation of a fine colorless powder. After 3 days, the suspension was filtered and the solid **4** was dried under vacuum. Complex **4** was washed with cold hexanes (2 × 2 mL). The yield was 71%. Anal. Calcd for IrClP$_3$SiC$_{17}$H$_{47}$: C, 34.02; H, 7.89. Found: C, 33.74; H, 7.71. ^{13}C[^{1}H] (C$_6$D$_6$): 51.5 (pseudo s, 3P(CH$_3$)$_3$); 44.7 (s, *C*(CH$_3$)$_3$); 39.2 (s, C(*C*H$_3$)$_3$). ^{31}P[^{1}H] (CDCl$_3$): −61.4 (d, 16 Hz, 2P); −63.8 (t, 16 Hz, 1P).

Synthesis of IrH$_2$(PMe$_3$)$_3$SiPh$_3$, 4. To a stirred solution of IrH(PMe$_3$)$_4$ (0.10 g, 0.20 mmol) in toluene (1 mL) was added SiHPh$_3$ (0.05 g, 0.20 mmol). A vigorous reaction took place followed by the precipitation of colorless crystals. The mixture was filtered and allowed to sit overnight, causing a second crop of crystals to form. The total yield was 81%. The solvent was removed under vacuum, and the product **4** was recrystallized from toluene, yielding crystals which were

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Table 3. Summary of Crystallographic Data for 1, 3, and 4

	1	3	4
formula	$IrP_3SiC_{21}H_{40}$	$IrClP_3SiC_{17}H_{47}$	$IrP_3SiC_{27}H_{44}$
formula wt, amu	605.76	600.23	681.80
crystal syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)	*C2/c* (No. 15)
a, Å	9.793(2)	18.519(3)	34.011(7)
b, Å	16.385(2)	15.264(2)	9.779(2)
c, Å	16.807(4)	18.982(3)	18.733(4)
α, deg	88.32(2)	90	90
β, deg	99.70(2)	90	105.46(3)
γ, deg	94.72(2)	90	90
V, $Å^3$	2649.(1)	5636(2)	5998(2)
Z	4	8	8
ϱ(calcd), g cm^{-1}	1.52	1.49	1.51
cryst dimens, mm^3	0.1 × 0.3 × 0.3	0.2 × 0.2 × 0.4	0.2 × 0.3 × 0.3
diffractometer	Syntex $P2_1$	Syntex $P2_1$	Syntex $P2_1$
radiation	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
temp, K	296	296	130
scan type	$2\theta-\theta$	$2\theta-\theta$	ω
2θ scan limits, deg	3.0−50.0	3.0−50.0	3.5−50.0
linear abs coeff, cm^{-1}	52.51	52.81	46.44
total no. of rflns scanned	103 17 (322 stds)	5446 (165 stds)	5580 (173 stds)
unique rflns	8901	4048	3950
final no. of variables	469	208	289
goodness of fit	1.1879	1.1164	0.98
R(*F*)	0.038 ($F_o^2 \geq 3\sigma(F_o^2)$)	0.037 ($F_o^2 \geq 3\sigma(F_o^2)$)	0.061 ($F_o \geq 4\sigma(F_o)$)
$R_w(F)$	0.042 ($F_o^2 \geq 3\sigma(F_o^2)$)	0.040 ($F_o^2 \geq 3\sigma(F_o^2)$)	0.075 ($F_o \geq 4\sigma(F_o)$

suitable for X-ray analysis. Anal. Calcd for $IrP_3SiC_{27}H_{44}$: C, 47.56; H, 6.50. Found: C, 47.63; H, 6.32. $^{31}P[^1H]$ (C_6D_6): −58.8 (pseudo s, 2P); −61.4 (pseudo t, 1P). ^{29}Si (DEPT, C_6D_6): 0.094 (d of t, 134 Hz, 8 Hz).

X-ray Structures for Compounds 1, 3, and 4. A colorless single crystal of each compound was chosen for examination by X-ray diffraction methods. The dimensions of the crystals were as follows: **1**, 0.1 × 0.3 × 0.3 mm^3; **3**, 0.2 × 0.2 × 0.4 mm^3; and **4**, 0.2 × 0.3 × 0.3 mm^3. Each crystal was mounted on the end of a thin glass fiber in air. Diffraction measurements were performed on a Syntex $P2_1$ automated four-circle diffractometer at room temperature for **1** and **3** and at 130 K for **4**. Compound **1** is triclinic, and no systematic absences were observed, suggesting the space group $P\bar{1}$. Compound **3** is orthorhombic with systematic absences ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) indicating the centrosymmetric space group *Pbca*. Compound **4** is monoclinic with systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) indicating the space group *C*2/*c* with one molecule per asymmetric unit, or the space group *Cc* with two molecules per asymmetric unit. The structure refined satisfactorily in the space group *C*2/*c*. Data were corrected for Lorentz and polarization factors and reduced to [F_o] values. Details relevant to data collection and refinement appear in Table 3.

The analytical form of the scattering factors for neutral iridium, chlorine, phosphorus, silicon, and carbon was used throughout the analyses,[15a] and the contributions of all non-hydrogen atoms were corrected for both real (Df') and imaginary (Df'') components of anomolous dispersion.[15b] Structures **1**, **3**, and **4** were solved by direct methods.[16] The remaining atoms were located via a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. The unit cells of **1**, **3**, and **4** contain two, one, and one molecules per asymmetric unit, respectively. For all three complexes, all hydrogen atoms, except those bound to iridium or silicon, whose approximate positions could be obtained from the electron density maps were placed in idealized positions. The remaining hydrogen atoms were included by calculation (based upon C−H = 0.95 Å, tetrahedral or trigonal angles, and idealized thermal parameters with B = 1.0 $Å^2$ greater than those of the carbon atom to which they are attached).[17] The hydrogen atoms bound to iridium or silicon were selected from among the highest maxima surrounding the metal and the silicon atoms in the final difference-Fourier syntheses, and their existence is consistent with the ^1H NMR and IR data as well as the coordination of the iridium and silicon atoms. In **4** the hydrogen atoms on iridium were not located. Numerical absorption corrections were performed for all the structures of **1** and **3** and were based on the indexed and measured faces of each crystal and the contents of each unit cell. An empirical absorption correction was performed on the structure of **4**. Refinement for **1** and **3** was based on F^2 and included reflections with $F_o^2 \geq 3(F_o^2)$. Refinement for **4** was based on F and included reflections with $F_o > 4(F_o)$. Full-matrix least-squares refinement of positional and anisotropic thermal parameters of **1** and **3** for all non-hydrogen atoms led to final convergence with R = 0.038, R_w = 0.042, and GOF = 1.19 for 469 variables and 8901 reflections for **1**; R = 0.037, R_w = 0.040, and GOF = 1.16 for 208 variables and 4272 reflections for **3**; and R = 0.061, R_w = 0.075, and GOF = 0.98 for 289 variables and 5288 reflections for **4**. Positional parameters for the structures of **1**, **3**, and **4** are provided in Tables 4, 5, and 6, respectively.

Results and Discussion

The reactions of several phenyl- or *tert*-butylsilanes with $IrH(PMe_3)_4$ proceed at room temperature and produce the complexes **1**−**4** in high yield (eq 1). In each case the net reaction involves the loss of a trimethylphosphine ligand from the iridium reagent and oxidative addition of a Si−H (or Si−D) bond to the iridium, leading to the formation of Ir−Si and Ir−H (or Ir−D) bonds. As expected, preferential oxidative addition of Si−H instead of Si−Cl to the iridium center occurred in the case of $(t\text{-Bu})_2SiHCl$ to give **3**. Interestingly, an

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Table 4. Positional Parameters for the Non-Hydrogen Atoms of $IrH_2(PMe_3)_3(SiHPh_2)$ (1)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ir(1)	0.80250(4)	0.74430(2)	0.58140(2)
Ir(2)	0.82810(4)	0.74014(2)	0.09079(2)
P(1)	0.9740(3)	0.7981(2)	0.5117(1)
P(2)	0.7248(3)	0.8654(2)	0.6177(2)
P(3)	0.6289(3)	0.7052(2)	0.4755(2)
P(4)	0.8921(3)	0.7201(2)	−0.0321(2)
P(5)	0.7846(3)	0.6054(2)	0.1309(2)
P(6)	0.6043(3)	0.7760(2)	0.0456(2)
Si(1)	0.9021(3)	0.6172(2)	0.5978(1)
Si(2)	0.9326(3)	0.8758(2)	0.1021(2)
C(1)	1.0919(9)	0.6230(5)	0.6511(5)
C(2)	1.1299(10)	0.6606(6)	0.7262(6)
C(3)	1.2671(11)	0.6669(7)	0.7636(6)
C(4)	1.3683(11)	0.6363(7)	0.7300(7)
C(5)	1.3344(11)	0.5972(7)	0.6570(7)
C(6)	1.1958(9)	0.5903(6)	0.6188(5)
C(7)	0.8175(9)	0.5312(5)	0.6560(5)
C(8)	0.7204(11)	0.5409(6)	0.7047(6)
C(9)	0.6682(12)	0.4756(7)	0.7493(7)
C(10)	0.7125(12)	0.4001(7)	0.7438(6)
C(11)	0.8040(13)	0.3878(7)	0.6923(7)
C(12)	0.8567(11)	0.4517(6)	0.6499(6)
C(13)	1.1429(11)	0.8293(8)	0.5751(7)
C(14)	1.0359(11)	0.7314(7)	0.4408(6)
C(15)	0.9434(12)	0.8887(7)	0.4479(7)
C(16)	0.8566(12)	0.9335(7)	0.6793(7)
C(17)	0.5913(11)	0.8530(7)	0.6822(7)
C(18)	0.6447(14)	0.9383(7)	0.5427(7)
C(19)	0.6072(13)	0.5969(7)	0.4522(8)
C(20)	0.4546(12)	0.7217(9)	0.4893(7)
C(21)	0.6285(12)	0.7506(7)	0.3750(6)
C(22)	1.1156(9)	0.8877(5)	0.1631(5)
C(23)	1.1543(10)	0.8420(6)	0.2335(6)
C(24)	1.2847(13)	0.8548(7)	0.2787(7)
C(25)	1.3824(11)	0.9108(8)	0.2537(7)
C(26)	1.3493(12)	0.9533(7)	0.1833(7)
C(27)	1.2175(11)	0.9418(6)	0.1367(6)
C(28)	0.8458(9)	0.9553(6)	0.1511(5)
C(29)	0.7965(11)	0.9438(6)	0.2241(6)
C(30)	0.7426(11)	1.0025(7)	0.2616(6)
C(31)	0.7286(11)	1.0800(7)	0.2260(7)
C(32)	0.7762(13)	1.0938(7)	0.1550(7)
C(33)	0.8346(11)	1.0329(7)	0.1180(6)
C(34)	1.0773(14)	0.7183(10)	−0.0276(9)
C(35)	0.8290(15)	0.6264(9)	−0.0881(7)
C(36)	0.8549(15)	0.7975(8)	−0.1116(6)
C(37)	0.6318(14)	0.5403(7)	0.0848(8)
C(38)	0.7707(15)	0.5947(7)	0.2377(6)
C(39)	0.9201(14)	0.5362(7)	0.1257(8)
C(40)	0.4921(13)	0.7619(8)	0.1215(8)
C(41)	0.5776(13)	0.8821(8)	0.0089(8)
C(42)	0.4994(11)	0.7195(9)	−0.0380(7)

iridium reagent similar to the one in this study, $IrCl(PMe_3)_3(C_8H_{14})$, was found to oxidatively add to the Si−Cl bond of $MeSiCl_3$ at room temperature in 90% yield.[6] The complexes **1**−**4** are moderately air-stable solids, but in solution they are air-sensitive. Recently the rhodium analog of **4** was reported.[18]

$$\mathrm{HIr(PMe_3)_4} + \mathrm{XSiRR'_2} \xrightarrow{-\mathrm{PMe_3}} \mathrm{IrH(X)(SiRR'_2)(PMe_3)_3} \qquad (1)$$

X = H or D

1: X = R = H, R′ = Ph
1(D): X = R = D, R′ = Ph
2: X = R = H, R′ = *t*-Bu
2(D): X = R = D, R′ = *t*-Bu
3: X = H, R = Cl, R′ = *t*-Bu
4: X = H, R = R′ = Ph

Table 5. Positional Parameters for the Non-Hydrogen Atoms of $IrH_2(PMe_3)_3(SiCl(t\text{-}Bu)_2)$ (3)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ir(1)	0.94772(2)	0.21924(3)	0.58867(2)
Cl(1)	1.1408(2)	0.2299(2)	0.5286(2)
P(1)	0.8731(2)	0.3281(2)	0.6339(2)
P(2)	0.8731(2)	0.1089(2)	0.5817(2)
P(3)	0.9477(2)	0.2668(2)	0.4723(2)
Si(1)	1.0709(1)	0.2440(2)	0.6207(2)
C(1)	1.1059(6)	0.3569(8)	0.6552(7)
C(2)	1.0640(7)	0.3855(10)	0.7217(8)
C(3)	1.0963(8)	0.4237(8)	0.5979(8)
C(4)	1.1874(7)	0.3602(9)	0.6748(8)
C(5)	1.1110(7)	0.1500(9)	0.6786(7)
C(6)	1.0837(9)	0.0597(9)	0.6550(9)
C(7)	1.0890(9)	0.1607(10)	0.7568(7)
C(8)	1.1949(7)	0.1433(11)	0.6752(9)
C(9)	0.7762(6)	0.3237(9)	0.6099(7)
C(10)	0.8619(7)	0.3294(11)	0.7288(6)
C(11)	0.8899(7)	0.4452(9)	0.6147(9)
C(12)	0.9013(7)	0.0013(8)	0.5702(8)
C(13)	0.7894(7)	0.1049(10)	0.5160(9)
C(14)	0.8104(9)	0.0903(11)	0.6638(9)
C(15)	0.8613(7)	0.3009(10)	0.4341(7)
C(16)	1.0031(7)	0.3594(9)	0.4444(7)
C(17)	0.9788(8)	0.1836(10)	0.4099(7)

Table 6. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non−Hydrogen Atoms of $IrH_2(PMe_3)_3(SiPh_3)$ (4)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Ir(1)	0.3708(1)	0.3079(1)	0.0795(1)	0.026(1)
Si(1)	0.3587(1)	0.1861(4)	−0.0345(2)	0.028(1)
P(1)	0.3436(1)	0.4490(4)	0.1539(2)	0.035(1)
P(2)	0.3977(1)	0.1320(5)	0.1615(2)	0.037(1)
P(3)	0.4314(1)	0.4174(5)	0.0827(2)	0.038(1)
C(1)	0.3154(4)	0.2595(14)	−0.1107(8)	0.024(5)
C(2)	0.2894(5)	0.359(2)	−0.1004(10)	0.053(7)
C(3)	0.2557(5)	0.4026(18)	−0.1582(9)	0.047(6)
C(4)	0.2485(6)	0.3483(18)	−0.2279(10)	0.050(7)
C(5)	0.2746(5)	0.2474(18)	−0.2413(9)	0.043(6)
C(6)	0.3061(5)	0.2051(17)	−0.1843(8)	0.036(5)
C(7)	0.3402(5)	0.0002(17)	−0.0358(8)	0.040(6)
C(8)	0.3134(5)	−0.0332(16)	0.0072(9)	0.042(6)
C(9)	0.2962(6)	−0.1629(18)	0.0072(11)	0.052(7)
C(10)	0.3069(6)	−0.2645(19)	−0.0381(10)	0.055(7)
C(11)	0.3320(7)	−0.2325(17)	−0.0813(10)	0.055(8)
C(12)	0.3489(5)	−0.1046(17)	−0.0799(9)	0.045(6)
C(13)	0.4023(5)	0.1758(17)	−0.0807(8)	0.038(6)
C(14)	0.4084(5)	0.2734(15)	−0.1296(9)	0.039(6)
C(15)	0.4421(5)	0.2753(18)	−0.1561(9)	0.045(7)
C(16)	0.4709(5)	0.171(2)	−0.1384(11)	0.054(8)
C(17)	0.4659(5)	0.071(2)	−0.0902(10)	0.051(7)
C(18)	0.4329(5)	0.0712(19)	−0.0631(8)	0.043(6)
C(19)	0.3471(6)	0.417(2)	0.2517(9)	0.057(8)
C(20)	0.2880(5)	0.457(2)	0.1195(11)	0.059(7)
C(21)	0.3557(6)	0.6305(19)	0.1582(10)	0.049(7)
C(22)	0.4225(6)	−0.0130(19)	0.1305(11)	0.059(8)
C(23)	0.4376(6)	0.182(2)	0.2462(11)	0.071(7)
C(24)	0.3626(5)	0.0371(19)	0.2016(9)	0.049(7)
C(25)	0.4278(7)	0.547(2)	0.0132(11)	0.068(9)
C(26)	0.4756(5)	0.3209(19)	0.0750(10)	0.048(6)
C(27)	0.4562(5)	0.517(3)	0.1645(11)	0.071(9)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The different possible isomers that could be formed from the reaction of $IrH(PMe_3)_4$ and $XSiRR'_2$ (X = H or D) are shown in Scheme 1. Scheme 1 was formulated on the basis of accepted mechanisms[19] of *cis* addition to the 16-electron square planar Ir(I) intermediate $HIr(PMe_3)_3$. Loss of a PMe_3 ligand from $IrH(PMe_3)_4$ would result in the formation of such an intermediate. The Si−H (or Si−D) bond of the silane could oxidatively

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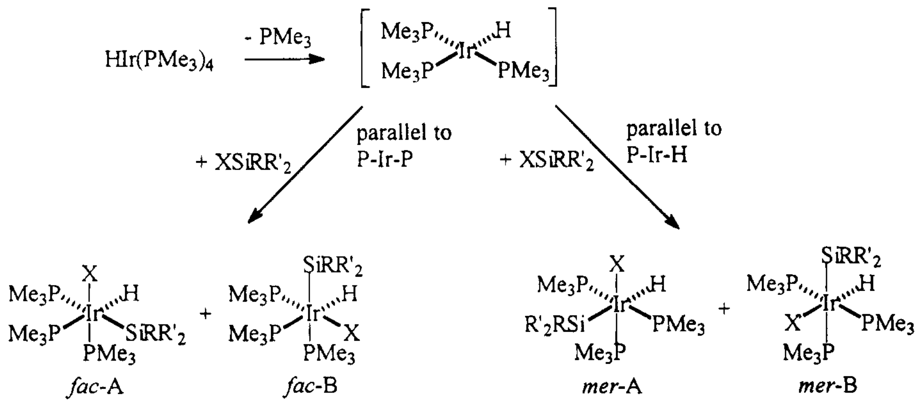
Scheme 1



add to the planar intermediate either parallel to the P–Ir–P axis or parallel to the P–Ir–H axis. Addition parallel to the P–Ir–P axis would give two *fac* isomers which are mirror images of each other and therefore indistinguishable by NMR spectroscopy. In both *fac* isomers the H and X substituents occupy *cis* positions. Addition parallel to the P–Ir–H axis would give two *mer* isomers which are not mirror images of each other. In only one of the two *mer* isomers (*mer*-A) are the H and X substituents found in *cis* positions.

The ^{1}H NMR spectra of **1**–**4** are listed in Table 1. All complexes show a similar pattern for the protons of the PMe_3 ligands with a resonance for two equivalent (or nearly equivalent in **1(D)** and **2(D)**) phosphine ligands and a seperate resonance for the third phosphine, in the range 1.04–1.37 ppm with the appropriate integrations. Each ^{1}H NMR signal for the methylphosphines is split into a doublet, $^1J(PH) = 6.9–7.7$ Hz, by the phosphorus to which it is attached. The ^{1}H NMR signal of the phosphines is only consistent with the facial isomers. Two trimethylphosphine ligands situated in a *trans* orientation as in the meridional isomers would give rise to a pseudo triplet/doublet pattern.[20,21] The silicon hydride resonances of complexes **1** and **2** are quartets with overlapping splittings from the phosphorus atoms, in the appropriate regions of the ^{1}H NMR spectra (4.50–5.51 ppm). The iridium hydride signals are observed as multiplets with a chemical shift range of −12.01 to −13.16 ppm.[22] The iridium hydride resonances for the undeuterated **1**–**4** exhibit second-order behavior because they are chemically equivalent but magnetically inequivalent with respect to the phosphine ligands. The iridium hydride signal for each undeuterated compound is an apparent doublet of doublets, showing two very different couplings to phosphorus atoms ($^2J(PH) = 16–18$ and 90–92 Hz). On the basis of similarities with the spectra of related iridium hydride complexes, the smaller $^2J(PH)$ is assigned to coupling to *cis* phosphines and the larger to coupling to *trans* phosphines.[6,7,19,23] The Ir–H signal of the complexes containing only one iridium hydride, **1(D)** and **2(D)**, appears as the expected doublet of triplets showing two very different couplings to phosphorus atoms ($^2J(PH_{cis}) = 20–23$ Hz and $^2J(PH_{trans}) = 100–116$ Hz) and unresolved deuterium splittings.

Other NMR spectra of **1**–**4** were obtained. The ^{31}P-[^{1}H] NMR spectra of **1**, **1(D)**, **2(D)**, and **3** all show the presence of two different types of phosphine ligands, one of which is split into a doublet by one phosphorus atom and the other of which is split into a triplet by two equivalent phosphorus atoms. Apparently in **1(D)** and **2(D)** two of the three inequivalent phosphines of the *fac* isomers are in almost identical environments. The DEPT ^{29}Si NMR spectra of compounds **1**, **2**, and **4** were obtained. The ^{29}Si signals are observed in the range 0–24 ppm, each as a doublet of doublets due to splitting from *trans* ($^2J(PSi_{trans}) = 126–128$ Hz) and *cis* ($^2J(PSi_{cis}) = 8–10$ Hz) phosphine ligands. No evidence for agostic Ir–H–Si interactions, in the form of a significant silicon–hydrogen coupling in the range of 20–136 Hz,[24] is observed. The solution ^{13}C[^{1}H] NMR spectra for the compounds **1**–**4** show the expected resonances and splitting patterns and are consistent with the other NMR results. There was no evidence for fluxional behavior or slow interconversions between species at room temperature.

The infrared stretching frequencies of the Ir–H and the Si–H bands for the solid state samples (Nujol mulls) of **1**–**4** are summarized in Table 2. Because the Ir–H and Si–H bands occur at similar regions of the IR spectrum,[25] assignments of the Si–H bands for complexes **1** and **2** have been positively made by synthesizing their deuterated analogs **1(D)** and **2(D)** and comparing their spectra. The band that disappears from the 2200–1950 cm^{-1} region of the spectrum of **1** and **2** on deuteration is assigned to the Si–H stretch. In each case a new band appears with approximately $(1/\sqrt{2})(\bar{\nu}(\text{Si–H}))$ of **1** and **2** in the spectrum of **1(D)** and **2(D)**, respectively. This new band is thought to be the Si–D stretch, but it could also be the Ir–D stretch as at least one band is expected for each. The presence of unrelated signals in the region, however, does not allow for more precise assignments. On the basis of the deuteration studies, two Ir–H stretches are assigned

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Table 7. Selected Bonding Parameters for $IrH_2(PMe_3)_3(SiHPh_2)$ (1)

Bond Lengths (Å)			
Ir(1)−Si(1)	2.361(3)	Si(1)−C(7)	1.905(9)
Ir(2)−Si(2)	2.369(3)	Si(2)−C(22)	1.907(9)
Si(1)−H(c)	1.184	Si(2)−C(28)	1.891(10)
Si(2)−H(f)	1.219	Ir(1)−P(1)	2.308(3)
Ir(1)−H(a)	1.218	Ir(1)−P(2)	2.316(3)
Ir(1)−H(b)	1.215	Ir(1)−P(3)	2.310(3)
Ir(2)−H(d)	1.119	Ir(2)−P(4)	2.297(3)
Ir(2)−H(e)	1.341	Ir(2)−P(5)	2.316(3)
Si(1)−C(1)	1.918(9)	Ir(2)−P(6)	2.313(3)
Bond Angles (deg)			
Ir(1)−Si(1)−C(1)	114.6(3)	P(5)−Ir(2)−Si(2)	156.3(1)
Ir(1)−Si(1)−C(7)	118.9(3)	P(6)−Ir(2)−Si(2)	96.0(1)
Ir(2)−Si(2)−C(22)	115.6(3)	P(1)−Ir(1)−P(2)	99.0(1)
Ir(2)−Si(2)−C(28)	119.0(3)	P(1)−Ir(1)−P(3)	100.6(1)
Ir(1)−Si(1)−H(c)	104.0	P(2)−Ir(1)−P(3)	100.7(1)
Ir(2)−Si(1)−H(f)	107.1	P(4)−Ir(2)−P(5)	100.0(1)
C(1)−Si(1)−H(c)	109.0	P(4)−Ir(2)−P(6)	98.6(1)
C(7)−Si(1)−H(c)	107.4	P(5)−Ir(2)−P(6)	100.7(1)
C(28)−Si(1)−H(f)	106.1	P(5)−Ir(2)−H(e)	77.0
C(1)−Si(1)−C(7)	102.5(4)	P(6)−Ir(2)−H(d)	152.5
C(22)−Si(2)−C(28)	100.6(4)	P(6)−Ir(2)−H(e)	98.4
Si(1)−Ir(1)−H(a)	81.9	P(1)−Ir(1)−H(a)	76.4
Si(1)−Ir(1)−H(b)	81.3	P(1)−Ir(1)−H(b)	162.3
Si(2)−Ir(2)−H(d)	57.6	P(2)−Ir(1)−H(a)	81.9
Si(2)−Ir(2)−H(e)	84.1	P(2)−Ir(1)−H(b)	83.4
H(a)−Ir(1)−H(b)	86.7	P(3)−Ir(1)−H(a)	176.3
H(d)−Ir(2)−H(e)	87.2	P(3)−Ir(1)−H(b)	96.1
P(1)−Ir(1)−Si(1)	91.2(1)	P(4)−Ir(2)−H(d)	77.5
P(2)−Ir(1)−Si(1)	158.3(1)	P(4)−Ir(2)−H(e)	163.0
P(3)−Ir(1)−Si(1)	96.1(1)	P(5)−Ir(2)−H(d)	106.8
P(4)−Ir(2)−Si(2)	93.9(1)		

Table 8. Selected Bonding Parameters for $IrH_2(PMe_3)_3(SiCl(t\text{-}Bu)_2)$ (3)

Bond Lengths (Å)			
Ir(1)−Si(1)	2.291(3)	Ir(1)−H(b)	1.244
Cl(1)−Si(1)	2.187(4)	Ir(1)−P(1)	2.326(3)
Si(1)−C(1)	1.95(1)	Ir(1)−P(2)	2.329(3)
Si(1)−C(5)	1.96(1)	Ir(1)−P(3)	2.325(3)
Ir(1)−H(a)	1.365		
Bond Angles (deg)			
P(1)−Ir(1)−P(2)	97.4(1)	Ir(1)−Si(1)−Cl(1)	110.3(2)
P(1)−Ir(1)−P(3)	97.3(1)	Ir(1)−Si(1)−C(1)	122.8(4)
P(2)−Ir(1)−P(3)	99.9(1)	Ir(1)−Si(1)−C(5)	112.9(4)
P(1)−Ir(1)−Si(1)	111.1(1)	Cl(1)−Si(1)−C(1)	99.1(4)
P(2)−Ir(1)−Si(1)	141.8(1)	Cl(1)−Si(1)−C(5)	98.8(4)
P(3)−Ir(1)−Si(1)	101.1(1)	C(1)−Si(1)−C(5)	109.5(6)
P(1)−Ir(1)−H(a)	81.1	P(3)−Ir(1)−H(b)	96.9
P(1)−Ir(1)−H(b)	161.6	Si(1)−Ir(1)−H(a)	66.4
P(2)−Ir(1)−H(a)	85.9	Si(1)−Ir(1)−H(b)	62.6
P(2)−Ir(1)−H(b)	90.0	H(a)−Ir(1)−H(b)	84.1
P(3)−Ir(1)−H(a)	176.5		

Table 9. Selected Bonding Parameters for $IrH_2(PMe_3)_3(SiPh_3)$ (4)

Bond Lengths (Å)			
Ir(1)−P(1)	2.323(5)	Si(1)−C(1)	1.90(2)
Ir(1)−P(2)	2.324(4)	Si(1)−C(7)	1.92(2)
Ir(1)−P(3)	2.306(5)	Si(1)−C(13)	1.91(2)
Ir(1)−Si(1)	2.382(4)		
Bond Angles (deg)			
Ir(1)−Si(1)−C(1)	113.5(5)	P(2)−Ir(1)−Si(1)	99.6(2)
Ir(1)−Si(1)−C(7)	117.6(5)	P(1)−Ir(1)−Si(1)	146.4(1)
Ir(1)−Si(1)−C(13)	117.6(5)	P(3)−Ir(1)−Si(1)	101.3(2)
C(1)−Si(1)−C(7)	99.3(6)	P(1)−Ir(1)−P(2)	101.1(2)
C(7)−Si(1)−C(13)	103.6(8)	P(1)−Ir(1)−P(3)	101.8(2)
C(1)−Si(1)−C(13)	102.7(7)	P(2)−Ir(1)−P(3)	97.8(2)

for each complex **1**−**4**. Two stretches are expected for the *fac* isomers according to symmetry. This result is consistent with the solid state X-ray crystallographic results for **1** and **3** (see below) and the above solution ^{1}H NMR results. For the deuterated compounds **1(D)** and **2(D)** two Ir−H stretches are observed whereas only one would be expected. We attribute this to solid state effects.

The observation of the formation of exclusively facial isomers can be best rationalized by invoking the accepted mechanisms of oxidative addition to Ir(I) centers shown in Scheme 1. Only preferential *cis* addition of R_3Si−H parallel to the P−Ir−P axis yields *cis* dihydride products in which the silicon is *trans* to a phosphine (*fac* isomers), as is implied spectroscopically for complexes **1**−**4** and is observed crystallographically for **1**, **3**, and **4** (see below). Either orientation of R_3SiH parallel to the P−Ir−P axis is sterically and electronically equivalent and produces *cis* dihydride products. Thereby apparent scrambling of the H and D positions in **1(D)** and **3(D)** observed in the infrared spectra can also be accounted for.

The X-ray crystal structures of **1**, **3**, and **4** have been determined. Selected distances and angles for the structures of **1**, **3**, and **4** are listed in Tables 7, 8 and 9, respectively. ORTEP drawings of **1**, **3**, and **4** are shown in Figures 1−3, respectively. Two independent molecules of **1** are present in the unit cell. Though the arrangement of the substituents around the silicon atoms in the two molecules of **1** is different (see below), the differences between the angles and distances are minor and therefore only one of the molecules is represented in Figure 1. The hydrogen atoms on iridium were located for **1** and **3** but not for **4**. The crystal structure of **4** had to be determined at 130 K because at room temperature only a poor structure (R = 12.2%, carbon atoms left isotropic) could be obtained.

In the solid state, both **1** and **3** assume distorted octahedral arrangements in which a PMe_3 ligand and the silyl group occupy the axial positions, and the four equatorial positions are occupied by two iridium hydrides and two PMe_3 ligands such that each iridium hydride is roughly *trans* to a phosphine. Complex **4** assumes a similar structure, but the quality of the refinement did not permit the location of the iridium hydrides. The solid state geometries for complexes **1**, **3**, and **4** show a *facial* arrangement of the phosphine ligands.

Trends in the *cis*-P−Ir−P, *trans*-Si−Ir−P, and C−Si−C angles and Ir−Si and Si−C distances allow us to conclude that the steric bulk of the silyl fragments increases in the order $SiPh_2H$ (**1**) < $SiPh_3$ (**4**) < $Si(t\text{-}Bu)_2Cl$ (**3**). The long Si−Cl bond length of 2.184 Å in **3** is also consistent with the greater steric bulk of the $Si(t\text{-}Bu)_2Cl$ fragment. Other Si−Cl bond lengths in iridium(III) complexes of less sterically hindered silanes range from 2.094 to 2.139 Å.[26] The Ir−Si distances of the two molecules of **1** (2.361(3) and 2.369(3) Å) and that of **4** (2.382(4) Å) are shorter than that of **3** (2.392(3) Å). These distances are also short when compared to other Ir(III)−Si distances of mononuclear unstrained complexes, which range from 2.390 to 2.416 Å[26,27] with the exception of the 2.299 Å distance observed in the

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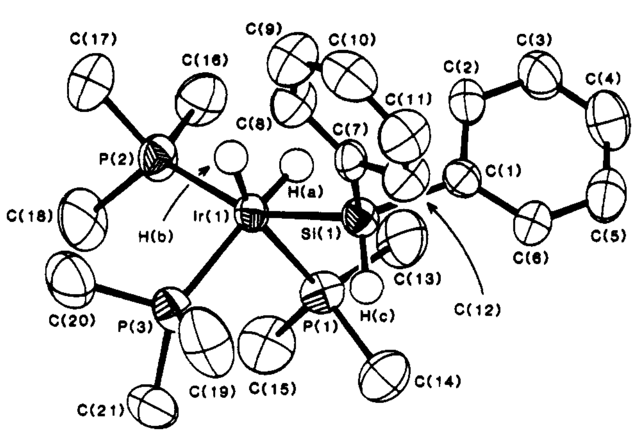

Figure 1. ORTEP labeling diagram for one molecule of $IrH_2(PMe_3)_3(SiHPh_2)$ (**1**). The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms, except those bound to iridium and silicon, have been omitted for clarity.

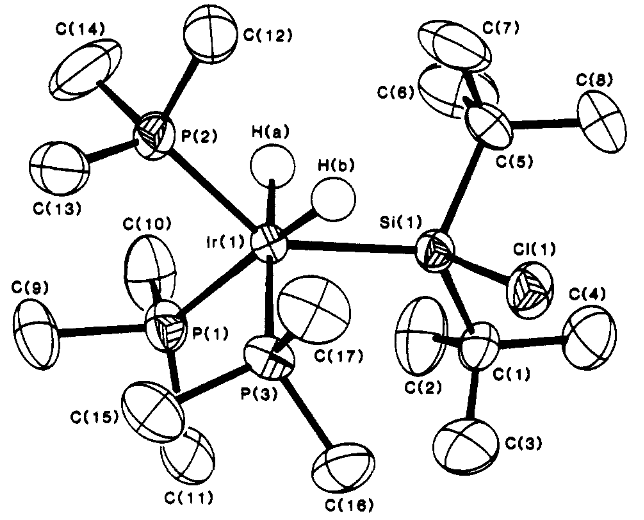

Figure 2. ORTEP labeling diagram for $IrH_2(PMe_3)_3(SiCl(t\text{-}Bu)_2)$ (**3**). The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms, except those bound to iridium, have been omitted for clarity.

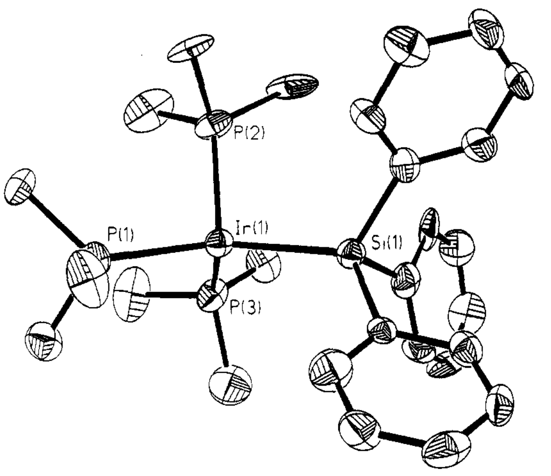

Figure 3. Thermal ellipsoid labeling diagram for $IrH_2(PMe_3)_3(SiPh_3)$ (**4**). The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms on iridium were not found, and all other hydrogen atoms have been omitted for clarity.

complex $Ir(PMe_3)_3Cl_2(SiMeCl_2)$.[6] The tendency toward shorter Ir(III)−Si bond lengths in complexes with three PMe_3 ligands may be due to the small steric requirements of the PMe_3 ligand relative to other phosphine ligands. In all three complexes the Ir−P(*trans*) (with respect to the silicon atom) distance is marginally longer than Ir-P(*cis*) distances. The range of Ir−P bond distances in **1**, **3**, and **4** are comparable to each other and to those of other Ir(III) complexes with three PMe_3 ligands.[6,7,28]

The hydrides on iridium and silicon of **1** and **3** were located in the difference maps but were not refined. The lack of long Ir−Si bonds and the positions of the hydrides of **1** and **3** indicate that all hydrides are terminal, and no evidence was found for agostic Si−H or H−H bonding to iridium, in agreement with NMR spectral data. This is consistent with the observation that agostic Si−H interactions with iridium have been only observed at low temperatures.[29] A computational study of the oxidative addition of SiH_4 to the related 14-electron complex $RhCl(PH_3)_2$ indicates that an agostic η^2-SiH_4 complex is a transition state but not an intermediate.[30]

Crystallographic studies of mononuclear complexes of diphenylsilane are available when the metal is iridium (**1**), ruthenium,[31] chromium,[32] and manganese[33] (two examples). There exists a relationship between the C−Si−C angle of the diphenylsilane ligand and the extent of oxidative addition. In the former two complexes the C−Si−C angle is in the range 100.5−102.5° and the Si−H has fully oxidatively added to the metal, whereas in the latter three complexes the angle increases to 105.9−107.0° and the Si−H interacts in an agostic fashion.

A long-range goal of this research is to find ways to induce elimination of X−Y from an X−Ir−Si−Y moiety to give Ir=Si bonds or $(Ir-Si)_2$ rings. The success of an elimination process may depend on the relative arrangement of the X and Y substituents around the Ir−Si bond and/or whether steric interactions impede X and Y from attaining the correct arrangement. Views of both the molecules of **1** and the complexes **3** and **4** are shown in Figure 4. Each molecule has been drawn looking down the Si−Ir axis with the Si atom forward such that the phosphine is *trans* to the silicon and the two iridium hydrides are toward the bottom of the drawing. The two molecules of **1** have very different orientations of the phenyl groups; however, in both, the phenyl groups are staggered relative to the *cis*-phosphines. In the first molecule of **1** the hydrides are symmetrically disposed whereas in the second molecule a hydride on silicon H(f) is nearly opposite to the iridium hydride H(e) (dihedral angle = 169°). In **3** and **4** a *cis*-phosphine is eclipsed with a hydrocarbon substituent

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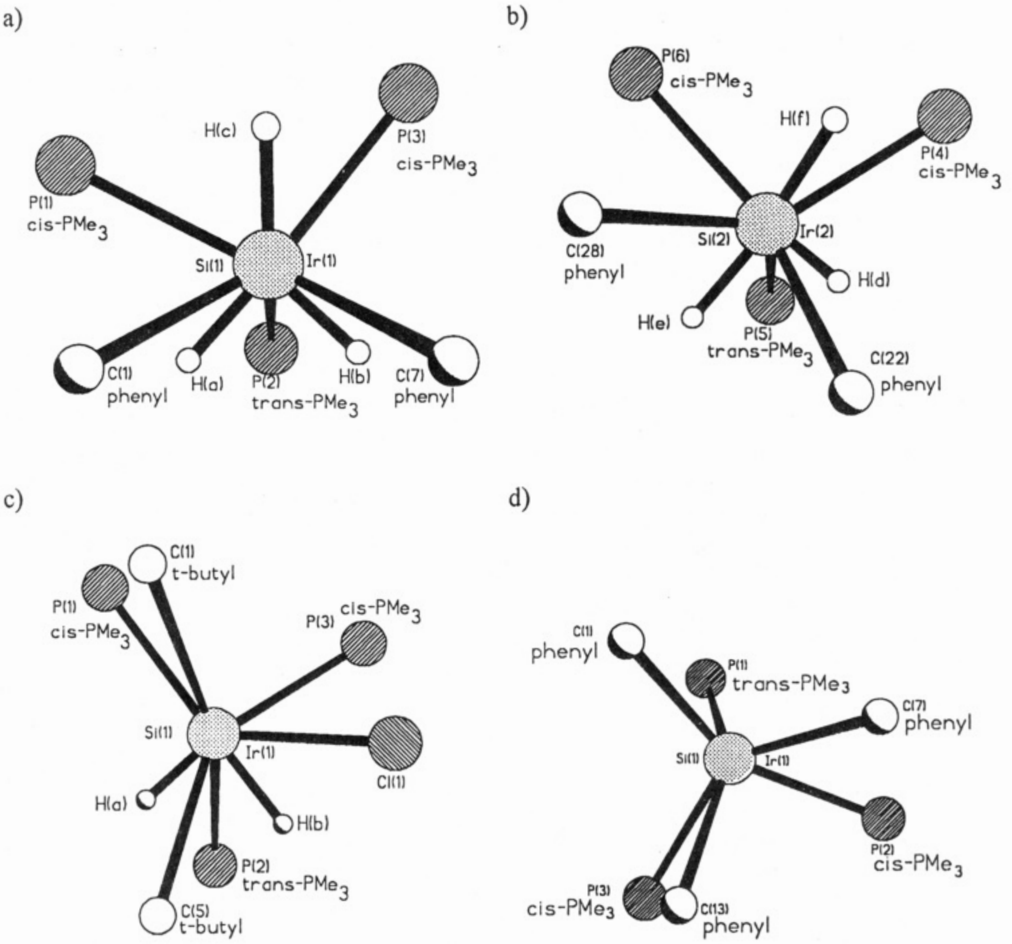

Figure 4. Projections of both molecules of **1** (a and b), **3** (c), and **4** (d) down the Ir−Si bond with the silicon atom in front.

on the silicon. Crystal-packing forces cannot be eliminated as a reason, though there are no close intermolecular contacts. In **3** the silyl chloride is on the same side of the Ir−Si bond as the iridium hydride H(b) (dihedral angle = 46°).

The spectroscopic and crystallographic results presented within this paper show that monomeric iridium−silyl complexes are formed by the reaction of a silane with an iridium(I) phosphine compound. Though spectral results indicate free rotation around the Ir−Si bond, crystallographic results of **3** and preliminary reaction studies indicate that steric hindrance may impede reactions of the di(*tert*-butyl)silyl complexes.[34] Further studies of **1**−**4** will be directed toward understanding the reaction chemistry of the hydride or chloride substituents on the silyl groups or the iridium center with the goal of forming Ir=Si bonds or $(Ir-Si)_2$ rings. Other reactions pathways are possible. Recently, thermolysis of $Ir(PMe_3)_3(SiPh_3)(Me)H$ gave methane and an iridasilacyclobutane complex in which the *ortho* C−H on the phenyl ring had been activated.[7] Loss of H_2 from **4** could give a similar complex. The reactions of silanes which contain more than one reactive substituent with $IrCl(PMe_3)_4$ are also being investigated.

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Supplementary Material Available: Complete data collection parameters, thermal parameters, and complete tables of bond lengths and angles for the structures of **1**, **3**, and **4** (15 pages). Ordering information is given on any current masthead page.

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