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# Facial (Methyl)(hydrido)(silyl) Complexes of Iridium: Synthesis, X-ray Structures, and Reductive Elimination Reactions. Facile Formation of Silametallacycles by Metalation of Silyl Ligands

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**Abstract:** Facial complexes $L_3Ir(CH_3)(H)(SiR_3)$ ($L = PMe_3$; R = EtO (**2**), Ph (**3**), Et (**4**)) result from oxidative addition of the corresponding silanes to $MeIrL_4$. The three compounds are fully characterized spectroscopically and the mutual cis arrangement of H, $CH_3$, and $SiR_3$ groups is confirmed by X-ray crystallographic studies of **3** and **4**. Crystal data for **3**: monoclinic, $P2_1/n$, $a = 10.050(2)$ Å, $b = 31.459(6)$ Å, $c = 10.325(2)$ Å, $\beta = 114.61(3)°$, $Z = 4$. Crystal data for **4**: triclinic, $P\bar{1}$, $a = 8.653(2)$ Å, $b = 10.090(2)$ Å, $c = 14.988(3)$ Å, $\alpha = 92.43(3)°$, $\beta = 94.53(3)°$, $\gamma = 113.69(3)°$, $Z = 2$. Based on the X-ray structural data, the following order of increasing trans influence is deduced: $CH_3 < H < SiPh_3 < SiEt_3$. On heating to 100 °C, **2** and **3** reductively eliminate methane exclusively. The resulting Ir(I) silyls quantitatively cyclometalate to produce novel iridasilacycles $L_3\overline{Ir(H)(CH_2CH_2OSi}(OEt)_2)$ (**5**) and $L_3\overline{Ir(H)(o\text{-}C_6H_4Si}Ph_2)$ (**6**). **5** and **6** are fully characterized spectroscopically and complex **6** also crystallographically. Compound **4** on heating eliminates C–H, C–Si, and H–Si bonds competitively (the latter one reversibly). The upper limit of the relative rates of C–H and C–Si bond formation is estimated as $k_{C-H}/k_{C-Si} \approx 4$. The resulting highly reactive intermediate complexes $[HIrL_3]$, $[MeIrL_3]$, and $[Et_3SiIrL_3]$ react further with the solvent benzene and triethylsilane to yield a mixture of C–H and Si–H addition products. These were identified by carrying out independent oxidative addition reactions of $HSiEt_3$, $H_2$, and $C_6H_6$ to $HIrL_4$ and $PhIrL_3$. A plausible scheme accounting for the formation of the observed complexes is proposed.

## Introduction

Transformations of organosilicon compounds catalyzed by transition metal complexes,[1] being of importance because they lead to materials possessing valuable properties,[2] are still in many aspects not well-understood mechanistically. For example, the product-forming step of the industrially important olefin hydrosilation reaction[3] that is postulated in various versions of the Chalk–Harrod mechanism[4,5] is C–Si reductive elimination. On the other hand, a significant body of evidence exists which indicates that it may not be the only possibility. Seitz and Wrighton proposed[6] an alternative mechanism in which migration of an $R_3Si$ group to an alkene ligand takes place at a Co center and the product is released by C–H rather than C–Si reductive elimination. Their observation of vinylsilane formation in the reaction provided strong evidence in favor of this mechanism. Later Duckett and Perutz[7] thoroughly investigated hydrosilation of alkenes catalyzed by a $\eta^5$-CpRh complex and postulated a two-silicon catalytic cycle in which the product-forming step was, again, C–H reductive elimination.

There are numerous examples of C–H bond formation by reductive elimination.[8] In contrast, formation of a C–Si bond by this process since the first report by Gladysz et al.[9] has very rarely been observed.[10–13] Needless to say, a study of a direct competition between the two processes may contribute to better

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(2) See, for example: (a) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 1207–1240; (b) Seyferth, D. In *Organosilicon Chemistry. From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH Verlagsgesellschaft: Weinheim, 1994; pp 269–274. (c) Hengge, E. *Ibid.*, pp 275–283.

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(13) (a) Kinetic evidence for this process to occur from (dtbpm)Pt(Me)($SiMe_3$) (dtbpm = $^tBu_2PCH_2P^tBu_2$) was presented in: Hofmann, P.; Heiss, H.; Neiteler, P.; Müller, G.; Lachmann, J. *Angew. Chem.* **1990**, *102*, 281; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880. (b) The analogous (dtbpm)-Pt(Et)($SiEt_3$) reductively eliminates $Et_4Si$ cleanly: Hofmann, P. In *Organosilicon Chemistry. From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH Verlagsgesellschaft: Weinheim, 1994; pp 231–250.

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mechanistic understanding of homogeneous hydrosilation and related reactions. To our knowledge no well-defined system capable of both these reductive elimination reactions has been studied. There are several reports where C−H bonds were generated upon reactions of alkyl or aryl complexes of transition metals with hydrosilanes.[6,10a,14] However, in only one case was an intermediate that bears alkyl, silyl, and hydride substituents on a metal center, namely $Cp_2Ta(CH_3)(H)(SiMe_2Cl)$,[14e] observed in solution. For this complex, as earlier for its analog $Cp^*_2Ta(CH_3)(H)(SiH_3)$,[15] an arrangement with $CH_3$ in the lateral position is proposed, excluding even a possibility in principle of the aforementioned competition. Of particular relevance are the results obtained by Thorn and Harlow,[16] who reported formation of methane in the reaction between $MeRh(PMe_3)_{3,4}$ and $HSiPh_3$. They also mentioned that in an analogous reaction with $HSiEt_3$ both $CH_4$ and $CH_3SiEt_3$ were formed, but no intermediate complexes were detected, and the relative disposition of the groups of interest in them is unknown.

We report here in full on the synthesis and reductive elimination reactivity of three fully characterized facial complexes $(Me_3P)_3Ir(CH_3)(H)(SiR_3)$ (R = EtO (**2**), Ph (**3**), Et (**4**)), that possess the required all-cis arrangement of $CH_3$, H, and $SiR_3$ ligands. We present X-ray structural characterization of **3** and **4**, and using these data we compare the trans influence of the ligands involved and discuss the differences in reactivity of the complexes. We also report on C−H activation reactions of Ir(I) silyls, which in the case of triphenylsilyl and triethoxysilyl derivatives are intramolecular and regioselective leading to novel iridasilacycles, while for the corresponding triethylsilyl complex intermolecular C−H activation processes prevail. Part of this work has been published as a preliminary communication.[17]

## Experimental Section

**General.** Most of the compounds described herein are air and moisture sensitive and they were handled under inert atmosphere, usually in a Vacuum Atmospheres nitrogen-filled glovebox or using Schlenk techniques. The solvents used were purified by established procedures, degassed by purging with dry $N_2$, and stored over molecular sieves in the glovebox. $C_6D_6$ (99% D) and $(CD_3)_2CO$ (99% D) were purchased from Riedel-de Haën, degassed, and used after prolonged storage over molecular sieves. All the reagents were of reagent grade. $HSiEt_3$ (Petrarch Systems Inc.) and $HSi(OEt)_3$ (Silar Laboratories Inc.) were degassed prior to use. $HSiPh_3$ (Aldrich) was used as received. $Ir(PMe_3)_4Cl$,[18] $MeIr(PMe_3)_4$,[19] and $HIr(PMe_3)_4$[20] were synthesized as described. NMR spectra were obtained with a Bruker AMX 400 spectrometer at ambient probe temperature in $C_6D_6$ unless otherwise specified. $^{1}H$-NMR spectra (400 MHz) were referenced to residual internal $C_6D_5H$ at 7.15 ppm, $^{31}P\{^{1}H\}$-NMR spectra (162 MHz) were measured against external 85% $H_3PO_4$ in $D_2O$ at 0.0 ppm, and in $^{13}C\{^{1}H\}$-NMR spectra (100 MHz) peaks of the solvent (128.0 ppm for $C_6D_6$; 205.1 ppm for $(CD_3)_2CO$) were used as the standards. Elemental analyses were obtained from the Microanalysis Laboratory of The Hebrew University of Jerusalem. Mass spectra (FAB, sulfolane) were obtained from the Mass Spectroscopy Laboratory, Technion, Haifa, and are reported for the more abundant isotope, namely $^{193}$Ir.

**Preparation of *fac*-$(Me_3P)_3Ir(CH_3)(H)(Si(OEt)_3)$ (2).** To a solution of 51 mg (0.10 mmol) of $MeIr(PMe_3)_4$ (**1**) in 3 mL of benzene was added 18 mg (0.11 mmol) of $HSi(OEt)_3$. After 1 h the solvent was removed under vacuum to afford 57 mg (95%) of a yellowish oil. Anal. Calcd for $C_{16}H_{46}O_3P_3SiIr$: C, 32.04; H, 7.73. Found: C, 31.54; H, 7.86. $^{31}P\{^{1}H\}$-NMR: $\delta$ −63.4 (dd, $J_1$ = 24.1 Hz, $J_2$ = 18.8 Hz, 1P); −56.6 (dd, $J_1$ = 24.1 Hz, $J_2$ = 16.3 Hz, 1P); −55.4 (dd, $J_1$ = 18.6 Hz, $J_2$ = 16.5 Hz, 1P). $^{1}H$-NMR: $\delta$ −12.12 (dt, $^{2}J$(H,P,trans) = 126 Hz, $^{2}J$(H,P,cis) = 17.8 Hz, 1H; Ir−*H*), 0.3 (m, 3H; Ir−C$H_3$), 1.13 (d, $^{2}J$(H,P) = 6.9 Hz, 9H; P$Me_3$), 1.34 (d, $^{2}J$(H,P) = 7.9 Hz, 9H; P$Me_3$), 1.51 (d, $^{2}J$(H,P) = 8.3 Hz, 9H; P$Me_3$), 1.4 (t, $^{3}J$(H,H) = 7 Hz, 9H; C$H_3$C$H_2$O), 4.17 (AB q ($J$ = 10.1 Hz) of q ($^{3}J$(H,H) = 7 Hz), 6H; Si−OC$H_2$).

**Preparation of *fac*-$(Me_3P)_3Ir(CH_3)(H)(SiPh_3)$ (3).** This compound was prepared earlier,[16] but no experimental details and $^{31}P$-NMR data were reported. To a solution of 51 mg (0.10 mmol) of **1** in 3 mL of benzene was added a solution of 29 mg (0.11 mmol) of $HSiPh_3$ in 1 mL of benzene. After 1 h the solvent was removed under vacuum. **3** was isolated in 98% yield as a white microcrystalline powder after washing with pentane (0.5 mL). Colorless crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent from a concentrated benzene solution of **3** at room temperature. Anal. Calcd for $C_{28}H_{46}P_3SiIr$: C, 48.33; H, 6.66. Found: C, 48.63; H, 6.92. $^{31}P\{^{1}H\}$-NMR: $\delta$ −63.4 ("t", $J$ = 16.1 Hz, 1P); −60.1 (dd, $J_1$ = 19.5 Hz, $J_2$ = 16.6 Hz, 1P); −59.2 (dd, $J_1$ = 19.6 Hz, $J_2$ = 15.8 Hz, 1P). $^{1}H$-NMR: $\delta$ −11.79 (dt, $^{2}J$(H,P,trans) = 123.5 Hz, $^{2}J$(H,P,cis) = 15.4 Hz, 1H; Ir−*H*), 0.15 (m, 3H; Ir-C$H_3$), 0.72 (d, $^{2}J$(H,P) = 7.3 Hz, 9H; P$Me_3$), 1.10 (d, $^{2}J$(H,P) = 7.6 Hz, 9H; P$Me_3$), 1.17 (d, $^{2}J$(H,P) = 7.2 Hz, 9H; P$Me_3$), [7.1 (m), 7.25 (t, $J$(H,H) = 7.4 Hz), 8.11 (m), 15H; SiC$_6H_5$].

**Preparation of *fac*-$(Me_3P)_3Ir(CH_3)(H)(SiEt_3)$ (4).** The procedure and molar amounts of the reactants, namely **1** and $HSiEt_3$, were the same as for the synthesis of **2**. Complex **4** was isolated as a white light solid in 92% yield after washing with a minimum amount of cold pentane. Colorless crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent from a pentane solution of **4** at room temperature. Anal. Calcd for $C_{16}H_{46}P_3SiIr$: C, 34.83; H, 8.40. Found: C, 34.58; H, 8.53. $^{31}P\{^{1}H\}$-NMR: $\delta$ −64.7 (dd, $J_1$ = 19.7 Hz, $J_2$ = 17.7 Hz, 1P); −59.0 (6-line second order m, 2P). $^{1}H$-NMR: $\delta$ −12.15 (dt, $^{2}J$(H,P,trans) = 135.1 Hz, $^{2}J$(H,P,cis) = 19.0 Hz, 1H; Ir−*H*), 0.20 (m, 3H; Ir−C$H_3$), 1.09 (d, $^{2}J$(H,P) = 6.8 Hz, 9H; P$Me_3$), 1.14 (d, $^{2}J$(H,P) = 7.1 Hz, 9H; P$Me_3$), 1.29 (d, $^{2}J$(H,P) = 7.3 Hz, 9H; P$Me_3$), 1.09 (AB q ($J$ = 14 Hz) of qd ($^{3}J$(H,H) = 7.8 Hz, $^{4}J$(H,P,trans) = 1.4 Hz), 6H; SiC$H_2$),[21] 1.43 (t, $^{3}J$(H,H) = 7.8 Hz, 9H; SiCH$_2$C$H_3$).

**Preparation of *fac*-$(Me_3P)_3Ir(H)_2(SiEt_3)$ (7).** To a solution of 42 mg (0.085 mmol) of $HIr(PMe_3)_4$ (**13**) in 3 mL of benzene was added a 3-fold excess of $HSiEt_3$. After several hours the solvent was removed under vacuum to yield 52 mg (96%) of a yellowish light solid. Anal. Calcd for $C_{15}H_{44}P_3SiIr$: C, 33.50; H, 8.25. Found: C, 33.23; H, 8.35. $^{31}P\{^{1}H\}$-NMR: $\delta$ −63.7 (t, $J$ = 19.8 Hz, 1P); −58.0 (d, $J$ = 19.8 Hz, 2P). $^{1}H$-NMR: $\delta$ −12.60 (symmetrical second order m, $J_1$ = 95.5 Hz, $J_2$ = 20.2 Hz, 2H; Ir-*H*), 1.26 (d, $^{2}J$(H,P) = 7.4 Hz, 9H; unique P$Me_3$), 1.31 (dd, $^{2}J$(H,P) = 7.2 Hz, $^{4}J$(H,H) = 0.5 Hz, 18H; P$Me_3$ trans to H), 1.07 (qd, $^{3}J$(H,H) = 7.8 Hz, $^{4}J$(H,P,trans) = 1.9 Hz, 6H; SiC$H_2$), 1.41 (t, $^{3}J$(H,H) = 7.8 Hz, 9H; SiCH$_2$C$H_3$).

**Preparation of $(Me_3P)_3Ir(C_6H_5)$ (12).** To a stirred suspension of 200 mg (0.377 mmol) of $Ir(PMe_3)_4Cl$ in 14 mL of THF/$Et_2O$ (1.4:1) were added 0.45 mL of a 1.5 M solution of PhMgCl in $Et_2O$ (1.8 equiv). After the addition was complete (ca. 10 min) the stirring was continued for 10 min after which the solvent was removed under vacuum. The viscous mass left was extracted with warm pentane (3 × 2 mL), the extract was filtered, and the solvent was removed under vacuum to

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(21) This multiplet was assigned by using $^{1}H\{^{31}P\}$ NMR data.

(22) **12** is an extremely air-sensitive compound, and for this reason it was not characterized by combustion analysis.

yield 80 mg of crude product as an orange solid. Analytically pure red crystalline material was obtained by recrystallization of the crude from a minimum amount of pentane at −20 °C.[22] $^{31}P\{^1H\}$-NMR: $\delta$ −35.4 (t, $J$ = 20.4 Hz, 1P); −24.8 (d, $J$ = 20.3 Hz, 2P). $^1H$-NMR: $\delta$ 1.09 (vt, $J$ = 2.8 Hz, 18H; mutually *trans*-P$Me_3$), 1.29 (d, $^2J$(H,P) = 6.3 Hz, 9H; unique P$Me_3$), [7.06 ("t", $J$ = 7.2 Hz, 1H), 7.26 ("t", $J$ = 7.4 Hz, 2H), 7.89 (m, 2H); $C_6H_5$].

**Preparation of *fac*-$(Me_3P)_3Ir(C_6H_5)(H)(SiEt_3)$ (11).** To a red-orange solution of 25 mg (0.05 mmol) of $PhIr(PMe_3)_3$ in $C_6D_6$ (0.5 mL) was added dropwise a solution containing 1.05 equiv of $HSiEt_3$ in $C_6D_6$ (0.5 mL). The color immediately discharged. NMR analysis showed formation of **11** in >95% yield. $^{31}P\{^1H\}$-NMR: $\delta$ −62.3 (second order m, 2P); −58.2 (dd, $J_1$ = 20.5 Hz, $J_2$ = 16.7 Hz, 1P). $^1H$-NMR: $\delta$ −11.57 (dt, $^2J$(H,P,trans) = 135.2 Hz, $^2J$(H,P,cis) = 18.2 Hz, 1H; Ir−$H$), 0.88 (d, $^2J$(H,P) = 6.9 Hz, 9H; P$Me_3$), 1.24 (d, $^2J$(H,P) = 6.8 Hz, 9H; P$Me_3$), 1.33 (d, $^2J$(H,P) = 6.7 Hz, 9H; P$Me_3$), 0.74 (m, 3H; Si$CH_2$), 1.07 (m, 3H; Si$CH_2$), 1.27 (t, $^3J$(H,H) = 7.8 Hz, 9H; $SiCH_2CH_3$), [7.05 (m), 7.5 (vbr), 8.1 (vbr), 5H; $C_6H_5$]. FAB-MS (positive ions): 615.6; 537.3.

**Thermolysis of *fac*-$(Me_3P)_3Ir(CH_3)(H)(Si(OEt)_3)$ (2). Formation of Iridasilacycle 5.** Complex **2** (20 mg) was dissolved in $C_6D_6$ (0.8 mL) and transferred into a screw-capped 5-mm NMR tube. The capped tube was heated in an oil bath at 100 °C for 1 day. After the sample was cooled to room temperature the $^{31}P\{^1H\}$, $^1H$, $^{13}C\{^1H\}$, and $^{13}C$ DEPT135 NMR spectra were measured, showing complete disappearance of **2** and exhibiting the following signals: $^{31}P\{^1H\}$-NMR: $\delta$ −61.4 (dd, $J_1$ = 23.2 Hz, $J_2$ = 19.1 Hz, 1P); −57.2 ("t", $J$ = 17.7 Hz, 1P), −56.4 (dd, $J_1$ = 23.0 Hz, $J_2$ = 16.5 Hz, 1P). $^1H$-NMR: $\delta$ −12.54 (dt, $^2J$(H,P,trans) = 122.8 Hz, $^2J$(H,P,cis) = 16.6 Hz, 1H; Ir-$H$), 1.10 (d, $^2J$(H,P) = 6.9 Hz, 9H; P$Me_3$), 1.30 (d, $^2J$(H,P) = 7.8 Hz, 9H; P$Me_3$), 1.46 (d, $^2J$(H,P) = 8.0 Hz, 9H; P$Me_3$), 1.42 (t, $^3J$(H,H) = 7.0 Hz, 3H; $SiOCH_2CH_3$), 1.48 (t, $^3J$(H,H) = 7.0 Hz, 3H; $SiOCH_2CH_3$), 1.94 (m, 1H; Ir−$CH_2$; the second H is obscured by the other lines, but appears in COSY spectrum as a cross peak at ~1.57 ppm), 4.0−4.4 (series of m; Ir−$SiOCH_2CH_3$ + Ir−$SiOCH_2CH_2$), 0.15 (s; $CH_4$ free). $^{13}C\{^1H\}$-NMR: $\delta$ 3.0 (dt, $J_d$ = 59.3 Hz, $J_t$ = 5.7 Hz; Ir−$CH_2$; negative in DEPT), [18.8 (s), 19.5 (s); $Si(OCH_2CH_3)_2$; positive in DEPT], [20.5 (dm), 21.4 (dm), 25.1 (dm); $P(CH_3)_3$; positive in DEPT], [56.3 (d, $J$ = 1.6 Hz), 57.1 (d, $J$ = 2.5 Hz); $Si(OCH_2CH_3)_2$; negative in DEPT], [68.7 (dt, $J_d$ = 10 Hz, $J_t$ = 2.6 Hz; $SiOCH_2CH_2$; negative in DEPT]. The purity of **5** (as determined by $^{31}P\{^1H\}$- and $^1H$-NMR) exceeded 98%. No insoluble material was formed. The solvent was removed under vacuum, the resulting oily residue was extracted with pentane, and the extract was dried in high vacuum to yield 18 mg (92%) of pure **5** as a yellow oil. Anal. Calcd for $C_{15}H_{42}O_3P_3SiIr$: C, 30.87; H, 7.25. Found: C, 31.14; H, 7.32.

**Thermolysis of *fac*-$(Me_3P)_3Ir(CH_3)(H)(SiPh_3)$ (3). Formation of Iridasilacycle 6.** A suspension of 25 mg of a white powder (25 mg) of **3** in 0.8 mL of $C_6D_6$ was transferred into a screw-capped NMR tube. The capped tube was treated as in the case of thermolysis of **2**. On heating, all the material quickly dissolved. After 1 day at 100 °C the sample was cooled to room temperature and the following spectral data were obtained. $^{31}P\{^1H\}$-NMR: $\delta$ −60.9 (dd, $J_1$ = 14.6 Hz, $J_2$ = 20.7 Hz, 1P), −60.2 (dd, $J_1$ = 14.4 Hz, $J_2$ = 18.4 Hz, 1P), −56.7 ("t", $J$ = 19.6 Hz, 1P). $^1H$-NMR: $\delta$ −9.8 (dt, $^2J$(H,P,trans) = 122.2 Hz, $^2J$(H,P,cis) = 18.4 Hz, 1H; Ir−$H$), 0.81 (d, $^2J$(H,P) = 7.7 Hz, 9H; P$Me_3$), 1.27 (d, $^2J$(H,P) = 7.7 Hz, 9H; P$Me_3$), 1.31 (d, $^2J$(H,P) = 7.3 Hz, 9H; P$Me_3$), [7.05−7.40 (several m), 8.01 (m, 2H), 8.10 (m, 1H), 8.36 (m, 2H); $Si(C_6H_5)_2$ + $Si(C_6H_4)$-cycle], 0.15 (s; $CH_4$ free). On prolonged standing colorless crystals of **6** suitable for X-ray analysis slowly precipitated from the solution.

**Thermolysis of *fac*-$(Me_3P)_3Ir(CH_3)(H)(SiEt_3)$ (4).** This reaction was carried out at temperatures in the range of 85−125 °C, with or without added $PMe_3$, in $C_6D_6$ or $C_6H_6$ as a solvent. The methane that eliminated was quantified by GC analysis of the gas phase, and the amount of $CH_3SiEt_3$ formed was determined by $^1H$-NMR using as an internal standard 1,4-dioxane, added after the reaction was interrupted. The reaction was monitored by $^{31}P\{^1H\}$- and $^1H$-NMR. The Ir complexes formed in the reaction were identified by comparing the spectral data obtained with those of independently prepared compounds.

**Reaction of 4 with $HSi(OEt)_3$.** The reaction was conducted in $C_6H_6$ at 25 °C. The amount of **4** taken was 12 mg, and the **4**: $HSi(OEt)_3$ molar ratio was 1:5. The progress of the reaction was monitored by $^{31}P\{^1H\}$- and $^1H$-NMR. After 3 h the reaction mixture contained **2**, as a major organometallic product (56.3%), along with 10.7% of the starting material, **4**, and 33.0% of a new complex, most probably *fac*-$(Me_3P)_3Ir(H)(Si(OEt)_3)_2$. $^{31}P\{^1H\}$-NMR of the mixture in addition to resonances, belonging to **2** and **4**, exhibited the following signals: $\delta$ −63.0 (d, $J$ = 24.2 Hz, 2P); −57.5 (t, $J$ = 24.2 Hz, 1P). $^1H$-NMR indicated quantitative liberation of $HSiEt_3$ and also formation of methane.

**Thermolysis of *fac*-$(Me_3P)_3Ir(C_6H_5)(H)(SiEt_3)$ (11).** Ten milligrams of the waxy yellowish solid of **11** obtained by evacuation of its solution in $C_6D_6$ was redissolved in $C_6H_6$ (0.8 mL). The solution was heated at 95 °C for 1 day and then for 2 days at 110 °C. Reaction progress was followed by periodical measurement of $^{31}P\{^1H\}$-NMR of the solution.

**Preparation of *mer,trans*-$(Me_3P)_3Ir(C_6H_5)_2(H)$ (8).** An orange solution of 10 mg (0.02 mmol) of **12** in 0.8 mL of $C_6H_6$ was heated in a screw-capped NMR tube at 100 °C for 2 days. During this time the color of the solution gradually became yellow. $^{31}P\{^1H\}$-NMR of the reaction mixture indicated 80% conversion to **8**, the rest being unreacted **12**. The solvent was removed under vacuum, and the dry solid left was washed with cold pentane (0.5 mL) and vacuum dried to yield 8 mg (69%) of pure **8**. $^{31}P\{^1H\}$-NMR: $\delta$ −54.3 (t, $J$ = 19.9 Hz, 1P); −45.5 (d, $J$ = 19.9 Hz, 2P). $^1H$-NMR: $\delta$ −11.37 (dt, $^2J$(H,P,trans) = 147.0 Hz, $^2J$(H,P,cis) = 21.7 Hz, 1H; Ir−$H$), 1.09 (vt, $J$ = 3.4 Hz, 18H; mutually *trans*-P$Me_3$), 1.27 (dd, $^2J$(H,P) = 6.7 Hz, $^4J$(H,H) = 0.9 Hz, 9H; unique P$Me_3$), [7.1 (m), 7.8 (m), 10H; mutually *trans*-$C_6H_5$]. $^{13}C\{^1H\}$-NMR (acetone-$d_6$): $\delta$ 18.9 (vtd, $J_{vt}$ = 18.7 Hz, $J_d$ = 3.8 Hz; mutually *trans*-$P(CH_3)_3$); 18.9 (dt, $J_d$ = 24.3 Hz, $J_t$ = 2.3 Hz; unique $P(CH_3)_3$); [119.5 (s), 125.5 (s), 143.0 (m), 147.6 (dt, $J_d$ = 6.8 Hz, $J_t$ = 2.7 Hz); mutually *trans*-$C_6H_5$]. FAB-MS (positive ions): 575.3; 498.5.

**Reaction of $(Me_3P)_3Ir(C_6H_5)$ (12) with $H_2$.** Dry hydrogen gas was bubbled for 2 min through an orange solution of **12** (15 mg, 0.03 mmol) in 0.6 mL of $C_6D_6$. The reaction mixture rapidly decolorized and formation of *fac*-$(Me_3P)_3Ir(H)_2(C_6H_5)$ (**10**) was detected in >80% yield by NMR. $^{31}P\{^1H\}$-NMR: $\delta$ −58.3 (t, $J$ = 14.9 Hz, 1P); −56.1 (d, $J$ = 15.0 Hz, 2P). $^1H$-NMR: $\delta$ −10.76 (symmetrical second order m, $J_1$ = 120.2 Hz, $J_2$ = 21.0 Hz, 2H; Ir−$H$), 1.23 (d, $^2J$(H,P) = 7.2 Hz, 18H; P$Me_3$ trans to H), 1.30 (d, $^2J$(H,P) = 7.9 Hz, 9H; unique P$Me_3$), [8.09 (m), 7.15 (m), 5H; $C_6H_5$].

**Reaction of $HIr(PMe_3)_4$ (13) with $C_6H_6$.** Sixteen milligrams of **13** was dissolved in 1.0 mL of benzene and then heated in a screw-capped NMR tube at 108 °C for 1 day. $^{31}P\{^1H\}$-NMR indicated formation of a mixture, containing 29.7% of *mer,cis*-$(Me_3P)_3Ir(H)_2(C_6H_5)$ (**9**), 4.9% of **10**, and 2.0% of **8**, the rest being unreacted **13**. Further heating for 1 day resulted in a mixture, containing 55.7% of the starting material, 35.1% of **9**, 5.8% of **10**, and 3.7% of **8**. At this stage the reaction was interrupted. The spectral data for **9** are as follows. $^{31}P\{^1H\}$-NMR: $\delta$ −57.0 (t, $J$ = 22.3 Hz, 1P); −47.5 (d, $J$ = 22.3 Hz, 2P). $^1H$-NMR: $\delta$ −14.19 (qd, $^2J$(H,P,cis) = 17.8 Hz, $^2J$(H,H) = 5.2 Hz, 1H; Ir−$H$, trans to $C_6H_5$), −11.59 (dtd, $^2J$(H,P,trans) = 134.3 Hz, $^2J$(H,P,cis) = 22.4 Hz, $^2J$(H,H) = 5.0 Hz, 1H; Ir−$H$, trans to $PMe_3$), 1.32 (vt, $J_{vt}$ = 7.1 Hz, 18 H; mutually *trans*-P$Me_3$), 1.36 (dd, $^2J$(H,P) = 7.2 Hz, $^4J$(H,H) = 0.8 Hz, 9H; unique P$Me_3$), signals of $C_6H_5$ could not be assigned definitely, because they overlapped with signals of the solvent benzene and of other components of the mixture.[23]

**Crystallographic Methods. $(Me_3P)_3Ir(CH_3)(H)(SiPh_3)$ (3).** The structural data of compound **3** were collected using a CAD 4 (Enraf-Nonius diffractometer with Mo K$\alpha$ radiation (graphite monochromator, $\lambda$ = 0.71073 Å). Unit cell dimensions were determined from 25 reflections. Details of crystal parameters and data collection are presented in Table 1. Two standards were collected 30 times each with a 4% change in intensity. The structure was solved by direct methods (SHELXTL-PC)[24] and refined using the full-matrix least-

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(23) Complex **9** was synthesized independently in the reaction between $PhIr(PMe_3)_3$ and $CH_3OH$, resulting in $^{31}P\{^1H\}$ and $^1H$ NMR data that agree with that reported herein: Blum, O.; Milstein, D. Unpublished results.

(24) Sheldrick, G. M. *SHELXTL-PC*, Release 4.1; Siemens Analytical X-ray Instruments, Inc.: Madison, Wisconsin, 1990.

**Table 1.** Crystallographic Parameters for the Structures of 3 and 4

| | **3** | **4** |
|---|---|---|
| empirical formula | $C_{28}H_{46}P_3SiIr$ | $C_{16}H_{46}P_3SiIr$ |
| formula mass, amu | 695.85 | 551.73 |
| color and habit | colorless plates | colorless plates |
| crystal size, mm | 0.5 × 0.5 × 0.5 | 0.3 × 0.2 × 0.1 |
| crystal system | monoclinic | triclinic |
| space group | $P2_1/n$ (No. 14) | $P\bar{1}$ (No. 2) |
| $a$, Å | 10.050(2) | 8.653(2) |
| $b$, Å | 31.459(6) | 10.090(2) |
| $c$, Å | 10.325(2) | 14.988(3) |
| $\alpha$, deg | | 92.43(3) |
| $\beta$, deg | 114.61(3) | 94.53(3) |
| $\gamma$, deg | | 113.69(3) |
| $V$, Å$^3$ | 2967.9(10) | 1190.6(4) |
| $Z$ | 4 | 2 |
| density (calcd), g/cm$^3$ | 1.555 | 1.539 |
| $\mu$, mm$^{-1}$ | 4.716 | 5.855 |
| diffractometer | CAD 4 Enraf-Nonius | Rigaku AFC 5R |
| radiation (wavelength, Å) | Mo K$\alpha$ ($\lambda = 0.71073$) | Mo K$\alpha$ ($\lambda = 0.71073$) |
| monochromator | graphite | graphite |
| temp, K | 110 | 110 |
| mode | $\omega$ | $\omega$ |
| $\theta_{max}$, deg | 26.97 | 27.4 |
| scan speed, deg/min | 6 | 16 |
| scan width, deg | 1.2 | 0.8 |
| collection range | $-12 \le h \le 12$;<br>$-2 \le k \le 40$;<br>$-13 \le l \le 13$ | $-11 \le h \le 11$;<br>$-13 \le k \le 13$;<br>$-19 \le l \le 19$ |
| no of reflcns: | | |
| collected | 13653 | 11325 |
| unique | 6447 | 5393 |
| obsd | 4438 ($I > 2\sigma(I)$) | 4907 ($I > 2\sigma(I)$) |
| no. of variables | 312 | 203 |
| corrections applied | Lorentz, polarization | Lorentz, polarization |
| solution | direct method | direct method |
| refinement | full-matrix least-squares | full-matrix least-squares |
| $R_1$ | 0.0696 | 0.0385 |
| $wR_2$ | 0.1265 | 0.0972 |

**Table 2.** Selected Interatomic Bond Lengths (Å) in the Molecule of 3

| atoms | bond length | atoms | bond length |
|---|---|---|---|
| Ir(1)−C(5) | 2.178(11) | P(2)−C(22) | 1.815(12) |
| Ir(1)−P(3) | 2.297(3) | P(2)−C(23) | 1.836(14) |
| Ir(1)−P(1) | 2.339(3) | P(3)−C(31) | 1.822(12) |
| Ir(1)−P(2) | 2.346(3) | P(3)−C(32) | 1.824(12) |
| Ir(1)−Si(4) | 2.381(3) | P(3)−C(33) | 1.831(11) |
| P(1)−C(11) | 1.828(11) | Si(4)−C(41) | 1.922(12) |
| P(1)−C(12) | 1.813(13) | Si(4)−C(42) | 1.916(11) |
| P(1)−C(13) | 1.824(13) | Si(4)−C(43) | 1.919(11) |
| P(2)−C(21) | 1.816(12) | | |

**Table 3.** Selected Bond Angles (deg) in the Molecule of 3

| atoms | bond angle | atoms | bond angle |
|---|---|---|---|
| C(5)−Ir(1)−P(3) | 179.3(3) | P(1)−Ir(1)−Si(4) | 102.33(10) |
| C(5)−Ir(1)−P(1) | 86.4(3) | P(2)−Ir(1)−Si(4) | 152.28(11) |
| P(3)−Ir(1)−P(1) | 94.26(11) | C(42)−Si(4)−C(43) | 105.2(5) |
| C(5)−Ir(1)−P(2) | 83.8(3) | C(42)−Si(4)−C(41) | 104.7(5) |
| P(3)−Ir(1)−P(2) | 95.86(11) | C(43)−Si(4)−C(41) | 94.8(4) |
| P(1)−Ir(1)−P(2) | 100.71(11) | C(42)−Si(4)−Ir(1) | 116.2(4) |
| C(5)−Ir(1)−Si(4) | 82.5(3) | C(43)−Si(4)−Ir(1) | 117.7(3) |
| P(3)−Ir(1)−Si(4) | 97.58(11) | C(41)−Si(4)−Ir(1) | 115.4(4) |

**Table 4.** Selected Interatomic Bond Lengths (Å) in the Molecule of 4

| atoms | bond length | atoms | bond length |
|---|---|---|---|
| Ir(1)−P(1) | 2.339(2) | P(2)−C(22) | 1.843(6) |
| Ir(1)−P(2) | 2.359(2) | P(2)−C(23) | 1.841(7) |
| Ir(1)−P(3) | 2.302(2) | P(3)−C(31) | 1.837(7) |
| Ir(1)−Si(1) | 2.424(2) | P(3)−C(32) | 1.832(6) |
| Ir(1)−C(2) | 2.177(6) | P(3)−C(33) | 1.847(6) |
| P(1)−C(11) | 1.828(6) | Si(1)−C(111) | 1.922(6) |
| P(1)−C(12) | 1.848(7) | Si(1)−C(121) | 1.935(6) |
| P(1)−C(13) | 1.846(7) | Si(1)−C(131) | 1.926(5) |
| P(2)−C(21) | 1.842(7) | | |

**Table 5.** Selected Bond Angles (deg) in the Molecule of 4

| atoms | bond angle | atoms | bond angle |
|---|---|---|---|
| P(1)−Ir(1)−P(2) | 105.14(6) | P(3)−Ir(1)−C(2) | 175.3(2) |
| P(1)−Ir(1)−P(3) | 96.87(6) | Si(1)−Ir(1)−C(2) | 87.3(2) |
| P(2)−Ir(1)−P(3) | 96.95(6) | Ir(1)−Si(1)−C(111) | 116.7(2) |
| P(1)−Ir(1)−Si(1) | 98.89(6) | Ir(1)−Si(1)−C(121) | 119.3(2) |
| P(2)−Ir(1)−Si(1) | 153.08(5) | Ir(1)−Si(1)−C(131) | 112.9(2) |
| P(3)−Ir(1)−Si(1) | 91.97(6) | C(111)−Si(1)−C(121) | 101.4(3) |
| P(1)−Ir(1)−C(2) | 87.9(2) | C(111)−Si(1)−C(131) | 99.7(2) |
| P(2)−Ir(1)−C(2) | 81.7(2) | C(121)−Si(1)−C(131) | 104.2(3) |

**Table 6.** Selected Interatomic Bond Lengths (Å) in the Molecule of 6

| atoms | bond length | atoms | bond length |
|---|---|---|---|
| Ir(1)−P(1) | 2.342(3) | P(3)−C(26) | 1.85(1) |
| Ir(1)−P(2) | 2.314(3) | P(3)−C(27) | 1.82(1) |
| Ir(1)−P(3) | 2.343(3) | Si(1)−C(2) | 1.87(1) |
| Ir(1)−Si(1) | 2.404(3) | Si(1)−C(7) | 1.92(1) |
| Ir(1)−C(1) | 2.16(1) | Si(1)−C(13) | 1.92(1) |
| P(1)−C(19) | 1.83(1) | C(1)−C(2) | 1.41(1) |
| P(1)−C(20) | 1.82(1) | C(1)−C(6) | 1.37(1) |
| P(1)−C(21) | 1.83(1) | C(2)−C(3) | 1.37(1) |
| P(2)−C(22) | 1.81(1) | C(3)−C(4) | 1.40(2) |
| P(2)−C(23) | 1.82(1) | C(4)−C(5) | 1.39(2) |
| P(2)−C(24) | 1.84(1) | C(5)−C(6) | 1.39(1) |
| P(3)−C(25) | 1.82(1) | | |

squares method based on $F^2$ (SHELXL 93).[25] Hydrogens were found from the difference Fourier map and refined in with group temperature factors and scattering factors from the literature.[26] For 312 parameters the following final discrepancy factors were obtained: $R_1$ (based on $F$) = 0.0696 and $wR_2$ (based on $F^2$) = 0.1265 ($I > 2\sigma(I)$); $R_{1'}$ = 0.1137, $wR_{2'}$ = 0.1551 (all data). GOF (on $F^2$) = 1.144. The largest residual electron density of about 4 e Å$^{-3}$ appeared close to the iridium center (0.87 Å). Selected interatomic bond lengths and angles are listed in Tables 2 and 3.

**$(Me_3P)_3Ir(CH_3)(H)(SiEt_3)$ (4).** The structure of **4** was determined on a Rigaku AFC5R diffractometer using Mo K$\alpha$ radiation (graphite monochromator, $\lambda$ = 0.71073 Å). The unit cell was obtained by a random search of 20 reflections in the 2$\theta$ range of 11.52−14.50°, which were refined prior to data collection by a high-angle search (2$\theta$ range: 25.30−29.37°). Information on crystal parameters and data collection is given in the Table 1. Monitoring of three standard reflections every 120 min indicated no decay of the crystal in the X-ray beam. The structure was solved by direct methods (SHELXTL-PC)[24] and refined using the full-matrix least-squares method based on $F^2$ (SHELXL 93).[25] Hydrogens were found from the difference Fourier map and refined in a free mode with group temperature factors and scattering factors from the literature.[26] For 203 parameters the following final $R$-factors were obtained: $R_1$ = 0.0385, $wR_2$ = 0.0972 ($I > 2\sigma(I)$); $R_{1'}$ = 0.0433 and $wR_{2'}$ = 0.1025 (all data). GOF (on $F^2$) = 0.927. The largest electron density of about 3 e Å$^{-3}$ appeared in close proximity from the iridium center (0.94 Å). Selected interatomic bond lengths and angles are presented in Tables 4 and 5.

**$(Me_3P)_3\overline{Ir(H)(o\text{-}C_6H_4Si}Ph_2)$ (6).** The structure of this complex was published in the preliminary account of this work[17] with which supplementary material was deposited. In the present paper selected structural data for **6** are reproduced for the sake of comparison with that of **3**. Selected interatomic bond lengths and angles are presented in Tables 6 and 7.

Full crystallographic data for complexes **3** and **4** are given in the supplementary material.

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[25] Sheldrick, G. M. *SHELXL93*, Program for crystal structure refinement; University of Göttingen: Germany, 1993.

[26] *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, 1974; Vol. IV.

**Table 7.** Selected Bond Angles (deg) in the Molecule of 6

| atoms | bond angle | atoms | bond angle |
|---|---|---|---|
| P(1)–Ir(1)–P(2) | 97.7(1) | Ir(1)–Si(1)–C(13) | 128.0(4) |
| P(1)–Ir(1)–P(3) | 97.3(1) | C(2)–Si(1)–C(7) | 109.3(4) |
| P(1)–Ir(1)–Si(1) | 94.6(1) | C(2)–Si(1)–C(13) | 110.5(5) |
| P(1)–Ir(1)–C(1) | 92.9(3) | C(7)–Si(1)–C(13) | 101.0(4) |
| P(2)–Ir(1)–P(3) | 97.1(1) | Ir(1)–C(1)–C(2) | 108.1(7) |
| P(2)–Ir(1)–Si(1) | 100.38(9) | C(2)–C(1)–C(6) | 117.9(9) |
| P(2)–Ir(1)–C(1) | 164.2(3) | Si(1)–C(2)–C(1) | 99.4(7) |
| P(3)–Ir(1)–Si(1) | 157.3(1) | C(1)–C(2)–C(3) | 121(1) |
| P(3)–Ir(1)–C(1) | 93.2(3) | C(2)–C(3)–C(4) | 121(1) |
| Si(1)–Ir(1)–C(1) | 66.9(3) | C(3)–C(4)–C(5) | 118(1) |
| Ir(1)–Si(1)–C(2) | 85.1(3) | C(4)–C(5)–C(6) | 120.5(9) |
| Ir(1)–Si(1)–C(7) | 120.6(3) | C(1)–C(6)–C(5) | 121(1) |

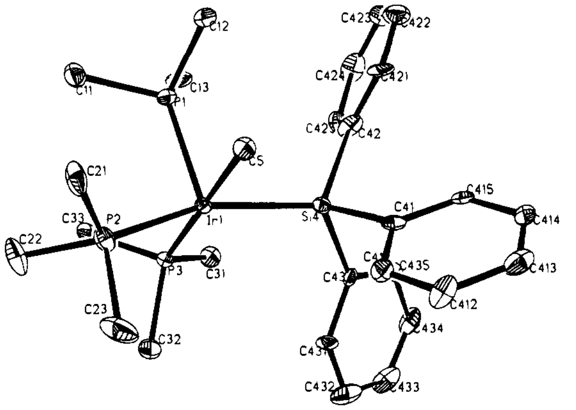
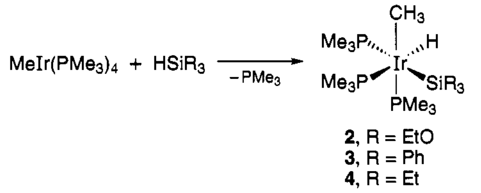


**Figure 1.** Perspective view of a molecule of **3**. Hydrogen atoms are omitted for clarity.

## Results and Discussion

**Reactions between MeIr(PMe$_3$)$_4$ and HSiR$_3$.** Mixing of tertiary silanes HSiR$_3$ (R = EtO, Ph, Et) with MeIr(PMe$_3$)$_4$ in benzene at room temperature resulted in clean formation of the corresponding complexes **2**–**4** (eq 1).



$$\mathrm{MeIr(PMe_3)_4 + HSiR_3 \xrightarrow[-PMe_3]{} fac\text{-}Ir(CH_3)(H)(SiR_3)(PMe_3)_3} \qquad (1)$$

**2**, R = EtO
**3**, R = Ph
**4**, R = Et

The three compounds exhibit similar patterns in $^1$H-NMR, i.e. doublets ($^2J$(H,P) ~ 6.8 – 8.3 Hz) for three different $(CH_3)_3$P groups, widely spaced doublet ($^2J$(H,P,trans) ~ 123–135 Hz) of pseudotriplets ($^2J$(H,P,cis) ~ 15–19 Hz) in the hydride region, high-field multiplet for coordinated C$H_3$, and signals of appropriate intensity and multiplicity corresponding to the SiR$_3$ group bound to Ir. $^{31}$P{$^1$H}-NMR spectra for compounds **2** and **3** contain signals of three inequivalent mutually coupled phosphorus atoms (doublets of doublets or pseudotriplets), while compound **4** exhibits a second order multiplet for two of three phosphines that have close chemical shifts. On the basis of these data the formulation and facial configuration of complexes **2**–**4** are unequivocal. It was also verified in the case of **3** and **4** by X-ray structure analysis.

**X-ray Structures of Complexes 3 and 4.** The solid-state structures of the adducts **3** and **4** determined by single-crystal X-ray studies, exhibit several common features (Figures 1 and 2; Tables 2–5). Both compounds possess a distorted octahedral coordination geometry around the Ir centers. Fully in accord with the NMR spectroscopy data, the arrangement of phosphine ligands is facial. This arrangement places methyl, hydrido, and silyl ligands in mutually cis positions, thus making all three elimination pathways, namely C–H, C–Si, and H–Si, possible in principle without a need for prior isomerization. Importantly, the facial configuration of **3** and **4** enables direct qualitative comparison of the *trans* influence of CH$_3$, H, SiPh$_3$, and SiEt$_3$ ligands. As seen from Tables 2 and 4, in both complexes the Ir–P$_{\text{(trans to CH}_3)}$ bonds are the shortest, Ir–P$_{\text{(trans to H)}}$ bonds are intermediate in length, and Ir–P$_{\text{(trans to Si)}}$ bonds are the longest. Moreover, the Ir1–P2$_{\text{(trans to SiPh}_3)}$ bond (2.346(3) Å) in **3** is shorter than the Ir1–P2$_{\text{(trans to SiEt}_3)}$ bond (2.359(2) Å) in **4**. This indicates the following order of increasing trans influence: CH$_3$ < H < SiPh$_3$ < SiEt$_3$. It is known[27] that silyl ligands have a strong trans influence. It was discussed that it is inductive in nature and is higher when less electronegative substituents are attached to silicon. Our structural data are fully in accord with these considerations.

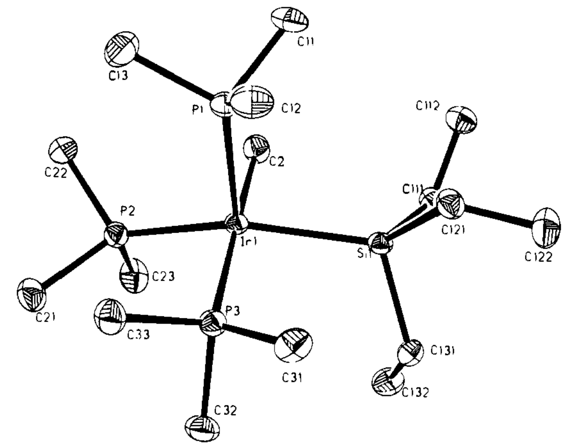


**Figure 2.** Perspective view of a molecule of **4**. Hydrogen atoms are omitted for clarity.

One more important observation can be made when comparing the crystal structures of **3** and **4**. The length of the Ir–SiPh$_3$ bond in **3** (2.381(3) Å) lies in the normal range,[28] while the corresponding Ir–SiEt$_3$ bond in **4** (2.424(2) Å) is among the longest Ir–Si bond ever measured.[29] This is incompatible with simple steric arguments because the SiEt$_3$ ligand is smaller in volume than SiPh$_3$ (isoelectronic PEt$_3$ and PPh$_3$ ligands are characterized by the cone angle values of 132° and 145°, respectively,[30] while P and Si have similar covalent radii[31]). The elongation of the Ir–SiEt$_3$ bond, as compared to Ir–SiPh$_3$, may be a reflection of the former being weaker than the latter, which is in agreement with the reported[32] dependence of the strength of M–SiR$_3$ bonds on the electronegativity of the

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[27] (a) Chatt, J.; Eaborn, C.; Ibekwe, S. *Chem. Commun.* **1966**, 700. (b) Haszeldine, R. N.; Parish, R. V.; Setchfield, J. H. *J. Organomet. Chem.* **1973**, *57*, 279 and references therein.

[28] For other examples of structurally characterized Ir–silyl complexes see: (a) ref 1, pp 264 and 343. (b) Hays, M. K.; Eisenberg, R. *Inorg. Chem.* **1991**, *30*, 2623.

[29] The recently measured Os–SiEt$_3$ bond length in the complex Os(H)(SiEt$_3$)(PPh$_3$)(CO) was found to be the longest known for osmium complexes: Clark, G. R.; Flower, K. R.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *J. Organomet. Chem.* **1993**, *462*, 331.

[30] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[31] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins College Publishers: New York, 1993; p 292.

[32] Haszeldine, R. N.; Parish, R. V.; Taylor, R. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2311. Although in this paper the order of stability of the complexes L$_2$Rh(H)(SiR$_3$)(Cl) (R = Et, Ph) toward reductive elimination of a silane was found to be reversed, i.e. the HSiPh$_3$ adduct was less stable than the one of HSiEt$_3$, it was attributed to steric rather than electronic factors. In the bimetallic Ir–Ta system, however, the Ir(H)(SiEt$_3$) moiety reductively eliminated the Si–H bond much faster than Ir(H)(SiPh$_3$) did, thus indicating that in the absence of steric congestion the Ir–SiPh$_3$ bond is stronger than Ir–SiEt$_3$—see ref 5c.

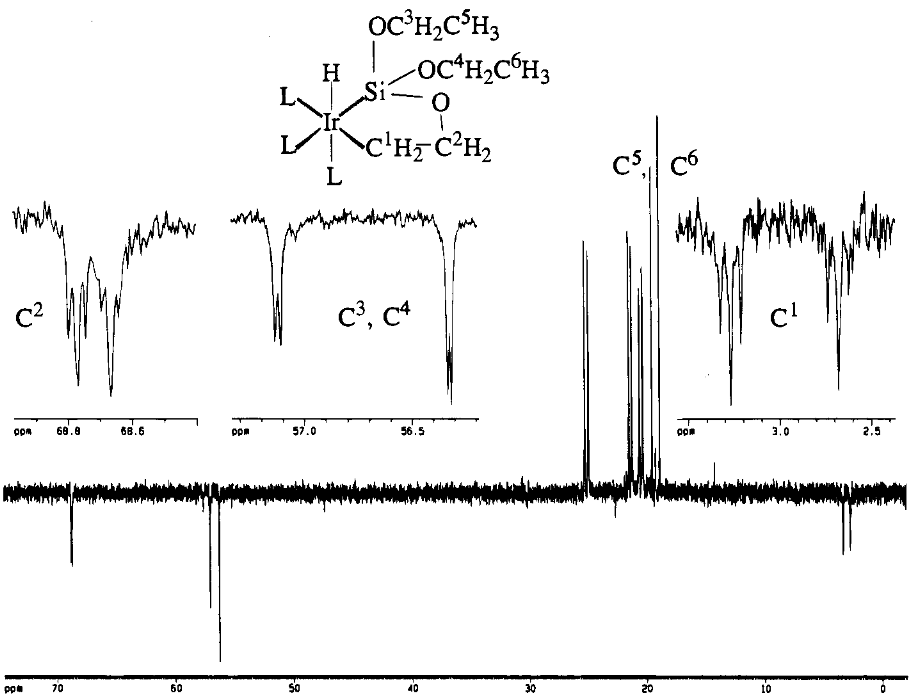
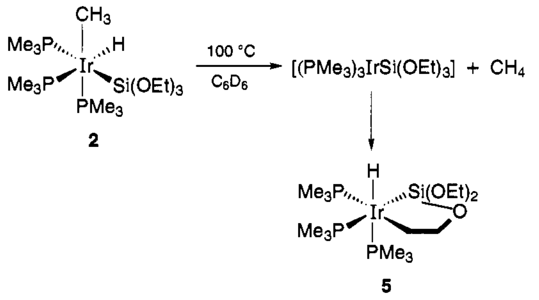


**Figure 3.** $^{13}C$ DEPT 135 NMR spectrum of the reaction mixture resulting from the thermolysis of **2**.

substituents R. This relative weakness of the Ir−SiEt$_3$ bond is, probably, one of the main reasons for the rich reductive elimination reactivity of **4** as compared to that of **2** and **3** (see below). To our knowledge, **3** and **4** are the first structurally characterized complexes that have alkyl, hydrido, and silyl ligands assembled at the same metal center.

**Reductive Eliminations from Complexes 2 and 3. Formation of Iridasilacycles 5 and 6. (a) Thermolysis of 2.** When heated in $C_6D_6$ in a closed vessel at 90 °C for 12 h **2** appeared to be surprisingly stable. Only slight decomposition during this treatment was observed in $^{31}P\{^1H\}$-NMR. However, at 100 °C, the signals in the $^{31}P\{^1H\}$-NMR spectrum, attributable to **2**, completely disappeared after 1 day. Instead, a new set of three mutually coupled signals appeared, indicating quantitative and selective formation of a new facial complex (**5**, see below). The $^1H$-NMR spectrum of the resulting solution contained a sharp singlet at $\delta$ 0.15 ppm whose chemical shift exactly matched that of $CH_4$ dissolved in $C_6D_6$. Methane formation was also confirmed by GC analysis of the gas phase taken from the reaction vessel. $^1H$-NMR also indicated formation of a *fac*-Ir(III) complex that had a hydride, a silyl, bearing inequivalent ethoxy groups, and some other ligand. Final elucidation of the structure of the complex formed in the reaction (eq 2) was achieved using $^{13}C\{^1H\}$ and $^{13}C$ DEPT 135 NMR data. These showed (Figure 3) the presence of a high-field signal at $\delta$ 3.0 ppm which appeared as a doublet of triplets ($^2J_d$(C,P,trans) = 59.3 Hz, $^2J_t$(C,P,cis) = 5.7 Hz) and became negative in DEPT (Ir-bound methylene group, $C^1$), as well as a low-field doublet of triplets at $\delta$ 68.7 ppm ($^3J_d$(C,P,trans) = 10 Hz, $^3J_t$(C,P,cis) = 2.6 Hz) which also became negative in DEPT, indicating an even number of hydrogens (the second methylene group in the iridacycle, $C^2$). Importantly, signals of the methylene carbons $C^3$ and $C^4$ appeared as doublets due to coupling to the trans phosphorus atom ($^4J$(C,P,trans) = 1.6 and 2.5 Hz). Other signals corresponded to three different $PMe_3$ ligands and to two different $OCH_2CH_3$ groups.



(2)

All this taken together excludes the possibility of formation of a 4-membered ring and makes assignment of the cyclic structure to **5** unequivocal. Unfortunately, **5**, like its precursor **2**, is an oil, which makes impossible determination of their solid-state structures by X-ray crystallography.

The selectivity and purity of reaction 2 are vividly seen from the fact that Figure 3 represents the $^{13}C$ NMR spectrum of the reaction mixture, rather than of the purified compound, and they deserve some comment. First, activation of an aliphatic C−H bond occurs intramolecularly, distinctly in preference to intermolecular activation of the aromatic solvent benzene. Second, the reaction is regioselective, resulting in $\delta$-metalation and formation of a 5-membered ring. This takes place despite the fact that C−H bonds of $OCH_2$ groups are expected to be more activated toward metalation as compared to those of the methyl groups in the triethoxysilyl ligand. Analogous preference for formation of more stable 5-membered rings, when there is a choice, was reported for a number of systems involving, e.g., cyclometalated phosphines,[33] phosphites,[34] and hydrocarbyl ligands.[35] We observe that this selectivity holds in the cyclometalation of alkoxysilyls as well. To our knowledge **5** is the first isolated complex resulting from cyclometalation of an organosilyl ligand that does not involve an aryl group.

**Thermolysis of 3.** This complex was also found to be relatively stable to heating. Thermolysis at 90 °C in $C_6D_6$ after 5 h resulted in less than 5% conversion to a new facial complex (**6**, see below). When the temperature of the reaction was raised

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(33) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* **1971**, 3833.

(34) Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 639.

(35) Calabrese, J. C.; Colton, M. C.; Herskovitz, T.; Klabunde, U.; Parshall, G. W.; Thorn, D.; Tulip, T. H. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 302.

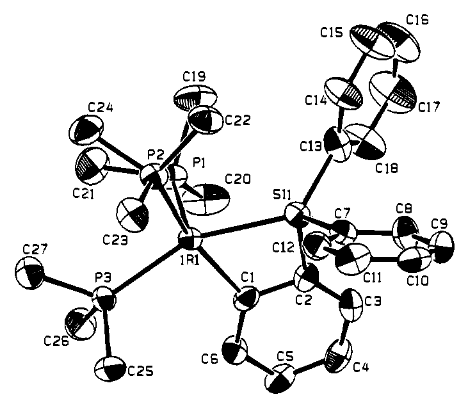
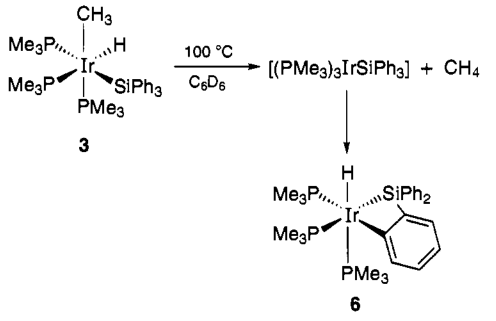


**Figure 4.** Perspective view of a molecule of **6**. Hydrogen atoms are omitted for clarity.

to 100 °C the rate of decomposition increased, and after 1 day the $^{31}$P{$^{1}$H}-NMR spectrum of the reaction mixture indicated quantitative formation of **6** at the expense of the starting material. GC analysis of the gas phase and $^{1}$H-NMR spectrum of the resulting solution showed that methane was produced in the reaction. $^{1}$H-NMR also indicated the presence of a hydride ligand in the complex formed and confirmed the facial disposition of PMe$_3$ groups in it. Importantly, inequivalence of the aromatic rings bound to the silicon was observed. This was expressed by the presence of three signals of relative intensity 2:1:2 in the "ortho-region" (multiplets at $\delta$ 8.36, 8.10, and 8.01 ppm), which showed no coupling to each other in the COSY spectrum. These spectral data are compatible with the formation of an Ir(III) complex with an ortho-metalated SiPh$_3$ ligand (eq 3).



(3)

Final verification of the structure of **6** was achieved by X-ray analysis.

**X-ray Structure of Complex 6.**[17] One can easily see from Figure 4 and Tables 6 and 7 that the coordination geometry around the Ir center in **6** is a distorted octahedron formed by three mutually cis phosphine ligands, a silyl ligand, a carbon of the metalated aromatic ring, and a hydride, which was not located. The four-membered iridasilacycle is clearly visible. The Ir–Si bond is relatively long (2.404(3) Å) as compared to the one in the non-metalated precursor **3** (2.381(3) Å). This is, probably, due to the greater steric crowding in the former, which has also resulted in a higher deviation of $\mathrm{P}_{(\text{trans to C})}$–Ir–C angle from 180° (compare 164.2(3)° in **6** and 179.3(3)° in **3**). At the same time the $\mathrm{P}_{(\text{trans to Si})}$–Ir–Si angle in **6** slightly opens up as compared to the corresponding one in **3** (157.3(1)° *vs* 152.28(11)°). The iridasilacycle itself is not far from being planar. The torsion angles involving Ir1, Si1, C2, and C1 atoms are equal to −5.2(8)°, 6.2(8)°, 3.7(8)°, and −5.3(8)°, the deviation of the iridasilacycle from planarity being less than 0.04 Å. This is in accord with almost undisturbed geometry of the metalated phenyl ring as seen from the values of the bond lengths and angles in it. However, as in similar complexes with a metalated arylphosphine moiety,[36] certain strain is evident in distortion of angles within the 4-membered ring from ideal geometry: C1–Ir1–Si1 66.9(3)° instead of 90°; Ir1–C1–C2 108.1(7)° instead of 120°; C1–C2–Si1 99.4(7)° instead of 120°; C2–Si1–Ir1 85.1(3)° instead of the ideal tetrahedral angle. To our knowledge this is the first structural characterization of a complex resulting from metalation of a silyl ligand.

In contrast to the very well precedented cyclometalation of the isoelectronic phosphine ligands,[37] and quite a number of known examples of distal C–H activation by iridium,[38] cyclometalation of organosilyl ligands is surprisingly rare. We are aware of only one other example of an isolated complex resulting from the orthometalation of an arylsilyl ligand, namely (dcpe)Pt(C$_6$H$_4$)Si(SiMe$_3$)$_2$.[39] In that work and in a number of others[33,40] it was proposed that the cyclometalation reaction can be facilitated in the presence of sterically demanding substituents at a donor atom and at a metal center. We believe that steric effects are unlikely to play an important role in the cyclometalation reaction leading to PMe$_3$ complex **6** and even less likely in the case of the PMe$_3$ complex **5**, because the triethoxysilyl ligand is very small in volume. We still do not know why cyclometalations of organosilyl ligands are that rare. This may be a reflection of much less accessibility of corresponding precursors.[41] Nevertheless, we demonstrate here that formation of silametallacycles can be a facile, selective, and high-yield reaction if appropriate starting complexes are available.

**Reductive Eliminations from Complex 4.** The reactivity of complex **4** is much more complex than that of compounds **2** and **3**. Under no conditions studied was selective C–H reductive elimination observed. Initial experiments on thermolysis of **4** showed that in fact both elimination reactions, namely C–H and C–Si, had occurred. This was concluded on the basis of the following results. $^{1}$H-NMR of the reaction mixture and GC analysis of the gas phase taken from the reaction vessel indicated formation of both methane ($^{1}$H-NMR (C$_6$D$_6$): $\delta$ 0.15, s) and methyltriethylsilane ($^{1}$H-NMR (C$_6$D$_6$): $\delta$ −0.07, s, 3H; 0.47, q (7.9 Hz), 6H; 0.93, t(7.9 Hz), 9H). In the experiment that was run at 100 °C the ratio of CH$_4$ and CH$_3$SiEt$_3$ formed was about 4:1 (yields based on the amount of **4** taken: CH$_4$, *ca.* 80% by GC; CH$_3$SiEt$_3$, *ca.* 20% by $^{1}$H NMR). Similar results were obtained when complex **4** was thermolyzed at 125 °C: CH$_3$SiEt$_3$ was produced in 16% yield. $^{31}$P- and $^{1}$H-NMR spectra of the solution that underwent thermolysis indicated that a mixture of several hydride-containing organometallic products was formed. Neither [(Me$_3$P)$_3$IrSiEt$_3$] nor [(Me$_3$P)$_3$IrH], both of which are expected to be very reactive under the reaction conditions, were detected in the mixture. However, when the reaction was run in the presence of excess PMe$_3$, [(Me$_3$P)$_3$IrH] was trapped and the known (Me$_3$P)$_4$IrH[20] was detected. To accomplish the identification of the Ir complexes formed in the subsequent reactions, which undoubtedly included C–H activation of the solvent benzene,[42] we carried out severalindependent reactions which are shown in the eq 4–8.

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(36) Countryman, R.; McDonald, W. S. *Acta Crystallogr.* **1977**, *B33*, 3580.

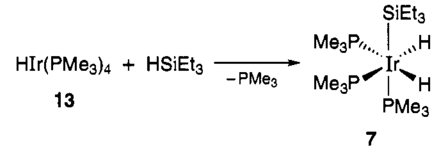
(37) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.

(38) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448.

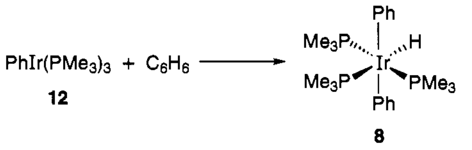
(39) Chang, L. S.; Johnson, M. P.; Fink, M. *Organometallics* **1991**, *10*, 1219.

(40) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. D* **1970**, 1176.

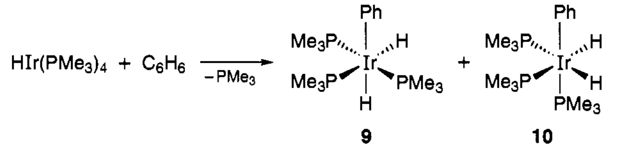
(41) To our knowledge there are only two reports on isolated Ir(I)–silyl complexes—(a) Ir(PCH$_2$CH$_2$SiMe$_2$)(CO)$_2$(PPh$_3$): Auburn, M. J.; Grundy, S. L.; Stobart, S. R.; Zaworotko, M. *J. Am. Chem. Soc.* **1985**, *1037*, 266. (b) Ir(PCy$_3$)(CO)$_3$(SiPh$_3$): Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 4246.



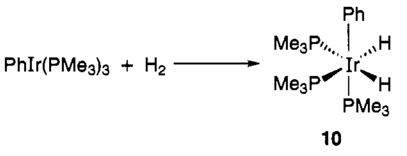
(4)



(5)



(6)



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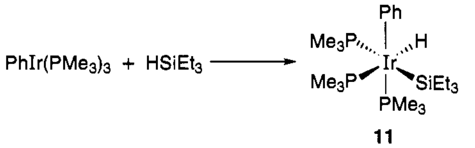

(8)

These reactions and the products formed are worth comment. Reactions 4 and 8 are regular oxidative additions of $Et_3Si-H$ to electron-rich complexes of Ir(I). Both reactions proceed quantitatively and the products **7** and **11** can be readily isolated as light solids. However, while reaction 8 is instantaneous when stoichiometric amounts of the reactants are used, reaction 4, which obviously involves predissociation of $PMe_3$ from the 18-electron $HIr(PMe_3)_4$, is much slower. In order to be completed during several hours, it requires about a 3-fold excess of the silane. This is in accord with the reported[20] very low lability of the $PMe_3$ ligands in $HIr(PMe_3)_4$. Both **7** and **11** have facial configuration and are the only isomers formed. $C_6H_5-H$ oxidative addition reactions 5 and 6 do not proceed at room temperature and require thermal initiation. Here, again, unsaturated $PhIr(PMe_3)_3$ (**12**) was noticeably more active than the saturated $HIr(PMe_3)_4$ (**13**). As a consequence, reaction 5 was 80% complete after 2 days at 100 °C, while the reaction mixture resulting from heating **13** in $C_6H_6$ at 108 °C still contained about 56% of the starting material after 2 days, thus precluding isolation of the resulting mixture of **9** and **10**. Importantly, reaction 6 yields *mer,cis*-$(Me_3P)_3Ir(H)_2(C_6H_5)$ (**9**) as a major product, the ratio **9**:**10** being about 6:1, while direct oxidative addition of dihydrogen to **12** leads to the facial isomer **10** exclusively (eq 7). Activation of Ar−H bonds by the related complex $[Ir(COD)(PMe_3)_3]Cl$ was studied in detail by Merola and Selnau.[43] They reported that only the meridional isomer with H trans to Cl resulted from benzene activation. In our systems we observe formation of both a single isomer (eq 5) and a mixture (eq 6).[44]

Analysis of the mixtures which resulted from a number of experiments on the thermolysis of **4** in $C_6H_6$ or $C_6D_6$ revealed that **7**, **8**, **9**, **10**, **11**, and even **12** along with unreacted **4** can be found in different amounts at different stages of the reaction. The most abundant after heating at 95 °C for 2 days (which appeared to be the optimum conditions leading to the least complicated mixture) were, however, **7** and **8** in approximately a 1.37:1 ratio. The complex nature of the processes that can simultaneously go on in the system makes it difficult to completely understand the reactivity of every complex being formed, but some important conclusions can nevertheless be drawn. Scheme 1 depicts the reaction sequences that we believe can account for the generation of the complexes detected in the reaction mixtures.

We propose that complex **4** can, in fact, undergo all three possible elimination reactions. The fact that the H−Si bond can reductively eliminate[5bc,28b,32] was confirmed by two additional experiments. In the first one **4** was combined in $C_6H_6$ with 5 equiv of another silane, $(EtO)_3SiH$. $^{31}P\{^1H\}$-NMR, after 3 h at room temperature, revealed that the reaction mixture contained 56.3% of **2**, 10.7% of unreacted **4**, and 33.0% of some other complex, most probably *fac*-$(Me_3P)_3Ir(H)(Si(OEt)_3)_2$. $^1H$-NMR indicated formation of free $HSiEt_3$ and $CH_4$. In the second experiment **4** was heated at 85 °C in the presence of excess $PMe_3$, resulting in formation of $MeIr(PMe_3)_4$. These results strongly support the ability of **4** to reductively eliminate $H-SiEt_3$.

Some other observations regarding the reactions depicted in Scheme 1 must be pointed out. It is not surprising that when the solvent used was $C_6D_6$ (and not $C_6H_6$) the $^{31}P$-NMR signals of all phenyl-containing complexes appeared distorted due to $^{31}P-^2H$ coupling. But, more importantly, the signals of **7** were also affected, and $CH_3D$ was detected in $^1H$-NMR ($\delta$ 0.14 ppm, 1:1:1 triplet ($J$ = 2 Hz)). This indicates that one of two (or, most probably, both) reactions can go on in the system: (i) $CH_3D$ elimination from **4** which was reformed on addition of $DSiEt_3$ (formed by other routes) to $[CH_3Ir(PMe_3)_3]$; (ii) oxidative addition of $C_6D_6$ to $[CH_3Ir(PMe_3)_3]$ with subsequent $CH_3D$ elimination and formation of $C_6D_5Ir(PMe_3)_3$. Our observation that **11** can be detected in the reaction mixture can account for D/H exchange between $HSiEt_3$ and $C_6D_6$ and, consequently, for the partial deuteration of the hydrides in **7**. Phenyltriethylsilane was observed as a minor product[45] in a separate experiment, in which independently prepared **11** was heated in benzene. It was identified by comparing the signals in $^1H$-NMR with those of an authentic sample ($\delta$ [7.45 m, 7.22 m, 5H, $C_6H_5$]; 0.96 overlapped triplets, 9H, $Si(CH_2CH_3)_3$; 0.74 overlapped quartets, 6H, $Si(CH_2CH_3)_3$). However, it was detected only in small amounts in experiments in which **4** was heated in benzene under the same conditions. No formation of $Et_3Si-SiEt_3$ was observed. This is in contrast with the reactivity of Ir−dppe complexes toward $HSiEt_3$[46] and in agreement with the results obtained for $(PPh_3)_2Pt(C_2H_4)$.[47] Some signals of olefinic protons, probably due to compounds resulting from C−H activation of $Et_3Si$ groups and subsequent $\beta$-H elimination, were detected. These processes together with $\beta$-H elimination from the $SiEt_3$ ligand[48] could serve as additional sources for the formation of the hydridoiridium(I) intermediate, which, when captured by free $HSiEt_3$, leads to additional amounts of **7**. The

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[42] This was clearly evidenced by characteristic distortion due to deuterium−phosphorus coupling of some of the signals observed in $^{31}P\{^1H\}$ NMR when the thermolysis was carried out in $C_6D_6$.

[43] (a) Merola, J. S. *Organometallics* **1989**, *8*, 2975. (b) Selnau, H. E.; Merola, J. S. *Organometallics* **1994**, *12*, 1583.

[44] The C−H activation reactions depicted in eqs 5 and 6 and complexes **8**, **9**, and **10** are of interest in their own right. Aspects of kinetic preference and thermodynamic stability of isomers formed are currently under study. They are beyond the scope of this paper and will be reported separately.

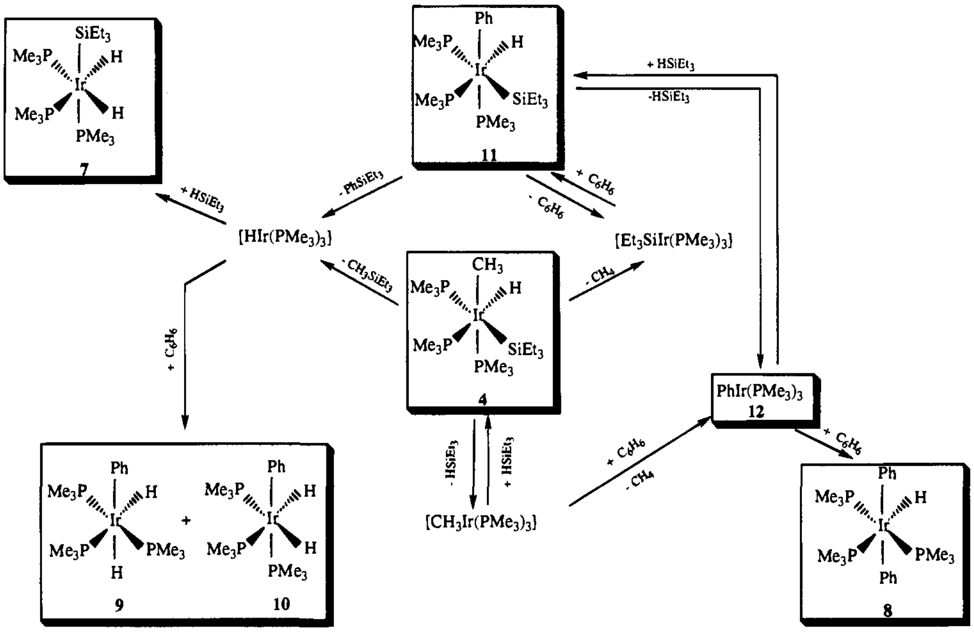
[45] Major decomposition pathways of **11** were, probably, $H-SiEt_3$ and $H-C_6H_5$ reductive eliminations, leading to mixtures, which contained **8** and **7** along with other complexes.

[46] Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531.

[47] Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.

[48] (a) Berry, D. H.; Procopio, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 4099. (b) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1826. (c) Yamashita, H.; Kawamoto, N.; Tanaka, M.; Goto, M. *Chem. Lett.* **1991**, 2107. (d) Djurovich, P. I.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 2551. (e) Djurovich, P. I.; Dolich, A. R.; Berry, D. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1897.

**Scheme 1**



apparent very complicated nature of the system described precluded complete analysis and it was not investigated further.

**Competition between C−H and C−Si Bond Formation.** As seen from the results above, there is a distinct difference in the reductive elimination reactivity of complexes **2** and **3**, on one hand, and **4**, on the other, despite the very close analogy in their structures. Whereas **2** and **3** eliminate $CH_4$ exclusively, **4** is prone to all three elimination reactions. As the yield of $CH_3SiEt_3$, observed at 100 °C, is about 20%, and assuming C−H and C−Si bond formation is irreversible, one can roughly estimate the upper limit[49] of their relative rates as $k_{C-H}/k_{C-Si} \approx 4$.

The reasons for the aforementioned difference in reactivity can be both thermodynamic and kinetic in nature. C−H reductive elimination which requires reorientation of one directional orbital toward the spherical one is usually more facile than C−C reductive elimination which involves reorientation of two directional orbitals. This leads to a higher kinetic barrier for the latter,[50] although thermodynamics of C−C reductive elimination are favorable. When a highly electropositive metal is bound to a silyl ligand it can direct a high degree of s-character to the silicon contribution to the M−Si bond[51] as was discussed for stannyl derivatives.[52] This can facilitate the required reorientation. This effect, however, is expected to be expressed more as the electronegativity of the substituents at the silicon increases. On the other hand, the thermodynamic driving force for C−Si reductive elimination is stronger when the metal−silicon bond is weaker, i.e. it goes in the opposite direction. So, what we, most probably, observe is a combination of thermodynamic and kinetic factors[53] which results in the C−Si reductive elimination becoming competitive with C−H when one deals with **alkylsilyl** complexes. It should be stressed, however, that with electronegative substituents at silicon C−H reductive elimination definitely wins the competition.

## Conclusions

We have synthesized a series of *facial* (methyl)(hydrido)(silyl) complexes of Ir(III) and determined the X-ray structures for two of them. These data enabled us to arrange $CH_3$, H, $SiPh_3$, and $SiEt_3$ ligands according to their *trans* influence as well as revealed that the less sterically demanding $SiEt_3$ ligand is involved in longer and, probably, weaker bonding to the Ir center than $SiPh_3$. We have demonstrated that the $Si(OEt)_3$ and $SiPh_3$ derivatives **2** and **3** under the conditions when C−H, C−Si, and H−Si reductive elimination reactions can compete form the C−H bond exclusively. The resulting very reactive Ir(I) silyls undergo quantitative and regioselective *intra*molecular C−H activation reactions and produce novel iridasilacycles, which we unequivocally characterized spectroscopically (complex **5**) and structurally (complex **6**). We have shown that the $SiEt_3$ derivative **4**, in which the Ir−Si bond is weaker, on heating eliminates all three possible bonds, namely, C−H, C−Si, and H−Si, competitively. We have also studied the reactivity of the resulting electron-rich Ir(I) complexes in C−H activation of benzene. These findings indicate that generalizations on mechanisms of catalytic transformations of organosilicon compounds should be viewed with much caution if they do not take into consideration the nature of the silicon substrates involved.

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**Supplementary Material Available:** Tables of atomic coordinates, bond distances and angles, and ansitropic displacement coefficients for **3** and **4** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[49] The H−Si reductive elimination, although reversible, results in the secondary $CH_4$ formation, thus preventing exact determination of the relative rates for C−H and C−Si elimination from 4 based solely on the absolute yields of $CH_4$ and $CH_3SiEt_3$.

[50] Low, J. J.; Goddard, W. A., III *Organometallics* **1986**, *5*, 609.

[51] Reference 1, p 266.

[52] Ho, B. Y. K.; Zuckerman, J. J. *J. Organomet. Chem.* **1973**, *49*, 1.

[53] For a recent discussion of the factors affecting reductive elimination and oxidative addition of Si−E (E = C, Si) bonds see: Schubert, U. *Angew. Chem.* **1994**, *106*, 435; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419.