ELSEVIER
www.elsevier.nl/locate/jorganchem
Journal of Organometallic Chemistry 593–594 (2000) 154–160
Journal of Organometallic Chemistry

Catalytic and stoichiometric reactions of tertiary silanes with [Ir(Me)$_2$Cp*L] (Cp* = η^5-C$_5$Me$_5$; L = PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$) in the presence of one-electron oxidants. A unique case of Si–H, Si–C, Ir–C and P–F bonds one-step activation: crystal structure of [Ir(Ph)(SiPh$_2$F)Cp*(PMe$_3$)]

Pietro Diversi [a,*], Fabio Marchetti [b], Valentina Ermini [a], Simona Matteoni [a]

[a] *Dipartimento di Chimica e Chimica Industriale dell'Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy*
[b] *Dipartimento di Ingegneria Chimica dei Materiali e delle Materie Prime e Metallurgia dell'Università 'La Sapienza', Via del Castro Laurenziano 7, I-00195 Rome, Italy*

Received 28 May 1999; accepted 2 August 1999

Abstract

The iridium(III) dimethyl derivatives [Ir(Me)$_2$Cp*L] (Cp* = η^5-C$_5$Me$_5$; L = PMe$_3$ **1a**, PPh$_3$ **1d**) catalyze the dehydrogenative coupling of dimethylphenylsilane in the presence of one-electron oxidants to yield Me$_2$PhSiSiPhMe$_2$. Compounds **1a**–**d** react with triphenylsilane in the presence of [FeCp$_2$]PF$_6$ to give methane and [Ir(Ph)(SiFPh$_2$)Cp*L] (L = PMe$_3$ (**2a**), PMe$_2$Ph (**2b**), PMePh$_2$ (**2c**), PPh$_3$ (**2d**)). **2a** was structurally characterized by single-crystal X-ray diffraction experiments. The 'three-legged piano stool' coordination polyhedron is slightly deformed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iridium; Electron-transfer catalysis; Silanes; Dehydrocoupling

1. Introduction

We have described in previous papers [1] the reactions of the Ir(III) dimethyl complexes [Ir(Me)$_2$Cp*L] (L = PMe$_3$ (**1a**), PMe$_2$Ph (**1b**), PMePh$_2$ (**1c**), PPh$_3$ (**1d**)) with arenes under oxidative conditions to give methane and the corresponding methylaryl derivatives [Ir(Me)(Ar)Cp*L] via a 'σ-bond metathesis' reaction of Ir–C and C–H bonds. With the aim to extend the applicability of this reaction we have moved our attention to the activation of Si–H bonds, which are known to undergo a variety of catalytic [2] and stoichiometric [3] reactions in the presence of transition metals. Here we report that the above iridium derivatives in the presence of one-electron oxidants are able to catalyze the deydrogenative coupling of PhMe$_2$SiH to the disilane and react with Ph$_3$SiH to give new iridium complexes resulting from a novel one-step rearrangement of Si–H, Si–C, Ir–C, and P–F bonds.

2. Results and discussion

The reaction of PhMe$_2$SiH in the presence of catalytic amounts of **1a** or **1d** and one-electron oxidants ([FeCp$_2$]PF$_6$, AgBF$_4$) in CH$_2$Cl$_2$ showed formation of the product of dehydrogenative coupling PhMe$_2$SiSiMe$_2$Ph (Table 1):

$$2\text{PhMe}_2\text{SiH} \rightarrow \text{PhMe}_2\text{SiSiMe}_2\text{Ph} + \text{H}_2$$

Compound **1a** proved to be a better catalyst precursor than **1d**. The yields depend significantly on the temperature and on silane/catalyst ratio, being quite low (2%) at room temperature (r.t.) and at a silane/iridium ratio of 1000, but increasing remarkably (up to 71%) with the temperature (80°C) and by decreasing the silane:iridium ratio (400). No detectable amounts of disilane form in the absence of the oxidant agent.

---

* Corresponding author. Fax: +39-050-918-260.
E-mail address: div@dcci.unipi.it (P. Diversi)

0022-328X/00/$ - see front matter
PII: S0022-328X(99)00469-6

Table 1
Dehydrocoupling of $PhMe_2SiH$ in the presence of $[Ir(Me)_2Cp^*L]$/oxidant

Complex	Ox [a]	Ox/Ir [b]	Si/Ir [b]	*T* (°C)	Time (days)	$(PhMe_2Si)_2$ yield (%)	Ph_2MeSiH yield (%)
1a	$[FeCp_2]^+$	2.0	1000	25	6	2.5	–
1a	$[FeCp_2]^+$	2.0	1000	40	6	8	–
1a	$[FeCp_2]^+$	2.5	400	80	1	37	3.4
1a	$[FeCp_2]^+$	2.5	400	80	2	71	–
1d	$[FeCp_2]^+$	2.0	1000	25	6	0.6	–
1d	$[FeCp_2]^+$	2.0	1000	40	6	2.2	–
1a	Ag^+	2.5	400	80	2	5 [c]	–
1a	Ag^+	2.5	400	80	2	25	17.5

[a] Ox, oxidant; reactions carried out using 6.3 mmol of silane in 1.6 ml of CH_2Cl_2.
[b] Molar ratio.
[c] In a sealed tube.

The yields are lower in the presence of $AgBF_4$ or in a sealed system, as it is to be expected for a reaction which proceeds with formation of dihydrogen.

It has to be noted that, depending on the experimental conditions, formation of Ph_2MeSiH was also observed. This product does not form at all if the reaction is carried out in a closed system. It is possible that Ph_2MeSiH formed by disproportionation of the starting silane.

$$2PhMe_2SiH \rightarrow Ph_2MeSiH + Me_3SiH$$

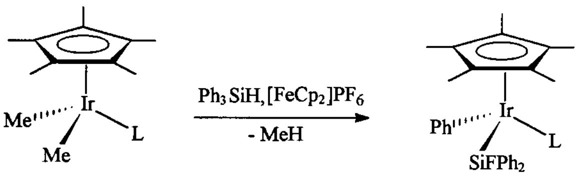
Transition-metal catalyzed redistribution reactions, which exchange groups bonded to silicon are well known [2c,4].

In general the catalytic systems reported in the literature are inactive or poorly active for the dehydrogenative coupling of tertiary silanes, the order of reactivity being tertiary < secondary < primary [2]. Then the activity of our system towards $PhMe_2SiH$ is an interesting peculiarity since only a few catalysts are able to catalyze the dehydrogenative coupling of monohydrosilanes ($PhMe_2SiH$, Ph_2MeSiH) [5]. The best yields (71%) of $(PhMe_2Si)_2$ we have obtained are remarkably high, if compared with those reported in the literature for tertiary silanes: for instance, dehydrogenative coupling of $PhMe_2SiH$ proceeds only with 7% yield in the presence of $[Pt(PMe_2Ph)_4]$ at 150°C [5b].

In the literature two main reaction pathways have been proposed for dehydrocoupling reactions, a concerted mechanism for the early transition-metal catalyzed reactions, and an oxidative addition/reductive elimination sequence for the late transition-metal catalyzed reactions [5]. However we are inclined to prefer the first one in analogy to what we have proposed for some arene C–H activation reactions observed with the same iridium/oxidant system [1]. As for the role of the one-electron oxidant we believe that its presence is necessary in order to trigger the reductive elimination steps of methane which lead eventually to the active species $[Ir(SiMe_2Ph)Cp^*(L)]^+$.

Other silanes such as Ph_2MeSiH and Ph_3SiH do not give dehydrocoupling products under the above conditions probably because of the greater steric requirements due to the presence of the aromatic groups (although in the case of Ph_3SiH small amounts of $Ph_3SiOSiPh_3$ have been occasionally observed, as it is reported to occur for dehydrocoupling reactions catalyzed by late transition metal systems [2a,b] in the presence of adventitious traces of water or dioxygen). Instead Ph_3SiH reacts stoichiometrically with **1a–d** to give new organometallic complexes which have been isolated and characterized. When a slight excess of triphenylsilane and a 1:1 ferrocenium:iridium ratio are used, formation of the new organometallic complexes **2** takes place, which contain an Ir–Ph and an Ir–$SiFPh_2$ bond (Scheme 1).

The reaction proceeds rapidly at r.t. by adding equimolar amounts of $[FeCp_2]PF_6$ to a solution of **1a–d** in dichloromethane containing an excess of triphenylsilane. A gas evolves from the surface of the oxidant which by monitoring the reaction by ^{1}H-NMR spectroscopy in CD_2Cl_2 was identified as methane (δ 0.20 ppm, s). After ca. 1 h at r.t., it was found that **1a–d** have been almost quantitatively converted into the new organometallic compounds **2a–d**. These products were isolated from the reaction mixture as pale–yellow crystals, soluble in dichloromethane, benzene and relatively stable in the air. The ^{1}H-NMR spectrum



1a	L = PMe_3	**2a**
1b	L = PMe_2Ph	**2b**
1c	L = $PMePh_2$	**2c**
1d	L = PPh_3	**2d**

Scheme 1.

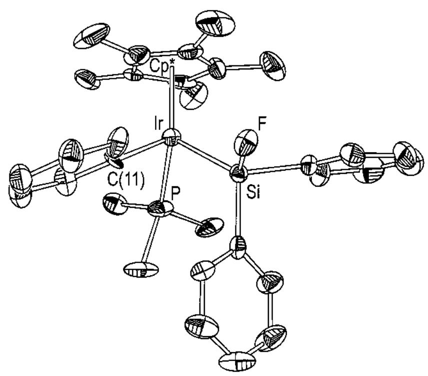


Fig. 1. Molecular structure of [Ir(Ph)(SiFPh$_2$)Cp*(PMe$_3$)] (**2a**).

is characterized by the presence of signals due to the pentamethylcyclopentadienyl ligand, the phosphine, and a series of aromatic multiplets. For instance the spectrum of **2a** in CD$_2$Cl$_2$ shows two doublet resonances at 1.32 ppm ($J_{HP} = 1.79$ Hz) and 1.57 ppm ($J_{HP} = 9.9$ Hz) assigned to the C$_5$Me$_5$ and PMe$_3$ proton atoms, and a multiplet between 6.9 and 7.7 ppm due to the aromatic protons. The ^{31}P-NMR spectrum in C$_6$D$_6$ shows a singlet at -45.5 ppm, which is consistent with the observed values of related half-sandwich trimethylphosphino complexes of Ir(III) [1b,6]. Moreover the ^{19}F-NMR resonances of **2a–d** present the ^{29}Si (nuclear spin 1/2, 4.7% abundance) satellites which indicate that the Si and F atoms are connected. The chemical shifts of the fluorine nuclei are in agreement with those reported in the literature for systems containing Si–F bonds [6,7].

In order to clarify the nature of these products, crystals of **2a** suitable for an X-ray analysis were prepared by slow crystallization from dichloromethane/pentane solutions. The X-ray structure determination has established that in addition to the Cp* and phosphine ligands the iridium center is bonded to a phenyl and a SiFPh$_2$ group. The molecular structure of **2a** is shown in Fig. 1. The coordination around the metal is the usual 'three-legged piano stool' generally found in half-sandwich derivatives of Ir(III). The bonding geometry around the metal is listed in Table 2. The coordination distances are in keeping, within the standard deviations, with the values generally found in (η^5 - pentamethylcyclopentadienyl) – phosphino – silyl derivatives of Ir(III) [3,8]. The Ir–C(11) distance may instead be compared with those found in other Ir(III)–phenyl derivatives: by instance 2.076 Å in (η^5-pentamethylcyclopentadienyl)–trimethylphosphino–trifluoromethanesulfonyl–phenyl–iridium [9], 2.063 Å in (η^5 - ethyl(tetramethyl) – cyclopentadienyl) – fluoro–phenyl–trimethylphosphine–iridium [6] or 2.094 Å in (*Z*) - (η^5 - pentamethylcyclopentadienyl)–trimethylphosphino–(1 - hydroxy - 1,2 - bis(methoxycarbonyl)ethenyl)–phenyl–iridium [9]. Provided that the 'three-legged piano stool' may be considered as an octahedral coordination where three corners are occupied by the Cp*, the bond angles among the 'legs' of the 'stool' are normally found closely near to 90°. This value is observed also in this case, with minor deviations ($<3°$) due to the different hindrance of the ligands, the greatest angles being those adjacent to the iridium phosphorus bond.

Table 2
Selected bond distances (Å) and angles (°) around the metal in **2a** [a,b]

Ir–C(11)	2.08(2)	Ir–Cp′	1.979(13)
Ir–P	2.266(6)	Ir–Si	2.318(7)
Si–F	1.653(14)		
Cp′–Ir–C(11)	119.8(7)	Cp′–Ir–Si	124.0(4)
C(11)–Ir–P	91.1(6)	P–Ir–Si	92.8(3)
Cp′–Ir–P	128.6(4)	C(11)–Ir–Si	90.4(6)

[a] Estimated standard deviations are given in parentheses.

[b] Cp′ denotes the centroid of the Cp* ligand.

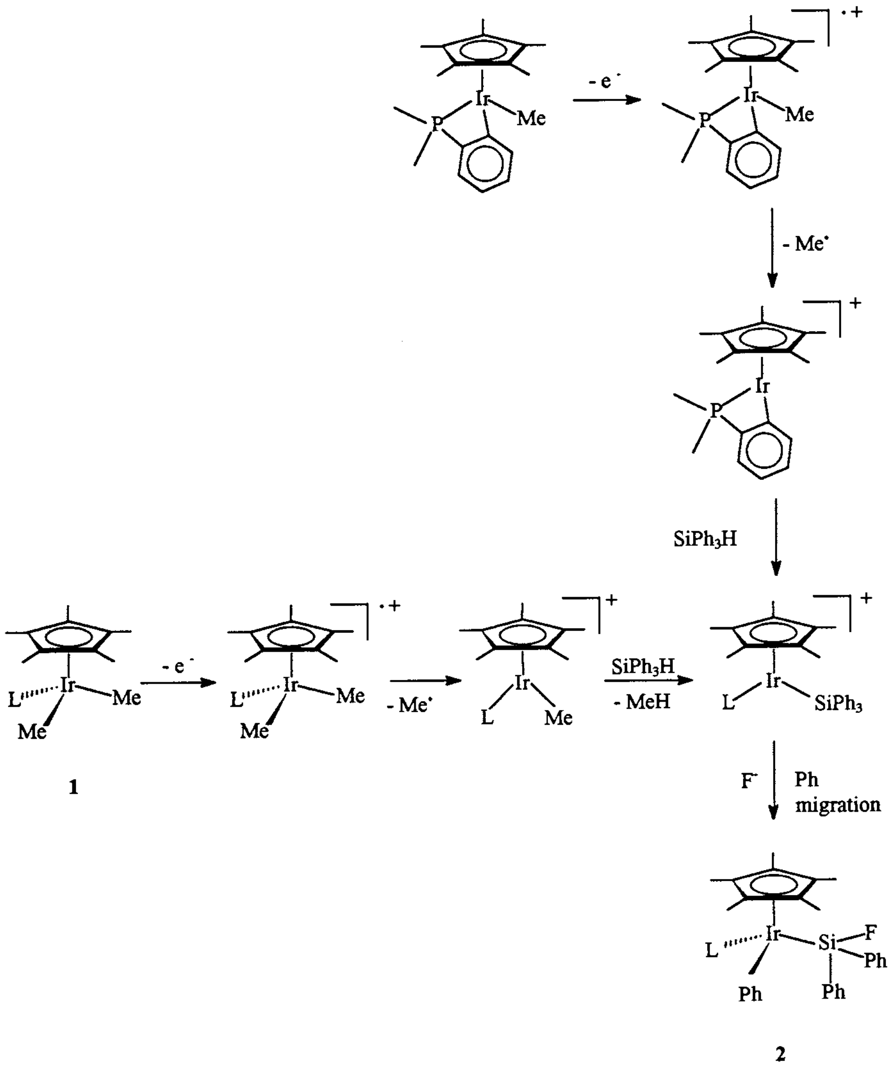
It is interesting to observe that Ph$_3$SiH does also react with [Ir(C$_6$H$_4$PPh$_2$)(Me)Cp*] [1a,b] in the presence of [FeCp$_2$]PF$_6$ to give **2d**, with similar rates and reaction times. Analogously **2c** is also obtained by reaction of Ph$_3$SiH with [Ir(C$_6$H$_4$PMePh)(Me)Cp*] [1c].

Under the above stoichiometric conditions PhSiMe$_2$H gave poor yields of complex mixtures of organometallic compounds which we have not been able to characterize.

The formation of **2a–d** is a complex reaction by which two Ir–C bonds, the Si–H and Si–C bonds of triphenylsilane and a P–F bond of the PF$_6^-$ anion are cleaved, and Ir–Si, Ir–C and Si–F bonds are formed, with concurrent elimination of 2 mol of methane per mole of complex. A plausible mechanism is shown in the Scheme 2.

The role of the oxidant, besides being the source of fluorine which is bonded to the silicon atom in the final product, is that of triggering the homolysis reaction of the Ir–Me bond which is a prerequisite for the activation of silane. Since methane does not incorporate deuterium in the reaction carried out in CD$_2$Cl$_2$, at least half of the methane produced is eliminated intramolecularly. Although at the moment we have no other evidence, we think that a 'tucked-in' intermediate [10] is operating in both the methane elimination steps. The intermediacy of such species has been already demonstrated for C–H activation reactions under oxidative conditions [1c] with the same iridium systems, but other routes are of course possible [11].

Then metathesis of Ir–Me and Si–H bonds produces a SiPh$_3$ ligand, which undergoes Si–Ph cleavage with the phenyl group migrating to the iridium center and a fluoride ion moving from the hexafluorophosphate anion to the silicon atom. The route from the orthometallated derivatives after the addition of the silane is identical.



Scheme 2.

An interesting mechanistic question concerns the transfer of a phenyl group from silicon to the iridium atom. Transfer of an aryl group from silicon to a transition metal to form a metal–aryl bond has been previously observed [6,12]. The occurrence of a cationic silylene intermediate (possibly generated via 1,2-shifts between the metal and silicon) may be involved (Scheme 2). A related cationic silylene ruthenium complex has been recently isolated [13]. Alternatively the cationic silyl intermediate may undergo F^- attack and migration of the phenyl group to the iridium center.

These mechanistic pathways have been already proposed for other rearrangement reactions of substituted silyl groups bonded to an iridium center [6,12b]. In particular the same cationic methyl intermediate $[Ir(Me)Cp^*(PMe_3)]^+$, which is reported to derive from ionization of the starting trifluoromethanesulfonato complex $[Ir(Me)(OSO_2CF_3)Cp^*(PMe_3)]$ [12b], in our case is produced by the reductive elimination of methane promoted by the one electron oxidation of the dimethyl compound **1**.

Finally, a crucial point is the mechanistic significance of these results in connection with the catalytic reactions. Our opinion is that the same intermediate which has been proposed in the Scheme 2, $[Ir(SiR_3)Cp^*(L)]^+$, is the active species for the dehydrocoupling and that only a delicate balance of steric and electronic properties of the silane, according to the nature of the groups attached to silicon, may decide which is the preferred reaction pattern. Work is in progress in order to verify these ideas.

3. Experimental

The reactions and manipulation of organometallics were carried out under dinitrogen or argon, using standard techniques. The solvents were dried and distilled prior to use. The compounds [Ir(Me)$_2$Cp*(L)] (L = PMe$_3$ (**1a**) [1b], PMe$_2$Ph (**1b**) [1c], PMePh$_2$ (**1c**) [1c], PPh$_3$ (**1d**) [1b]), were prepared according to literature procedures. Commercial reagents, AgBF$_4$, [FeCp$_2$]PF$_6$, Ph$_3$SiH, PhMe$_2$SiH and Ph$_2$MeSiH were used as supplied. ^{1}H, ^{13}C, ^{31}P, ^{19}F, ^{2}H-NMR spectra were recorded on Varian Gemini 200 and VXR 300 instruments. Elemental analyses were performed by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, University of Pisa.

*3.1. Reaction of dimethylphenylsilane in the presence of **1a** or **1b** and [FeCp$_2$]PF$_6$ or AgBF$_4$: general procedure*

The reaction of Ph$_2$MeSiH in the presence of **1a** and [FeCp$_2$]PF$_6$ is reported as an example. Ph$_2$MeSiH (1 ml, 6.3 mmol), **1a** (6.8 mg, 0.016 mmol) and [FeCp$_2$]PF$_6$ (13.0 mg, 0.039 mmol) were introduced under argon atmosphere in a two-necked flask equipped with a reflux condenser and a stirbar, and 1.6 ml of anhydrous deoxygenated CH$_2$Cl$_2$ were added. The reaction mixture was heated for the desired time at constant temperature, then, after removal of the volatiles, the residue was eluted through a column of alumina by using a benzene/pentane mixture. The oily residue was examined by ^{1}H-NMR spectroscopy. (Me$_2$PhSi)$_2$ [14] and Ph$_2$MeSiH were identified on the basis of spectroscopic data.

(Me$_2$PhSi)$_2$: ^{1}H-NMR (CDCl$_3$): $\delta = 0.32$ (12H, s, SiMe); 7.25–7.60 (10H, m, Ph) (Ref. [14] $\delta = 0.32$). (C$_6$D$_6$): $\delta = 0.31$ (12H, s, SiMe); 7.20 (12H, m, Ph), 7.55 (8H, m, Ph). MS: *m*/*z* 270 (M$^+$), 135.

Ph$_2$MeSiH: ^{1}H-NMR (CDCl$_3$): $\delta = 0.63$ (3H, d, J = 3.7 Hz, SiMe); 4.95 (1H, q, J = 3.9 Hz, SiH); 7.25–7.60 (10H, m, Ph). (CD$_2$Cl$_2$): 0.68 (3H, d, SiMe); 4.97 (1H, q, SiH); 7.35–7.70 (10H, m, Ph).

*3.2. General procedure for the reaction of [Ir(Me)$_2$Cp*L] (**1a–d**) with SiPh$_3$H and [FeCp$_2$]PF$_6$: formation of [Ir(Ph)(SiPh$_2$F)Cp*L] (**2a–d**)*

Complexes **1a–d** (20–30 mg), ferrocenium hexafluorophosphate (equimolar amounts) and triphenylsilane (Si:Ir molar ratio = 2) were reacted in CH$_2$Cl$_2$ (0.75 ml) under stirring. A vigorous formation of methane was observed (δ 0.20 ppm in CD$_2$Cl$_2$). Ferrocene was formed (δ 4.18 ppm in CD$_2$Cl$_2$). After 1–2 h the reaction mixture was dried under vacuum. The yellow oily residue was chromatographed on an alumina column by eluting with pentane/benzene. The eluted product was crystallized from dichloromethane/pentane to give **2a** (83%), **2b** (81%), **2c** (75%), **2d** (70%) as white crystals.

*3.2.1. Complex **2a***

Anal. Found: C, 55.2; H, 5.7. C$_{31}$H$_{39}$FIrPSi Calc.: C, 54.6; H, 5.8%; ^{1}H-NMR (CD$_2$Cl$_2$): δ 1.32 (9H, d, $J_{HP} = 9.9$ Hz, PMe$_3$), 1.57 (15H, d, $J_{HP} = 1.8$ Hz, C$_5$Me$_5$), 6.9–7.7 (15H, bm, Ph); (C$_6$D$_6$): δ 1.11 (9H, d, PMe$_3$), 1.47 (15H, d, C$_5$Me$_5$), 6.7–7.4 (bm, Ph). ^{13}C-NMR (C$_6$D$_6$): 9.81 (s, C$_5$Me$_5$), 18.41 (d, $J_{CP} = 38$ Hz, PMe$_3$), 97.32 (s, C$_5$Me$_5$), 122.5, 127.4, 127.5, 127.6, 127.7, 128.6, 135.1, 135.3, 144.6 (d, $J_{CP} = 3.7$ Hz) (Ph). ^{19}F-NMR (C$_6$D$_6$): δ −151.12 (d, $J_{SiF} = 316$ Hz).

*3.2.2. Complex **2b***

Anal. Found: C, 57.8; H, 5.4. C$_{31}$H$_{39}$FIrPSi Calc.: C, 58.1; H, 5.5%; ^{1}H-NMR (CD$_2$Cl$_2$): δ 1.23 (3H, d, $J_{HP} = 10.1$ Hz, PMe), 1.42 (3H, d, $J_{HP} = 9.7$ Hz, PMe), 1.48 (15H, d, $J_{HP} = 1.9$ Hz, C$_5$Me$_5$), 6.8–7.7 (bm, Ph); (C$_6$D$_6$): δ 1.17 (3H, d, PMe), 1.26 (3H, d, PMe), 1.40 (15H, d, C$_5$Me$_5$), 7.0–8.0 (bm, Ph). ^{19}F-NMR (C$_6$D$_6$): δ −148.9 (d, $J_{SiF} = 312$ Hz).

*3.2.3. Complex **2c***

Anal. Found: C, 60.9; H, 5.5. C$_{41}$H$_{43}$FIrPSi Calc.: C, 61.1; H, 5.4%. ^{1}H-NMR (CD$_2$Cl$_2$): δ 1.05 (3H, d, $J_{HP} = 10.1$ Hz, PMe), 1.46 (15H, d, $J_{HP} = 1.7$ Hz, C$_5$Me$_5$), 6.8–7.7 (bm, Ph). ^{19}F-NMR (C$_6$D$_6$): δ −145.7 (d, $J_{SiF} = 308.5$ Hz).

*3.2.4. Complex **2d***

Anal. Found: C, 64.0; H, 5.3. C$_{46}$H$_{45}$FIrPSi Calc.: C, 63.6; H, 5.2%. ^{1}H-NMR (CD$_2$Cl$_2$): δ 1.45 (15H, d, $J_{HP} = 2.0$ Hz, C$_5$Me$_5$), 6.8–7.0 (bm, Ph). ^{19}F-NMR (C$_6$D$_6$): δ −142.3 (d, $J_{SiF} = 305.4$ Hz). ^{13}C-NMR (C$_6$D$_6$): 9.75 (s, C$_5$Me$_5$), 100.00 (s, C$_5$Me$_5$), 121.01–145.39 (m, Ph).

3.3. Crystallographic studies

Single crystals of **2a** are colorless prisms. One of them was mounted in nitrogen atmosphere on a Siemens P4 diffractometer. Details about the crystal parameters and intensity data collection are summarized in Table 3. The diffraction symmetry and systematic absences suggested the *Cc* or *C*2/*c* as possible space groups. The first was chosen on the basis of the cell volume and the possible symmetry elements of the molecule. The collected data were corrected for Lorentz, polarization and absorption effects by means of a Ψ-scan method [15]. The structure solution was obtained by means of direct methods by using the TREF procedure contained in SHELXTL package [16]. Some degree of disorder in molecule conformation is revealed by abnormally high values of some thermal factors and by the inconsistent geometry of some rings. The refinement was performed by constraining the phenyl ring C(11) > C(16) and the pentamethylcyclopentadienyl ring C(1) > C(5) to have an ideal geome-

Table 3
Crystal data and structure refinement

Empirical formula	$C_{31}H_{39}FIrPSi$
Formula weight	681.88
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	
a (Å)	14.066(3)
b (Å)	13.739(3)
c (Å)	15.918(2)
β (°)	108.14(1)
Volume (Å^3)	2923.3(10)
Z	4
D_{calc} (g cm^{-3})	1.549
Absorption coefficient (mm^{-1})	4.687
F(000)	1360
Crystal size (mm)	0.24 × 0.20 × 0.12
θ Range for data collection (°)	2.13–25.00
Index ranges	$-1 \leq h \leq 16$, $-1 \leq k \leq 16$, $-18 \leq l \leq 18$
Reflections collected	3176
Independent reflections	2909 [$R_{int} = 0.0318$]
Completeness to $\theta = 22.50°$	49.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2909/2/292
Goodness-of-fit [a] on F^2	1.051
Final *R* indices [a] [$I > 2\sigma(I)$]	$R_1 = 0.0520$, $wR_2 = 0.1281$
R indices [a] (all data)	$R_1 = 0.0669$, $wR_2 = 0.1384$
Absolute structure parameter	−0.04(3)
Largest difference peak and hole (e·Å^{-3})	2.458 and −2.343

[a] Goodness-of-fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N-P)\}^{0.5}$, where *N* and *P* are the no. of observations and parameters, respectively; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$; $w = 1/[\sigma^2(F_o^2) + (0.0750Q)^2 + 38.34Q]$ where $Q = [\max(F_o^2, 0) + 2F_c^2]/3$.

try. The hydrogen atoms were introduced in calculated positions as riding atoms in the last refinement cycles. In the final cycles the heavy atoms were refined with anisotropic thermal parameters. Details on the refinement and some statistical reliability data are listed at the bottom of Table 3.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 124099 for compound **2a**. A full list of observed and calculated structure factors has been deposited with the editor as supplementary material and is available upon request. Geometric calculations have been made by means of the PARST-97 program [17].

Acknowledgements

This work was supported by the CNR (Rome).

References

[1] (a) P. Diversi, S. Iacoponi, G. Ingrosso, F. Laschi, A. Lucherini, P. Zanello, J. Chem. Soc. Dalton Commun. (1993) 351. (b) P. Diversi, S. Iacoponi, G. Ingrosso, F. Laschi, A. Lucherini, C. Pinzino, G. Uccello-Barretta, P. Zanello, Organometallics 14 (1995) 3275. (c) F. de Biani Fabrizi, P. Diversi, A. Ferrarini, G. Ingrosso, F. Laschi, A. Lucherini, C. Pinzino, G. Uccello-Barretta, P. Zanello, Gazz. Chim. Ital. 126 (1996) 391.

[2] (a) K.A. Brown-Wensley, Organometallics 6 (1987) 1590. (b) L.S. Chang, J.T. Corey, Organometallics 8 (1989) 1885. (c) T.D. Tilley, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, p. 1415. (d) I. Ojima, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, p. 1479. (e) H. Woo, T.D. Tilley, J. Am. Chem. Soc. 111 (1989) 8043. (f) T.D Tilley, Comments Inorg. Chem. 10 (1990) 37. (g) J. Harrod, Y. Mu, E. Samuel, Polyhedron 10 (1991) 1239. (h) B. Marciniec, J. Gulìnski, J. Organomet. Chem. 446 (1993) 15. (i) T.D. Tilley, Acc. Chem. Res. 26 (1993) 22. (j) C. Herzig, in: N. Avrer, J. Weis (Eds.), Organosilicon Chemistry, VCH, Weinheim, 1994, p. 253. (k) C.A. Recatto, Aldrichim. Acta 28 (1995) 85.

[3] J.Y. Corey, J. Braddock-Wilking, Chem. Rev. 99 (1999) 175 and Refs. cited therein.

[4] (a) M.D. Curtis, P.S. Epstein, Adv. Organomet. Chem. 19 (1981) 213. (b) S.K. Grumbine, T.D. Tilley, J. Am. Chem. Soc. 116 (1994) 6951.

[5] (a) M. Tanaka, T. Kobayashi, T. Hayashi, T. Sakakura, Appl. Organomet. Chem. 2 (1988) 91. (b) H. Yamashita, M. Tanaka, Bull. Chem. Soc. Jpn. 68 (1995) 403. (c) L. Rosenberg, M.D. Fryzuk, S.J. Rettig, Organometallics 18 (1999) 958.

[6] J.E. Veltheer, P. Burger, R.G. Bergman, J. Am. Chem. Soc. 117 (1995) 12478.

[7] S.E. Johnson, R.O. Day, R.R. Holmes, Inorg. Chem. 28 (1989) 3182.

[8] (a) L. Andreucci, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio, M. Nardelli, J. Chem. Soc. Dalton Trans. (1986) 803. (b) L. Andreucci, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio, M. Nardelli, J. Chem. Soc. Dalton Trans. (1986) 477. (c) B.K. Campion, R.H. Heyn, T.D. Tilley, J. Am. Chem. Soc. 112 (1990) 4079. (d) M.J. Auburn, R.D. Holmes-Smith, S.R. Stobart, P.K. Bakshi, T.S. Cameron, Organometallics 15 (1996) 3032.

[9] K.A. Woerpel, R.G. Bergman, J. Am. Chem. Soc. 115 (1993) 7888.

[10] M.E. Thompson, S.E. Baxter, A. Ray Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.

[11] C. Hinderling, D. Feichtinger, D.A. Plattner, P. Chen, J. Am. Chem. Soc. 119 (1997) 10793.

[12] (a) L.S. Chang, M.P. Johnson, M.J. Fink, Organometallics 10 (1991) 1219. (b) P. Burger, R.G. Bergman, J. Am. Chem. Soc. 115 (1993) 10462.

[13] (a) D.A. Straus, C. Zhang, G.E. Quimbita, S.D. Grumbine, R.H. Heyn, T.D. Tilley, A.L. Rheingold, S.J. Geib, J. Am. Chem. Soc. 112 (1990) 2673. (b) S. Grumbine, T.D. Tilley, F. Arnold, A. Rheingold, J. Am. Chem. Soc. 115 (1993) 7884.

[14] I. Fleming, R.S. Roberts, S.C. Smith, J. Chem. Soc. Perkin Trans. (1998) 1209.

[15] (a) A.C. T. North, C. Phillips, F.S. Mathews, Acta Crystallogr., Sect. A 24 (1968) 351. (b) XSCANS, X-ray Single Crystal Analysis System, Version 2.1, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.

[16] G.M. Sheldrick, SHELXTL, Version 5.03, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1992.

[17] M. Nardelli, J. Appl. Cryst. 28 (1995) 659.