ELSEVIER

Journal of Organometallic Chemistry 654 (2002) 224–228

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Note

Synthesis and characterization of the sterically hindered iridium(III)–silyl complex: $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$ and the generation of the cationic iridium(III)-silylene complex: $[(Et_3P)_3(H)_2Ir{=}Si(H)(C_6H_3\text{-}Mes_2\text{-}2,6)][B(C_6F_5)_4]$

Richard S. Simons [a], Judith C. Gallucci [b], Claire A. Tessier [a,*], Wiley J. Youngs [a,*]

[a] *Department of Chemistry, University of Akron, Room 111, 190 Buchtel Commons, Akron, OH 44325-3601, USA*
[b] *Department of Chemistry, Ohio State University, Columbus, OH 43210, USA*

Received 4 February 2002; received in revised form 5 March 2002; accepted 5 March 2002

Abstract

The oxidative addition reaction of $(Et_3P)_3IrCl$ with $H_3Si(C_6H_3\text{-}Mes_2\text{-}2,6)$ (Mes = 2,4,6-trimethylphenyl) affords the sterically hindered iridium(III)–silyl complex $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$ (**1**) via a H/Cl exchange reaction at silicon. Complex **1** is characterized by ^{1}H-, ^{13}C-, ^{31}P-, and ^{29}Si-NMR and IR spectroscopy. The solid state structure of **1** is determined by X-ray crystallography. Complex **1** undergoes a halide abstraction reaction with $LiB(C_6F_5)_4(OEt_2)$ to afford the cationic iridium(III)–silylene complex $[(Et_3P)_3(H)_2Ir{=}Si(H)(C_6H_3\text{-}Mes_2\text{-}2,6)][B(C_6F_5)_4]$ (**4**). Complex **4** is characterized by ^{1}H-, ^{13}C-, ^{31}P-, and ^{29}Si-NMR spectroscopy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sterically hindered; Iridium(III)–silyl complex; Cationic iridium(III)–silylene complex

---

1. Introduction

The most common method of synthesizing transition metal silyl complexes involves the oxidative addition of a Si–H bond of a hydrosilane to a transition metal center with open coordination sites [1,2]. We have been investigating the oxidative addition reactions of silanes to the iridium(I) complex, $(Me_3P)_4IrH$ [3]. In general, these reactions afford hydrido-iridium(III)–silyl complexes according to Eq. (1).

$$(Me_3P)_4Ir(H) \;+\; H\text{-}SiR_3 \xrightarrow[-PMe_3]{} (Me_3P)_3(H)_2Ir(SiR_3) \qquad (1)$$

R = alkyl, aryl, hydride, chloride

We postulated that the reaction of the sterically hindered silane, $H_3Si(C_6H_3\text{-}Mes_2\text{-}2,6)$ (Mes = 2,4,6-trimethylphenyl) with $(Et_3P)_3IrCl$ would afford iridium–silyl complexes that exhibit chemistry rarely observed with less sterically hindered silanes. We based this hypothesis on related work. For example, the reaction of $H_3Si(C_6H_3\text{-}Mes_2\text{-}2,6)$ with $(Pr_3P)_3Pt$ provided the mono(silyl)Pt(II) complex, *cis*-$(2,6\text{-}Mes_2C_6H_3(H)_2Si)\text{-}Pt(H)(PPr_3)_2$ [4], which is a rare example of a monomeric species obtained from a primary silane and a platinum(0) metal complex [5]. With less sterically hindered silanes, Pt_2Si_2 dimeric complexes are obtained [6–12].

We report herein the synthesis and structure of $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$ (**1**). Complex **1** is an example of a H/Cl exchange reaction between iridium and silicon. Also, we report that the reaction of **1** with $LiB(C_6F_5)_4(OEt_2)$ affords the cationic iridium(III)–silylene $[(Et_3P)_3(H)_2Ir{=}Si(H)(C_6H_3\text{-}Mes_2\text{-}2,6)][B(C_6F_5)_4]$ (**4**).

---

* Corresponding authors. Fax: +1-330-972-7370.
E-mail addresses: tessier@chemistry.uakron.edu (C.A. Tessier), youngs@uakron.edu (W.J. Youngs).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)01374-8

2. Experimental

2.1. General considerations

All manipulations were carried out under anaerobic conditions in an atmosphere of nitrogen or Ar. The compounds $(Et_3P)_3IrCl$ [13], $[Ir(COE)_2Cl]_2$ [14] and 2,6-$Mes_2C_6H_3SiH_3$ [15] were prepared according to literature procedures. $LiB(C_6F_5)_4(OEt_2)$ was purchased from Boulder Scientific Corporation and used as received. Hexane and THF were freshly distilled from sodium benzophenone ketyl. ^1H-, ^{13}C- and ^{29}Si-NMR data were recorded on a Varian 400 MHz instrument. ^1H-NMR data was referenced to the residual protons in C_6D_6 or CD_2Cl_2 and ^{13}C-NMR data was referenced to the deuterated solvent. ^{29}Si-NMR data was referenced to external Me_4Si. ^{31}P-NMR data was recorded on a Gemini 300 MHz instrument and referenced to external H_3PO_4. IR data was recorded on a Bomem FTIR instrument.

2.2. Synthesis of $(Et_3P)_3(Cl)Ir$

PEt_3 (0.7 ml, 4.7 mmol) was added by syringe to a THF solution (50 ml) of $[Ir(COE)_2Cl]_2$ (0.7 g, 0.8 mmol) while stirring at ambient temperature. Stirring was continued for ca. 1 h. The solution became red and this was used in situ for the synthesis of $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$.

2.3. Synthesis of $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$ (**1**)

A THF solution (50 ml) of $(Et_3P)_3(Cl)Ir$ (1.6 mmol), synthesized and used in situ from PEt_3 (0.7 ml, 4.7 mmol) and $[Ir(COE)_2Cl]_2$ (0.7 g, 0.8 mmol), was added dropwise to $H_3Si(C_6H_3\text{-}Mes_2\text{-}2,6)$ (0.6 g, 1.6 mmol) in THF (20 ml) while stirring at dry ice–acetone bath temperature. The solution was warmed to ambient temperature and stirred for an additional 16 h. The volatile components were removed under reduced pressure to yield a light yellow solid. The solid was washed with 50 ml of hexane and collected on a glass frit to afford $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$ (**1**) as an off-white solid. Yield: 0.9 g, 1.0 mmol, 63%. M.p.: 150–152 °C. Anal. Calc. for $C_{42}H_{73}ClIrP_3Si$: C, 54.44; H, 7.94. Found: C, 54.52; H, 8.09%. ^1H-NMR (C_6D_6): δ −14.5 (ddd, 1H, $J_{H-Pcis} = 16$ Hz, $J_{H-Ptrans} = 100$ Hz, Ir–H), −13.8 (ddd, 1H, $J_{H-Pcis} = 18$ Hz, $J_{H-Ptrans} = 112$ Hz, Ir–H) 0.82 (m, 27H, $P(CH_2C\underline{H}_3)_3$), 1.5 (m, 12H, $P(C\underline{H}_2CH_3)_3$) 1.7 (m, 6H, $P(C\underline{H}_2CH_3)_3$), 2.32 (s, 6H, *p*-Mes), 2.46 (s, 12H, *o*-Mes), 6.41 (ddd, 1H, $J_{H-P} = 16$ Hz, $J_{H-Si} = 188$ Hz, Si–H), 6.92 (s, 2H, *m*-Mes), 6.94 (d, 2H, $J = 7.2$ Hz, *m*-C_6H_3), 6.97 (s, 2H, *m*-Mes), 7.26 (t, 1H, $J = 7.6$ Hz, *p*-C_6H_3). ^{13}C-NMR (C_6D_6): δ 8.9 (d, $J_{C-P} = 2$ Hz, $P(CH_2\underline{C}H_3)_3$), 9.8 (d, $J_{C-P} = 4$ Hz, $P(CH_2\underline{C}H_3)_3$), 10.2 (d, $J_{C-P} = 4$ Hz, $P(CH_2\underline{C}H_3)_3$), 21.37 (*o*-Mes), 22.4 (dt, $J_{C-P} = 24$ Hz, $J_{C-P-Ir-P} = 3$ Hz, $P(\underline{C}H_2CH_3)_3$), 22.6 (s, *p*-Mes), 24.0 (dt, $J_{C-P} = 25$ Hz, $J_{C-P-Ir-P} = 3$ Hz, $P(\underline{C}H_2CH_3)_3$), 24.6 (dt, $J_{C-P} = 21$ Hz, $J_{C-P-Ir-P} = 3$ Hz, $P(\underline{C}H_2CH_3)_3$), 127.89, 128.44, 128.69, 134.87, 137.42, 143.00, 144.15, 148.15 (Ar). ^{31}P-NMR (C_6D_6): δ −31.7 (t, 1P, $J = 24$ Hz), −25.0 (m, 2P). ^{29}Si-NMR (C_6D_6): δ −7.1 (dt, $J_{Si-Ptrans} = 173$ Hz, $J_{Si-Pcis} = 10$ Hz). IR (Nujol, cm^{-1}): 2132(s), 2079(s), 2030(s) (Ir–H, Si–H).

2.4. Formation of $[(Et_3P)_3(H)_2Ir{=}Si(H)(C_6H_3\text{-}Mes_2\text{-}2,6)][B(C_6F_5)_4]$ (**4**)

A dichloromethane-*d*$_2$ solution (1 ml) of $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$ (0.05 g, 0.05 mmol) was added to $LiB(C_6F_5)_4(OEt_2)$ (0.04 g, 0.05 mmol) at ambient temperature to produce a yellow solution and a fine white precipitate. The solution was filtered and sealed in a NMR tube under an atmosphere of argon. ^1H- and ^{31}P-NMR spectroscopy indicated that the generation of $[(Et_3P)_3(H)_2Ir{=}Si(H)(C_6H_3\text{-}Mes_2\text{-}2,6)][B(C_6F_5)_4]$ (**4**) was nearly quantitative. ^1H-NMR (C_6D_6): δ −12.89 (dm, 2H, $J_{H-Ptrans} = 83.2$ Hz, Ir–H), 0.82 (m, 27H, $P(CH_2C\underline{H}_3)_3$), 1.16 (t, 6H, $OCH_2C\underline{H}_3$), 1.5 (m, 12H, $P(C\underline{H}_2CH_3)_3$) 1.7 (m, 6H, $P(C\underline{H}_2CH_3)_3$), 2.09 (s, 12H, *o*-Mes), 2.28 (s, 6H, *p*-Mes), 3.44 (q, 4H, $OC\underline{H}_2CH_3$), 6.91 (s, 4H, *m*-Mes), 7.01 (d, 2H, $J = 7.2$ Hz, *m*-C_6H_3), 7.55 (t, 1H, $J = 5.6$ Hz, *p*-C_6H_3), 10.54 (dt, 1H, $J_{H-Ptrans} = 24$ Hz, $J_{H-Pcis} = 6$ Hz, $J_{H-Si} = 168$ Hz, Si–H). ^{13}C-NMR (C_6D_6): δ 8.6 (d, $J_{C-P} = 2$ Hz, $P(CH_2\underline{C}H_3)_3$), 9.22 (s, *o*-Mes), 9.7 (d, $J_{C-P} = 4$ Hz, $P(CH_2\underline{C}H_3)_3$), 10.3 (d, $J_{C-P} = 4$ Hz, $P(CH_2\underline{C}H_3)_3$), 15.67 (*p*-Mes), 22.6 (d, $J_{C-P} = 24$ Hz, $P(\underline{C}H_2CH_3)_3$), 24.3 (d, $J_{C-P} = 25$ Hz, $P(\underline{C}H_2CH_3)_3$), 24.8 (d, $J_{C-P} = 22$ Hz, $P(\underline{C}H_2CH_3)_3$), 127.88, 128.39, 129.51, 129.63, 131.75, 137.39, 138.86, 144.59 (Ar), 135.5, 147.5, 149 9 (m, C–F). ^{31}P-NMR (C_6D_6): δ −14.7 (dm, 2P, $J_{P-Pcis} = 3.1$ Hz), −10.3 (t, 1P, $J = 14$ Hz). ^{29}Si-NMR (C_6D_6): δ 239.3 (dm, $J_{Si-Ptrans} = 178$ Hz).

2.5. X-ray crystallography

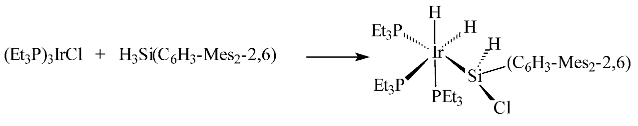
A colorless crystal of **1** with dimensions 0.2 × 0.2 × 0.05 mm was coated in paraffin oil and mounted on a glass fiber and placed under a stream of nitrogen [16]. All manipulations were carried out at 200 K using Mo–K$_\alpha$ (0.71073 Å) radiation on an Enraf–Nonius KappaCCD diffraction system. Unit cell parameters were obtained by indexing the peaks of the first 10 frames and refined using the entire data set. All frames were integrated and corrected for Lorentz and polarization effects using DENZO [17]. The structure of **1** was solved by direct methods [18]. The hydrogen atoms attached to the iridium (Ir–H1 = 1.69(11) Å, Ir–H2 = 1.80(10) Å) and silicon (Si–H = 1.52(8) Å) atoms were located from a difference map and refined using isotropic thermal parameters. Phenyl and alkyl hydrogen atoms were placed in idealized positions and refined using a riding model. Compound **1** was refined to convergence using anisotropic thermal parameters for all non-hydrogen atoms (Table 1).

3. Results and discussion

The iridium(III)–silyl complex $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$ (**1**) is prepared in 60% yield by the reaction of $(Et_3P)_3IrCl$ and $H_3Si(C_6H_3\text{-}Mes_2\text{-}2,6)$ (Eq. (2)). Complex **1** is isolated as colorless crystals that are thermally stable up to the temperature at which they melt (150–152 °C). The ^{1}H-, ^{13}C-, ^{31}P- and ^{29}Si-NMR and IR spectroscopic data and the X-ray crystallographic analysis are consistent with the structure of **1**. In the ^{1}H-NMR spectrum the two inequivalent iridium hydrides each appear as a set of doublets of doublets of doublets centered at -14.5 and -13.8 ppm due to coupling to three inequivalent phosphine ligands. For similar reasons, the silicon hydride appears at 6.41 ppm as an overlapping doublet of doublets of doublets. The proton decoupled ^{31}P-NMR spectrum shows a triplet at -31.7 ppm for the phosphine ligand oriented *trans* to the silyl ligand and a multiplet at -25.0 ppm for the two phosphine ligands oriented *cis* to the silyl ligand. The two phosphine ligands oriented *cis* to the silyl ligand are diastereotopic and we presume that the multiplet is due to overlapping doublet of doublets for each phosphine ligand. The proton decoupled ^{29}Si-NMR spectrum shows a doublet of triplets centered at -7.1 ppm due to coupling to one phosphine ligand oriented *trans* and two phosphine ligands oriented *cis* to the silicon atom. The IR spectroscopic data shows three stretching frequencies that can be assigned to Ir–H and Si–H at 2132, 2079 and 2030 cm^{-1}. The Ir–H and Si–H regions in the IR spectroscopic data are overlapping making complete assignment unavailable [19]. However, the values are consistent with the assignment of three element-hydrides.

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{42}H_{73}ClIrP_3Si$
Formula weight	926.65
Temperature (K)	200
Wavelength (Å)	0.71073
Crystal system, space group, *Z*	Orthorhombic, *Pna*2(1), 4
Unit cell dimensions	
a (Å)	16.112(3)
b (Å)	20.487(4)
c (Å)	13.572(3)
V (Å^3)	4480.0(15)
D_{calc} (Mg m^{-3})	1.374
Absorption coefficient (mm^{-1})	3.201
Theta range for data collection (°)	2.36–27.48
Reflections collected/unique	9942/9942 [$R_{int} = 0.03$]
Goodness-of-fit on F^2	1.027
Final *R* indices [$I > 2\sigma(I)$]	0.0459
R indices (all data)	0.1284
Largest difference peak and hole (e Å^{-3})	1.757 and -0.687



1

(2)

The X-ray crystal structure of **1** (Fig. 1) shows that the iridium(III) atom has distorted octahedral geometry with two *cis*-phosphine ligands (P1–Ir–P3 = 99.67(7)) and two *cis* hydride ligands defining a plane and a silyl ligand and phosphine ligand oriented perpendicular to this plane and *trans* to each other (Si–Ir–P2 = 154.43(7)). The most notable features of the structure of **1** are at the silicon atom. It has a distorted tetrahedral geometry with a large C1–Si–Ir angle of 123.8(3)°. This large angle is most likely due to the steric crowding caused by the large terphenyl substituent. The larger C1–Si–Cl bond angle of 118.0(1)° as compared to Cl–Si–Ir (101.4(3)°) is also indicative of a crowded situation imposed by the terphenyl ligand. The Si–Ir bond length for **1** (2.341(2) Å) is normal for iridium(III)–silyl complexes and is within the range of reported Si–Ir bond lengths (2.235–2.454 Å) [1]. It can be compared to the same parameter for $(Me_3P)_3(H)_2Ir[SiCl(t\text{-}Bu)_2]$ (2.391(3) Å), $(Me_3P)_3(H)_2Ir[SiPh_3]$ (2.382(4) Å) and $(Me_3P)_3(H)_2Ir[SiHPh_2]$ (2.361(3) Å) [3]. The silicon–carbon (1.947(8) Å) and silicon–chloride (2.148(3) Å)

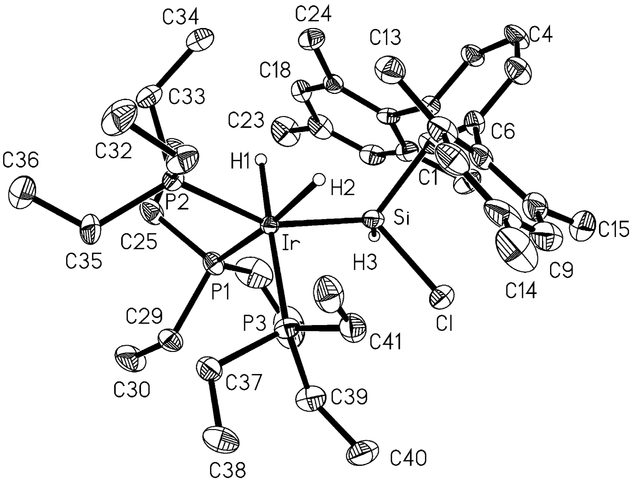


Fig. 1. Molecular structure of **1** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms attached to carbon atoms have been omitted for clarity. Selected bond lengths (Å), and angles (°): Ir–Si = 2.341(2), Si–C1 = 1.947(8), Si–Cl = 2.148(3), Ir–Si–C1 = 123.8(3), C1–Si–Cl = 118.0(1), Cl–Si–Ir = 101.4(3).

bond lengths are quite normal when compared to the same parameters for the aforementioned compounds.

The one-step synthesis of **1** is notable as it involves a H/Cl exchange reaction at the silicon atom. The exact mechanism for the formation of **1** is unclear but it may occur through a hydride migration with subsequent chloride abstraction. The oxidative addition reaction of $H_3Si(C_6H_3\text{-}Mes_2\text{-}2,6)$ with $(Et_3P)_3IrCl$ should afford the sterically crowded $(Et_3P)_3(H)(Cl)Ir[Si(H)_2(C_6H_3\text{-}Mes_2\text{-}2,6)]$ (**2**). The dissociation of a phosphine from **2**, imposed by steric crowding, would provide an unsaturated iridium(III)–silyl species, $(Et_3P)_2(H)(Cl)Ir[Si(H)_2(C_6H_3\text{-}Mes_2\text{-}2,6)]$, which could undergo a 1,2-hydride migration to give an iridium–silylene species, $(Et_3P)_3(H)_2(Cl)Ir[=Si(H)(C_6H_3\text{-}Mes_2\text{-}2,6)]$. Abstraction of a chloride ligand by the silylene ligand followed by complexation of a phosphine would provide **1**. A similar mechanism has been proposed to afford the complex $(R_3P)(TFB)(H)_2Ir[Si(OTf)Ph_2]$ (R = *i*-Pr, Cy) (TFB = tetraflourobenzobarrelene) [20]. In this case, a H/OTf exchange reaction is observed at the silicon atom. H/OTf exchange reactions have also been reported by Tilley and Bergman to generate the iridium silylene complex $[Cp^*(PMe_3)(H)Ir{=}SiMes_2][OTf]$ [21].

An alternative mechanism for the formation of **1** involves the reductive elimination of $H_2ClSi(C_6H_3\text{-}Mes_2\text{-}2,6)$ (**3**) from **2** with the formation of $(Et_3P)_3IrH$. Oxidative addition of **3** to $(Et_3P)_3IrH$ could hypothetically lead to **1**. Reversible oxidative additions and reductive eliminations have been observed with rhodium complexes and the net result is a H/Cl exchange at the silicon atom [22]. We do not rule out this mechanism, however, we did not detect any $(Et_3P)_3IrH$ or **3** when analyzing the crude reaction products by ^1H- and ^{31}P-NMR spectroscopy.

In an effort to elucidate the mechanism for the formation of **1**, two additional experiments were performed. First, the reaction of $(Et_3P)_3IrCl$ and $H_3Si(C_6H_3\text{-}Mes_2\text{-}2,6)$ in the presence of excess Et_3P was examined. If the mechanism involved the dissociation of phosphine ligand, this would be expected to inhibit the H/Cl exchange. Second, $(Et_3P)_3IrCl$ was treated with a large excess of $H_3Si(C_6H_3\text{-}Mes_2\text{-}2,6)$ to trap $(Et_3P)_3IrH$ and yield $(Et_3P)_3(H)_2Ir[Si(H)_2(C_6H_3\text{-}Mes_2\text{-}2,6)]$. In both cases, the formation of **1** was observed by ^1H- and ^{31}P-NMR spectroscopy as the major product. The exact mechanism for the formation of **1** is still unclear and further investigations are underway.

Metal–silyl complexes that have anionic functional groups are potential precursors for the formation of cationic metal–silylene complexes. For example, Tilley has demonstrated the utility of exchanging halides and pseudo-halides with less coordinating anions such as trimethylsilyltriflate or tetra-arylborates to afford cationic metal–silylene complexes [23–27]. Similarly, the cationic iridium(III)–silylene complex $[(Et_3P)_3(H)_2Ir{=}Si(H)(C_6H_3\text{-}Mes_2\text{-}2,6)][B(C_6F_5)_4]$ (**4**) was generated by the halide abstraction reaction of $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$ (**1**) with $LiB(C_6F_5)_4(OEt_2)$ in methylene chloride-d_2 (Eq. (3)).

$$\underset{\mathbf{1}}{(Et_3P)_3(H)_2IrSi(H)(Cl)(C_6H_3\text{-}Mes_2\text{-}2,6)} \xrightarrow[\text{-LiCl}]{LiB(C_6F_5)_4(OEt_2)} \underset{\mathbf{4}}{[(Et_3P)_3(H)_2Ir(=Si(H)(C_6H_3\text{-}Mes_2\text{-}2,6))][B(C_6F_5)_4]} \qquad (3)$$

^1H- and ^{31}P-NMR spectroscopy indicated that the generation of a yellow solution of silylene **4** is nearly quantitative. The proposed structure of **4** is consistent with the ^1H-, ^{13}C-, ^{31}P-, and ^{29}Si-NMR spectroscopy. In the ^1H-NMR spectrum, the Si–H resonance is observed at 10.54 ppm as a doublet of triplets with a silicon–hydride coupling constant of 168 Hz. In comparison with the same parameter for **1**, this value is shifted downfield by more than 4 ppm and is consistent with a hydride bonded to an electron deficient silicon atom. In the Ir–H region of the ^1H-NMR spectrum, two hydride ligands are equivalent and appear as a doublet of multiplets at -12.9 ppm. The resonances for the Et_2O appear at 1.16 and 3.44 ppm and these values are indicative of a non-coordinated molecule. The ^{31}P-NMR spectrum shows a doublet of multiplets at -14.7 ppm and a triplet at -10.3 ppm. The ^1H-NMR and ^{31}P-NMR data are consistent with two equivalent hydrides oriented *cis* to each other and *cis* to the silylene ligand. In the ^{29}Si-NMR spectrum, the silicon atom is observed at 239 ppm as a doublet of multiplets and this is consistent with our assignment of **4** as containing a silylene ligand. Whereas cationic metal–silylenes are known and the cationic iridium(III)–silylene complex, $[(Me_3P)_3(H)_2Ir(SiMes_2)][MeB(C_6F_5)_3]$, has recently been synthesized by the Tilley group [28], **4** is notable because it represents the first example of a metal–silylene complex with only one organic substituent bonded to the silicon atom.

4. Conclusion

In conclusion, the sterically hindered silane, $H_3Si(C_6H_3\text{-}Mes_2\text{-}2,6)$ reacts with $(Et_3P)_3IrCl$ to afford $(Et_3P)_3(H)_2Ir[Si(H)Cl(C_6H_3\text{-}Mes_2\text{-}2,6)]$ (**1**). Complex **1** is an example of a H/Cl exchange reaction at silicon that we presume is promoted by the steric crowding imposed by the terphenyl ligand. Complex **1** undergoes an halide abstraction reaction with $LiB(C_6F_5)_4(OEt_2)$ to afford the cationic iridium(III)–silylene complex $[(Et_3P)_3(H)_2Ir{=}Si(H)(C_6H_3\text{-}Mes_2\text{-}2,6)][B(C_6F_5)_4]$ (**4**).

5. Supplementary material

Crystallographic data (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 178637. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We wish to thank the National Science Foundation, the University of Akron and the Ohio Board of Reagents for financial support. We wish to thank Dr. Judith A. McCune for helpful discussions.

References

[1] J.Y. Corey, J. Braddock-Wilking, Chem. Rev. 99 (1999) 175.

[2] M.S. Eisen, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2 (Part 3, Chapter 35), Wiley, New York, 1998.

[3] E.A. Zarate, V.O. Kennedy, J.A. McCune, R.S. Simons, C.A. Tessier, Organometallics 14 (1995) 1802.

[4] R.S. Simons, L.M. Sanow, K.J. Galat, C.A. Tessier, W.J. Youngs, Organometallics 19 (2000) 3994.

[5] J. Braddock-Wilking, Y. Levchinsky, N.P. Rath, Organometallics 19 (2000) 5500.

[6] E.A. Zarate, C.A. Tessier-Youngs, W.J. Youngs, J. Am. Chem. Soc. 110 (1988) 4068.

[7] E.A. Zarate, C.A. Tessier-Youngs, W.J. Youngs, J. Chem. Soc. Chem. Commun. (1989) 577.

[8] A.B. Anderson, P. Shiller, E.A. Zarate, C.A. Tessier-Youngs, W.J. Youngs, Organometallics 8 (1989) 2320.

[9] R.H. Heyn, T.D. Tilley, J. Am. Chem. Soc. 114 (1992) 1917.

[10] L.M. Sanow, M. Chai, D.B. McConnville, K.J. Galat, R.S. Simons, P.L. Rinaldi, W.J. Youngs, C.A. Tessier, Organometallics 19 (2000) 192.

[11] S. Shimada, M. Tanaka, K. Honda, J. Am. Chem. Soc. 117 (1995) 8289.

[12] Y. Levchinsky, N.P. Rath, J. Braddock-Wilking, Organometallics 18 (1999) 2583.

[13] J.R. Bleeke, W-J. Peng, Organometallics 6 (1987) 1576.

[14] J.L. Herde, J.C. Lambert, C.V. Senoff, Inorg. Synth. 15 (1974) 18.

[15] R.S. Simons, S.T. Haubrich, B.V. Mork, M. Niemeyer, P.P. Power, Main Group Chem. 2 (1998) 275.

[16] H. Hope, in: A.L. Wayda, A.M.Y. Darensbourg (Ed.), Experimental Organometallic Chemistry ACS Symposium Series 357, American Chemical Society, Washington, DC, 1987, Chapter 10.

[17] Z. Otwinowsky, W. Minor, Methods in Enzymology, Vol. 276, in: C.W. Carter, Jr., R.M. Sweet (Eds.), Macromolecular Crystallography, part A, Academic Press, New York, 1997, pp. 307.

[18] SHELXTL, Version 5.11, Siemens Analytical Instruments, Madison, WI, 1997.

[19] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley, New York, 1986, p. 323, 384.

[20] W. Chen, A.J. Edwards, M.A. Esteruelas, F.J. Lahoz, M. Oliván, L.A. Oro, Organometallics 15 (1996) 2185.

[21] S.R. Klei, T.D. Tilley, R.G. Bergman, J. Am. Chem. Soc. 122 (2000) 1816.

[22] T. Koizumi, K. Osakada, T. Yamamoto, Organometallics 16 (1997) 6014.

[23] S.K. Grumbine, G.P. Mitchell, D.A. Straus, T.D. Tilley, Organometallics 17 (1998) 5607.

[24] D.A. Straus, S.K. Grumbine, T.D. Tilley, J. Am. Chem. Soc. 112 (1990) 7801.

[25] S.K. Grumbine, R.K. Chadha, T.D. Tilley, J. Am. Chem. Soc. 114 (1992) 1518.

[26] P.W. Wanandi, P.B. Glaser, T.D. Tilley, J. Am. Chem. Soc. 122 (2000) 972.

[27] G.P. Mitchell, T.D. Tilley, J. Am. Chem. Soc. 120 (1998) 7635.

[28] J.C. Peters, J.D. Feldman, T.D. Tilley, J. Am. Chem. Soc. 121 (1999) 9871.