

Short Communication

Formation of a sterically crowded iridium(III)-silyl complex from the bulky terphenyl silane $\text{H}_3\text{Si}(\text{C}_6\text{H}_3\text{-Mes}_2\text{-2,6})$

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Abstract

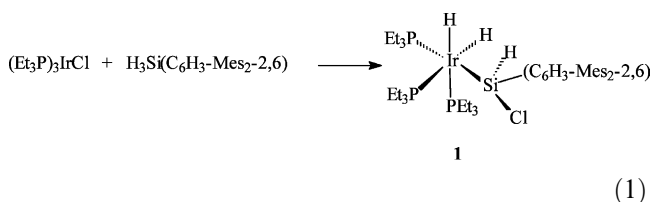
The reaction of $[\text{Ir}(\text{COE})\text{Cl}]_2$ and Et_2PhP in a 1:6 ratio affords the iridium(I) complex $(\text{Et}_2\text{PhP})_3(\text{Cl})\text{Ir}$ (**4**) as orange crystals in good yield (80%). The ^1H - and ^{31}P -NMR data are consistent with the structure of **4**. The structure of **4** was determined by X-ray crystallography. The sterically hindered iridium(III)-silyl complex **5** is prepared in 63% yield by the reaction of **4** and $\text{H}_3\text{Si}(\text{C}_6\text{H}_3\text{-Mes}_2\text{-2,6})$ (Eq. 5). Complex **5** is isolated as colorless crystals that are thermally stable up to the temperature at which they melt (162–163 °C). The ^{31}P - and ^{29}Si -NMR and IR spectroscopic data and the X-ray crystallographic analysis are consistent with the structure of **5**.

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Keywords: Silyl complexes; Iridium; Silanes; Cyclometallation

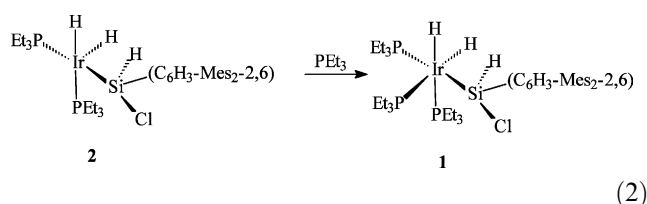
1. Introduction

Our group previously reported that the iridium(III)-silyl complex $(\text{Et}_3\text{P})_3(\text{H})_2\text{Ir}[\text{Si}(\text{H})\text{Cl}(\text{C}_6\text{H}_3\text{-Mes}_2\text{-2,6})]$ (**1**) forms from a H/Cl exchange reaction during the reaction of $(\text{Et}_3\text{P})_3\text{IrCl}$ and $\text{H}_3\text{Si}(\text{C}_6\text{H}_3\text{-Mes}_2\text{-2,6})$ (Eq. 1) [1].



In other groups, similar H/anion exchange chemistry was observed during the formation of the iridium(III)-silyl complex $(\text{R}_3\text{P})(\text{TFB})(\text{H})_2\text{Ir}[\text{Si}(\text{OTf})\text{Ph}_2]$ ($\text{R} = i\text{-Pr}$, Cy ; $\text{OTf} = \text{triflate}$; $\text{TFB} = \text{tetrafluorobenzobarrelene}$) [2]

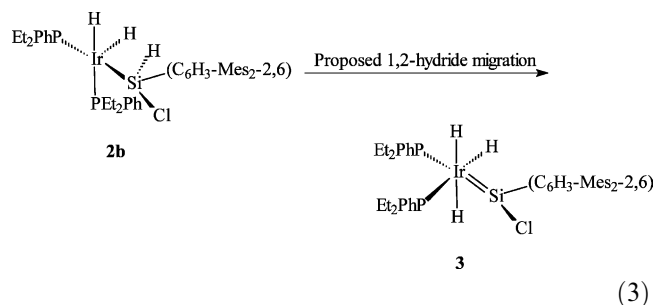
and the iridium silylene complex $[\text{Cp}^*(\text{PMe}_3)(\text{H})\text{Ir}=\text{SiMe}_2][\text{OTf}]$ [3]. In both cases, a H/OTf exchange reaction is observed at the silicon atom. During the formation of **1**, we proposed that the iridium-silyl complex $(\text{Et}_3\text{P})_2(\text{H})_2\text{Ir}[\text{Si}(\text{Cl})(\text{H})(\text{C}_6\text{H}_3\text{-Mes}_2\text{-2,6})]$ (**2a**) is generated and it affords **1** by complexation of an additional phosphine ligand (Eq. 2).



Increasing the steric bulk of the phosphine from Et_3P to Et_2PhP was expected to prevent the complexation of three phosphine ligands. Ideally, this would promote an additional 1,2 hydride migration to afford the neutral iridium silylene complex $(\text{Et}_2\text{PhP})_2(\text{H})_3\text{Ir}=[\text{Si}(\text{Cl})(\text{C}_6\text{H}_3\text{-Mes}_2\text{-2,6})]$ (**3**), which has a Si–Cl bond (Eq. 3). We report herein, the complex isolated from the reaction of $\text{H}_3\text{Si}(\text{C}_6\text{H}_3\text{-Mes}_2\text{-2,6})$ with $(\text{Et}_2\text{PhP})_3\text{IrCl}$.

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2. Experimental

2.1. General considerations

All manipulations were carried out under anaerobic conditions in an atmosphere of nitrogen or argon. The compounds, $[\text{Ir}(\text{COE})_2\text{Cl}]_2$ [4] and 2,6-Mes₂C₆H₃SiH₃ [5] were prepared according to literature procedures. Hexane and THF were freshly distilled from sodium benzophenone ketyl. ¹H-, ¹³C- and ²⁹Si-NMR data were recorded on a Varian 400 MHz instrument. ¹H-NMR data were referenced to the residual protons in C₆D₆ and ¹³C-NMR data was referenced to the deuterated solvent. ²⁹Si-NMR data were referenced to external Me₄Si. ³¹P-NMR data were recorded on a Gemini 300 MHz instrument and referenced to external H₃PO₄. IR data were recorded on a Bomem FTIR instrument.

2.2. Synthesis of (Et₂PhP)₃(Cl)Ir (**4**)

PEt₂Ph (1.0 g, 6.0 mmol) was added by syringe to a THF solution (50 ml) of $[\text{Ir}(\text{COE})_2\text{Cl}]_2$ (0.89 g, 1.0 mmol) while stirring at ambient temperature. Stirring was continued for ca. 1 h. The volume of the solution was reduced to incipient crystallization and stored at ca. –20 °C to afford (Et₂PhP)₃(Cl)Ir (**4**) as orange crystals. Yield: 0.6 g, 0.8 mmol, 80%. Anal. Calc. for C₃₀H₄₅P₃IrCl: C, 49.61; H, 6.25. Found: C, 49.99; H, 6.01%. ¹H-NMR (C₆D₆): δ 0.57, 2.14 (m, 12H, PCH₂), 1.1 (m, 18H, PCH₂CH₃), 7.0, 7.6 (m, 15H, C₆H₅). ³¹P-NMR (C₆D₆): δ –1.3 (t, 1P, *J* = 24 Hz), 10.5 (m, 2P).

2.3. Synthesis of **5**

A THF solution (50 ml) of **4** (0.6 g, 0.8 mmol) was added to H₃Si(C₆H₃–Mes₂–2,6) (0.8 g, 0.8 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 **5** as an off-white solid. Yield: 0.5 g, 0.5 mmol, 63%. Anal. Calc. for C₅₄H₇₁P₃IrClSi: C, 60.68; H, 6.70. Found: C, 61.10; H, 6.00%. ³¹P-NMR (C₆D₆): δ –16.7 (m, 1P), –17.7 (m, 1P), –23.2 (m, 2P). ²⁹Si-NMR (C₆D₆): δ –0.8 (dt, *J*_{Si–Ptrans} = 168 Hz, *J*_{Si–Pcis} = 10 Hz). IR (Nujol, cm^{–1}): 2132(s), 2079(s), 2030(s) (Ir–H, Si–H).

2.4. X-ray crystallography

Crystals of **4** and **5** were coated in paraffin oil and mounted on a glass fiber and placed under a stream of nitrogen [6]. Additional experimental data are given in Table 1. All manipulations were carried out at 100 K using Mo–K_α (0.71073 Å) radiation on an Bruker APEX CCD diffraction system. Unit cell parameters were obtained by indexing the peaks of the first 60 frames and refined using the entire data set. All frames were integrated and corrected for lorentz and polarization effects using the Bruker Saint program. The structures of **4** and **5** were solved by direct methods [7]. For **5**, the hydrogen atoms attached to the iridium (H1 and H2) were located from the difference map and refined using the DFIX restraint (Ir–H = 1.68 Å). Phenyl and alkyl hydrogen atoms were placed in idealized positions and refined using a riding model. Compounds **4** and **5** were refined to convergence using anisotropic thermal parameters for all non-hydrogen atoms.

Table 1
Crystal data and structure refinement for **4** and **5**

| Empirical formula | 4 , C ₃₀ H ₄₅ ClIrP ₃ | 5 , C ₅₄ H ₉₅ ClIrP ₃ –Si |
|---|---|---|
| Formula weight | 726.22 | 1092.95 |
| Temperature (K) | 100 | 100 |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system, space group, <i>Z</i> | Triclinic, <i>P</i> $\bar{1}$, 4 | Triclinic, <i>P</i> $\bar{1}$, 2 |
| Unit cell dimensions | | |
| <i>a</i> (Å) | 10.9277(7) | 12.7418(12) |
| <i>b</i> (Å) | 15.0014(10) | 12.9520(13) |
| <i>c</i> (Å) | 19.4813(13) | 18.2470(18) |
| α (°) | 102.2170(10) | 69.250(2) |
| β (°) | 95.4280(10) | 71.954(2) |
| γ (°) | 94.9610(10) | 66.686(2) |
| <i>V</i> (Å ³) | 3088.6(4) | 2535.2(4) |
| <i>D</i> _{calc} (Mg m ^{–3}) | 1.562 | 1.432 |
| Absorption coefficient (mm ^{–1}) | 4.582 | 2.840 |
| Theta range for data collection (°) | 1.08–27.51 | 1.22–27.55 |
| Reflections collected/unique | 38 531/13 842/ [<i>R</i> _{int} = 0.0208] | 21 912/11 169 [<i>R</i> _{int} = 0.0616] |
| Goodness-of-fit on <i>F</i> ² | 0.650 | 1.138 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | 0.0188 | 0.0662 |
| <i>R</i> indices (all data) | 0.0473 | 0.1426 |
| Largest difference peak and hole (e Å ^{–3}) | 1.128 and – | 0.371 |

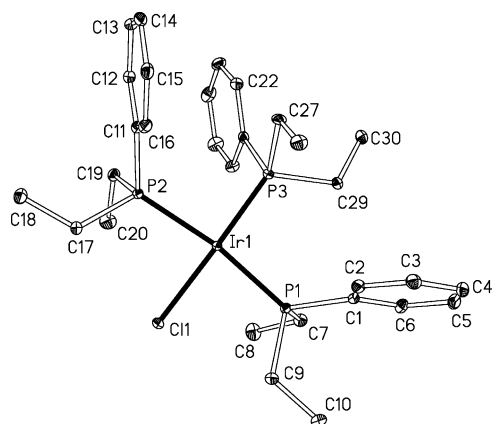


Fig. 1. Molecular structure of **4** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

3. Results and discussion

The reaction of $[\text{Ir}(\text{COE})\text{Cl}]_2$ and Et_2PhP in a 1:6 ratio affords the iridium(I) complex **4** as orange crystals in good yield (80%). The ^1H - and ^{31}P -NMR data are consistent with the structure of **4**. The structure of **4** was determined by X-ray crystallography (Fig. 1). Selected bond distances and angles are given in Table 2. Complex **4** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit that have equivalent structural parameters within experimental error. For this reason, the structural parameters of only one of the molecules will be discussed. The geometry of **4** is square planar with $\text{P1}-\text{Ir1}-\text{P2}$ ($171.15(2)^\circ$), $\text{P3}-\text{Ir1}-\text{Cl1}$ ($172.00(2)^\circ$), $\text{P3}-\text{Ir1}-\text{P1}$ ($96.04(2)^\circ$), $\text{P3}-\text{Ir1}-\text{P2}$ ($92.66(2)^\circ$) bond angles and $\text{Ir1}-\text{P1}$ ($2.305(1) \text{ \AA}$), $\text{Ir1}-\text{P2}$ ($2.328(1) \text{ \AA}$), $\text{Ir1}-\text{P3}$ ($2.211(1) \text{ \AA}$) and $\text{Ir}-\text{Cl1}$ ($2.395(1) \text{ \AA}$) bond distances.

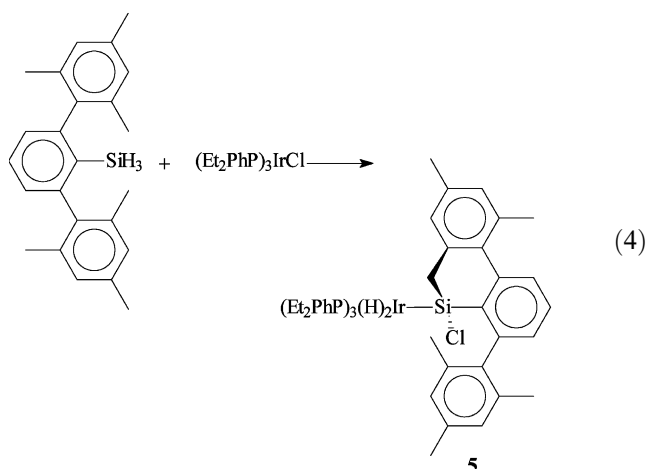
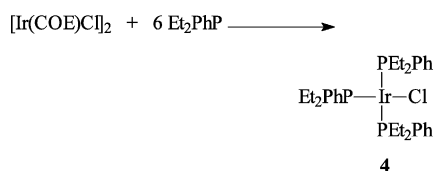


Table 2
Selected bond distances and angles for **4** and **5**

| 4 | | 5 | |
|-----------------------------------|-----------|------------------------------------|------------|
| <i>Bond distances (Å)</i> | | | |
| $\text{Ir1}-\text{Cl1}$ | 2.3945(5) | $\text{Ir1}-\text{P1}$ | 2.347(2) |
| $\text{Ir1}-\text{P1}$ | 2.3045(5) | $\text{Ir1}-\text{P2}$ | 2.336(2) |
| $\text{Ir1}-\text{P2}$ | 2.3276(6) | $\text{Ir1}-\text{P3}$ | 2.363(2) |
| $\text{Ir2}-\text{P3}$ | 2.2107(5) | $\text{Ir1}-\text{Si1}$ | 2.358(2) |
| | | $\text{Si1}-\text{C11}$ | 2.159(3) |
| | | $\text{Si1}-\text{C1}$ | 1.943(8) |
| | | $\text{Si1}-\text{C13}$ | 1.910(8) |
| <i>Bond angles (°)</i> | | | |
| $\text{P1}-\text{Ir1}-\text{P2}$ | 171.15(2) | $\text{Si1}-\text{Ir1}-\text{P2}$ | 143.39(7) |
| $\text{Cl1}-\text{Ir1}-\text{P3}$ | 172.00(2) | $\text{Ir1}-\text{Si1}-\text{C1}$ | 117.1(2) |
| $\text{P2}-\text{Ir1}-\text{P3}$ | 92.66(2) | $\text{Cl1}-\text{Si1}-\text{Ir1}$ | 118.15(11) |
| $\text{P1}-\text{Ir1}-\text{P3}$ | 96.04(2) | | |
| $\text{P1}-\text{Ir1}-\text{Cl1}$ | 85.07(2) | | |
| $\text{P2}-\text{Ir1}-\text{Cl1}$ | 86.08(2) | | |

The iridium(III)-silyl complex **5** is prepared in 63% yield by the reaction of **4** and $\text{H}_3\text{Si}(\text{C}_6\text{H}_3-\text{Mes}_2-2,6)$ (Eq. 5). Complex **5** is isolated as colorless crystals that are thermally stable up to the temperature at which they melt ($162-163^\circ\text{C}$). The ^{31}P - and ^{29}Si -NMR and IR spectroscopic data and the X-ray crystallographic analysis are consistent with the structure of **5**. The isolation of **5** suggests the formation of a reactive intermediate. One possible explanation is the formation of the anticipated iridium silylene species **3** that undergoes a C–H insertion reaction with simultaneous reductive elimination of H_2 (Eq. 6). Presumably, the electron withdrawing chloride atom further destabilizes the electron deficient silicon atom in **3**. A similar insertion reaction was reported by West and coworkers during defluorination of the terphenyl substituted silane $\text{F}_3\text{Si}(\text{C}_6\text{H}_3-\text{Mes}_2-2,6)$ [8]. In this case, a reactive fluor-

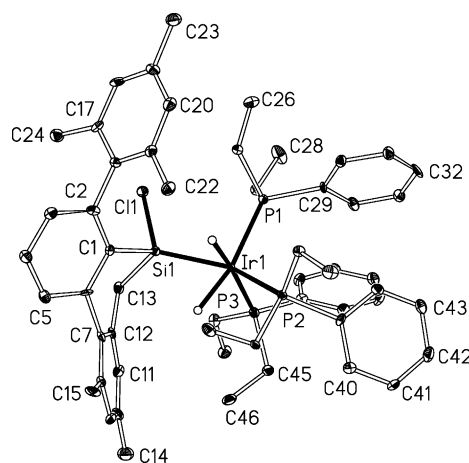
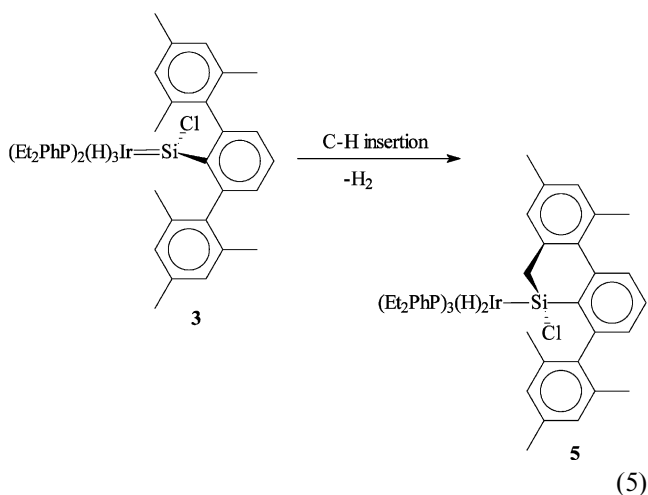


Fig. 2. Molecular structure of **5** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms attached to carbon atoms have been omitted for clarity.

osilylene or disilyne is proposed to undergo a C–C bond insertion reaction (Fig. 2).

The structure of **5** reveals an octahedral iridium(III) complex that has a silyl ligand *trans* to one phosphine and *cis* to two remaining phosphines ligands. The hydride ligands are oriented *cis* to each other and *cis* to the silyl ligand. The geometry at the silicon atom is distorted tetrahedral with one of the substituents being the cyclometallated C13 atom (Si1–C13 = 1.910(8) Å) to produce a puckered six-member ring. The Si1–C11 (2.159(3) Å), Si1–C1 (1.943(8) Å) and Ir1–Si1 (2.358(2) Å) bond distances and are quite standard. The bond angles at the silicon atom are normal with the exception of the Ir1–Si1–C1 (117.1(2)°) and C13–Si1–Ir1 (125.1(3)°) bond angles.



4. Conclusion

In conclusion, the sterically hindered silane, $\text{H}_3\text{Si}(\text{C}_6\text{H}_3\text{-Mes}_{2,6})$ reacts with $(\text{Et}_2\text{PhP})_3\text{IrCl}$ to afford a sterically hindered iridium(III)-silyl complex that

results from the cyclometallation of an *ortho*-mesityl C–H bond.

5. Supporting information available

Crystallographic data (excluding structure factors) for **4** and **5** have been deposited with the Cambridge Crystallographic Data Center as supplemental publications numbers CCDC 202586 and 202587. Copies of the data can be obtained, free of charge, on application to 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>).

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References

- [1] R.S. Simons, J.C. Gallucci, C.A. Tessier, W.J. Youngs, J. Organomet. Chem. 654 (2002) 224.
- [2] W. Chen, A.J. Edwards, M.A. Esteruelas, F.J. Lahoz, M. Oliván, L.A. Oro, Organometallics 15 (1996) 2185.
- [3] S.R. Klei, T.D. Tilley, R.G. Bergman, J. Am. Chem. Soc. 122 (2000) 1816.
- [4] J.L. Herde, J.C. Lambert, C.V. Senoff, Inorg. Synth. 15 (1974) 18.
- [5] R.S. Simons, S.T. Haubrich, B.V. Mork, M. Niemeyer, P.P. Power, Main Group Chem. 2 (1998) 275.
- [6] H. Hope, in: A.L. Wayda, A.M.Y. Darensbourg (Eds.), Experimental Organometallic Chemistry ACS Symposium Series 357, American Chemical Society, Washington, DC, 1987 (Chapter 10).
- [7] SHELXTL, Version 5.11, Siemens Analytical Instruments, Madison, WI, 1997.
- [8] R. Pietschnig, R. West, D.R. Powell, Organometallics 19 (2000) 2724.