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Note

Comparative reactivity of triorganosilanes, $HSi(OEt)_3$ and $HSiEt_3$, with $IrCl(CO)(PPh_3)_2$. Formation of $IrCl(H)_2(CO)(PPh_3)_2$ or $Ir(H)_2(SiEt_3)(CO)(PPh_3)_2$ depending on the substituents at Si

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ABSTRACT

Reaction of HSi(OEt)₃ with IrCl(CO)(PPh₃)₂ (5:1 molar ratio) at room temperature for 1 h gives $IrCl(H){Si(OEt)_3}(CO)(PPh_3)_2$ (1), which is observed by the ¹H and ³¹P{¹H} NMR spectra of the reaction mixture. The same reaction, but in 20:1 molar ratio at 50 °C for 24 h produces IrCl(H)₂(CO)(PPh₃)₂ (2) rather than the expected product Ir(H)₂{Si(OEt)₃}(CO)(PPh₃)₂ (3) that was previously reported to be formed by this reaction. Accompanying formation of Si(OEt)₄, (EtO)₃SiOSi(OEt)₃, and (EtO)₂HSiOSi(OEt)₃ is observed. On the other hand, trialkylhydrosilane HSiEt₃ reacts with IrCl(CO)(PPh₃)₂ (10:1 molar ratio) at 80 °C for 84 h to give Ir(H)₂(SiEt₃)(CO)(PPh₃)₂ (4) in a high yield, accompanying with a release of ClSiEt3.

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1. Introduction

Syntheses of the silvliridium complexes having a thermodynamically stable Ir-Si bond are reported and they are known to show high reactivities under some conditions [1–7]. Typical synthetic methods for the silvliridium complexes are the reactions of hydrosilanes with low-valent iridium complexes, which causes cleavage of H-Si bond by oxidative addition to form the Ir-Si bond. For instance, the reaction of HSiR₃ with Vaska's complex IrCl(CO)(PPh₃)₂ was reported to produce Ir(H)₂(SiR₃)(CO)(PPh₃)₂ via the proposed pathway shown in Scheme 1 [8]. This transformation involves three steps: the reversible oxidative addition of HSiR₃ to the starting Ir(I) complex affording the octahedral silyliridium(III) complex, the irreversible reductive elimination of Cl-SiR₃ [9] from the formed Ir(III) intermediate through trans-cis isomerization [10], and oxidative addition of the second HSiR₃ to the in situ formed IrH(CO)(PPh₃)₂.

The above reaction has been known to be applicable to preparation of the analogous $Ir(H)_2(MR_3)(CO)(PPh_3)_2$ (M = Ge and Sn) by the reactions of triorganogermanes [2,11] and triorganostannanes [12,13] with IrCl(CO)(PPh₃)₂.

From a viewpoint of the irreversible reductive elimination of chlorosilanes Cl-SiR₃ in Group 9 transition metals, we have already reported that a hexacoordinated $RhCl(H){Si(C_6H_5CF_3)_3}(PMe_3)_3$ with the chloro and silvl ligands at cis position underwent the

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concerted reductive elimination of chlorosilanes [14]. In addition, a kinetic study on the thermal reaction of RhCl(H){Si(OEt)_n- Me_{3-n} (PPh₃)₂ (n = 1-3) with a pentacoordinated structure revealed different rates of reductive elimination of chlorosilanes, depending on the substituents at Si; RhCl(H){Si(OEt)₃}(PPh₃)₂ liberates $ClSi(OEt)_3$ (k = 2.01 × 10⁻⁵ s⁻¹) at 60 °C much more slowly than RhCl(H){SiMe₂(OEt)}(PPh₃)₂ ($k = 3.7 \times 10^{-3} \text{ s}^{-1}$) [15]. This slow reductive elimination of ClSi(OEt)₃ from the Rh(III) complex is a sharp contrast with the above reaction in Scheme 1, in which the apparent double oxidative addition of HSi(OEt)₃ to IrCl(CO)-(PPh₃)₂ gave rise to the formation of Ir(H)₂{Si(OEt)₃}(CO)(PPh₃)₂ via a facile release of ClSi(OEt)₃ from the analogous Ir(III) complex [8b]. The different reactivities between Rh and Ir complexes bearing the Si(OEt)₃ ligand prompted us to investigate the reactions of two different hydrosilanes, HSi(OEt)3 and HSiEt3, with IrCl(CO)(PPh₃)₂.

2. Results and discussion

An NMR tube experiment of HSi(OEt)₃ with IrCl(CO)(PPh₃)₂ in 5:1 molar ratio at room temperature resulted in the formation of IrCl(H){Si(OEt)₃}(CO)(PPh₃)₂ (1) in 41% NMR yield (see, Eq. (1)). The ¹H NMR spectrum of the reaction mixture showed a triplet assigned to the hydrido ligand of **1** at δ –5.93 (J_{PH} = 15 Hz), indicating that two equivalent phosphorus atoms are located at cis positions of the hydrido ligand. The earlier studies by Chalk in 1969 on the same reaction was reported to give the complex that showed the ¹H NMR signal of the hydrido ligand at a similar position





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 $(\delta = -6.1 \ (J_{PH} = 14 \text{ Hz})$ in benzene) [8b]. Our several attempts to isolate **1** from the reaction mixture failed due to the reversible reductive elimination of HSi(OEt)₃ from **1** to regenerate the starting IrCl(CO)(PPh₃)₂ during evaporation under reduced pressure. This observation is compatible to the reported results; the HSi(OEt)₃ adduct thermally decomposes in vacuo to yield the original IrCl(CO)(PPh₃)₂. Bennett also reported that CO reacted with a pentacoordinated IrCl(H){Si(OEt)₃}(PPh₃)₂ to generate not **1**, but IrCl(CO)(PPh₃)₂ and HSi(OEt)₃ [16]. This result suggests the tentative formation of **1**, but the spontaneous reductive elimination of HSi(OEt)₃ from the unstable **1** occurs to recover IrCl(CO)(PPh₃)₂ and HSi(OEt)₃.

 $IrCl(CO)(PPh_{3})_{2} + HSi(OEt)_{3} \xrightarrow[]{PPh_{3}} H \xrightarrow[]{PPh_{3}} PPh_{3}$ $(1:5) \qquad C_{6}D_{6} \qquad Ph_{3}P' \mid Cl \qquad (1)$ 1 41% (NMR yield)

On the contrary, the reaction of a large excess amounts (20 molar equivalents) of HSi(OEt)₃ with IrCl(CO)(PPh₃)₂ at 50 °C gave the isolable IrCl(H)₂(CO)(PPh₃)₂ (**2**) in 82% yield (see, Eq. (2)). Complex **2** was identified by comparison of the IR and NMR (¹H and ³¹P{¹H}) data with those reported in the literature [17]. GC–MS and ²⁹Si{¹H} NMR analyses of the reaction mixture revealed the formation of Si(OEt)₄, (EtO)₃SiOSi(OEt)₃, and (EtO)₂HSiOSi(OEt)₃ as organic by-products. The formation of **2** was also evidenced by the molecular structure determination by X-ray diffraction. An ORTEP drawing of **2** is depicted in Fig. 1. Complex **2** has a slightly distorted octahedral coordination around the Ir center with two trans PPh₃ ligands and with the chloro and carbonyl ligands at mutually cis positions. The Ir–Cl bond distance (2.460(2) Å) is within the range of the bonds reported in hexacoordinate Ir(III)–Cl complexes (2.367(9)–2.518(1) Å) [18,19].



Although the reaction of $HSi(OEt)_3$ with $IrCl(CO)(PPh_3)_2$ has been reported to afford $Ir(H)_2\{Si(OEt)_3\}(CO)(PPh_3)_2$ (**3**), according to the reported literature [8b], reaction depicted in Eq. (2) did not form **3** at all. We thus prepared complex **3** according to another synthetic



Fig. 1. ORTEP drawing of IrCl(H)₂(CO)(PPh₃)₂ (**2**) at the 30% ellipsoid level. Hydrogen atoms except for the Ir–H hydrogen are omitted for simplicity. Selected bond distances (Å) and angles (deg): Ir1–Cl1 2.4602(17), Ir1–P1 2.3269(15), Ir1–P2 2.3215(13), Ir1–C1 1.904(7), Ir1–H1 1.536, and Ir1–H2 1.520; Cl1–Ir1–P1 91.84(5), Cl1–Ir1–P2 87.13(5), Cl1–Ir1–C1 103.4(2), P1–Ir1–P2 168.34(5), P1–Ir1–C1 94.5(2), P2–Ir1–C1 97.0(2), Cl1–Ir1–H1 176.5, Cl1–Ir1–H2 98.3, P1–Ir1–H1 89.3, P1–Ir1–H2 85.3, P2–Ir1–H1 92.4, P2–Ir1–H2 83.4, C1–Ir1–H1 73.2, C1–Ir1–H2 158.3, and H1–Ir1–H2 85.1.

method in the literature [20] in order to determine its structure unequivocally and to compare its detailed NMR data with those of the complex from the reaction in Eq. (2). Reaction of HSi(OEt)₃ (2 equivalents) with IrCl(CO)(PPh₃)₂ in toluene at 50 °C for 1 h cleanly formed Ir(H)₂{Si(OEt)₃}(CO)(PPh₃)₂ (**3**) in 72% yield (see, Eq. (3)). The ¹H NMR spectrum of **3** exhibits two Ir–H signals at δ –10.70 (ddd, J_{PH} = 110 Hz, J_{PH} = 19 Hz, and J_{HH} = 5 Hz) and δ –9.55 (ddd, J_{PH} = 22 Hz, J_{PH} = 15 Hz, and J_{HH} = 5 Hz). A large coupling constant of the former signal indicates that this hydrogen atom is located trans to one of the phosphorus atoms. The ³¹P{¹H} NMR spectrum of **3** shows two doublets at δ 3.51 and 7.25, which are assigned to the two inequivalent PPh₃ ligands. The stereochemistry of **3** with two bulky PPh₃ ligands at mutually cis positions is attributed to the large trans influence of the hydrido and silyl ligands.

$$IrH(CO)(PPh_{3})_{3} + HSi(OEt)_{3} \xrightarrow{toluene} OC - Ir - PPh_{3} \\ (1:2) 50 °C, 1 h H (3) \\ 3 \\ 72\%$$

In order to compare the reactivity of hydrosilanes bearing different substituents, reaction of HSiEt₃ with IrCl(CO)(PPh₃)₂ in a 10:1 molar ratio at 80 °C in toluene yielded Ir(H)₂(SiEt₃)(CO)(PPh₃)₂ (**4**) in 75% isolated yield and ClSiEt₃ in 96% yield, based on Cl, respectively (see, Eq. (4)). The obtained results are consistent with the reactions of HSiMe₃ and HSiCl₃ with IrCl(CO)(PPh₃)₂ [11c], giving the corresponding complexes Ir(H)₂(SiR₃)(CO)(PPh₃)₂ (R = Me and Cl) whose structures are similar to **4**. The structure of **4** was determined unambiguously by IR and NMR (¹H, ³¹P{¹H}, and ¹³C{¹H}) spectroscopy as well as elemental analysis. The ¹H NMR spectrum of **4** exhibited two Ir–H signals at δ –10.57 (ddd, *J*_{PH} = 15 Hz, *J*_{HH} = 5 Hz) and at δ –9.51 (ddd, *J*_{PH} = 23 Hz, *J*_{PH} = 15 Hz, *J*_{HH} = 5 Hz). These peak positions and coupling constants are similar to those of **3**. Complex **4** showed a characteristic signal of the carbony carbon at δ 183.51 in the ¹³C{¹H} NMR spectrum and IR band at 1956 cm⁻¹.



Scheme 2. A plausible sequence for the formation of 2, Si(OEt)₄, and the disiloxanes.



As described above, both $HSi(OEt)_3$ and $HSiEt_3$ react with $IrCl-(CO)(PPh_3)_2$ to give the Ir(III) intermediates through the initial oxidative addition. The final products of the reactions, however, were different from each other; complexes $IrCl(H)_2(CO)(PPh_3)_2$ (2) and $Ir(H)_2(SiEt_3)(CO)(PPh_3)_2$ (4), respectively. The former reaction did not involve reductive elimination of $ClSi(OEt)_3$ from 1, which is consistent with the high stability of the Rh [15] and Ir [21] complexes with the Cl and $Si(OEt)_3$ ligands.

Scheme 2i depicts a plausible reaction pathway for the formation of **2**, Si(OEt)₄, and the other ethoxysiloxanes. Conversion of the Ir–Si(OEt)₃ bond in the formed complex **1** into the Ir–O– Si(OEt)₃ bond would be accelerated by the contaminating O₂ [22,23], which smoothly reacts with HSi(OEt)₃ (or H₂Si(OEt)₂) to form ethoxysiloxanes [22] those are detected by the ²⁹Si{¹H} NMR spectrum and GC–MS [24] (see Section 4). On the other hand, complex **1** might decompose by hydrolysis with the contaminating water to form **2** and triethoxysilanol, which easily converts into ethoxysiloxanes via the known condensation, as shown in Scheme 2ii. Accompanying generation of H₂Si(OEt)₂ and Si(OEt)₄ is attributed to the Ir-catalyzed disproportionation of HSi(OEt)₃ (Scheme 2iii) [24].

In order to elucidate a role of O₂ or H₂O, we carried out several reactions of HSi(OEt)₃ with IrCl(CO)(PPh₃)₂ in toluene under different conditions. In a flame-sealed NMR tube containing carefully evacuated benzene- d_6 , the reaction at 50 °C proceeded much more slowly than that in a standard NMR tube experiment and resulted in a lower yield of 2 (28%), accompanied with the unreacted 1 (64%) even after 144 h. This results support that complex 1 it self is rather stable under an Ar atmosphere, but it would suffer from the contaminating O_2 in the reaction mixture to convert into the postulated silyloxoiridium complex. In addition, the reaction of HSi(OEt)₃ with IrCl(CO)(PPh₃)₃ in the presence of 20 molar equivalents of water under Ar smoothly generated 2 in 80% yield. In addition, when 20 molar equivalents of D₂O was added to the reaction mixture, again complex 2 was formed in 98% yield with D incorporation (22% at δ –17.58 and 27% at δ –6.66). On the other hand, the reaction under an O_2 atmosphere without water gave only 17% of **2** along with some unidentified products. These results suggest that incorporation of H₂O and/or O₂ contained in the reaction mixture can accelerate the reaction toward the formation of **2**, although no example of reactivities of silyliridium complexes toward water or oxygen has been reported to date.

Another possible reaction pathway for the formation of 2 is a direct hydrogenation of **1**. Parish et al. reported that in the Ir-catalyzed condensation of $HSi(OEt)_3$ with R^1OH ($R^1 = Me$ and Et), giving $(R^1O)Si(OEt)_3$ with a release of H₂, the starting IrCl- $(CO)(PPh_3)_2$ converts into a mixture of $IrCl(H)_2(CO)(PPh_3)_2$ (2), IrCl₂(H)(CO)(PPh₃)₂, and IrH₃(CO)(PPh₃)₂ [25]. Since neither IrCl₂(H)(CO)(PPh₃)₂ nor IrH₃(CO)(PPh₃)₂ were contaminated in the present reaction mixture, the hydrogenation pathway can be ruled out. Although they also postulated formation of IrH-(CO)(PPh₃)₂ and ClSi(OEt)₃ during the reaction, their formation might be attributed to reduction of IrCl(CO)(PPh₃)₂ by alcohol and the intermolecular transfer of the Cl ligand, respectively, rather than the formation of IrH(CO)(PPh₃)₂ from 1 via elimination of ClSi(OEt)₃. In a sharp contrast, the reaction of HSiEt₃ with IrCl-(CO)(PPh₃)₂, forming complex **4** and ClSiEt₃, follow the reaction pathway depicted in Scheme 1.

3. Summary

This study showed that HSiEt₃ reacts with IrH(CO)(PPh₃)₂ to give Ir(H)₂(SiEt₃)(CO)(PPh₃)₂ (**4**) and CISiEt₃, in agreement with reports of Chalk et al. in 1969. The reaction of HSi(OEt)₃, however, does not produce an analogous complex Ir(H)₂(SiR₃)(CO)(PPh₃)₂ due to a slow reductive elimination of Cl–Si(OEt)₃ from the Cl-Ir–Si(OEt)₃ species in complex **1** and causes the formation of **2** and disiloxanes by acceleration of the contaminating oxygen and water at 50 °C.

4. Experimental

4.1. General

All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure before use. Hexane and toluene were distilled from sodium and benzophenone prior to use or purchased from Kanto Chemicals Co. Ltd. Benzene- d_6 was dried over MS-4A and deoxygenated by three freeze-thaw cycles under reduced pressure. HSi(OEt)₃ and HSiEt₃ were was purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. IrCl(CO)(PPh₃)₂ was prepared according to published procedure [26]. NMR spectra (¹H, ¹³C{¹H}, ²⁹Si{¹H}, and ³¹P{¹H}) were recorded on JEOL EX-400 or Varian Mercury 300 spectrometers. The IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer in KBr. GC-MS analyses were carried out on a Hitachi M-80 spectrometer or a Shimadzu QP-5000 GC-MS system. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

4.2. Synthesis and characterization

4.2.1. Reaction of HSi(OEt)₃ with IrCl(CO)(PPh₃)₂ at room temperature To a solution of IrCl(CO)(PPh₃)₂ (31 mg, 0.04 mmol) in 1.0 mL of benzene-*d*₆ was added HSi(OEt)₃ (38 µL, 0.20 mmol) in an NMR tube at room temperature. After 1 h, the solution became dark yellow. ¹H and ³¹P{¹H} NMR spectra showed the formation of **1** in 41% NMR yield and the presence of unreacted IrCl(CO)(PPh₃)₂. **1**: ¹H NMR (300 MHz, benzene-*d*₆, 25 °C): δ –5.93 (t, *J*_{PH} = 15 Hz, 1H), 0.89 (t, *J*_{HH} = 7 Hz, 9H), 3.30 (q, *J*_{HH} = 7 Hz, 6H), 6.99–7.09 (m, 18H, PPh₃), 8.05–8.07 (m, 12H, PPh₃); ³¹P{¹H} NMR (121.5 MHz, benzene-*d*₆, 25 °C): δ 9.17. Attempts to isolate **1** were unsuccessful due to its facile conversion into IrCl(CO)(PPh₃)₂ during evaporation of volatiles.

4.2.2. Reaction of HSi(OEt)₃ with IrCl(CO)(PPh₃)₂ at 50 °C: formation of **2**

To a toluene (10 mL) dispersion of IrCl(CO)(PPh₃)₂ (500 mg, 0.65 mmol) was added HSi(OEt)₃ (2.5 mL, 12.8 mmol) at room temperature. The reaction mixture was heated to 50 °C with stirring for 24 h to result in the deposition of a pale yellow solid. The volatiles were removed and washed with hexane (5 mL \times 3 times), and dried in vacuo to give $IrCl(H)_2(CO)(PPh_3)_2$ (2) as pale yellow powder (512 mg, 82%). Recrystallization from toluene/hexane afforded dark yellow prisms suitable for X-ray crystallography. **2**: ¹H NMR (300 MHz, benzene- d_6 , 25 °C) [17e]: δ –17.58 (dt, J_{PH} = 15 Hz, J_{HH} = 5 Hz, 1H), -6.66 (dt, J_{PH} = 18 Hz, J_{HH} = 5 Hz, 1H), 6.92-7.05 (m, 18H, PPh₃), 7.87-7.95 (m, 12H, PPh₃); ³¹P{¹H} NMR (121.5 MHz, benzene-*d*₆, 25 °C): δ 9.81; ¹³C{¹H} NMR (100.5 MHz, dichloromethane- d_2 , 25 °C): δ 128.56 (t, J_{CP} = 5.5 Hz, PPh₃-ortho), 130.90 (PPh₃-para), 135.12 (t, J_{CP} = 27.5 Hz, PPh₃-ipso), 135.38 (t, $J_{CP} = 5.5 \text{ Hz}$, PPh₃-meta), 177.17 (t, $J_{CP} = 5.5 \text{ Hz}$, CO); IR (KBr, cm⁻¹): 1979 (v_{CO}), 2106 (v_{Ir-H} trans to CO), 2193 (v_{Ir-H} trans to Cl). Anal. Calc. for C₃₇H₃₂ClOPIr: C, 56.81; H, 4.21; Cl, 4.53. Found: C, 56.99; H, 4.28; Cl, 4.81%.

The reaction of IrCl(CO)(PPh₃)₂ (3.91 g, 5.0 mmol) and HSi(OEt)₃ (18.8 mL, 100 mmol) in toluene (55 mL) was carried out in order to characterize various tetraethoxysilane and ethoxysiloxanes. GC–MS of the reaction mixture indicated the presence of the silicon-containing by-products whose major fragments [*m*/*z* (relative intensity, ion)] are shown below. Si(OEt)₄: [208(5, M+), 193(77), 179(34), 163(52, M+ – OEt), 149(100), 119(24), 79(80), 63(72)]. (EtO)₂HSiOSi(OEt)₃: [297 (4, M⁺ – H), 253 (100, M⁺ – OEt), 225 (17), 209 (13), 197 (13), 181 (15), 169 (18), 155 (15), 141 (50), 123 (14)]. (EtO)₃SiOSi(OEt)₃: [342 (2, M⁺), 297 (100, M⁺ – OEt), 269 (30), 253 (35), 241 (17), 225 (25), 197 (22), 185 (19), 169 (18), 157 (39), 141 (28), 123 (13)] [24].

The ²⁹Si{¹H} NMR spectrum of the products after removal of **2** showed the following signals (relative intensity); Si(OEt)₄: δ –82.29 (100); (EtO)₂HSiOSi(OEt)₃: δ –68.65 (3), –77.29 (5); (EtO)₃SiOSi(OEt)₃: δ –88.77 (10). The volatiles were removed and washed with hexane (5 mL × 3 times), and distillation of hexane washings (110 °C/155 Torr) gave Si(OEt)₄ (961 mg, 4.62 mmol, 92% yield, based on IrCl(CO)(PPh₃)₂) as a colorless liquid.

4.2.3. Reaction of HSi(OEt)₃ with IrH(CO)(PPh₃)₃: preparation of 3

Complex **3** was prepared as modified to the literature [20]. To a yellow dispersion of $IrH(CO)(PPh_3)_3$ (600 mg, 0.60 mmol) in toluene (12 mL) was added $HSi(OEt)_3$ (2.25 mL, 1.20 mmol) at room

temperature. The reaction mixture was stirred at 50 °C for 1 h to result in pale yellow suspension. The volatiles were removed and the residue was washed with hexane (15 mL \times 3 times), and dried in vacuo to give $Ir(H)_2$ {Si(OEt)₃}(CO)(PPh₃)₂(**3**) as pale yellow powder (395 mg, 0.55 mmol, 72%). ¹H NMR (300 MHz, benzene-d₆, 25 °C): δ –10.70 (ddd, J_{PH} = 110 Hz, J_{PH} = 19 Hz, J_{HH} = 5 Hz, 1H), -9.55 (ddd, $J_{PH} = 22$ Hz, J(PH) = 15 Hz, $J_{HH} = 5$ Hz, 1H), 1.21 (t, $J_{\rm HH}$ = 7 Hz, 9H), 3.98 (dq, $J_{\rm HH}$ = 7 Hz, $J_{\rm PH}$ = 2 Hz, 6H), 6.82–7.01 (m, 18H, PPh₃), 7.25–7.32 (m, 6H, PPh₃), 7.59–7.66 (m, 6H, PPh₃); ³¹P{¹H} NMR (121.5 MHz, benzene- d_6 , 25 °C): δ 3.51 (d, $J_{PP} = 16 \text{ Hz}$), 7.25 (d, $J_{PP} = 16 \text{ Hz}$); ¹³C{¹H} NMR (100.5 MHz, dichloromethane-d₂, 25 °C): δ 18.16 (CH₃), 57.38 (CH₂), 127.81 (d, $J_{CP} = 11.0 \text{ Hz}$, PPh₃-ortho), 128.11 (d, $J_{CP} = 9.2 \text{ Hz}$, PPh₃-ortho), 129.60 (PPh₃-para), 129.71 (PPh₃-para), 133.95 (d, J_{CP} = 11.0 Hz, PPh₃-*meta*), 135.30 (dd, J_{CP} = 35.9, J_{CP} = 2.5 Hz, PPh₃-*ipso*), 135.32 (d, $J_{CP} = 11.0 \text{ Hz}$, PPh₃-meta), 136.83 (dd, $J_{CP} = 36.5$, $J_{CP} = 2.3 \text{ Hz}$, PPh₃-*ipso*), 185.77 (dd, J_{CP} = 16.5, J_{CP} = 7.1 Hz, CO); IR (KBr, cm⁻¹): 1094 (v_{Si-O}), 1968 (v_{CO}), 2080 (v_{Ir-H} trans to CO).

4.2.4. Reaction of HSiEt₃ with IrCl(CO)(PPh₃)₂

To a toluene (10 mL) dispersion of IrCl(CO)(PPh₃)₂ (512 mg, 0.65 mmol) was added HSiEt₃ (1.07 mL, 6.7 mmol) at room temperature. The reaction mixture was heated to 80 °C with stirring for 84 h to result in a dark yellow homogeneous solution. The volatiles were removed and the residue was washed with hexane $(5 \text{ mL} \times 3 \text{ times})$ and dried in vacuo to give $Ir(H)_2(SiEt_3)$ - $(CO)(PPh_3)_2$ (4) as pale yellow powder (517 mg, 75%). Data of 4: ¹H NMR (300 MHz, benzene- d_6 , 25 °C): δ –10.57 (ddd, J_{PH} = 113 Hz, J_{PH} = 19 Hz, J_{HH} = 5 Hz, 1H), -9.51 (ddd, J_{PH} = 23 Hz, J_{PH} = 15 Hz, $J_{\text{HH}} = 5 \text{ Hz}, 1\text{H}$, 1.06 (dq, $J_{\text{HH}} = 7 \text{ Hz}, J_{\text{PH}} = 2 \text{ Hz}, 6\text{H}$), 1.25 (t, $J_{\text{HH}} = 7 \text{ Hz}, 9\text{H}$), 6.86–6.92 (m, 18H, PPh₃), 7.35–7.51 (m, 6H, PPh₃), 7.53–7.50 (m, 6H, PPh₃); ³¹P{¹H} NMR (121.5 MHz, benzene- d_6 , 25 °C): δ 1.21 (d, J_{PP} = 13 Hz), 9.90 (d, J_{PP} = 13 Hz); ¹³C{¹H} NMR (100.5 MHz, dichloromethane- d_2 , 25 °C): δ 5.59 (CH₃), 12.76 (dd, *J*_{CP} = 5.5 Hz, *J*_{CP} = 3.7 Hz, CH₂), 128.01 (PPh₃-ortho), 128.09 (PPh₃-ortho), 129.55 (PPh₃-para), 129.86 (PPh₃-para), 133.96 (d, J_{CP} = 10.9 Hz, PPh₃-meta), 135.35 (d, J_{CP} = 10.9 Hz, PPh₃meta), 136.32 (d, I_{CP} = 52.3 Hz, PPh₃-ipso), 137.68 (d, I_{CP} = 52.3 Hz, PPh₃-*ipso*), 183.51 (t, J_{CP} = 3.6 Hz, CO); IR (KBr, cm⁻¹): 1956 (v_{CO}), 2080 (v_{Ir-H} trans to CO), 2126 (v_{Ir-H} trans to PPh₃). Anal. Calc. for C43H47OP2Silr: C, 59.91; H, 5.50. Found: C, 60.08; H, 5.58%. An NMR tube reaction of IrCl(CO)(PPh₃)₂ (31 mg, 0.04 mmol) and HSi-Et₃ (32 μ L, 0.20 mmol) in benzene- d_6 (0.7 mL) in an NMR tube at

Crystal data	a and details	of the structu	re refinement of 2

Table 1

Formula	C ₃₇ H ₃₂ ClOP ₂ Ir
Molecular weight	782.28
Crystal system	orthorhombic
Space group	<i>Pbca</i> (No. 61)
a (Å)	21.936(3)
b (Å)	17.782(5)
c (Å)	16.696(3)
V (Å ³)	6512.4(23)
Ζ	8
μ (mm ⁻¹)	4.320
F (000)	3088
D_{calcd} (g cm ⁻³)	1.596
Crystal size (mm ³)	0.45 imes 0.25 imes 0.20
2θ range (°)	5.0-55.0
Number of unique reflections	7474
Number of used reflections	4701
Number of variables	409
$R_1 (I > 3.00\sigma (I))$	0.032
R _w 2 ^a	0.044
GOF	1.002

^a Weighting scheme $[\sigma (F_0)^2]^{-1}$.

80 °C showed the formation of ¹H NMR signals of both **4** and ClSi-Et₃ (96%).

4.3. X-ray crystallography of 2

Single crystals of 2 suitable for X-ray diffraction studies were obtained by recrystallization from toluene/hexane. Crystallographic data and details of refinement were summarized in Table 1. The crystals were sealed in glass capillary tubes and mounted, and the X-ray data were collected with a Rigaku R-AXIS RAPID II imaging plate area detector using graphite-monochromated Mo K α radiation (λ = 0.7107 Å). Calculations were carried out by using the CrystalStructure crystallographic software package [27]. A full-matrix least-squares refinement was used for the nonhydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters.

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Appendix A. Supplementary material

CCDC 186010 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc. cam.ac.uk/data request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.12.033.

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