Synthesis of a Bis(silyl)iridium(III) Complex *via* Oxidative Addition of an Si-Si Linkage to Ir(I) and Its Crystal Structure

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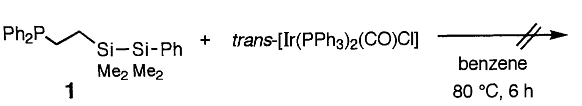
(Received September 18, 1995)

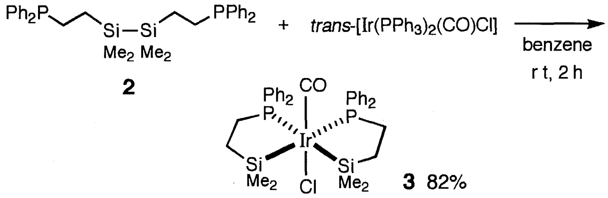
A new bis(trialkylsilyl)iridium(III) complex is synthesized by a process of oxidative addition of an Si–Si linkage to an iridium(I) complex, and the crystal structure is determined by an X-ray analysis.

Organosilicon compounds are widely utilized in organic synthesis. Bis(silylation), *i.e.*, the addition of an Si–Si linkage to an unsaturated organic molecule, has attracted much attention since two Si–C bonds are created in a single reaction.[1] Due to its synthetic utility, the mechanism of bis-silylation has recently become the subject of theoretical[2] and experimental investigations. Bis(organosilyl)palladium[3] and -platinum[4] complexes have been synthesized and characterized by several groups. These studies corroborated the postulated oxidative addition of an Si–Si linkage as one of the key steps of bis(silylation). Whereas hydrosilylation is promoted by a variety of catalysts,[5] transition metals of catalytic activities for bis(silylation) are mostly limited to palladium, platinum, and nickel. Very little is known about the behavior of other low-valent transition metals toward disilanes. Of particular interest is the possibility for the metals, capable of catalyzing hydrosilylation, to cleave an Si–Si linkage. A disilane having phosphine tethers like **2** seems to be an appropriate tool for probing the reactivity of various transition metals. The phosphine tethers are expected to force the Si–Si linkage into the proximity of the metal by precoordination accelerating the oxidative addition, and to stabilize the resulting complex by anchoring the split silyl groups onto the metal.[6] This paper describes the synthesis of a bis(silyl)iridium(III) complex **3** by a process of oxidative addition of an Si–Si linkage to Ir(I) and its structural determination.

A disilane (**1**) equipped with one phosphine tether[7] was treated with *trans*-[Ir(PPh_3)$_2$(CO)Cl] in benzene at 80 °C. No reaction took place after 6 h, being in marked contrast to the case with an Si–H linkage.[8] Pre-coordination with a single tether could not provide the Si–Si group with enough geometrical constraint to cause oxidative addition.



Next, we examined the reaction of a disilane (**2**) winged with two phosphine tethers. A solution of **2** (120 mg, 0.221 mol) and *trans*-[Ir(PPh_3)$_2$(CO)Cl] (155 mg, 0.199 mol) in benzene (3.5 mL) was stirred at room temperature for 2 h. The characteristic lemon-yellow color of the Ir(I) complex was completely discharged, suggesting the occurrence of the oxidative addition of the Si–Si bond. The solvent was removed under vacuum, and the residue was subjected to column chromatography to remove the free triphenylphosphine. The subsequent recrystallization from CH_2Cl_2/hexane afforded a bis(silyl)iridium(III) complex (**3**, 131 mg, 82%) as colorless and air-stable crystals.[9]



The presence of a single resonance in ^{31}P NMR spectra indicated a symmetric structure in which the carbonyl and chloro ligands are *trans*[10] rather than an asymmetric one with a *cis* arrangement. The proposed geometry was confirmed by an X-ray crystallographic analysis (Figure 1).[11] It adopts an octahedral geometry, where the two silicon atoms and the two phosphorous atoms lie on a plane with both pairs being *cis*. Selected bond lengths and angles are listed in Table 1. The Si–Ir bond lengths (2.444(2) and 2.447(2) Å) are among the longest Ir–Si bonds reported.[12] The distance between Si5 and Si6 was 3.49 Å, being suggestive of the absence of a considerable Si–Si interaction. The significantly longer Ir–C8 distance (1.835(6) Å) as well as the higher CO stretching frequency (1996 cm^{-1}) as compared with the corresponding values of *trans*-[IrP_2(CO)Cl] [P = (*o*-tolyl)$_3$P, Ir–CO = 1.67(4) Å, ν_{CO} = 1948 cm^{-1}][13] may reflect decreased backbonding due to the higher oxidation state of iridium.

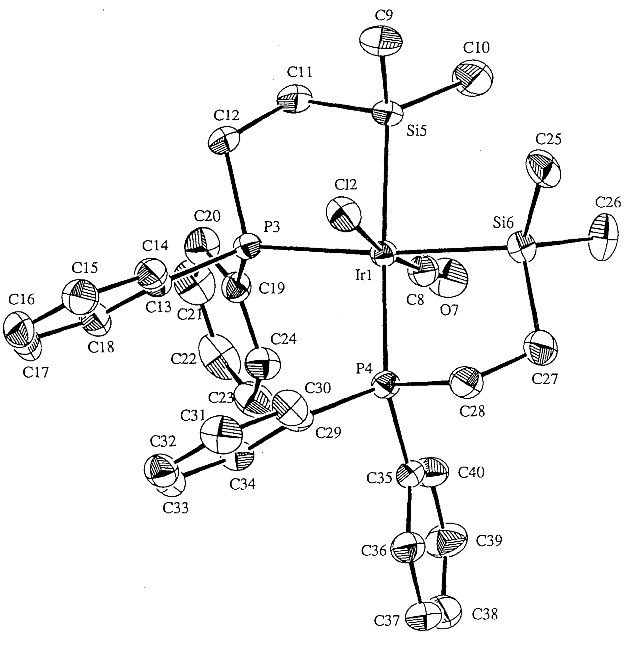


Figure 1. Molecular structure of **3** with the hydrogen atoms omitted for clarity.

Table 1. Selected interatomic bond lengths (Å) and angles (deg) in **3**

Ir1–Cl2	2.422(1)	Ir1–P3	2.440(2)
Ir1–P4	2.436(1)	Ir1–Si5	2.444(2)
Ir1–Si6	2.447(2)	Ir1–C8	1.835(6)
O7–C8	1.126(6)	Cl2–Ir1–P3	90.99(5)
Cl2–Ir1–P4	82.38(5)	Cl2–Ir1–Si5	88.61(6)
Cl2–Ir1–Si6	87.55(6)	P3–Ir1–Si5	83.59(5)
P3–Ir1–C8	93.3(2)	P4–Ir1–Si6	83.74(5)
P4–Ir1–C8	103.7(2)	Si5–Ir1–Si6	91.00(6)
Si5–Ir1–C8	84.8(2)	Si6–Ir1–C8	87.5(2)

All the attempted reactions of **3** with unsaturated organic substrates including alkynes failed to proceed. Moreover, **3** was recovered even upon treatment with $AgBF_4$ in benzene, in contrast to Vaska's complex.[14] The tight binding of the σ-donative chloro ligand can be also ascribed to the higher oxidation state of the iridium atom.

In summary, the present study provides the first example of the direct observation of oxidative addition of an Si–Si linkage to an iridium(I) complex, and thereby discloses the inherent reactivity of iridium(I) metal to undergo insertion into an Si–Si linkage. The inertness of the resulting bis(silyl)iridium(III) complex **3** toward ligand substitution may be relevant to the paucity of successful examples of Ir(I)-mediated bis-silylation. Unlike the nickel triad metals, an octahedral structure with the 18-electron configuration is most likely for a bis(silyl)iridium(III) complex, which is possibly too reluctant to open a coordination site for unsaturated organic molecules.

References and Notes

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9 **3**: ^1H NMR δ 0.45 (d, $J = 2.7$ Hz, 6H), 0.50 (d, $J = 1.3$ Hz, 6H), 0.54–0.80 (m, 2H), 0.88–1.27 (m, 2H), 2.26–2.64 (m, 4H), 6.94–7.42 (m, 20H); $^{31}P\{^1H\}$ NMR δ 11.61 (s); $^{13}C\{^1H\}$ NMR δ 0.45 (t, $J = 2.1$ Hz), 3.35 (t, $J = 3.1$ Hz), 17.88 (t, $J = 14.9$ Hz), 22.73 (the second-order complex coupling), 127.61 (t, $J = 4.2$ Hz), 128.43 (t, $J = 4.6$ Hz), 129.22, 130.02, 132.55 (t, $J = 5.4$ Hz), 132.77 (t, $J = 4.3$ Hz), 132.82–134.09 (m), 172.44. Anal. Found: C, 49.38; H, 5.07%. Calcd for $C_{33}H_{40}ClIrOP_2Si_2$: C, 49.64; H, 5.05%.

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11 Crystal data: $C_{33}H_{40}ClIrOP_2Si_2$, $M = 798.5$, monoclinic, space group $P2_1/c$, $a = 16.475(4)$, $b = 11.513(2)$, $c = 19.264(3)$ Å, $\beta = 110.93(2)°$, $V = 3412(1)$ Å^3, $Z = 4$, $D_c = 1.554$ g/cm^3, $\mu = 41.62$ cm^{-1}. Intensity data were measured on a Rigaku AFC7R diffractometer using ω-2θ scan technique with graphite monochromated Mo K_α radiation ($\lambda = 0.71069$ Å). 10402 unique reflections within $3 \le 2\theta \le 60°$ were collected. No decay correction was applied. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on azimuthal scans of several reflections was applied. The structure was solved by a direct method and refined by the full-matrix least-squares to $R = 0.035$ ($R_w = 0.034$) for 5883 reflections [$I > 3.0\sigma(I)$]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement with isotropic thermal parameters.

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