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Oxidative Addition of Halo(methyl)silanes to an In Situ Generated Ir(I) Complex and β-Hydride Elimination Reaction of the Resulting (Methylsilyl)iridium Complexes

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Halomethylsilanes ($MeSiCl_3$, Me_3SiI, Me_2SiCl_2, Me_3SiCl, and Me_3SiBr) undergo oxidative addition to $IrH(P^iPr_3)_2$ in situ generated from $IrH_5(P^iPr_3)_2$ and two equivalent neohexene to form halo(organosilyl)iridium(III) complexes. In addition, the resulting (methylsilyl)iridium complexes undergo β-hydride elimination reactions leading to the formation of dihydroiridium species.

In relation to the versatile uses and functions of silicon-containing polymers,[1)] homogeneous catalysis for silicon monomers and reactivities of silicon compounds toward transition metal complexes are attracting increasing interests. Of particular importance which warrants further fundamental investigations might be the oxidative addition of halosilanes, especially chlorosilanes since some of them are industrially available in large quantities. However, unlike the well documented oxidative addition of organic halides enabling a wide range of applications,[2)] corresponding reactions of halosilanes are still very rare.[3-7)] Previously we have reported the unequivocal examples in which Si-X (X = Cl, Br, I) bonds readily undergo oxidative addition to $Pt(PEt_3)_n$ (n = 3, 4).[5,6)] During the progress of the further studies, we have come across halo(silyl)iridium complexes being formed on the treatment of halosilanes with "$IrH(P^iPr_3)_2$"[8)] in situ generated from $IrH_5(P^iPr_3)_2$ and two equivalent neohexene.[9)] On the other hand, recently, Milstein et al.[7)] have reported that $MeSiCl_3$ reacts with $(C_8H_{14})IrCl(PMe_3)_3$ (C_8H_{14} = cyclooctene) to give mer-$(MeCl_2Si)IrCl_2(PMe_3)_3$, claiming the first example of oxidative addition of the very strong Si-Cl bond.[4,6)] This publication prompts us to report our results of oxidative addition reaction of Si-X bond (X = Cl, Br, I) with the Ir complex.

When a benzene (0.2 cm^3) solution of $IrH_5(P^iPr_3)_2$ (0.05 mmol), $MeSiCl_3$ (0.10 mmol) and neohexene (0.10 mmol) was heated in an NMR tube at 60 °C for 15 min, the colorless solution turned to red. The ^1H NMR signal of the methine proton of the ligated triisopropylphosphine shifted from 1.46-1.95 (m) to 2.62-3.08 (m) ppm. At the same time, a new singlet signal assignable to $MeCl_2Si$-Ir species emerged at 1.51 ppm with concomitant decrease in intensity of a singlet of the starting $MeSiCl_3$ (0.51 ppm). The intensity ratio of these two Me-Si signals indicated that starting Ir complex had reacted to give the new Si-Ir complex in 92% yield. In agreement with this statement, neohexene charged was largely converted into neohexane (93% yield). Essentially the same results were obtained at 90 °C (in benzene-d_6), and monitoring the reaction by ^{31}P NMR showed that the signal at 44.42 ppm (referred to H_3PO_4) had nearly completely shifted to 37.42 ppm. The resulting complex was successfully isolated in a separate experiment using larger amounts of the starting materials (Ir complex, 0.26 mmol; $MeSiCl_3$, 0.95 mmol; neohexene, 0.6 mmol; benzene, 0.9 ml). After heating at 90 °C for 15 min, the reaction solution was concentrated in vacuo, and pentane (15 cm^3) was added.

Filtration of the resulting mixture and refrigeration of the filtrate down to -80 °C afforded 140 mg of $MeCl_2SiIrClH(P^iPr_3)_2$ (**1a**) as red crystals. The spectral and analytical data[10a)] fully support the proposed structure. In addition, the structure was unequivocally determined by X-ray diffraction analysis of the red crystal (Fig. 1).[11)] Thus, the occurrence of the reaction of Eq. 1 was verified.

$$IrH_5(P^iPr_3)_2 + R_3SiX \xrightarrow[\text{- neohexane}]{\text{neohexene}} R_3SiIrXH(P^iPr_3)_2 \qquad (1)$$

R_3Si, X = $MeCl_2Si$, Cl **Ia** (81%)
Me_3Si, I **Ib** (75%)
Me_2ClSi, Cl **Ic** (35%)

When Me_3SiI was used in place of $MeSiCl_3$, a similar reaction took place cleanly, and an analogous complex **1b**[10b)] could be isolated in good yield. Me_2SiCl_2 also afforded a similar product **1c**[10c)] in moderate yield. However, the reaction seemed to be less selective since other ^{31}P NMR signals, albeit weak, were also emerging (vide infra).

Similar Ir complexes have been reported to be formed from the reaction of $IrXL_3$[12a)] or $IrXL_2$[12b)] with R_3SiH. The spectral data of **1a-c** are consistent with those of reported complexes. Related Rh complexes have also been known, and X-ray diffraction analysis of $Cl_3SiRhClH(PPh_3)_2$ (**2**) has revealed distorted trigonal bipyramidal structure.[13)] On the other hand, we could not determine the location of the hydride ligand in **1a** clearly. However, as judged from the reasonable similarity of the bond angles of **2** with those values of **1a** shown in Fig. 1, it is safely concluded that **1a** is also distorted trigonal bipyramidal, the hydride ligand being at the equatorial site.

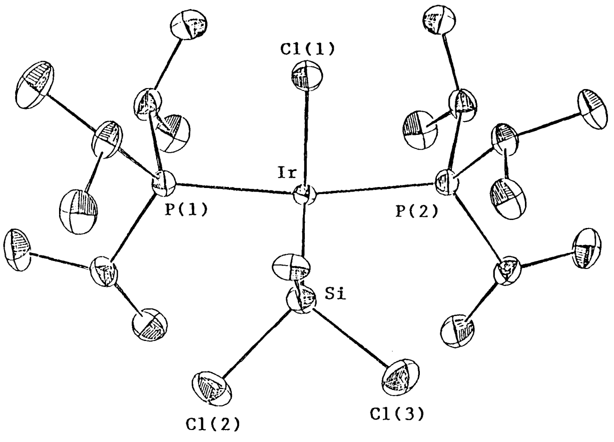

Fig.1. ORTEP drawing of the molecular structure of $MeCl_2SiIrClH(P^iPr_3)_2$ (**1a**).

Selected atomic distances (Å) and bond angles (°): Ir-Si, 2.235(5); Ir-Cl(1), 2.413(4); Ir-P(1), 2.360(4); Ir-P(2), 2.361(3); Si-Ir-Cl(1), 106.7(4); Si-Ir-P(1), 99.1(5); Si-Ir-P(2), 98.5(4); P(1)-Ir-P(2), 161.0(2); P(1)-Ir-Cl(1), 90.9(4); P(2)-Ir-Cl(1), 91.1(3).

As compared with $MeSiCl_3$, Me_3SiI, and Me_2SiCl_2, the reactivities of Me_3SiCl and Me_3SiBr seemed to be low. After the mixture of $IrH_5(P^iPr_3)_2$, neohexene, and a halosilane was heated at 90 °C for 2 h in a sealed NMR tube, ^1H and ^{31}P NMR signals assignable to $Me_3SiIrXH(P^iPr_3)_2$ (X = Cl, Br) could be observed; the ^1H NMR signals ascribable to Me_3Si-Ir and Ir-H emerged at 0.65 and -19.90 ppm (t, $J_{P\text{-}H}$ =13.7 Hz) for X = Cl, and 0.66 and -18.91 ppm (t, $J_{P\text{-}H}$ =13.9 Hz) for X = Br, while ^{31}P NMR signals of these chloro and bromo species appeared at 35.61 and 35.00 ppm, respectively. However, reactions did not proceed as cleanly as that with $MeSiCl_3$ and Me_3SiI, since other signals were also observed. In the mixture of the reaction with Me_3SiCl, we could detect a species which was identified with the known $H_2IrCl(P^iPr_3)_2$ (**3**).[14)] The same species was also observed in the reaction mixture of Me_2SiCl_2 (vide supra). Likewise, the reaction with

Me_3SiBr also seemed to give $H_2IrBr(P^iPr_3)_2$ (**4**) as a byproduct as judged from the NMR data[15] of the reaction mixture. Unless neohexene was added to the reaction system, the reactivity of halosilanes toward $IrH_5(P^iPr_3)_2$ was extremely low. For instance, $MeSiCl_3$ did not react at all with the Ir complex at 60 °C. On the other hand, two equivalent neohexene added to the system was nearly quantitatively converted into neohexane, and the reaction with the halosilanes took place. Accordingly, the present oxidative addition seems to take place as follows (Eq. 2), although the detailed mechanism is ambiguous; in the initial step, the coordinatively unsaturated species $IrH(P^iPr_3)_2$ is presumably generated from $IrH_5(P^iPr_3)_2$ and neohexene as proposed by Felkin et al.,[8] and subsequently halosilanes would undergo oxidative addition to the unsaturated Ir species.

$$IrH_5(P^iPr_3)_2 \xrightarrow[\text{2 neohexane}]{\text{2 neohexene}} IrH(P^iPr_3)_2 \xrightarrow{R_3SiX} \underset{\mathbf{1a\text{-}c}}{R_3SiIrXH(P^iPr_3)_2} \qquad (2)$$

As for the formation of the hydride complexes **3** and **4**, we can propose, among several possibilities, the β-hydride elimination from the organosilyliridium complex leading to silene generation as was unequivocally demonstrated for an Os complex by Berry et al.[16] (Eq. 3).

$$L_nM\text{-}SiMe_3 \longrightarrow L_nM\text{-}H + [Me_2Si{=}CH_2] \qquad (3)$$

The recent publication by Milstein et al. also describes the formation of a hydride complex in the reaction of $(C_8H_{14})IrCl(PMe_3)_3$ with Me_3SiCl, and the formation has been explained in terms of the β-hydride elimination although no evidence was given.[7] In our case, when benzene-d_6 solution of **1b** was heated at 120 °C in a sealed NMR tube, new ^1H and ^{31}P NMR signals which were reasonably assignable to $H_2IrI(P^iPr_3)_2$ (**5**) emerged at -33.19 ppm (t, $J_{P\text{-}H}$ = 13.0 Hz, Ir-H) and 56.27 ppm, respectively, with concomitant decline of the signals of initial silyliridium complex. The conversion of **1b** after 2 h was 47%, and the estimated yield of **5** by ^{31}P NMR was 64% based on the consumed **1b**. The result supports the occurrence of β-hydride elimination from Me_3Si group in the thermolysis of **1b**. However, the possibility of the disproportion reaction between two molecules of **1b** affording **5** and bis(silyl)iridium can not be completely eliminated.

In conclusion, Si-X bond (X = Cl, Br, I) can be readily cleaved with $IrH_5(P^iPr_3)_2$ in the presence of neohexene to result in halo(organosilyl)iridium complex formation. Resulting adducts, subject to the conditions, are prone to undergo β-hydride elimination. Further investigations to elucidate the reactivity of halosilanes toward transition metal organometallics are under way.

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10) a) **1a**: mp 136-138 °C; ^{1}H NMR (C_6D_6, TMS) δ -19.54 (t, $J_{\text{H-P}}$ = 11.7 Hz, 1H, IrH), 1.56 (s, 3H, $SiCH_3$), 0.87-1.57 (m, 36H, $C(CH_3)_2$), 2.52-3.17 ppm (m, 6H, PCH); ^{31}P NMR (C_6D_6, H_3PO_4) δ 37.42 ppm; IR (nujol): 2220 ($\nu_{\text{Ir-H}}$), 800 ($\rho_{\text{Si-Me}}$) cm^{-1}. Anal. Found: C, 34.29; H, 7.05; Cl, 16.19%. Calcd for $C_{19}H_{46}Cl_3IrP_2Si$: C, 34.41; H, 6.99; Cl, 16.04%; b) **1b**: mp 104-106 °C; ^{1}H NMR (C_6D_6, TMS) δ -16.28 (t, $J_{\text{H-P}}$ = 14.9 Hz, 1H, IrH), 0.63 (s, 9H, $SiCH_3$), 0.86-1.61 (m, 36H, $C(CH_3)_2$), 2.46-2.96 ppm (m, 6H, PCH); ^{31}P-NMR (C_6D_6, H_3PO_4) δ 33.80 ppm; IR (nujol): 2201 ($\nu_{\text{Ir-H}}$), 836 ($\rho_{\text{Si-Me}}$) cm^{-1}. Anal. Found: C, 35.13; H, 7.14%. Calcd for $C_{21}H_{52}IIrP_2Si$: C, 35.34; H, 7.34%; c) **1c**: mp 109-113 °C; ^{1}H NMR (C_6D_6, TMS) δ -19.64 (t, $J_{\text{H-P}}$ = 12.6 Hz, 1H, IrH), 1.12 (s, 6H, $SiCH_3$), 0.98-1.48 (m, 36H, $C(CH_3)_2$), 2.48-2.98 ppm (m, 6H, PCH); ^{31}P NMR (C_6D_6, H_3PO_4) δ 37.29 ppm; IR (nujol): 2217 ($\nu_{\text{Ir-H}}$), 806 ($\rho_{\text{Si-Me}}$) cm^{-1}. Anal. Found: C, 37.35; H, 7.43%. Calcd for $C_{20}H_{49}Cl_2IrP_2Si$: C, 37.37; H, 7.68%.

11) Crystal data of **1a**: $C_{19}H_{46}Cl_3IrP_2Si$, M = 663.186; The used crystal was sealed in a thin-walled glass capillary under nitrogen. Crystal size 0.7x0.4x0.4 mm^3; Triclinic, space group $P\bar{1}$; a = 8.862(2), b = 18.301(3), c = 18.372(3) Å, α = 105.10(2), β = 100.72(3), γ = 97.66(3)°, V = 2775(1) Å^3; Z = 4; d(cal) = 1.57 g/cm^3. Data collection: Enraf-Nonius CAD4 diffractometer, graphite monochromated Mo radiation ($\lambda_{\text{K}\alpha 1}$ = 0.70930 Å), scan range 2.0° ≤ 2θ ≤ 55°. An empirical absorption correction based on psi scans. The number of reflection used 10173 ($|F_0| \geq 3\sigma|F_0|$). The structure was solved by direct method and all non-hydrogen atoms were refined anisotropically by weighted full matrix least squares to R = 4.84% (Rw = 5.85%, $w = 1/(0.0047|F_0|^2 - 0.4828|F_0| + 20.60)$). Hydrogen atoms were not included in structure factor calculations. The unit cell contained two crystallographically independent molecules. The conformation of them were similar to each other.

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14) ^{1}H and ^{31}P NMR of the reaction mixture showed the signals at -32.42 ppm (t, $J_{\text{P-H}}$ =12.7 Hz, Ir-H) and 53.40 ppm, while reported values of ^{1}H and ^{31}P NMR signals for **3** are -32.50 ppm (t, $J_{\text{P-H}}$ =13.2 Hz, Ir-H) and 53.47 ppm, each respectively. See H. Werner, J. Wolf, and A. Hohn, *J. Organomet. Chem.*, **287**, 395 (1985).

15) ^{1}H NMR (C_6D_6, TMS) δ -33.15 ppm (t, $J_{\text{P-H}}$ =13.0 Hz, Ir-H); ^{31}P NMR (C_6D_6, H_3PO_4) δ 54.65 ppm.

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