Oxidative Addition of Si–Cl Bonds to Electron-rich Ir^I Complexes

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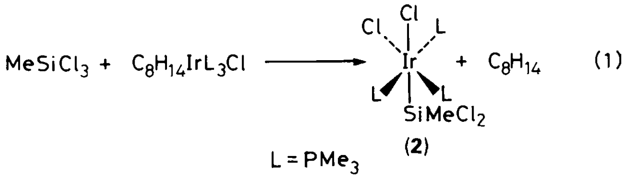
Si–Cl bonds undergo facile, rarely observed oxidative addition to $(C_8H_{14})Ir(PMe_3)_3Cl$ (**1**) to yield, when $MeSiCl_3$ is used, the crystallographically characterized *mer*-$Ir(PMe_3)_3(Cl)_2(SiMeCl_2)$, exhibiting a short Ir–Si bond; reaction of (**1**) and of other electron-rich Ir^I complexes with Me_3SiCl yields Ir–H complexes, probably arising from a rare silyl β-hydride elimination process.

Whereas oxidative addition reactions of C–X bonds (X = halogen) are common,[1] forming the basis of many synthetically useful transformations, and similar reactions involving Sn–Cl, Ge–Cl, and Pb–Cl are known,[2] oxidative addition of Si–X bonds to yield well characterized products has rarely been observed,[3—5] despite attempts to accomplish this.[6,7] In fact, thermochemical considerations led to the conclusion that cleavage of the Si–C bond in organohalogenosilanes would be preferable to that of the Si–X bond.[8] Also, halogenohydrosilanes undergo selective Si–H cleavage, with the Si–X bond remaining intact, even when the weak Si–I bond is involved.[9] Recently,[4] addition of Me_3Si–Br to $Pt(PEt_3)_3$ was described as the first example of oxidative addition of an Si–X bond, although the very strong Si–Cl bond [~112 kcal/mol (kcal = 4.184 kJ)][10] was not reactive in this reaction even at 120 °C. This publication prompts us to describe our findings that certain electron-rich Ir^I complexes are capable of cleaving the Si–Cl bond under exceedingly mild conditions, leading to isolable, fully characterized oxidative addition products. We have also isolated complexes resulting from apparent, rarely observed β-hydride elimination from a silyl ligand. Very recently, H/D exchange in alkylsilanes catalysed by osmium phosphine complexes was described as the first evidence for β-hydride elimination from a metal silyl.[11]

Addition of an excess of $MeSiCl_3$ to a red 0.1 M solution of $(C_8H_{14})Ir(PMe_3)_3Cl$ (**1**) (C_8H_{14} = cyclo-octene) in toluene under N_2 results, after 30 min, in decolouration and formation of a white precipitate which was isolated by filtration and washed with pentane to yield complex (**2**)† in 90% yield (equation 1). ^1H and ^{31}P NMR reveal that oxidative addition of the Si–Cl bond has taken place, although the exact stereochemistry of the octahedral product is not readily apparent from the spectroscopic data. This is revealed by an *X*-ray study of crystals obtained from pentane–toluene solution at −30 °C (Figure 1).‡ As expected, the silyl ligand, which is known to have a considerable *trans* effect,[12] is co-ordinated *trans* to Cl. The fact that Ir–Cl(6) is 0.065 Å longer than Ir–Cl(5) shows that $SiMeCl_2$ has an even larger *trans* effect than PMe_3. The Ir–Si bond length of 2.299 Å is significantly shorter (by 0.1 Å or more) than other Ir–Si bonds[13] and is among the shortest M–Si bonds.[14] This is probably a reflection of the high electron density of the iridium centre on one hand and the π-accepting properties of the $SiMeCl_2$ ligand, resulting in considerable back donation of d electron density to an acceptor orbital on silicon.[15]

The facility with which reaction (1) takes place is noteworthy. For comparison, oxidative addition of Me_3Si–Br to $Pt(PEt_3)_3$ requires heating at 90 °C for 2 h, whereas Me_3Si–Cl is not reactive.[4] Complex (**1**) proved to be very reactive in other oxidative addition reactions as well.[16]

Interestingly, reaction of (**1**) with Me_3SiCl, which also takes place at room temperature but is somewhat slower than the reaction with $MeSiCl_3$, results in the formation of the hydrido complex (**3**)§ (equation 2), probably because of a rare



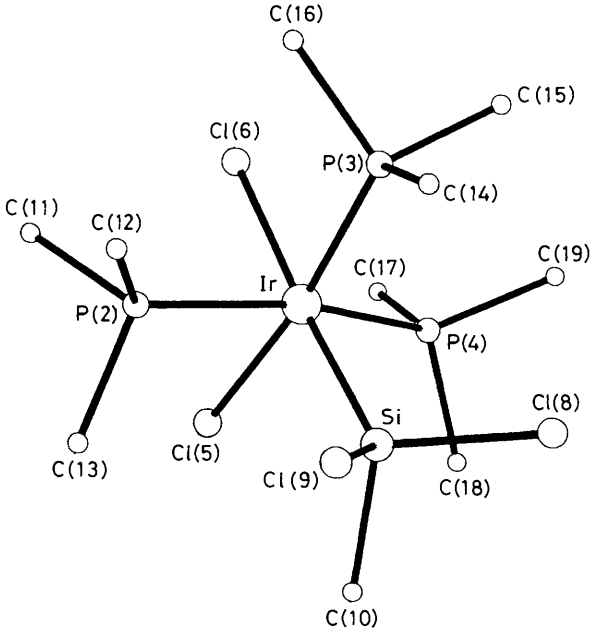


Figure 1. Molecular structure of (**2**). Selected bond distances (Å) and angles (°): P(2)–Ir 2.355(5), P(3)–Ir 2.294(5), P(4)–Ir 2.408(5), Cl(5)–Ir 2.425(5), Cl(6)–Ir 2.490(5), Si–Ir 2.299(5), C(10)–Si 1.923(12), P(3)–Ir–P(2) 94.0(2), P(4)–Ir–P(2) 164.1, P(4)–Ir–PI(3) 101.4, Si–Ir–P(2) 92.4(2), Si–Ir–P(3) 95.2(2), Si–Ir–P(4) 90.6(2).

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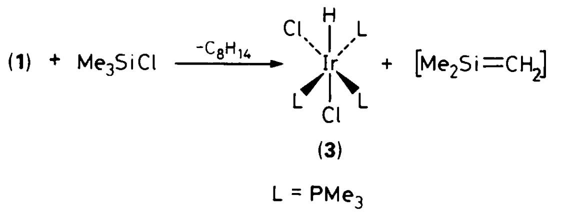
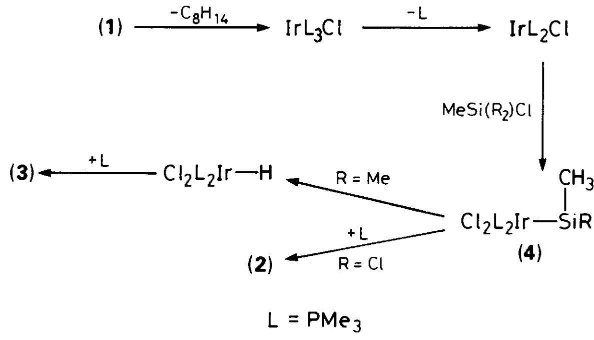
† For (**2**): ^1H NMR ([$^2H_5$]pyridine) δ 1.7—1.8 (m, 27H, $3PMe_3$), 1.26 (s, 3H, $MeSiCl_2$); $^1P\{^1H\}$ NMR ([$^2H_5$]pyridine) δ −40.9 (d, *J* 17.6 Hz, 2P), −45.1 p.p.m. (t, *J* 17.6 Hz, 1P).

‡ *Crystal data* for (**2**): $C_{10}H_{30}P_3Cl_4SiIr$, orthorhombic, space group *Pbca*, $a = 13.397(2)$, $b = 11.803(2)$, $c = 26.384(4)$, $U = 4171(2)$ Å^3, $T = 90$ K, $M = 605.386$, $Z = 8$, $D_c = 1.93$ g cm^{-3}, $F(000) = 2552$, μ(Mo-K_α) = 71.67 cm^{-1}, Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation; 6184 data collected using ω–2θ scan method; $4° < 2\theta < 54°$; 3033 unique reflections (R_{sym} = 0.02) corrected for absorption (DIFABS), with $F_o > 3\sigma(F_o)$ used in solution and refinement; solution by Patterson method (SHELXS), refinement by full-matrix least-squares technique (SHELX76), final max shifted/esd 0.02, max/min peaks ±2 eÅ^{-3} (in the vincinity of Ir), H atoms found in the difference Fourier map and fixed, all non-H atoms anisotropic, overall isotropic temperature factor for H, 209 parameters, $R = 0.044$, $R_w = 0.047$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ For (**3**): IR (Nujol) ν_{Ir-H} 2158s cm^{-1}; ^1H NMR (C_6D_6) δ 1.50 (t, *J* 3 Hz, 18H, $2PMe_3$), 1.26 (d, *J* 10 Hz, 9H, PMe_3), −21.67 (dt, J_{H-P1} 19, J_{H-P2} 14 Hz, 1H, Ir–H); $^{31}P\{H\}$ NMR (C_6D_6) δ −40 (d, *J* 20.6 Hz, 2P2), −44 p.p.m. (t, *J* 20.6 Hz, 1P).



(2)



Scheme 1

β-hydride elimination process from an organosilyl ligand.[11] This suggests that oxidative addition of the Si–Cl bond involves a co-ordinatively unsaturated Ir^{III} complex (**4**), formed *via* the 14e complex $Ir(PMe_3)_2Cl$. Complex (**4**) can undergo competing β-hydride elimination and ligand association processes, the former prevailing with Me_3SiCl and the latter with $MeSiCl_3$. This is perhaps because of (a) the number of β hydrogens involved and (b) the fact that the $Ir–SiMeCl_2$ bond is expected to be stronger than $Ir–SiMe_3$ (more back donation in the former case) (Scheme 1). β-Hydride elimination occurs also upon reaction of $Me_3Si–Cl$ with $Ir(PMe_3)_4{}^+PF_6{}^-$, as well as $Ir(PEt_3)_3Cl$. Clearly, further experiments are required to define the scope and mechanisms of these new interesting reactions, including utilization of labelled silyls and silylene trapping experiments. We are also exploring the synthetic aspects of these reactions for the easy generation of Si=C bonds.

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