

C–F Bond Activation by Iridium(I). A Unique Process involving P–C Bond cleavage, P–F Bond Formation and Net Retention of Oxidation State

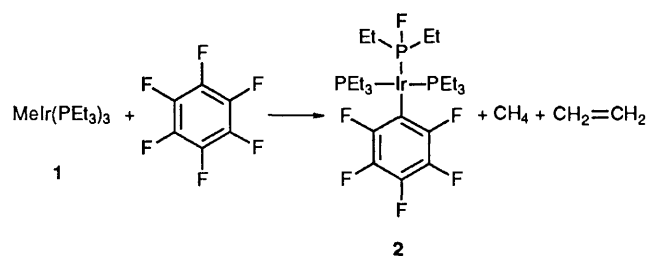
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Reaction of hexafluorobenzene with $\text{MeIr}(\text{PEt}_3)_3$ results in a unique process involving C–F bond cleavage, P–C bond cleavage and P–F bond formation, yielding the crystallographically characterized iridium(I) complex **2**.

Of the various chemical bonds capable of undergoing oxidative addition to metal centres, C–F is undoubtedly one of the least reactive. For example, whereas C–H oxidative addition is quite common, very few examples are reported for intermolecular¹ or even intramolecular² C–F bond activation processes. In fact, hexafluorobenzene has been used as an inert solvent in C–H activation reactions,³ although a Rh^{I} η^2 -complex of this compound was isolated.⁴ The relative inertness of C–F bonds is often attributed to bond strength (e.g. dissociation energy 154 kcal mol⁻¹ for Ph–F vs. 110 kcal mol⁻¹ for Ph–H;⁵ 1 cal = 4.184 J). However, since the M–F bond may be considerably stronger than M–H,⁶ the reason may be kinetic rather than thermodynamic.

Our recent observation⁷ that Ir^{I} alkylphosphine complexes are capable of oxidative addition of some of the strongest polar bonds (e.g. HO–H, 119 kcal mol⁻¹; Si–Cl, 112 kcal mol⁻¹) has prompted us to try the reaction of $\text{Ir}(\text{PEt}_3)_3\text{Cl}$ with hexafluorobenzene. However, no reaction occurred at 60 °C. Since higher reactivity towards oxidative addition is expected upon an increase in the electron density on the metal, we used the complex $\text{MeIr}(\text{PEt}_3)_3$ **1**, prepared by reaction of $\text{Ir}(\text{PEt}_3)_3\text{Cl}$ with MeLi. Upon reaction of **1** with



hexafluorobenzene at 60 °C, a unique C–F activation process takes place, involving C–F cleavage, P–C cleavage and P–F

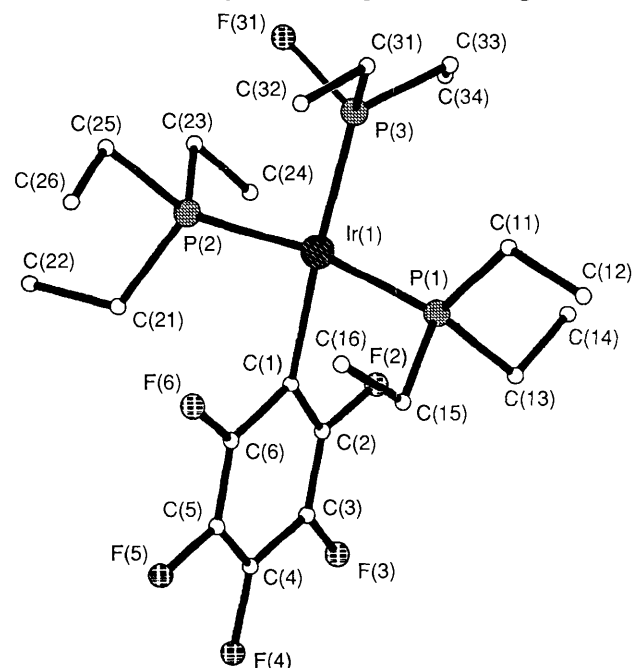
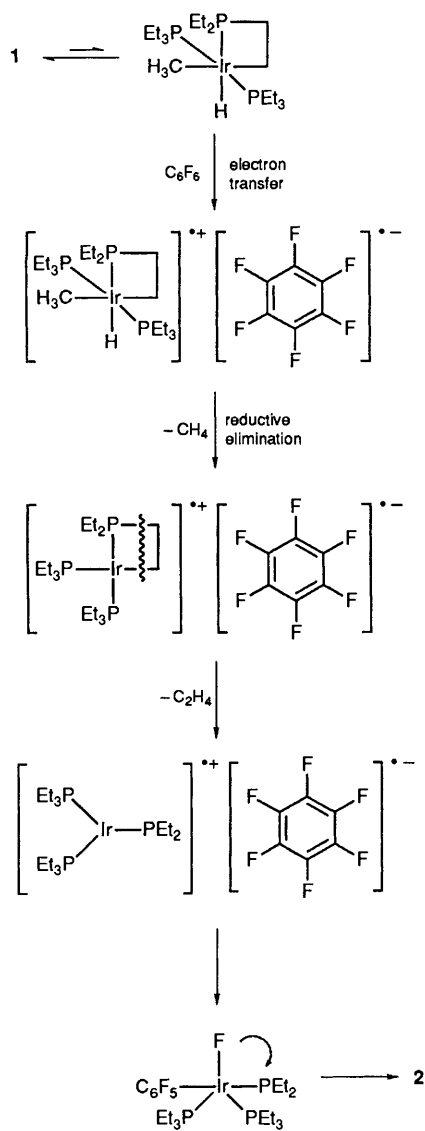


Fig. 1 A molecule of complex **2**. Selected bond distances (Å) and angles (°) are as follows: P(1)–Ir(1) 2.310(6), P(2)–Ir(1) 2.305(6), P(3)–Ir(1) 2.199(6), C(1)–Ir(1) 2.081(17), F(31)–P(3) 1.630(12), F(2)–C(2) 1.375(21), F(3)–C(3) 1.347(20), F(4)–C(4) 1.364(20), P(2)–Ir(1)–P(1) 170.3(2), C(1)–Ir(1)–P(3) 175.5(4), F(31)–P(3)–Ir(1) 115.6(5).



Scheme 2

generation. Methane and ethylene are evolved (as detected by GC), and the Ir^I complex **2** is generated in this process, the overall stoichiometry being as presented in Scheme 1.

The ¹⁹F NMR spectrum† of **2** exhibits the P–F resonance as a doublet at δ –143.5 with a large P–F coupling of 770 Hz, as well as three resonances for the C–F groups. The ³¹P NMR spectrum exhibits a low-field doublet at δ 186.1 for P–F. The *trans*-phosphines appear as a triplet at δ 8.7 as a result of identical ²J_{P–P} and ³J_{P–F} couplings.

An X-ray crystallographic study‡ of **2** (Fig. 1) reveals a distorted square-planar arrangement. The Ir–PEt₂F bond is significantly shorter (by about 0.1 Å) than the Ir–PEt₃ bond,

† ¹⁹F{¹H} NMR (referenced to CCl₃F at δ 0.0) (C₆D₆): δ –111.7 (t, ³J_{F–F} 22.5 Hz, 2F *ortho*); –143.5 (d, ¹J_{P–F} 770 Hz, PF); –164.0 (t, ³J_{F–F} 19 Hz, 1F *para*); –165.0 (t, ³J_{F–F} 17.5 Hz, 2F *meta*); ³¹P{¹H} NMR (referenced to 85% H₃PO₄ at δ 0.0) (C₆D₆): δ 186.1 (d × m, ¹J_{P–F} 769 Hz, 1P); 8.7 (t, ²J_{P–P} 20.5 Hz, ³J_{P–F} 20.5 Hz, 2P).

‡ Crystal data for **2**: monoclinic, P₂/c (No. 14), *a* = 9.205(2), *b* = 19.706(3), *c* = 15.106(3) Å, β = 90.50(2)°, from 25 reflections, *T* = 90 K, *V* = 2740.3(9) Å³, *Z* = 4, *D*_c = 1.706 g cm^{–3}, μ = 50.75 cm^{–1}, Mo-Kα radiation, 6514 reflection collected. The structure was solved by automated Patterson analysis (SHELXS-86) and Fourier method (SHELX-76). Hydrogens were found from a difference Fourier map and refined with an overall temperature factor, *U*_{over} = 0.032(2) Å² × 10³, final *R* = 0.060 *R*_w = 0.063. Atomic coordinates, thermal parameters, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

despite the larger *trans* influence of the aryl ligand as compared to that of the phosphine. The stronger Ir–PEt₂F bond may be a result of both its smaller size and its better π-acceptance capacity as compared with PEt₃. The latter feature may be of particular importance in stabilization of this electron-rich Ir^I complex. The C–F bond lengths are all somewhat longer than those of hexafluorobenzene (1.324 Å).⁵

It is noteworthy that under the conditions of Scheme 1, essentially no reaction is observed between benzene, fluoro-benzene or 1,3,5-trifluorobenzene and **1**. Reaction does take place upon heating above 80°C, leading only to C–H activation products, with no C–F activation observed. The lower reactivity of these substrates towards **1** may seem surprising when considering the fact that the C–F bond of hexafluorobenzene is stronger than the C–F and C–H bonds of these compounds.⁵ Although it is premature to draw mechanistic conclusions at this stage, an electron-transfer mechanism involving hexafluorobenzene, a better electron acceptor than other fluoroaromatic compounds, seems attractive.

A hypothetical mechanistic rationale is shown in Scheme 2. Assuming that some equilibrium concentration of a metalated ligand complex is present in this very electron-rich, unsaturated system, electron transfer to hexafluorobenzene may induce reductive elimination of methane, driving the equilibrium to the right. Metathetical-type expulsion of ethylene could lead to a highly unsaturated, low-valent complex. C–F oxidative addition to this complex, followed by P–F bond formation by reductive elimination can account for the observed reaction in Scheme 1.

Further work aimed at clarifying the mechanistic consequences of this unique reaction is now in progress.

We thank the Fund for Basic Research, administered by the Israel Academy of Science and Humanities for supporting this research.

Received, 23rd October 1990; Com. 0/04763E

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§ Electron transfer promoted reductive elimination was proposed for C–F activation *via* an intermediate titanocene–dienone complex: ref. 2(b).