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Electron-transfer Reactions in Iridium(III) Dialkyl Complexes: Activation of C–H Bonds on Oxidation of $[IrMe_2(\eta^5\text{-}C_5Me_5)(PR_3)]$ (R = Ph or Me)

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The iridium dimethyl complexes $[IrMe_2(\eta^5\text{-}C_5Me_5)(PR_3)]$ (R = Ph or Me) react slowly or not at all with C–H bonds of aromatics R′H under severe conditions, but in the presence of catalytic amounts of $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ or Ag^+ the activation proceeds at room temperature to give $[IrMe(R')(\eta^5\text{-}C_5Me_5)(PR_3)]$ and methane; the intermediacy of iridium(IV) species has been substantiated by electrochemical and EPR studies.

'σ-Bond metathesis'[1] of C–H bonds of aromatic hydrocarbons and M–R bonds has been observed both for early and late transition metals, under conditions of thermal activation [equation (1), R′ = aryl]. In this context we have now found

$$M\text{–}R + R'\text{–}H \longrightarrow M\text{–}R' + R\text{–}H \qquad (1)$$

that the half-sandwich iridium(III) dimethyl derivatives $[IrMe_2(\eta^5\text{-}C_5Me_5)(PR_3)]$ (R = Ph **1a** or Me **1b**),[2,3] which are able to activate C–H bonds of arenes only under rather drastic conditions or not at all, undergo a dramatic enhancement of reactivity in the presence of catalytic amounts of one-electron oxidants.*

Heating complex **1a** in benzene at 110 °C for 2 weeks led, with a 90% yield, to a mixture of the methyl(phenyl) derivative **2a** (24%) and the diphenyl derivative **6** (66%), along with CH_4 (see Scheme 1). By using methyl-substituted arenes the reaction stopped at the monoaryl complexes, affording a 3:2 mixture of the *m*- and *p*-tolyl isomer **3a** in the case of toluene, the 3,4-dimethyl **4a** and 3,5-dimethyl **5a** isomers in the case of *o*- and *m*-xylenes, respectively. No reaction was observed with *p*-xylene. Preliminary dissociation of the phosphine is probably important, as suggested by the suppression of the reaction in the presence of an excess of PPh_3, and by the lack of reactivity observed in the case of the trimethylphosphine derivative **1b**.

However when small amounts (3–10%) of ferrocenium hexafluorophosphate (or silver tetrafluoroborate) were added to the reaction mixture a remarkable acceleration of the activation of aromatic C–H bonds was observed. Thus **1a** reacted with benzene in the presence of $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$ at room temperature to give, within a few seconds, evolution of methane at the solid–oxidant surface and a transient red-violet colour. The orthometallated complex $[\overline{Ir(C_6H_4P}Ph_2)Me(\eta^5\text{-}C_5Me_5)]$ **7** was obtained (92% after 2 h), in addition to $[Fe(\eta^5\text{-}C_5H_5)_2]$. When left in the presence of the oxidant, **7** reacted with the solvent to give $[IrMe(Ph)(\eta^5\text{-}C_5Me_5)(PPh_3)]$ **2a** (85% conversion after 16 h). Under similar conditions, **7** is also able to activate toluene leading to essentially the same isomeric mixture **3a** obtained in the thermolysis of **1a** (Scheme 1). When the reaction of **1a** with the oxidant was carried out in CH_2Cl_2, **7** was easily formed, together with methane, and no interaction with the solvent was observed. The trimethylphosphine derivative **1b** behaves analogously (but in this case no phosphine cyclometallation reaction was observed) and the C–H activation of arenes occurred at room temperature resulting in about 1 h in the almost quantitative formation of $[IrMe(R')(\eta^5\text{-}C_5Me_5)(PMe_3)]$ (R′ = Ph **2b**, *m*- and *p*-tolyl **3b**, 3,4-dimethylphenyl **4b** or 3,5-dimethylphenyl **5b**). In all these catalysed reactions as well as in the thermolysis of **1a** the nature of the products seems

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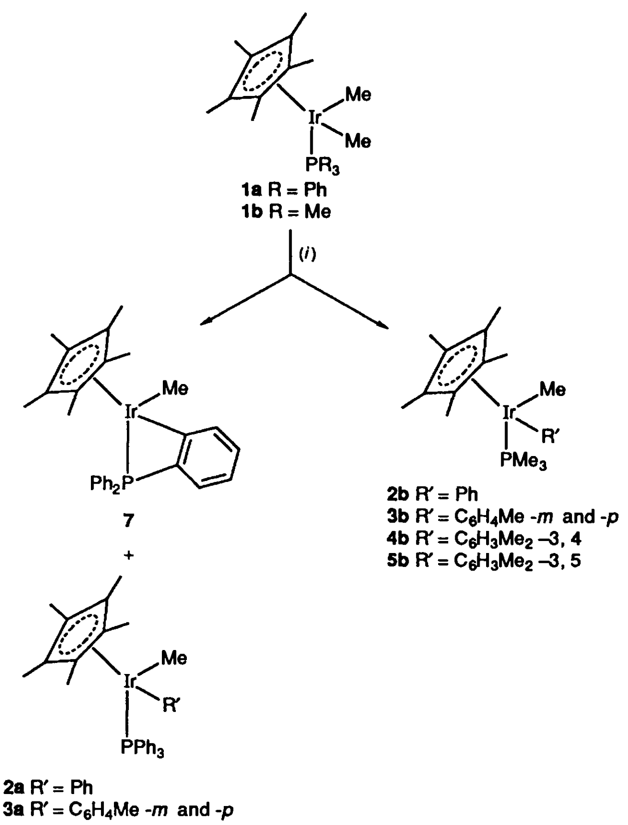
* In a typical experiment complex **1a** (or **1b**) (0.032 mmol) was treated with the arene (0.8–2 cm^3, *ca.* 8–30 mmol) at 110 °C, or at room temperature with stirring in the presence of the oxidant (0.0032 mmol). The reaction has been also scaled up to 0.100 g of starting material, and can be conveniently monitored by ^1H NMR spectroscopy, following the variation of the signals in the C_5Me_5 region. The new compounds were isolated by column chromatography on alumina using pentane or pentane–benzene as eluent. They were further purified by crystallization from pentane and characterized by elemental analysis, ^1H NMR spectra in C_6D_6, and, whenever possible, by comparison of their properties with samples prepared by independent synthesis. ^1H NMR: **2a**, δ 0.86 [d, 3 H, *J*(PH) 6.0, IrMe], 1.34 [d, 15 H, *J*(PH) 1.7, C_5Me_5], 6.8–7.5 (m, 20 H, Ph); **6**, 1.32 [d, 15 H, *J*(PH) 1.9, C_5Me_5], 6.8–7.6 (br m, 25 H, Ph); **3a** (*meta* isomer), 0.88 [d, 3 H, *J*(PH) 6.0, IrMe], 1.36 [d, 15 H, *J*(PH) 1.8, C_5Me_5], 2.15 (s, 3 H, Me), 6.8–7.8 (m, 19 H, PPh + C_6H_4Me); **3a** (*para* isomer), 0.89 [d, 3 H, *J*(PH) 6.0, IrMe], 1.36 [d, 15 H, *J*(PH) 1.7, C_5Me_5], 2.26 (s, 3 H, Me), 6.86 [d, 2 H, *J*(HH) 8.0, $C_6\mathit{H}_4Me$], 7.28 [d, 2 H, *J*(HH) 8.0, $C_6\mathit{H}_4Me$], 6.9–7.25 (m, 15 H, PPh); **4a**, 0.90 [d, 3 H, *J*(PH) 5.9, IrMe], 1.37 [d, 15 H, *J*(PH) 1.6, C_5Me_5], 2.08 (s, 3 H, Me), 2.19 (s, 3 H, Me), 6.8–7.8 (m, 18 H, PPh + $C_6\mathit{H}_3Me_2$); **5a**, 0.88 [d, 3 H, *J*(PH) 5.9, IrMe], 1.38 [d, 15 H, *J*(PH) 1.7, C_5Me_5], 2.19 (s, 6 H, Me), 6.6–7.8 (m, 18 H, PPh + $C_6\mathit{H}_3Me_2$); **2b**, 0.62 [d, 3 H, *J*(PH) 6.7, IrMe], 0.97 [d, 9 H, *J*(PH) 9.6, PMe], 1.51 [d, 15 H, *J*(PH) 1.7, C_5Me_5], 6.9–7.6 (m, 5 H, Ph); **3b** (*meta* isomer), 0.64 [d, 3 H, *J*(PH) 6.7, IrMe], 0.99 [d, 9 H, *J*(PH) 9.8, PMe], 1.52 [d, 15 H, *J*(PH) 1.8, C_5Me_5], 2.36 (s, 3 H, Me), 6.85–7.4 (m, 4 H, $C_6\mathit{H}_4Me$); **3b** (*para* isomer), 0.62 [d, 3 H, *J*(PH) 6.7, IrMe], 0.99 [d, 9 H, *J*(PH) 9.7, PMe], 1.52 [d, 15 H, *J*(PH) 1.8, C_5Me_5], 2.33 (s, 3 H, Me), 7.01 [d, 2 H, *J*(HH) 7.8, $C_6\mathit{H}_4Me$], 7.38 [d, 2 H, *J*(HH) 7.8, $C_6\mathit{H}_4Me$]; **4b**, 0.66 [d, 3 H, *J*(PH) 6.6, IrMe], 1.01 [d, 9 H, *J*(PH) 9.6, PMe], 1.54 [d, 15 H, *J*(PH) 1.8, C_5Me_5], 2.24 (s, 3 H, Me), 2.29 (s, 3 H, Me), 6.9–7.35 (m, 3 H, $C_6\mathit{H}_3Me_2$); **5b**, 0.66 [d, 3 H, *J*(PH) 6.6, IrMe], 1.01 [d, 9 H, *J*(PH) 9.7, PMe], 1.54 [d, 15 H, *J*(PH) 1.8, C_5Me_5], 2.37 (s, 6 H, Me), 6.73 (s, 1 H, $C_6\mathit{H}_3Me_2$), 7.16 (s, 2 H, $C_6\mathit{H}_3Me_2$); **7**, 0.76 [3 H, d, *J*(PH) 6.3, IrMe], 1.62 [15 H, d, *J*(PH) 2.4 Hz, C_5Me_5], 6.85–7.05 (6 H, m, Ph), 7.07–7.25 (4 H, m, Ph), 7.31 (2 H, m, C_6H_4), 7.70 (2 H, m, C_6H_4).



Scheme 1 (*i*) R′H, $[Fe(\eta^5\text{-}C_5H_5)_2]^+$, $-CH_4$

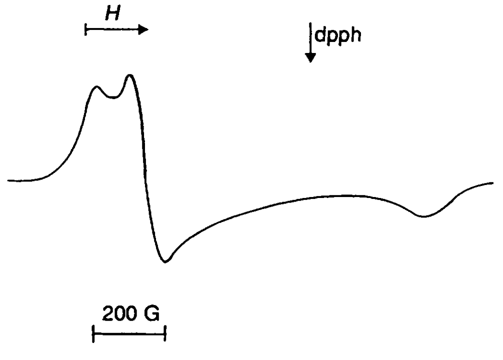


Fig. 1 X-Band EPR spectrum at 100 K in CH_2Cl_2 solution of the electrogenerated monocation **1a**$^+$. dpph = Diphenylpicrylhydrazyl; G = 10^{-4} T

to indicate that steric factors are important since the arene C–H bonds adjacent to the methyl substituents are not activated.

The above reactions can be rationalized in terms of electron-transfer catalysis[4] occurring through the following steps: on oxidation of **1a** (or **1b**) by ferrocenium hexafluorophosphate small amounts of the dimethyl cation **1a**$^+$ (or **1b**$^+$) are formed allowing the carbon–hydrogen activation to proceed rapidly at the level of the iridium(IV) complex (possibly because of the increased electrophilic properties of the metal centre); in a subsequent electron-transfer step the iridium(IV) methyl(aryl) species oxidizes the starting complex to give the final product and regenerate **1a**$^+$ (or **1b**$^+$) for further propagation.

Evidence for the intervention of iridium(IV) species in these reactions has been provided by electrochemical studies coupled to EPR measurements. The relevant apparatus and methods have been described elsewhere.[5] At room temperature, in CH_2Cl_2, complex **1a** undergoes an anodic process with features of chemical reversibility ($E^{\circ\prime} = +0.41$ V, *vs.* saturated calomel electrode, SCE), while **1b**, even at low temperatures, exhibits an anodic process ($E^{\circ\prime} = +0.27$ V) in which the primary electrogenerated species is involved in a relatively fast chemical reaction (at 2 V s^{-1}, $i_{pc}/i_{pa} = 0.4$).[6,*] Controlled-potential coulometry indicates that in both cases such oxidation processes involve the consumption of one electron per molecule. Interestingly, the presence of the more electron-donating PMe_3, while favouring the thermodynamic access to Ir^{IV}, makes it kinetically more labile. Despite the apparent stability of the monocation **1a**$^+$ in the short times of cyclic voltammetry, full decomposition occurs over the longer times of macroelectrolysis tests, performed at ambient temperature. The starting pale yellow solution first turns red-violet, which degrades slowly to yellow. At the end of the electrolysis, cyclic voltammetry gives no more evidence for the **1a**–**1a**$^+$ couple. However, when the macroelectrolysis test was performed at −20 °C the red-violet colour of **1a**$^+$ persisted for a long time, allowing its EPR characterization. Fig. 1 shows the X-band EPR spectrum, recorded at 100 K, of the monocation **1a**$^+$, obtained by macroelectrolysis in CH_2Cl_2 solution at −20 °C. The sample was withdrawn at the first stages of electrolysis (0.3 electron per molecule). It displays a well resolved signal of orthorhombic symmetry, which can be interpreted in terms of a $S = \frac{1}{2}$ spin Hamiltonian [g_l 2.387, g_m 2.315, g_h 1.846; $\langle g \rangle_{calc}$ 2.183 (0.005)]. There is no evidence for hyperfine structure, probably because of the relatively large overall linewidth which overlaps all narrow hyperfine signals [$\Delta H > a(^{191}Ir, ^{193}Ir), a(^{31}P)$]. When the temperature was raised beyond the glass–liquid phase transition, the signal rapidly disappared, but freezing the liquid solution restored it. This reversible temperature dependence, while underlining the 'metal' character of the absorption pattern, indicates that, under rapid thermal motion, active molecular distortions around the paramagnetic metal centre are present.

Work is in progress to clarify the mechanism of activation of these iridium systems and to test the generality of these electrocatalysed reactions.

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* Under the present experimental conditions the reversible one-electron oxidation of ferrocene occurs at $E^{\circ\prime} = +0.44$ V.

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