Kinetics and Mechanism of Cyclo- and Decyclo-metallation of some Iridium Triaryl Phosphite Complexes. Evidence for the Electrophilic Displacement Mechanism

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Summary The formation of $[IrH(P-C)(cod)L]X$ [P–C = $P(OC_6H_3Me-o)(OC_6H_4Me-o)_2$, cod = cyclo-octa-1,5-diene, L = $P(OC_6H_4Me-o)_3$ or PMe_2Ph] from $[Ir(P-C)(cod)L]$ and HX (X = ClO_4, PF_6, or BF_4) is proposed to occur by a mechanism involving direct proton attack at the metallated carbon for ring opening, followed by electrophilic displacement of a proton from an *ortho*-C–H by a preformed iridium(III) hydride in the ring closing step; a similar mechanism is proposed for the ring opening in the reaction of $[Ir(P-C)(cod)L]$ with halogen acids HX (X = Cl, Br, or I) to give $[IrHX_2(cod)L]$.

Two mechanisms[1] based on circumstantial evidence have been proposed for cyclometallations in metal–triaryl phosphite systems: (i) electrophilic substitution of a proton at the carbon centre by the metal, and (ii) oxidative addition of a ligand C–H unit to the metal. If either of these routes is operative in the metallation, then, by the microscopic reversibility principle, the demetallation step should occur by the reverse of one of these routes. From the very few demetallations in metal–triaryl phosphite systems known the reductive hydride migration mechanism[2] (the reverse of ii) seems to operate. Conclusive evidence for the reverse of either mechanisms (i) or (ii) as possible routes for decyclometallation has yet to appear. We now find that the halogen acids HX (X = Cl, Br, or I) split the metallated ring in $[Ir(P-C)(cod)L]$ [I; P–C = $P(OC_6H_3-Me-o)(OC_6H_4Me-o)_2$, cod = cyclo-octa-1,5-diene; L = $P(OC_6H_4Me-o)_3$ or PMe_2Ph] to afford $[IrHX_2(cod)L]$ (II). The reactions (*e.g.* for HCl) involved the formation of an intermediate orange-yellow solution which contained $[IrCl(cod)L]$ (III) (characterised for L = PMe_2Ph by comparing the solution u.v. visible spectrum with that of an authentic sample), and which appeared, at first sight, to provide evidence for the oxidative addition–reductive elimination route to demetallation (the reverse of ii), *e.g.* $[Ir(P-C)(cod)(PMe_2Ph)] + H^+ \rightarrow [IrH(P-C)(cod)(PMe_2Ph)]^+ \rightarrow [Ir(cod)(PMe_2Ph)\{P(OC_6H_4Me-o)_3\}]^+ + Cl^- \rightarrow [IrCl(cod)(PMe_2Ph)] + P(OC_6H_4Me-o)_3$.

When (I) was treated with acids, HX, having poorly co-ordinating anions (*e.g.* X = PF_6, ClO_4, or BF_4), the white hydride [IrH(P–C)(cod)L]X (IV) was formed. The u.v.–visible spectrum of the intermediate red solution, though slightly blue shifted, resembles the characteristic spectra of the known [Ir(cod)L_2]$^+$ [L = PPh_3, $PMePh_2$, or $P(OMe)Ph_2$] species. This consecutive ring opening and ring closing to hydride formation is only consistent with an electrophilic replacement of Ir^I by H$^+$ at the metallated carbon as part of the ring opening process. To confirm this and to elucidate the mechanism of the ring closing step a kinetic study of the reaction of $HClO_4$ with [I;L = P(OC$_6$-H$_4$Me-*o*)$_3$] in acetone has been completed. The two consecutive reactions were studied independently by stopped flow (Durrum D110) and conventional spectrophotometry (Cary 15) respectively by monitoring colour changes in the u.v.–visible absorption (λ 480 nm) of the red intermediate [Ir(cod){P(OC$_6$H$_4$Me-*o*)$_3$}$_2$]$^+$ (V). Both reactions are first order in [H$^+$] and in terms of total perchloric acid concentration (range: 0·0046M $\leqslant$ [HClO$_4$]$_{total}$ $\leqslant$ 0·365M) the rate laws take the form in equation (1), where K_a represents

$$K_{obs} = k[H^+] = kK_a^{\frac{1}{2}}[HClO_4]^{\frac{1}{2}}_{total} \qquad (1)$$

the acid dissociation constant. The slope values of the rate laws are $kK_a^{\frac{1}{2}} = 11\cdot6$ s^{-1} l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ (25 °C) for the first fast reaction and $kK_a^{\frac{1}{2}} = 30 \times 10^{-2}$ s^{-1} l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ (25 °C) for the second, slower reaction. The dependence of the reaction rate on the square root of the total perchloric acid concentration arises from the weak dissociation of $HClO_4$ in acetone solution which was verified in an independent experiment utilising conductivity measurements. The rate of reaction was retarded by addition of $LiClO_4$, thus demonstrating H$^+$ as the kinetically important species.

The mechanism in the Scheme is proposed.

In contrast to the generally proposed intramolecular oxidative addition cyclometallation of [(cod)Ir{P(OC$_6$H$_4$-Me-*o*)$_3$}$_2$]$^+$ (step k_3), the present study reveals that such an isomerization can also proceed by a catalytic pathway which entails oxidation of Ir^I by external protons (k_2) prior

$$\bigcirc\!\!\!\!\bigcirc = \text{cyclo-octa-1,5-diene; P–C} = P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2$$
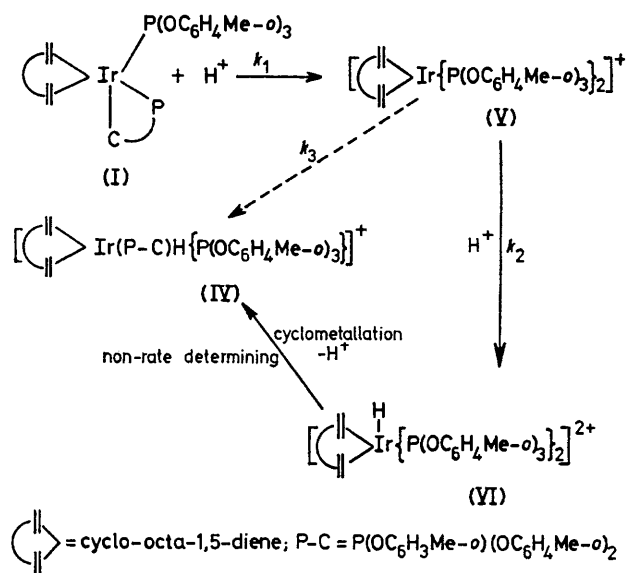
Scheme

to the cyclometallation step. Ring closing most probably occurs by an electrophilic replacement mechanism as the oxidative addition pathway would require an Ir^V dihydride intermediate, which seems unlikely.

It is probable that a corresponding demetallation step is involved in the reactions with halogen acids, and the formation of [IrX(cod)L] can be explained from earlier kinetic studies[3] which showed a rapid equilibrium [Ir(cod)L_2]$^+$ + Cl$^-$ $\rightleftharpoons$ [IrCl(cod)L] + L to occur in these systems. In the presence of acids, HX, containing poor co-ordinating anions (X = ClO_4, PF_6, or BF_4) the intermediate [Ir(cod)-L_2]$^+$ recyclometallates because of the inability of X to replace a phosphite ligand.

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[3] T. V. Ashworth, J. E. Singleton, D. J. A. de Waal, W. J. Louw, E. Singleton, and E. van der Stok, *J.C.S. Dalton*, 1978, 340.