Multiple Chlorinations of the Cyclometallated Ring in Iridium Triaryl Phosphite Complexes: the Crystal and Molecular Structure of $[IrCl_2\{P(OC_6Cl_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2\}(pyridine)(PMe_3)]$

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Summary Complete aromatic substitution of cyclometallated aromatic rings in a series of iridium triaryl phosphite complexes is found to occur rapidly with Cl_2 in benzene: the structure of $[IrCl_2\{P(OC_6Cl_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2\}(pyridine)(PMe_3)]$ has been elucidated by X-ray crystallography.

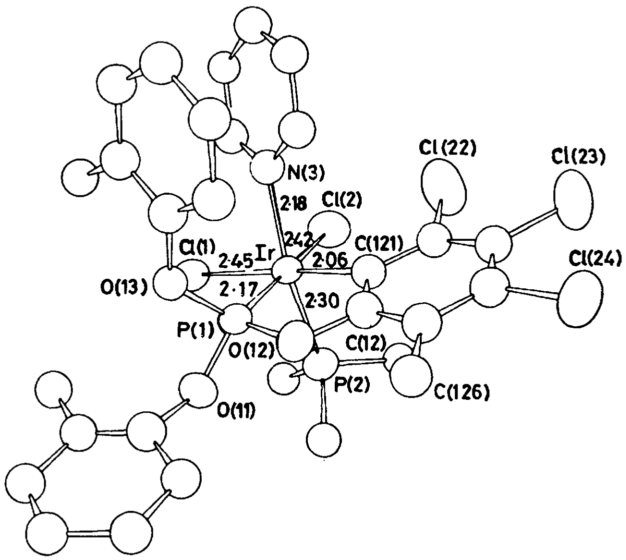
WE have recently found[1] that the cyclometallated ring in $[Ir(P\text{–}C)(cod)L]$ [I; P–C = $P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2$, L = $P(OC_6H_4Me\text{-}o)_3$; cod = cyclo-octa-1,5-diene] is demetallated with protic acids by direct electrophilic attack of H^+ on the metallated carbon atom. In extending this work to other potential electrophilic reagents we have now discovered a novel iridium-induced aromatic activation of cyclometallated rings in iridium(III) triaryl phosphite complexes towards chlorine.

Treatment of a solution of [I; P–C = $P(OC_6H_4)(OPh)_2$, L = $P(OPh)_3$; P–C = $P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2$, L = $P(OC_6H_4Me\text{-}o)_3$] in benzene with Cl_2 gave products of stoicheiometry $[IrCl_6\{P(OPh)_3\}_2]$ and $[IrCl_7\{P(OC_6H_4\text{-}Me\text{-}o)_3\}_2]$, respectively, the stereochemistries of which have not, as yet, been fully elucidated. Similar reactions of [I; P–C = $P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2$, L = PMe_3 or PMe_2Ph] gave an immediate white precipitate which for L = PMe_3 has been characterised as the doubly chlorine-bridged dimer $[IrX_2(P\text{–}C)L]_2$ (II; X = Cl) from microanalytical data and bridge-splitting reactions. Thus (II) and pyridine (py) gave $[IrCl_2(P\text{–}C)(py)(PMe_3)]$(III). The white precipitate, obtained when L = PMe_2Ph, is assumed to be (II; L = PMe_2Ph) by analogy. The precipitate (II; L = PMe_3 or PMe_2Ph) readily redissolved on further treatment with Cl_2 to give a clear solution from which a second white precipitate of stoicheiometry $[IrCl_5L\{P(OC_6H_4Me\text{-}o)_3\}]_x$ (IV; L = PMe_3 and PMe_2Ph) was deposited after a short period of time. Compound (IV) gave $[IrCl_5\{P(OC_6H_4Me\text{-}o)_3\}L(py)]$ (V; L = PMe_3 and PMe_2Ph) with py ($x = 2$) which was also formed for L = PMe_3 by chlorinating (III) in benzene. These compounds have now been shown to contain trichlorinated cyclometallated aromatic rings from an X-ray structural determination of (V; L = PMe_3) (Figure). Hence, (IV) is formulated as $[IrCl_2\{P(OC_6Cl_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2\}L]_2$.

Crystal Data: $[IrCl_2\{P(OC_6Cl_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2\}(py)(PMe_3)]$, M 875·0, colourless prisms, space group $P2_1/c$, $a = 9{\cdot}61$, $b = 22{\cdot}10$, $c = 16{\cdot}17$ ($\pm 0{\cdot}02$) Å, $Z = 4$, $D_m = 1{\cdot}74$, $D_c = 1{\cdot}76$ g cm^{-3}. Intensity data were collected on a Philips automatic four-circle diffractometer[†] with graphite-monochromatized Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). The structure was solved by Patterson and Fourier methods using the 3256 observed reflections [$I > 2\sigma(I)$] and was refined by full matrix least-squares to $R = 0{\cdot}056$.[‡]

[†] The measurements were carried out at N.P.R.L., C.S.I.R.

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



FIGURE

The iridium atom is octahedrally co-ordinated to two Cl atoms, one P(PMe$_3$), one N(py), and one P and one C atom of the chelated *o*-tolyl phosphite group. Relevant bond parameters are given in the Figure and compare closely with those found for the dimetallated complex [IrCl{P(OC$_6$H$_3$Me-*o*)$_2$(OC$_6$H$_4$Me-*o*)}(pyMe-4)$_2$].[2] The C–C distances in the cyclometallated ring average 1·40 Å, and this together with the root-mean-square deviations of 0·0003 Å for all the C atoms in this ring and the average endocyclic ring angles of 120° establish its aromaticity unambiguously.

We cannot say at this stage whether the mechanism involves radical or electrophilic attack on the cyclometallated ring. Excess of Bu^{t}OCl and (II; L = PMe$_3$) gave the monosubstituted complex [IrCl$_2${P(OC$_6$H$_2$ClMe-*o*)(OC$_6$H$_4$-Me-*o*)$_2$}(PMe$_3$)]$_2$ whereas the electrophilic reagents MeSO$_3$-CF$_3$, NOPF$_6$, and HY (Y = ClO$_4$ or PF$_6$) gave only the triply-halogen bridged cation [L(P–C)IrX$_3$Ir(P–C)L]$^+$ (VI; X = Cl), which was isolated as either the PF$_6$ or the BPh$_4$ salt. Friedel–Crafts reagents, *e.g.* MeCOCl–AlCl$_3$, have given as yet unidentified products.

Corresponding reactions of [I; P–C = P(OC$_6$H$_3$Me-*o*)-(OC$_6$H$_4$Me-*o*)$_2$, L = P(OC$_6$H$_4$Me-*o*)$_3$] with X$_2$ (X = Br or I) produced only the oxidised complexes (II; X = Br and I) which for X = I further converted into the cation (VI; X = I) with excess of I$_2$.

The generality of this subsitution process with a range of cyclometallated aromatic and non-aromatic rings is at present being studied. For example, treatment of the dimetallated complex [IrCl{P(OC$_6$H$_3$Me-*o*)$_2$(OC$_6$H$_4$Me-*o*)}-(PEt$_3$)$_2$][3] with Cl$_2$ has given the product [IrCl{P(OC$_6$Cl$_3$-Me-*o*)$_2$(OC$_6$H$_4$Me-*o*)}(PEt$_3$)$_2$] and in other tri-*o*-tolyl phosphite complexes it appears as if some chlorination of the *o*-methyl groups on the cyclometallated ring also occurs. This then would account for the higher chlorine content found from chlorination reactions of [I; P–C = P(OC$_6$H$_3$-Me-*o*)(OC$_6$H$_4$Me-*o*)$_2$, L = P(OC$_6$H$_4$Me-*o*)$_3$] when compared with [I; P–C = P(OC$_6$H$_4$)(OPh)$_2$, L = P(OPh)$_3$].

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[1] D. J. A. de Waal, E. Singleton, and E. van der Stok, *J.C.S. Chem. Comm.*, accepted for publication.

[2] M. J. Nolte, E. Singleton, and E. van der Stok, *J. Organometallic Chem.*, 1977, **142**, 387.

[3] E. Singleton and E. van der Stok, *J.C.S. Dalton*, 1978, 926.