

Carbon-Hydrogen Bond Cleavage in Metal Complexes: X-Ray Study of the Geometry of Iridium-*ortho*-Carbon (Aryl) Bonds in $\text{IrCl}[\text{P}(\text{OPh})_2(\text{OC}_6\text{H}_4)]_2\text{P}(\text{OPh})_3$

By J. M. Guss and R. MASON*

(Department of Chemistry, The University of Sheffield, S3 7HF)

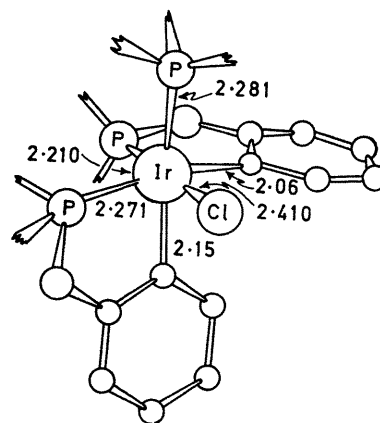
Summary The presence of metal-*o*-carbon bonds in the title compound, prepared by heating $\text{IrHCl}_2[\text{P}(\text{OPh})_3]_3$ with boiling decalin, has been confirmed by X-ray analysis.

non-bonded interactions between the *cis*-phosphite ligands. The Ir-P bond-lengths which are *trans*- to the σ -bonded

RECENTLY reactions involving the cleavage of aryl C-H bonds in tertiary-phosphine and -phosphite complexes of transition metals have been reported.¹⁻³ Ainscough and Robinson³ have isolated products tentatively formulated as having metal-*ortho*-carbon bonds; this suggestion is now confirmed by X-ray analysis.

The complex, prepared by heating $\text{IrHCl}_2[\text{P}(\text{OPh})_3]_3$ in boiling decalin, crystallises in the space group $P1$ with $a = 10.96 \text{ \AA}$, $b = 19.20 \text{ \AA}$, $c = 12.12 \text{ \AA}$, $\alpha = 95.9^\circ$, $\beta = 108.0^\circ$, $\gamma = 90.7^\circ$ and $Z = 2$. 5900 independent reflexions with $F^2(\text{obs})/\sigma[F^2(\text{obs})] \geq 3.0$ have been observed by automatic four-circle diffractometer methods but the present results are based on a conventional analysis of the 3759 reflexions for which $F^2(\text{obs})/\sigma[F^2(\text{obs})] \geq 8.0$; the present reliability index for these data is 0.045 and further refinement is continuing with the complete data corrected for absorption effects. Present standard deviations are 0.004 \AA for the Ir-P and Ir-Cl bond-lengths and 0.04 \AA for C-C bonds. The stereochemistry of the complex is shown in the Figure.

The ligand-metal-ligand bond-angles show the steric requirements of chelate ring-formation and the effects of



FIGURE

aryl groups are significantly longer than that *trans*- to the chlorine. The mean Ir-C bond-length of 2.10 \AA is identical with the value observed for the Ir-C (methyl) bond-length in di- μ -chloro-dichlorodimethyltetracarbonyldi-iridium(III)⁴ and comments on the apparent difference in the two bond-lengths must await our final refinement.

The mean Ir-P bond length of 2.25 Å is *ca.* 0.15 Å less than that found in a number of six-co-ordinate iridium-triphenylphosphine complexes such as Ir(C₆N₄H)CO[C₄(CN)₄](PPh₃)₂⁵ and IrO₂ICO(PPh₃)₂.CH₂Cl₂.⁶ This is rather striking and parallels, contrary to the suggestion of Coetzer and Gafner,⁷ the difference between the Rh-P bond-length of 2.14 Å in di- μ -chloro-bis(triphenyl phosphite)-(cyclo-octa-1,5-diene)dirhodium(I) and the mean values of 2.32 Å in RhH(CO)(PPh₃)₃,⁸ 2.29 Å in RhCl(PPh₃)₃, and 2.37 Å in Rh(C₃F₄)Cl(PPh₃)₂.⁹ These results must indicate the increased Lewis acidity of the phosphite compared with the phosphine ligand since steric effects seem unlikely to contribute to bond lengthening of this magnitude.

The chelate rings are almost planar. We note that the

P-O-C bond-angles in the phosphite ligands average 128° and 117° for carbon atoms which are respectively uncoordinated and co-ordinated to the metal. There is obviously much more flexibility for chelate ring formation in phosphite complexes than is possible for the triphenylphosphine-metal analogues. It remains to be seen whether an iridium complex containing two metal-carbon bonds from cleaved triphenylphosphine ligands can be synthesised; the triphenyl phosphite ligand has both electronic and steric factors in its favour. Other steric considerations which may be involved in intramolecular metal-carbon bond formation have been discussed by Cheney *et al.*¹⁰

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