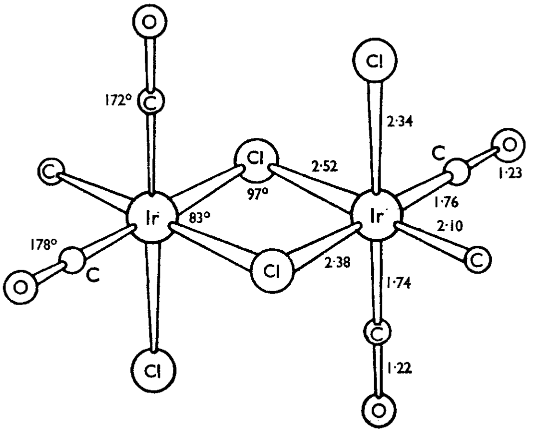
The Preparation and Crystal Structure of Di-μ-chloro-dichlorodimethyltetracarbonyldi-iridium(III)

By N. A. BAILEY* and C. J. JONES
(*Department of Chemistry, University of Sheffield, Sheffield* 10)
and B. L. SHAW and E. SINGLETON
(*School of Chemistry, University of Leeds, Leeds* 2)

WINKHAUS AND SINGER[1] have shown that cyclooctene reacts with chloroiridic acid in ethanol to give $[IrCl(CO)(C_8H_{14})_3]$; we have independently discovered this reaction and found that methane is evolved, showing that the carbonyl group is derived from the breakdown of the ethanol. On washing with ether the complex loses cyclo-octene to produce $[IrCl(CO)(C_8H_{14})_2]_2$ which, when treated with acyl chlorides (R·COCl), gives crystalline complexes of the formula $[Ir_2Cl_4R_2(CO)_4]$ (R = Me, Et, Pr^i or Ph). Infrared and other evidence suggest that the reaction is an oxidative addition of R·COCl to the iridium(I) complex, followed by alkyl (or phenyl) migration from carbonyl to the iridium. Since there are many possible isomers for the product and because of the novelty of the reaction, the crystal structure of the methyl complex, $[Ir_2Cl_4Me_2(CO)_4]$, has been determined by X-ray diffraction.

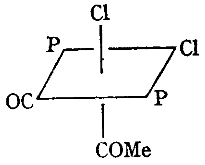
The complex forms very pale yellow needles which are monoclinic with $a = 7{\cdot}64$, $b = 10{\cdot}73$, $c = 8{\cdot}20$ Å, $\beta = 90°\ 5'$, $Z = 2$; the space group is $P2_1/n$ and the molecule is required to possess a strict inversion centre. Complete three-dimensional, room temperature, X-ray data $[(\sin\theta/\lambda)_{\max} = 0{\cdot}70]$ were collected by means of an automatic diffractometer and comprised 1072 independent reflexions. The structure was solved by conventional Patterson and difference Fourier synthesis techniques and has been refined by block-diagonal least-squares procedures to a current discrepancy index of 0·089 — anisotropic thermal parameter being allowed for all atoms. The molecular geometry is shown in the Figure.

A feature of the structure is the highly asymmetric chlorine bridging system consistent with the known *trans*-bond weakening effect of a methyl group as observed in, for example, *trans*-$[PtClMe(PEt_3)_2]$[2] and $[IrClMe_2(PMe_2Ph_3)]$[3] where the metal–chlorine stretching frequencies are 274 and 254 cm.$^{-1}$, respectively. The dependence of bond lengths on the *trans*-ligand is also observed in the organo-iridium complex $(C_{15}H_{13}O(Cl_2Ir(Me_2SO)_2$[4] where the iridium–chlorine bond lengths *trans* and *cis* to the σ-bonded carbon atom are, respectively, 2·49 and 2·38 Å.



FIGURE

On treatment with two moles of dimethylphenylphosphine, $[Ir_2Cl_4Me_2(CO)_4]$ gives $[Ir_2Cl_4(COMe)_2(CO)_2(PMe_2Ph)_2]$ and with a further two moles gives $[IrCl_2(COMe)(CO)(PMe_2Ph)_2]$ of configuration (II), showing that dimethylphenylphosphine induces methyl migration from iridium to carbonyl rather than causes simple chlorine bridge fission.



(II)

(*Received, August* 22*nd*, 1967; *Com.* 905.)

---

[1] G. Winkhaus and H. Singer, *Chem. Ber.*, 1966, **99**, 3610.
[2] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.
[3] B. L. Shaw and A. C. Smithies, *J. Chem. Soc.* (*A*), 1967, 1047.
[4] E. M. McPartlin and R. Mason, *Chem. Comm.*, 1967, 545.