The Preparation of the Complexes MX_4L_2 (M = Rh, Ir; X = Halogen; L = Phosphine or Phosphinite) from Reactions of X_2 with the $[ML_4]^+$ Cations. The Characterisation of $IrI_4(PMePh_2)_2$ as the Triply-Halo-Bridged Salt $[Ir_2I_5(PMePh_2)_4]I_3$ by X-ray Analysis

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Few complexes of stoichiometry $IrCl_4L_2$ (L = tertiary phosphine or arsine) are known. Their methods of preparation have been (i) single-electron oxidations of the salts $[LH][IrCl_4L_2]$ (L = PEt_2Ph, PEt_3, PPr_3^n, PMe_2Ph and $ASPr_3^n$) with Cl_2 [1,2] or (ii) oxidative addition reactions of chlorine with $IrClL(PPh_3)_2$ (L = N_2 [1] and PPh_3 [3]) and $[IrH_xCl_{3-x}(PPh_3)_3]$ (x = 1, 2).[3,4] These latter reactions are most unusual and would seem to involve, at some stage, a heterolytic fission of a Cl–Cl bond. Corresponding rhodium(IV) complexes are not known to date and this might be ascribed to the relative instability of the rhodium(IV) oxidation state when compared with that of iridium. It was apparent, however, from these iridium(IV) compounds characterised that L was usually bulky, and it was possibly that steric factors may play a significant role. This is especially true in the oxidative addition reactions where a five-coordinate d^6 system would necessarily[5] be an intermediate in the conversion of iridium(III) to iridium(IV). In attempts to assess the relative electronic and ligand size factors in forming iridium(IV) compounds we initially treated the cations $[IrL_4]^+$ [L = $P(OMe)Ph_2$ and $PMePh_2$] with an excess of the halogens Cl_2, Br_2 and I_2 in dichloromethane or acetone solution and found that only for I_2 was a complex of stoichiometry IrI_4L_2 obtained. Corresponding reactions with $[RhL_4]^+$ [L = $P(OMe)Ph_2$ and $PMePh_2$] gave the products RhX_4L_2 (X = Br and I). These complexes all analysed correctly, were dark brown or purple in colour, had intermediate to zero conductivity values and gave broad unresolved ^1H NMR methyl resonances. Molecular weights gave values in between a monomer and a dimer which could have been indicative of dissociation and dimerisation occurring in solution, though no anion exchange with PF_6^- or BPh_4^- could be effected from these solutions. It was unexpected that no MCl_4L_2 complexes were obtained with chlorine, the strongest of the three oxidising agents used, and because of this it was decided to fully characterise these MX_4L_2 species. Consequently an X-ray structural determination of the complex of stoichiometry $IrI_4(PMePh_2)_2$ was undertaken, and this established the compound as a salt of formula $[Ir_2I_5(PMePh_2)_4]^+I_3^-$ (I).

Crystal Data

$Ir_2I_8P_4C_{52}H_{52}$; M.W = 2200.57, $\lambda(Mo\text{-}K\alpha)$ = 0.7107 Å; Monoclinic space group $P2_1/c$, Z = 4, a = 12.45(2), b = 28.98(2), c = 17.38(2) Å, β = 107.7(1)°, μ = 90.57 cm^{-1}; D_m = 2.46, D_c = 2.45 g/cm^{-3}. The single crystal X-ray data have been collected with an automatic four-circle diffractometer and the structure solved by Patterson and Fourier methods and refined by least squares procedure. The actual R factor is 0.092 based on 3993 observed reflections with the intensity $I \geqslant 2\sigma(I)$. The refinement is still progressing. A prospective view of the structure is given in Figure 1. Significant bond lengths observed were Ir–P (mean) = 2.33(1) Å; Ir–I (terminal) = 2.68(1) Å (mean); Ir–I (bridged) = 2.69(1), 2.76(1) and 2.75(1) Å; I–I (mean) = 2.90(1) Å, I_1 is *trans* to the terminal I_4 and I_5 and at the same distance from the iridium, whereas the Ir–I_2 and Ir–I_3 distances are elongated presumably because of the structural *trans*-effect of the phosphine ligands. The Ir_1–I_1–Ir_2 angle of 85.5(1)° is larger than the mean Ir_1–I_2 or $_3$–Ir_2 angle of 82.8(1)°. Ligand steric effects are probably responsible for the distortion from ideal octahedral coordination about the iridium atoms, where angles vary from 166.9° to 171.0° and from 78.2° to 98.5°. The anion I–I–I angle of 177.2° and I–I bond lengths agree well with values previously reported.[6] The cation and the anion are both discreet and there is no indication from this structural determination as to why low conductivity values were obtained for these salts. Strong ion pair formation in solution may account for this as well as our inability to exchange anions with PF_6^- and BPh_4^-.

What is surprising from this work is that the physical evidence pointed to the formulation of these complexes as monomeric metal(IV) species, and though we assign all the other compounds prepared here the same stereochemistry as (I) only structural characterisation will reveal their true identity. We cannot comment at this stage on the mechanism of these reactions nor whether the known $IrCl_4L_2$ compounds have similar structures to (I) and that their instability is due to the instability of the Cl_3^- ion. This Cl_3^- ion instability may explain why no products corresponding to (I) were obtained from $[ML_4]^+$ and chlorine, though another factor may be the greater tendency to form bridging products along the series Cl < Br < I. The increased tendency to
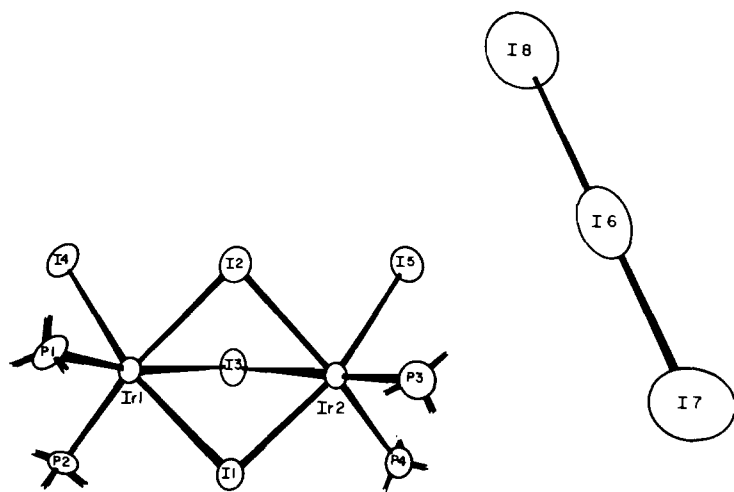
Figure 1.

dimerisation can also account for the greater range of rhodium products obtained than for iridium. Mechanistic studies on these reactions are in progress.

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