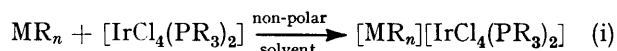


## Redox Properties of $[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$ : the Synthesis of Halide-bridged Mixed-metal Mixed-valence Complexes and the Crystal and Molecular Structure of $[(\text{Me}_3\text{As})\text{ClPd}(\mu\text{-Cl})_2\text{IrCl}_2(\text{PMe}_2\text{Ph})_2]\dagger$

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The potential of  $[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$  as a one-electron oxidising agent in organometallic chemistry has been evaluated. In complementary redox reactions with metallocenes, salts of the general form  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2][\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$  (1) are formed. In non-complementary reactions with platinum(0) and palladium(II) complexes some interesting mixed-metal mixed-valence complexes of the type  $[(\text{Ph}_3\text{P})_2\text{Pt}(\mu\text{-Cl})_2\text{IrCl}_2(\text{PMe}_2\text{Ph})_2][\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$  (2) and  $[(\text{Me}_3\text{As})\text{ClPd}(\mu\text{-Cl})_2\text{IrCl}_2(\text{PMe}_2\text{Ph})_2]$  (3) are formed. Complex (3) has been characterised by single-crystal X-ray diffraction studies. It crystallises in the space group  $P2_1/n$  of monoclinic symmetry in a cell of dimensions  $a = 12.218(2)$ ,  $b = 13.187(2)$ ,  $c = 17.832(2)$  Å,  $\beta = 91.80(1)^\circ$  and  $Z = 4$ , the final  $R$  and  $R'$  being 0.046 and 0.051 respectively based on full-matrix refinement of 167 variables and 4 273 observations. This structural determination confirms that (3) contains an octahedral iridium(III) unit linked to a square-planar palladium fragment by means of chloride bridges.

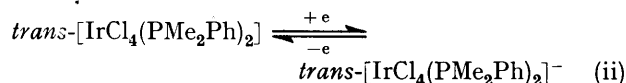
THE redox properties of  $[\text{IrCl}_6]^{2-}$  and its oxidation reactions with a wide range of organic and organometallic substrates have been studied extensively.<sup>1</sup> However, the low solubility of this anion in organic solvents and the inability to vary its redox potential by ligand substitution have limited its utility as a general reagent. Some years ago we synthesised a series of purple iridium(IV) complexes of the type  $\text{trans-}[\text{IrCl}_4(\text{PR}_3)_2]$ <sup>2,3</sup> which are soluble in a wide range of organic solvents, and therefore of potential interest as one-electron oxidising agents of organic molecules and organometallic complexes.<sup>4</sup> The latter possibility seemed to be particularly attractive since the formation of ionic complexes containing the large  $[\text{IrCl}_4(\text{PR}_3)_2]^-$  anion according to the redox reaction (i)



would result in their precipitation from non-polar organic solvents. The rapid removal of the oxidised organometallic species  $[\text{MR}_n]^+$  from the reaction medium could limit some of the decomposition pathways available to  $[\text{MR}_n]^+$  and thereby lead to the isolation of some interesting paramagnetic organometallic species.

### RESULTS AND DISCUSSION

Qualitative tests established that the oxidising ability of  $[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$ , which gives intensely coloured purple solutions in organic solvents, is intermediate between that of chlorine and bromine and that the reduced product of such reactions is  $[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]^-$ . Cyclic-voltammetry studies, the results of which are illustrated in Figure 1, show a well defined reduction wave for  $\text{trans-}[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$  in acetonitrile solutions at 0.90 V with respect to the Ag-AgCl electrode. This reduction step met the criteria for a diffusion-controlled one-electron redox process and is consistent with the reduction processes in (ii).



The utility of  $\text{trans-}[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$  as a one-electron oxidising agent in organometallic chemistry was first investigated with metallocenes, *viz.*  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$  and  $[\text{Ni}(\eta\text{-C}_5\text{H}_5)_2]$ , which are known to readily undergo oxidation to give stable cations. Benzene solutions of these metallocenes required 1 mol equivalent of *trans-*

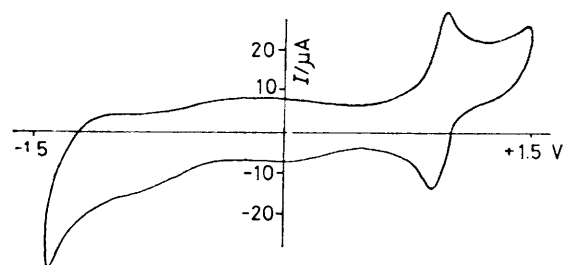


FIGURE 1 Cyclic voltammogram of  $\text{trans-}[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$  in  $\text{CH}_3\text{CN}$  with  $\text{Na}[\text{ClO}_4]$  as supporting electrolyte

$[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$ , as judged by the decolourisation of the iridium complex, for oxidation. Precipitates of the salts  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2][\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$  [ $\text{M} = \text{Fe}$  (1a) or  $\text{Ni}$  (1b)] separated in high yields very quickly from the solutions. These complexes were characterised as salts of the metallocenium cations  $[\text{M}(\eta\text{-C}_5\text{H}_5)_2]^+$  on the basis of elemental analyses and conductivity measurements (see Table 1). The u.v. and visible spectra of (1a) and (1b) showed bands at 622 (422) and 435 nm ( $\epsilon = 220 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), respectively, similar to those reported previously for  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^+$  and  $[\text{Ni}(\eta\text{-C}_5\text{H}_5)_2]^+$ .<sup>5,6</sup>

In contrast, addition of  $[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]$  to a solution of  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  in benzene required the addition of 2 mol equivalents of the iridium complex for complete reaction. The fawn precipitate which separated from the solution has been formulated as the di- $\mu$ -chloro-platinum(II)iridium(III) complex (2) on the basis of the analytical and conductivity measurements summarised in Table 1. The  $^1\text{H}$  n.m.r. spectrum of (2) in  $\text{CDCl}_3$  has

† *cd*-Di- $\mu$ -chloro-*agh*-trichloro-*ef*-bis(dimethylphenylphosphine)-*b*-trimethylarsinepalladium(II)iridium(III).

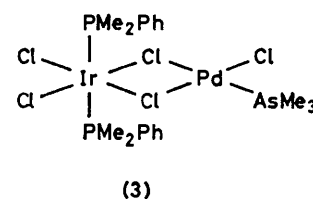
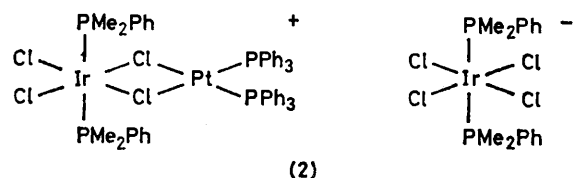
TABLE 1

Analytical, melting-point, and conductivity data for the complexes

| Complex   | Colour     | M.p. <sup>a</sup><br>(θ <sub>c</sub> /°C) | Analysis/% <sup>b</sup> |              |                | Λ/<br>Ω <sup>-1</sup> m <sup>2</sup> mol <sup>-1</sup> |
|---|------------|---|-------------------------|--------------|----------------|--|
|   |            |   | C                       | H            | Cl             |  |
| (1a) [Fe(η-C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ][IrCl <sub>4</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ]  | Blue-green | 168—171                                   | 38.6<br>(39.2)          | 4.2<br>(4.0) | 18.1<br>(17.9) | 56.5 <sup>c</sup>                                      |
| (1b) [Ni(η-C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ][IrCl <sub>4</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ]  | Pale brown | 240—243                                   | 39.1<br>(39.1)          | 4.0<br>(4.0) | 17.6<br>(17.8) | 57.4 <sup>c</sup>                                      |
| (2) [(Ph <sub>3</sub> P) <sub>2</sub> Pt(μ-Cl) <sub>2</sub> IrCl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ][IrCl <sub>4</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ] | Pink-brown | 165—170 <sup>d</sup>                      | 42.1<br>(42.2)          | 3.9<br>(3.8) | 13.8<br>(14.5) | 12.2 <sup>e</sup>                                      |
| (3) [(Me <sub>3</sub> As)ClPd(μ-Cl) <sub>2</sub> IrCl <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ]   | Orange-red | 186—190                                   | 26.2<br>(26.7)          | 3.6<br>(3.6) | 20.3<br>(19.5) | 1.2 <sup>e</sup>                                       |
| (4) [AsMe <sub>3</sub> H][IrCl <sub>4</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ]  | Pink       | 190—194                                   | 31.0<br>(31.2)          | 4.3<br>(4.4) | 19.0<br>(19.4) | 21.3 <sup>e</sup>                                      |

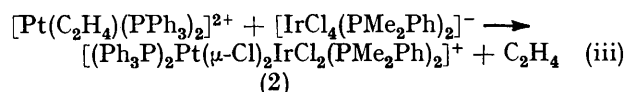
<sup>a</sup> Generally with decomposition. <sup>b</sup> Calculated values are given in parentheses. <sup>c</sup> In nitromethane solution. <sup>d</sup> Turns orange at this temperature, eventually decomposing at 288—290 °C. <sup>e</sup> In nitrobenzene solution.

a multiplet at δ 1.9 which is interpreted as a pair of overlapping triplets arising from two independent pairs of overlapping triplets arising from two independent pairs of *trans*-PMe<sub>2</sub>Ph ligands.<sup>7</sup> The proton-decoupled <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum of (2) in CDCl<sub>3</sub> shows singlets at 36.54 and 40.75 p.p.m. with respect to trimethyl



phosphate, and the latter can be assigned to the *trans*-[IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]<sup>-</sup> anion since the corresponding resonance in [PMe<sub>2</sub>PhH][IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] is observed at 40.98 p.p.m. In addition, the <sup>31</sup>P-{<sup>1</sup>H} spectrum shows a characteristic 1:4:1 triplet at 11.84 p.p.m. which can be assigned to *cis*-PPh<sub>3</sub> ligands co-ordinated to platinum [<sup>1</sup>J(Pt-P) = 3 732 Hz].<sup>8</sup>

For the platinum(0) phosphine complex [Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>] a two-electron oxidation reaction leading to a platinum(II) species [Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> appears to be preferred to a one-electron oxidation step. The ethylene ligand in the resultant intermediate must be sufficiently labile for it to be displaced by the chloride ligands of the [IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]<sup>-</sup> ion according to equation (iii). The utility of mixed-metal mixed-valence



complexes such as (2) as precursors for mixed-metal cluster compounds using reductive processes is currently under investigation.

Further support for structure (2) has been obtained by the characterisation of the related neutral palladium(II)-iridium(III) complex (3) by a single-crystal X-ray structural analysis. Addition of *trans*-[IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] to *trans*-[PdCl<sub>2</sub>(AsMe<sub>3</sub>)<sub>2</sub>] in acetone led to the formation of a mixture of products which were separated by fractional recrystallisation and identified as [(Me<sub>3</sub>As)ClPd(μ-Cl)<sub>2</sub>IrCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (3) and [AsMe<sub>3</sub>H][IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (4). Complex (3) crystallises as red cuboid crystals and (4)

pink hexagonal crystals. The relevant analytical and conductivity data are summarised in Table 1. The i.r. spectrum of (4) showed bands which could be attributed to Me<sub>3</sub>As and PMe<sub>2</sub>Ph moieties, but did not show a band

which could be attributed to ν(As-H). The <sup>1</sup>H n.m.r. spectrum of (4) in (CD<sub>3</sub>)<sub>2</sub>SO shows, in addition to the multiplet at δ ca. 7.5 (10 H) arising from the phenyl protons, a singlet at δ 2.10 (9 H) and a triplet at 1.75 (12 H). The latter is assigned to the *trans*-PMe<sub>2</sub> protons and the former to the AsMe<sub>3</sub>H<sup>+</sup> methyl protons. For AsMe<sub>4</sub><sup>+</sup> the methyl resonances have been observed at δ 2.0, in contrast to AsMe<sub>3</sub> for which the corresponding

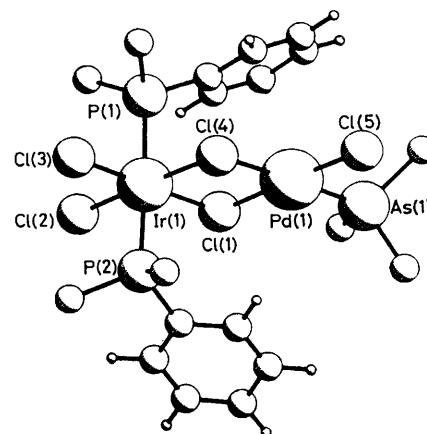


FIGURE 2 Molecular structure of [(Me<sub>3</sub>As)ClPd(μ-Cl)<sub>2</sub>IrCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]

resonance is observed at δ 0.88.<sup>9,10</sup> The absence of a resonance which can be attributed to H-As is consistent with reports that the corresponding resonance for PMe<sub>3</sub>H<sup>+</sup> could not be observed.<sup>11</sup> The electronic spectrum of (4) showed bands at 381 (160), 305 (8 × 10<sup>3</sup>),

and 257 nm ( $\epsilon = 7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) which are characteristic of the *trans*- $[\text{IrCl}_4(\text{PMe}_2\text{Ph})_2]^-$  anion.<sup>12</sup>

Compound (3) could not be obtained in sufficient quantities for spectroscopic studies but formed crystals of sufficient quality for a single-crystal structural determination. The molecular structure resulting from this determination is illustrated in Figure 2, and the important bond lengths and angles are summarised in Tables 3 and 4. The structure confirms that the complex

TABLE 2

Crystal data and details of data collection and structure analyses

| (a) Crystal data  |            |                                |          |
|---|------------|--------------------------------|----------|
| Formula weight $\text{C}_{19}\text{H}_{31}\text{AsCl}_5\text{IrP}_3\text{Pd}$ , $M$ 872 |            |                                |          |
| Crystal system  | Monoclinic |                                |          |
| $a/\text{\AA}$  | 12.218(2)  | $\alpha/^\circ$                | 90       |
| $b/\text{\AA}$  | 13.187(2)  | $\beta/^\circ$                 | 91.80(1) |
| $c/\text{\AA}$  | 17.832(2)  | $\gamma/^\circ$                | 90       |
| $U/\text{\AA}^3$  | 2 871.6    |                                |          |
| Space group   |            | $P2_1/n$                       |          |
| $Z$   |            | 4                              |          |
| $D_c/g \text{ cm}^{-3}$   |            | 2.02                           |          |
| $D_m/g \text{ cm}^{-3}$   |            | 1.98 (by flotation)            |          |
| $F(000)$  |            | 1 664                          |          |
| Linear absorption coefficient/ $\text{cm}^{-1}$   |            | 73.5                           |          |
| Crystal size/mm   |            | $0.78 \times 0.42 \times 0.22$ |          |
| (b) Data collection   |            |                                |          |
| $\lambda(\text{Mo-K}\alpha)/\text{\AA}$   |            | 0.710 69                       |          |
| $\theta_{\text{min.}}, \theta_{\text{max.}}/^\circ$                                     |            | 1.5–25                         |          |
| Scan width parameters,<br>$A$ and $B$ ( $^\circ$ ), in $\omega =$                       |            |                                |          |
| $A + B \tan \theta$   |            | 0.8, 0.15                      |          |
| Horizontal aperture parameters,<br>$A$ and $B$ (mm), in aperture =                      |            |                                |          |
| $A + B \tan \theta$   |            | 4, 0                           |          |
| Total unique data   |            | 5 602                          |          |
| Observed data<br>[ $F > 3\sigma(F)$ ]   |            | 4 273                          |          |
| (c) Refinement  |            |                                |          |
| No. of variables (full matrix)  |            | 167                            |          |
| Weighting scheme (Chebyshev) $A_r$  |            | 613.4 856.6 198.7              |          |
| Final $R$ ( $= \Sigma \Delta F / \Delta F_o$ )  |            | 0.046                          |          |
| $R'$ [ $= (\Sigma w \Delta F^2 / \Sigma w F_o^2)^{1/2}$ ]                               |            | 0.051                          |          |

TABLE 3

Selected intramolecular bond lengths ( $\text{\AA}$ ) for  $[(\text{Me}_3\text{As})\text{-ClPd}(\mu\text{-Cl})_2\text{IrCl}_2(\text{PMe}_2\text{Ph})_2]$

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| Ir(1)–Cl(1) | 2.382(2)  | Pd(1)–Cl(1) | 2.331(2)  |
| Ir(1)–Cl(2) | 2.346(2)  | Pd(1)–Cl(4) | 2.421(2)  |
| Ir(1)–Cl(3) | 2.333(2)  | Pd(1)–Cl(5) | 2.268(3)  |
| Ir(1)–Cl(4) | 2.390(2)  | Pd(1)–As(1) | 2.313(1)  |
| Ir(1)–P(1)  | 2.343(3)  | As(1)–C(1)  | 1.948(14) |
| Ir(1)–P(2)  | 2.344(3)  | As(1)–C(2)  | 1.958(14) |
| P(1)–C(11)  | 1.807(10) | As(1)–C(3)  | 1.929(13) |
| P(1)–C(12)  | 1.856(15) |             |           |
| P(1)–C(13)  | 1.813(14) |             |           |
| P(2)–C(21)  | 1.792(10) |             |           |
| P(2)–C(22)  | 1.839(14) |             |           |
| P(2)–C(23)  | 1.823(13) |             |           |

contains an octahedral iridium(III) unit linked to a square-planar palladium(II) fragment by means of chloride bridges. The long iridium–palladium bond distance [3.488(1)  $\text{\AA}$ ] effectively rules out any metal–metal bonding. The geometries about the octahedral and square-planar metal centres are close to those anticipated, with

TABLE 4

Selected intramolecular bond angles ( $^\circ$ ) for  $[(\text{Me}_3\text{As})\text{-ClPd}(\mu\text{-Cl})_2\text{IrCl}_2(\text{PMe}_2\text{Ph})_2]$

|                   |           |                   |            |
|-------------------|-----------|-------------------|------------|
| Cl(1)–Ir(1)–Cl(2) | 91.00(8)  | Cl(1)–Pd(1)–As(1) | 95.07(6)   |
| Cl(1)–Ir(1)–Cl(3) | 177.77(9) | Cl(1)–Pd(1)–Cl(4) | 85.95(8)   |
| Cl(1)–Ir(1)–Cl(4) | 85.52(7)  | Cl(1)–Pd(1)–Cl(5) | 178.44(11) |
| Cl(1)–Ir(1)–P(1)  | 91.74(8)  | As(1)–Pd(1)–Cl(4) | 176.99(8)  |
| Cl(1)–Ir(1)–P(2)  | 92.35(9)  | As(1)–Pd(1)–Cl(5) | 84.60(8)   |
| Cl(2)–Ir(1)–Cl(3) | 91.22(9)  | Cl(4)–Pd(1)–Cl(5) | 94.30(9)   |
| Cl(2)–Ir(1)–Cl(4) | 176.50(8) | Ir(1)–Cl(1)–Pd(1) | 95.47(8)   |
| Cl(2)–Ir(1)–P(1)  | 92.19(10) | Ir(1)–Cl(4)–Pd(1) | 92.92(8)   |
| Cl(2)–Ir(1)–P(2)  | 88.79(10) |                   |            |
| Cl(3)–Ir(1)–Cl(4) | 87.56(10) |                   |            |
| Cl(3)–Ir(1)–P(1)  | 88.34(10) |                   |            |
| Cl(3)–Ir(1)–P(2)  | 87.54(10) |                   |            |
| Cl(4)–Ir(1)–P(1)  | 91.72(9)  |                   |            |
| P(1)–Ir(1)–P(2)   | 175.78(9) |                   |            |

TABLE 5

Fractional co-ordinates ( $\times 10^4$ ) for  $[(\text{Me}_3\text{As})\text{ClPd}(\mu\text{-Cl})_2\text{IrCl}_2(\text{PMe}_2\text{Ph})_2]$

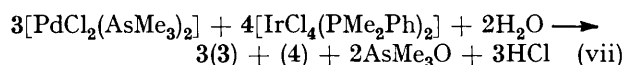
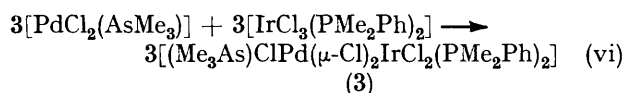
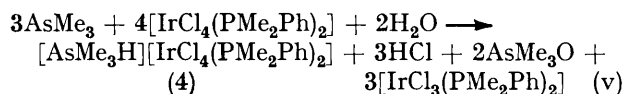
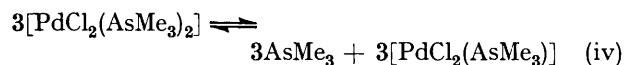
| Atom   | $x/a$       | $y/b$      | $z/c$      |
|--------|-------------|------------|------------|
| Ir(1)  | 517.7(3)    | 1 989.1(3) | 2 296.4(2) |
| Pd(1)  | –1 066.5(6) | 946.5(5)   | 3 695.7(4) |
| As(1)  | –2 319.7(9) | 1 496.9(8) | 4 552.7(5) |
| Cl(1)  | –774(2)     | 2 544(2)   | 3 181(1)   |
| Cl(2)  | 633(2)      | 3 628(2)   | 1 796(2)   |
| Cl(3)  | 1 783(2)    | 1 384(2)   | 1 451(2)   |
| Cl(4)  | 313(2)      | 356(2)     | 2 853(1)   |
| Cl(5)  | –1 321(3)   | –596(2)    | 4 223(2)   |
| P(1)   | –880(2)     | 1 532(2)   | 1 432(1)   |
| P(2)   | 2 005(2)    | 2 377(2)   | 3 108(2)   |
| C(1)   | –2 855(11)  | 2 872(10)  | 4 390(8)   |
| C(2)   | –3 663(12)  | 691(11)    | 4 590(8)   |
| C(3)   | –1 706(11)  | 1 483(10)  | 5 562(7)   |
| C(11)  | –2 218(8)   | 1 390(8)   | 1 824(5)   |
| C(111) | –2 602(9)   | 459(9)     | 2 066(7)   |
| C(112) | –3 620(13)  | 370(13)    | 2 368(9)   |
| C(113) | –4 226(13)  | 1 202(13)  | 2 437(9)   |
| C(114) | –3 890(11)  | 2 186(10)  | 2 226(8)   |
| C(115) | –2 864(10)  | 2 258(9)   | 1 918(6)   |
| C(12)  | –625(12)    | 289(11)    | 985(8)     |
| C(13)  | –1 079(11)  | 2 377(11)  | 638(8)     |
| C(21)  | 1 678(8)    | 3 116(8)   | 3 913(5)   |
| C(211) | 1 240(9)    | 2 648(9)   | 4 533(7)   |
| C(212) | 956(11)     | 3 200(10)  | 5 141(7)   |
| C(213) | 1 114(13)   | 4 236(12)  | 5 160(9)   |
| C(214) | 1 530(12)   | 4 685(12)  | 4 546(9)   |
| C(215) | 1 814(11)   | 4 149(10)  | 3 929(7)   |
| C(22)  | 2 737(11)   | 1 259(11)  | 3 480(8)   |
| C(23)  | 3 100(10)   | 3 086(10)  | 2 675(7)   |

the majority of interligand bond angles equal to  $90 \pm 3^\circ$ . The angles subtended at the metal atoms by the bridging chloride ligands and Cl(5)–Pd–AsMe<sub>3</sub> are, however, substantially smaller than  $90^\circ$  and are approximately equal to  $85^\circ$ .

The iridium–terminal chlorine bond lengths are essentially equal to those reported for the *trans*-chlorines in *mer*- $[\text{IrCl}_3(\text{PMe}_2\text{Ph})_3]$ ,<sup>13</sup> and the iridium–phosphorus bond lengths show a similar relationship. The metal–chlorine bond lengths to the bridging chlorides are longer than the terminal metal–chlorine bond lengths and in addition show an asymmetry arising from the *trans* influence of the AsMe<sub>3</sub> ligand, *i.e.* Pd–Cl(4) is *ca.* 0.09  $\text{\AA}$  longer than Pd–Cl(1).<sup>14</sup>

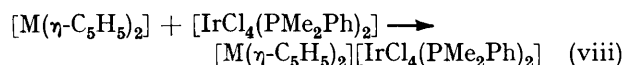
Another interesting structural feature of (3) concerns the relative orientation of the phenyl rings of the dimethylphenylphosphine ligands co-ordinated to the iridium atom. Both phenyl rings are directed towards

the empty co-ordination sites of the square-planar palladium fragment. An examination of the Pd...H (phenyl) distances has not revealed any particularly short metal-hydrogen contacts and therefore the observed phosphine conformation probably arises from crystal-packing effects rather than incipient metal-hydrogen bond formation. The identification of (3) and (4) as [(Me<sub>3</sub>As)ClPd(μ-Cl)<sub>2</sub>IrCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] and [AsMe<sub>3</sub>H][IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] respectively demonstrates that {IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>} is not a sufficiently strong oxidising agent to oxidise palladium(II) to palladium(IV) and the overall reaction is best represented by the sequence (iv)–(vi).

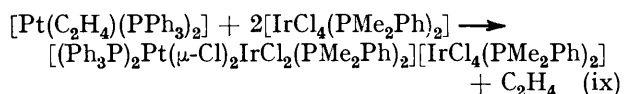


The overall oxidation process (vii) involves oxidation of AsMe<sub>3</sub> to AsMe<sub>3</sub>O rather than of the palladium complex. The formation of AsMe<sub>3</sub>O was detected by i.r. studies on the residue of the reaction.

**Conclusions.**—The preliminary experiments described in this paper have established that *trans*-[IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] is capable of acting as a simple one-electron oxidising agent with organometallic complexes such as metallocenes which form stable co-ordinatively saturated cations according to equation (viii). However, in



non-complementary redox reactions generating co-ordinatively unsaturated metal cations the [IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]<sup>−</sup> anion is sufficiently nucleophilic to behave as a bidentate ligand through its halide bridges to form mixed-metal complexes, *e.g.*, as in equation (ix).



## EXPERIMENTAL

Reactions were generally carried out under pure dry dinitrogen in dry dioxygen-free solvents. Microanalyses (C, H, and Cl) were performed by Mr. M. Gascoyne and his staff at Oxford University. N.m.r. spectra were recorded on JEOL JNM PMX-60 (<sup>1</sup>H) and Bruker WH-90 spectrometers (<sup>31</sup>P-<sup>1</sup>H}) operating at 36.43 MHz. The internal standard for the <sup>1</sup>H n.m.r. spectra was tetramethylsilane, and the external standard for the <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectra was trimethyl phosphate. Infrared spectra were obtained as Nujol mulls using a Pye Unicam Sp 2000 spectrometer. Melting points were measured using an Electrothermal

apparatus, and conductivities were recorded on a Philips PW 9505 bridge using a standard conductivity cell with a cell constant of 0.1 cm<sup>−1</sup>. Electrochemical measurements were made using an instrument constructed by Dr. K. R. Seddon and his co-workers at Oxford University, and recorded on a Bryans A3 X-Y recorder. The acetonitrile used for the electrochemical studies was thoroughly dried by repeated distillation over P<sub>2</sub>O<sub>5</sub>, and sodium perchlorate was used as supporting electrolyte.

The complexes *trans*-[IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>], [Fe(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], [Ni(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], [Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>], and [PdCl<sub>2</sub>(AsMe<sub>3</sub>)<sub>2</sub>] were prepared by standard literature methods.<sup>2,15-17</sup>

*Bis*(η-cyclopentadienyl)iron *Tetrachlorobis*(dimethylphenylphosphine)iridate(III), [Fe(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>].—The complex [Fe(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (0.1 g, 0.54 mmol) was dissolved in benzene (10 cm<sup>3</sup>) giving a yellow solution. When a solution of [IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.33 g, 0.54 mmol) in benzene (10 cm<sup>3</sup>) was added slowly the solution decolourised instantly and a green-blue precipitate separated. Recrystallisation of the solid from dichloromethane–light petroleum (b.p. 40–60 °C) gave dark blue-green crystals of [Fe(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>].

*Bis*(η-cyclopentadienyl)nickel *Tetrachlorobis*(dimethylphenylphosphine)iridate(III), [Ni(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>].—The complex [Ni(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] (0.9 g, 0.48 mmol) was dissolved in benzene (10 cm<sup>3</sup>) giving a green solution which turned yellow on slow addition of a solution of [IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.29 g, 0.48 mmol) in benzene (15 cm<sup>3</sup>). A sand-coloured precipitate rapidly separated from the solution and was filtered off and recrystallised from dichloromethane–light petroleum to give pale brown crystals (yield 0.23 g, 65%).

*cd-Di-μ-chloro-gh-dichloro-ef-bis*(dimethylphenylphosphine)-*ab-bis*(triphenylphosphine)platinum(II)iridium(III) *Tetrachlorobis*(dimethylphenylphosphine)iridate(III), (2).—The complex [Pt(C<sub>2</sub>H<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (0.3 g, 0.42 mmol) was dissolved in benzene (20 cm<sup>3</sup>) and [IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.48 g, 0.84 mmol) in benzene (20 cm<sup>3</sup>) was slowly added. The purple colour of the second complex was rapidly discharged and a slight excess was added. A pink-brown solid separated from the solution and was recrystallised from acetone–light petroleum to give crystals of [(Ph<sub>3</sub>P)<sub>2</sub>Pt(μ-Cl)<sub>2</sub>IrCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>][IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (yield 0.59 g, 78%).

*Reaction of* [PdCl<sub>2</sub>(AsMe<sub>3</sub>)<sub>2</sub>] *with* [IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>].—The complex [PdCl<sub>2</sub>(AsMe<sub>3</sub>)<sub>2</sub>] (0.40 g, 0.96 mmol) was dissolved in acetone (10 cm<sup>3</sup>) and [IrCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.66 g, 1.08 mmol) in acetone (30 cm<sup>3</sup>) was added dropwise. The volume of the resultant dark yellow solution was reduced and on addition of light petroleum yielded perfectly formed crystals of *trimethylarsonium tetrachlorobis*(dimethylphenylphosphine)iridate(III), (4). On reducing the volume further and adding more light petroleum an orange powder and orange-red cuboid crystals of *cd-di-μ-chloro-agh-trichloro-ef-bis*(dimethylphenylphosphine)-*b-trimethylarsinepalladium*(II)iridium(III), (3), separated from the solution.

*X-Ray Crystallography* of [(Me<sub>3</sub>As)ClPd(μ-Cl)<sub>2</sub>IrCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>].—Preliminary unit-cell parameters and the crystal system were determined from oscillation and Weissenberg photographs. The space group (*P*2<sub>1</sub>/*n*) was uniquely determined from the systematic absences *0k0* for *k* odd and *h0l* for *h* + *l* odd. The accurate cell parameters and the orientation matrix used for data collection were determined from least-squares refinement of the setting angles for 25 reflections (14 < θ < 18°) automatically centred on an Enraf-Nonius CAD4 diffractometer.

Three-dimensional  $X$ -ray intensity data ( $h, k, \pm l$ ;  $1.5 < \theta < 25^\circ$ ) were collected from a single crystal mounted on the CAD4 diffractometer using Mo- $K_\alpha$  radiation (graphite monochromator) and an  $\omega$ - $2\theta$  scan technique. A periodic check of standard reflections showed no significant fluctuations of intensity. The data were corrected for Lorentz and polarisation effects and for absorption. The relevant details of the crystallographic analysis are summarised in Table 2.

The positions of the iridium and palladium atoms were determined from a three-dimensional Patterson synthesis and the arsenic, phosphorus, chlorine, and carbon atoms were located from successive Fourier difference electron-density maps. In subsequent full-matrix least-squares refinement the Ir, Pd, As, P, and Cl atoms were refined with anisotropic temperature factors. The majority of the hydrogen atoms were located in the final difference map and were placed in idealised positions with C-H 1.00 Å and assigned  $U_{\text{iso}} = 0.05 \text{ \AA}^2$ . The refinement finally converged at  $R = 0.046$  and  $R' \{ = [\Sigma(w\Delta F^2)/\Sigma(wF_o^2)]^{1/2} \} = 0.051$ .

Each reflection was assigned a weight  $w = 1 / \sum_{r=1}^n A_r T_r(X)$  where  $n$  is the number of coefficients  $A_r$  for a Chebyshev series,  $T_r$  is the polynomial function, and  $X$  is  $F_o/F_o(\text{max.})$ .<sup>18</sup> Three coefficients, with values given in Table 2, were used. Fractional co-ordinates with their estimated standard deviations are given for non-hydrogen atoms in Table 5, selected intramolecular bond lengths and angles in Tables 3 and 4. Anisotropic thermal parameters, fractional co-ordinates of the hydrogen atoms, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 23032 (37 pp.).\*

The data reduction and absorption correction were performed on a CDC 7600 computer at the University of London using SHELX-76.<sup>19</sup> The structure solution and refinement were carried out at Oxford University on an ICL 2980 computer with the Oxford CRYSTALS package.<sup>20</sup> Neutral-atom scattering factors were taken from ref. 21, and those

\* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

of the heavier elements were modified for anomalous dispersion (taking the  $\Delta f'$  and  $\Delta f''$  values from ref. 22).

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