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Preliminary communication

A CYCLOMETALLATED IRIDIUM(III) DIMETHYLPHENYLPHOSPHINE COMPLEX

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Summary

$[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) reacts with PMe_2Ph in CH_3CN to give the red cation $[Ir(PMe_2Ph)_4]^+$. This complex in CH_3CN reacts with H_2 to give *cis*-$[IrH_2(PMe_2Ph)_4]^+$, but on reflux for 6 h in the absence of H_2, it gives the first example of a cyclometallated PMe_2Ph complex *fac*-$[IrH(PMe_2C_6H_4)(PMe_2Ph)_3]^+$, as shown by PMR spectroscopy and preliminary X-ray crystallographic data.

Cyclometallation [1] has often been observed among complexes of electron-rich transition metals containing bulky tertiary phosphine ligands [1,2]. Such reactions are also promoted by the presence of a group, such as hydride or alkyl, on the metal, that reductively eliminates irreversibly with the hydrogen originating from the cyclometallated group [3].

Few cases are known in which cyclometallation or intermolecular metallation of the smaller tertiary phosphines (cone angle <130° [4]) takes place. This has been observed on very electron-rich Fe^0 and Ru^0 systems, with PMe_3 [5] and $(Me_2PCH_2)_2$ [6], respectively, and in one case for a cluster complex $Os_3(CO)_{11}(PMe_3)$ which metallates at 150°C to give a cluster-bridging Me_2PCH system [7]. Phosphites, such as $P(OPh)_3$ (cone angle: 128°), also cyclometallate very readily [1], presumably because the 5-membered metallacycle so formed is less strained than the 3- or 4-membered rings formed by metallation of a PMe or PPh group. Cyclometallation has, as far as we are aware, never been observed in complexes of the ligand PMe_2Ph (cone angle: 122°).

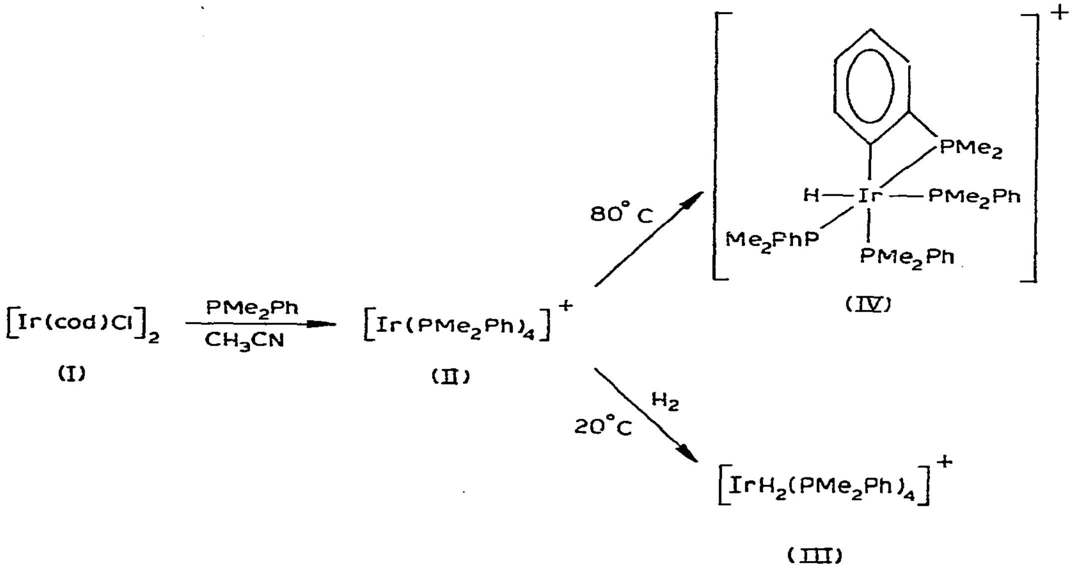
In the only case where phenyl and methyl substituents on phosphorus compete in what appears to be a cyclometallation reaction (but see below), the methyl group has been found to metallate rather than the Ph group. The reaction of $[PtCl_2L_2]$ with a bulky, phenyl-substituted, carboranyl-lithium reagent leads to the metallation of the tertiary phosphine groups to give $[\overline{\text{Pt(carboranyl)L\{P(C}}\text{HEt)(n-Pr)}_2\}]$ [8], where $L = P(n\text{-}Pr)_3$ (cone angle: 131°), and $[\overline{\text{Pt(carboranyl)L\{P(C}}\text{H}_2\text{)Ph}_2\}]$ [9], where $L = PMePh_2$ (cone angle: 136°). In these reactions both chloride ligands on platinum are presumed to be substituted by the carboranyllithium reagent, but one carboranyl ligand assists metallation by acting as a leaving group. Where a choice is possible ($L = PMePh_2$), the product is the one in which the metal is bonded to an alkyl, rather than an aryl carbon.

We now report the direct cyclometallation of the relatively small tertiary phosphine, PMe_2Ph, on an Ir^I centre, where we find that, in contrast to the platinum system, insertion into the aromatic CH bond is preferred over insertion into a CH bond of a PMe group. The reaction takes place under relatively mild conditions (refluxing acetonitrile) and does not appear to involve a leaving group.

The complex $[Ir(cod)Cl]_2$ (I; cod = 1,5-cyclooctadiene) was treated with excess PMe_2Ph in refluxing acetonitrile. After a few minutes a red solution is formed which probably contains the cation $[Ir(PMe_2Ph)_4]^+$ (II) [10], and addition of hydrogen at this stage gives the colorless hydrogen adduct *cis*-$[IrH_2(PMe_2Ph)_4]^+$ (III) which can be isolated conveniently as the hexafluorophosphate salt (85% yield).

If the original solution is refluxed for several hours, however, the red solution progressively turns light brown. After 6 h, a colourless product *fac*-$[\overline{\text{IrH\{PMe}_2\text{(C}}_6\text{H}_4)\}(PMe_2Ph)_3]PF_6$ (IV) was isolated with aqueous NH_4PF_6 (recryst. CH_2Cl_2/Et_2O; 60% yield). The complex was characterised by a preliminary X-ray crystallographic study (R = 5.7%; R_w = 6.6%).

The crystallographic data are: space group $P21/n$; a 15.920(5); b 18.081(8); c 13.374(5) Å; β 111.27(8)°, V 3587 Å^3, $Z = 4$; μ 42 cm^{-1}. The intensities were



SCHEME 1
The Reactions of the Iridium Complexes

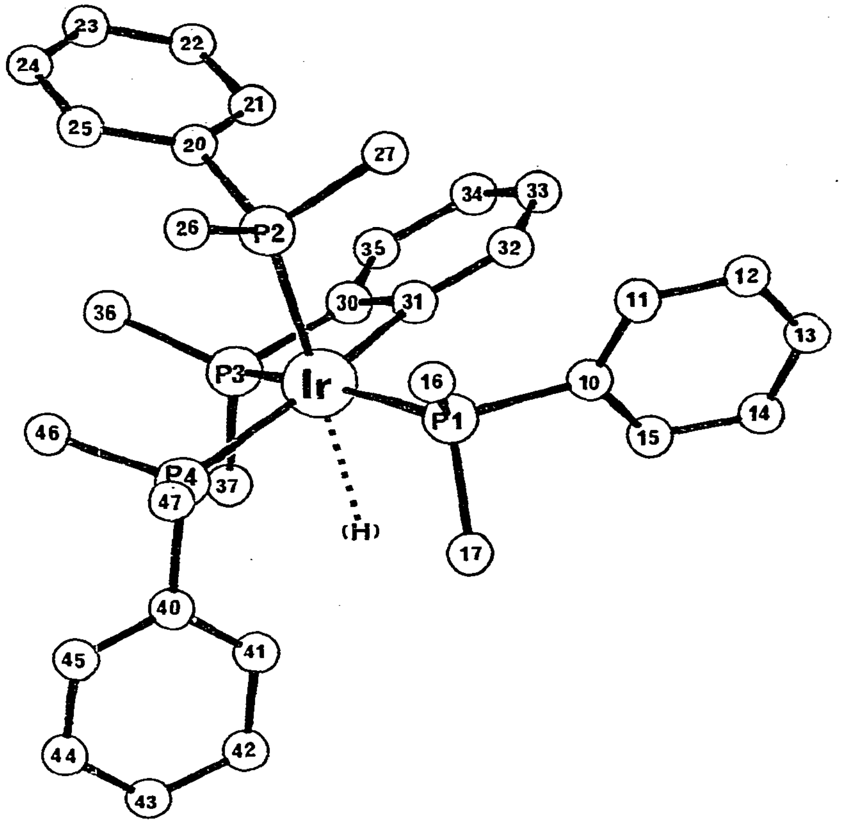


Fig. 1. An ORTEP diagram of the structure of *fac*-$[\overline{IrH(PMe_2C_6}H_4)(PMe_2Ph)_3]PF_6$ (IV). The coordination position assigned to the hydrogen ligand is shown although this ligand was not detected in the final difference map.

not corrected for extinction due to experimental difficulties. The full experimental data and results appear in the supplementary data, which are available from the authors on request.

Figure 1 shows the ORTEP diagram of the structure of IV. The main features of interest are the *ortho*-metallated PMe_2Ph ligand and the apparently empty position, *trans* to P(2), in the coordination sphere, which, from Ir{ν(IrH) = 2092 cm^{-1}} and PMR (see below) evidence is occupied by a hydride ligand.

The stereochemistry of the complex is analogous to that of the *cis*-dihydride (III) and is consistent with, though does not prove, a concerted mechanism for addition of the aromatic CH bond to the metal, similar to the mechanism that has been discussed for the addition of H_2 to iridium compounds [11].

There are no unexpected structural features, the cyclometallated $\overline{IrPC}_6H_4$ unit, for example, is normal [12], but the molecule is quite crowded, for instance the C(21)—C(30) non-bonded contact is 3.24 Å. The *trans*-effect of the hydride ligand is apparent in the long Ir—P(2) distance of 2.380(3) Å (average Ir—P: 2.333 Å, σ = 0.003 Å). The Ir—C bond (2.142(12) Å) is normal [13].

The PMR spectrum of IV (Brucker 270 MHz) shows a hydride resonance at δ −10.75 ppm due to a hydride ligand *trans* to one phosphorus nucleus (^2J(P,H) *trans* = 125 Hz) and *cis* to three further phosphorus nuclei (J(P,H) *cis* = 34 Hz). The "quartet" resonances have a slightly irregular appearance no doubt due to the inequivalence of the three *cis*-PMe_2Ph groups. The aromatic resonance pattern is unusually broad and has a structure that we have not interpreted, but the unusual features of the spectrum may be due to the *ortho*-inserted aromatic group.

The PMe region is complex but the ^{31}P decoupled spectrum is simple. Six sharp singlets at δ 1.6, 1.65, 1.7, 1.8, 1.85, and 1.9 ppm, arise from the six independent methyl groups of the three normal PMe_2Ph ligands. Two methyl groups (at δ 1.8, 1.5, 1.45, and 0.45 ppm), presumably those of the cyclometallated unit, resonate in the form of four broad or very broad peaks. This may indicate that two interconverting conformations of the molecule are populated in solution. One of these broad peaks lies considerably to high field of the others. We imagine that this peak may be due to the C(36) methyl which might be incrementally shielded by the ring current of the P(2) phenyl group.

In the undecoupled spectrum, four of the six sharp methyl resonances appear as doublets (^2J(P,H) = 10 Hz) and two as doublets of doublets (J(P,H) = 4 and 10 Hz). The principal broader peaks are also doublets of doublets (J(P,H) = 4 and 10 Hz).

We presume that the peaks that only show one coupling constant arise from the pair of mutually *cis*-PMe_2Ph ligands and that the peaks that show two coupling constants arise from the pair of mutually *trans* phosphorus ligands, although we would have expected the latter to show "virtual" coupling, as do the corresponding resonances in the *cis*-dihydride.

Possibly, the difference between Bresadola's results [9] and ours' is that the loss of the hydrogen by reductive elimination with the R group from the LiR reagent traps the kinetic product of metallation at the aliphatic CH. Under our conditions, the CH addition is in principle reversible and the thermodynamic addition product may be formed. This product could reasonably be expected to have the less strained, 4-membered ring resulting from PPh metallation. More likely, the lithium alkyl may directly deprotonate the coordinated $PMePh_2$ in the Bresadola system, leading to the observed product without any C—H activation by platinum at all [14].

We have shown that a relatively small tertiary phosphine, PMe_2Ph, can cyclometallate readily at an iridium centre at 80°C, without requiring either bulky substituents on phosphorus or a leaving group on the metal. We find, in contrast to previous systems [9], that metallation occurs preferentially at the PPh rather than the PMe group.

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