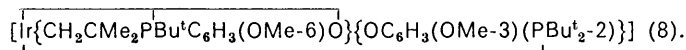


**Some Unusual Iridium Complexes formed from (2,6-Dimethoxyphenyl)- and (2,3-Dimethoxyphenyl)-di-*t*-butylphosphine: Crystal Structure of [2-Di-*t*-butylphosphino-3-methoxyphenoxo-*OP*]{2-[(2-hydroxy-6-methoxyphenyl)*t*-butylphosphino]-2-methylpropanato(2-)-*C*<sup>1</sup>*PO*<sup>2</sup>}- (methyl isocyanide)iridium(III)**

By H. David Empsall, Peter N. Heys, Walter S. McDonald,\* Michael C. Norton, and Bernard L. Shaw,\*  
School of Chemistry, The University, Leeds LS2 9JT

The compound  $\text{PBU}^t_2[\text{C}_6\text{H}_3(\text{OMe})_2-2,6]$  reacts with iridium trichloride in propan-2-ol to give the purple five-coordinate hydride  $[\text{IrH}\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBU}^t_2-2)\}_2]$  (1). This hydride in solution is converted by air into the red paramagnetic iridium(II) complex  $[\text{Ir}\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBU}^t_2-2)\}_2]$  (3) which can be converted back to (1) when treated with  $\text{Na}[\text{BH}_4]$ . The hydride (1) takes up small ligands (L) such as pyridine or carbon monoxide reversibly to give colourless adducts  $[\text{IrL}\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBU}^t_2-2)\}_2]$ . Complex (3) takes up dioxygen reversibly to give a purple complex, probably  $[\text{Ir}(\text{O}_2)\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBU}^t_2-2)\}_2]$ , reacts with NO to give brown diamagnetic  $[\text{Ir}(\text{NO})\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBU}^t_2-2)\}_2]$  and with CO to give a pale green complex which in air becomes intensely blue, then red, and finally gives the colourless *C*-cyclometallated iridium(III) complex  $[\text{Ir}(\text{CO})\{\text{CH}_2\text{CMe}_2\text{PBU}^t\text{C}_6\text{H}_3(\text{OMe})\text{O}\}\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBU}^t_2-2)\}]$  (7; L = CO). The dioxygen adduct is slowly converted into the purple, co-ordinatively unsaturated, *C*-cyclometallated complex



Complex (8) takes up small ligands such as CO, pyridine, or MeNC more strongly than (1) to give six-coordinate species. The structure of the title complex (7; L = MeNC) has been determined by X-ray diffraction. The crystals are monoclinic, space group  $P2_1/c$ , with  $a = 13.471(2)$ ,  $b = 16.043(3)$ ,  $c = 16.690(3)$  Å, and  $\beta = 104.22(1)^\circ$ . The complex has a five-membered  $\text{IrPC}_2\text{O}$  chelate ring bound to a highly strained four-membered  $\text{IrPC}_2$  ring. Complex (8) also takes up  $\text{PMe}_2\text{Ph}$ ; this addition is reversed on heating and the <sup>31</sup>P n.m.r. spectrum at 300 K shows that rapid  $\text{PMe}_2\text{Ph}$  exchange occurs (at 233 K exchange does not occur). Treatment of iridium carbonyl chloride solutions with  $\text{PBU}^t_2[\text{C}_6\text{H}_3(\text{OMe})_2-2,6]$  and  $\text{PBU}^t_2[\text{C}_6\text{H}_3(\text{OMe})_2-2,3]$  gives yellow complexes of the type  $[\text{IrH}(\text{CO})\{\text{OC}_6\text{H}_3(\text{OMe}-6)(\text{PBU}^t_2-2)\}_2]$ , isomeric and much more stable than the one described above. Hydrogen-1, <sup>13</sup>C, and <sup>31</sup>P n.m.r. and i.r. data are given.

We have described some unusual complexes of Ir<sup>III</sup>, Ir<sup>II</sup>, and Ir<sup>I</sup> formed from the bulky ligands  $\text{PBU}^t_2(\text{C}_6\text{H}_4\text{OH}-2)$  and  $\text{PBU}^t_2(\text{C}_6\text{H}_4\text{OMe}-2)$ .<sup>1,2</sup> In particular, a planar iridium(I) complex  $[\text{Ir}(\text{CO})\{\text{OC}_6\text{H}_4(\text{PBU}^t_2-2)\}\{\text{PBU}^t_2(\text{C}_6\text{H}_4\text{OH}-2)\}]$  was treated with air to give a purple five-coordinate iridium(III) hydride,  $[\text{IrH}\{\text{OC}_6\text{H}_4(\text{PBU}^t_2-2)\}_2]$ , which in turn was treated with dioxygen to give a red four-coordinate iridium(II) complex,  $[\text{Ir}\{\text{OC}_6\text{H}_4(\text{PBU}^t_2-2)\}_2]$ , and finally a purple *C*-metallated five-coordinate iridium(III) species,  $[\text{Ir}(\text{CH}_2\text{CMe}_2\text{PBU}^t\text{C}_6\text{H}_4\text{O})\{\text{OC}_6\text{H}_4(\text{PBU}^t_2-2)\}]$ .

In these, and related, reactions steric and conformational effects of the bulky ligands are clearly very important and it was therefore of interest to study some iridium chemistry with even more bulky ligands of a related type. We here describe our work with the ligands  $\text{PBU}^t_2\text{R}$  (R = 2,3- or 2,6-dimethoxyphenyl).<sup>3</sup> A preliminary account of some of this work has been published.<sup>1</sup>

† No reprints available.

<sup>1</sup> R. Mason, K. M. Thomas, H. D. Empsall, S. R. Fletcher, P. N. Heys, E. M. Hyde, C. E. Jones, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1974, 612.

<sup>2</sup> H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J.C.S. Dalton*, 1975, 1690.

## RESULTS AND DISCUSSION

When a solution of hydrated iridium trichloride in propan-2-ol was heated with  $\text{PBU}^t_2[\text{C}_6\text{H}_3(\text{OMe})_2-2,6]$  for 60 h the purple five-coordinate iridium hydride (1) (Scheme) was formed (use of a primary alcohol as solvent was avoided so as to prevent a carbonyl-abstraction reaction). The analogous complex  $[\text{IrH}\{\text{OC}_6\text{H}_4(\text{PBU}^t_2-2)\}_2]$  of type (1) which was described previously<sup>2</sup> was made by a different route *viz.* the aerial oxidation of  $[\text{Ir}(\text{CO})\{\text{OC}_6\text{H}_4(\text{PBU}^t_2-2)\}\{\text{PBU}^t_2(\text{C}_6\text{H}_4\text{OH}-2)\}]$  (see above). The structure (1) follows from the microanalytical and molecular-weight data (Table 1) and the <sup>1</sup>H and <sup>31</sup>P n.m.r. data (Table 2). The two 1 : 2 : 1 triplet resonances at  $\delta$  1.37 and 1.45 p.p.m. for the *t*-butyl hydrogens indicate two pairs of *t*-butyl groups which are mutually *trans* and equivalent with no plane of symmetry through the phosphorus-iridium bonds. The hydride resonance pattern at very high field ( $\delta = -47.8$  p.p.m.) is characteristic of square-pyramidal five-coordinate iridium(III) hydrides of this type.<sup>4</sup> The <sup>31</sup>P n.m.r. spectrum consists of a singlet. No i.r. absorption band due to  $\nu(\text{Ir}-\text{H})$

<sup>3</sup> H. D. Empsall, P. N. Heys, and B. L. Shaw, *J.C.S. Dalton*, 1978, 257.

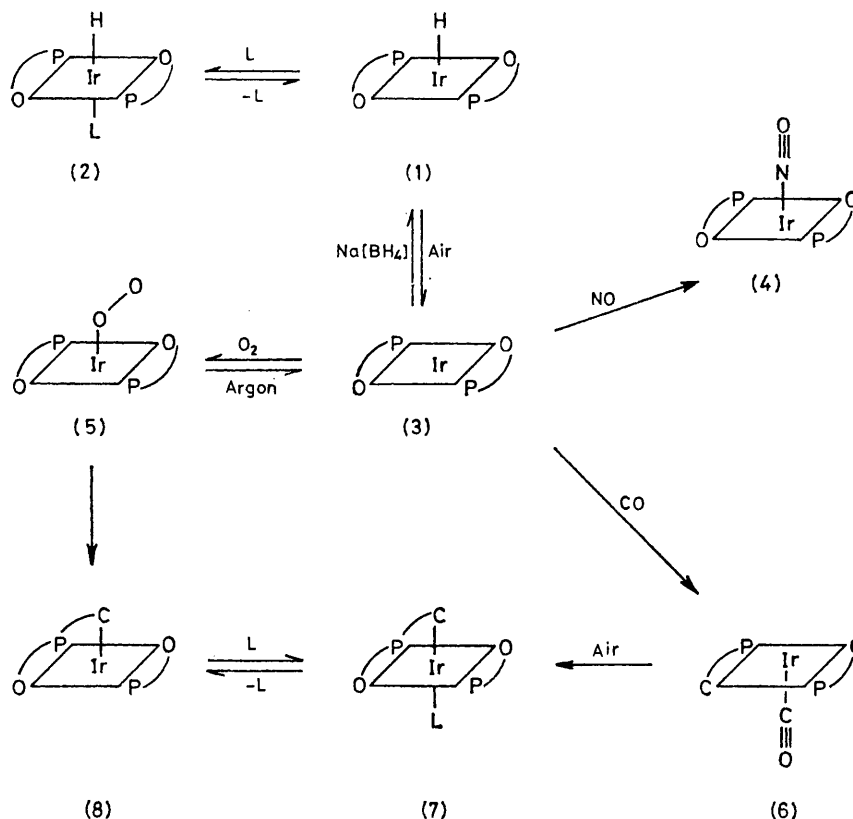
<sup>4</sup> C. Masters, B. L. Shaw, and R. E. Stainbank, *J.C.S. Dalton*, 1972, 664.

could be observed: often, absorption due to  $\nu(\text{Ir-H})$  in hydrides of this type is very weak or cannot be observed.

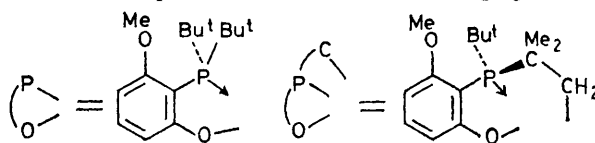
As expected, this purple co-ordinatively unsaturated complex readily took up small ligands (L) such as pyridine, carbon monoxide, or 4-methylpyridine to form colourless adducts (2). These addition reactions were

posed to air it rapidly became blood red. The conversion occurs more slowly in benzene but very rapidly in benzene-methanol (1 : 1). A deep red crystalline complex was isolated from these solutions. It was shown to be the planar iridium(II) complex

$\text{trans-}[\text{Ir}\{\text{OC}_6\text{H}_3(\text{OMe-3})\}(\text{P}^t\text{Bu}^t_2)_2]_2$  (3) by a single-



SCHEME Representations of the two chelating ligands:



readily reversible, an excess of added ligand being required to discharge the purple colour, and evaporation of the solvent (benzene) gave the five-co-ordinate hydride (1). Thus the solid adducts were not obtained pure, but their formation in solution was studied by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. and by i.r. spectroscopy (Table 2). The carbonyl adduct showed bands at  $2175\text{ cm}^{-1}$  due to  $\nu(\text{Ir-H})$  and at  $1990\text{ cm}^{-1}$  due to  $\nu(\text{C}\equiv\text{O})$  (in benzene solution). In the  $^1\text{H}$  n.m.r. spectrum of this carbonyl hydride the hydride absorbs at  $\delta = -7.07$  (t) p.p.m. [ $^2J(\text{PH})$  15 Hz]. The spectroscopic data for the pyridine adduct similarly showed it to have configuration (2).

**An Iridium(II) Complex.**—A purple solution of  $[\text{IrH}\{\text{OC}_6\text{H}_3(\text{OMe-3})\}(\text{P}^t\text{Bu}^t_2)_2]_2$ , configuration (1), in dichloromethane was stable under argon but when ex-

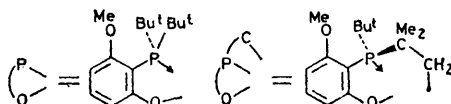
posed to air it rapidly became blood red. The conversion occurs more slowly in benzene but very rapidly in benzene-methanol (1 : 1). A deep red crystalline complex was isolated from these solutions. It was shown to be the planar iridium(II) complex  $\text{trans-}[\text{Ir}\{\text{OC}_6\text{H}_3(\text{OMe-3})\}(\text{P}^t\text{Bu}^t_2)_2]_2$  (3) by a single-crystal X-ray structural determination<sup>1</sup> and by magnetic measurements. At 298 K the magnetic molar susceptibility is  $1.08 \times 10^{-9}\text{ m}^3\text{ mol}^{-1}$ , measured for the solid by the Gouy method. A diamagnetic correction for the ligands of  $2.66 \times 10^{-10}\text{ m}^3\text{ mol}^{-1}$  was estimated from the molar susceptibility of  $\text{trans-}[\text{Pt}\{\text{OC}_6\text{H}_3(\text{OMe-3})\}(\text{P}^t\text{Bu}^t_2)_2]_2$ ,<sup>3</sup>  $\chi_m = 3.06 \times 10^{-10}\text{ m}^3\text{ mol}^{-1}$ , and Pascal's constants. This gives a magnetic moment for the iridium(II) complex of 1.78 B.M., close to the 'spin-only' value of 1.73 B.M. for one electron. The i.r. spectrum of (3) ( $250\text{--}4000\text{ cm}^{-1}$ ) is almost identical to that of the platinum analogue. When treated with  $\text{Na}[\text{BH}_4]$  in ethanol the iridium(II) species (3) was converted rapidly back into the hydrido-iridium(III) complex (2).

Previous to our preliminary note<sup>1</sup> no definite cases of

TABLE 1

Percentage yields, colours, melting points, and analytical data (calculated values in parentheses) for some iridium complexes

| Complex *  | Configur-<br>ation   | Yield<br>(%) | Colour | M.p.<br>(θ <sub>c</sub> /°C) | Analysis (%)         |                  |                | M             |              |
|--|--|--------------|--------|------------------------------|----------------------|------------------|----------------|---------------|--------------|
|  |  |              |        |                              | C                    | H                | N              |               |              |
| L = PBu <sub>2</sub> {2,6-C <sub>6</sub> H <sub>3</sub> (OMe) <sub>2</sub> }<br>[IrH(O-P) <sub>2</sub> ] | (1)  | 75           | Purple | 285—289 <sup>a</sup>         | 49.95<br>(49.5)      | 6.95<br>(6.80)   |                | 744<br>(728)  |              |
|  | [Ir(O-P) <sub>2</sub> ]  | (3)          | 78     | Red                          | 300—308 <sup>a</sup> | 49.9<br>(49.55)  | 6.65<br>(6.65) |               | 704<br>(727) |
|  | [Ir(NO)(O-P) <sub>2</sub> ]  | (4)          | 84     | Brown                        | 195—290 <sup>b</sup> | 47.9<br>(47.6)   | 6.35<br>(6.40) | 2.0<br>(1.85) |              |
|  | [Ir(O-P-C)(O-P)]   | (8)          | 88     | Purple                       | 228—232              | 49.6<br>(49.65)  | 6.45<br>(6.65) |               | 722<br>(726) |
|  | [Ir(O-P-C)(O-P)(py)]   | (7)          | 64     | White                        | 222—228 <sup>c</sup> | 52.3<br>(52.2)   | 6.5<br>(6.5)   |               |              |
|  | [Ir(CO)(O-P-C)(O-P)]   | (7)          | 79     | White                        | 215—218 <sup>c</sup> | 49.15<br>(49.4)  | 6.3<br>(6.3)   |               | 754<br>(754) |
|  | [Ir(PMe <sub>2</sub> Ph)(O-P-C)(O-P)]  | (7)          | 85     | Yellow                       | 138—141 <sup>c</sup> | 52.45<br>(52.8)  | 6.75<br>(7.0)  |               | 844<br>(846) |
|  | [Ir(CNMe)(O-P-C)(O-P)]   | (7)          | 81     | White                        | 238—242 <sup>c</sup> | 50.45<br>(50.15) | 6.55<br>(6.55) | 1.85<br>(1.9) | 765<br>(767) |
|  | [Ir(CO)H(O-P) <sub>2</sub> ]   | (10)         | 64     | Yellow                       | 234—238              | 49.15<br>(49.25) | 6.55<br>(6.55) |               | 748<br>(756) |
|  | L = PBu <sub>2</sub> {2,3-C <sub>6</sub> H <sub>3</sub> (OMe) <sub>2</sub> }<br>[Ir(CO)H(O-P) <sub>2</sub> ] | (10)         | 61     | Yellow                       | 195—200              | 49.2<br>(49.15)  | 6.55<br>(6.55) |               | 744<br>(756) |



<sup>a</sup> Decomposes without melting. <sup>b</sup> Sublimes. <sup>c</sup> Bubbles and forms prisms melting at 228—232 °C.

TABLE 2

Hydrogen-1<sup>a</sup> and <sup>31</sup>P<sup>b</sup> n.m.r. data, measured in CDCl<sub>3</sub>, unless stated otherwise: s = singlet, d = doublet, dd = doublet of doublets, t = triplet

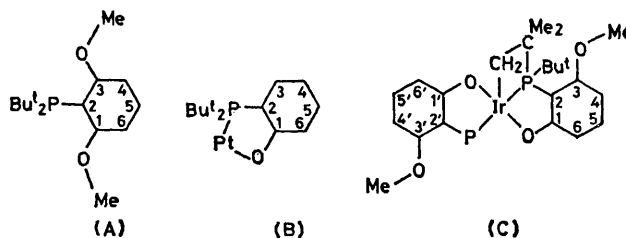
| Complex                          | <sup>1</sup> H |                     |                    |                  |                    | <sup>31</sup> P   |                    |
|----------------------------------|----------------|---------------------|--------------------|------------------|--------------------|-------------------|--------------------|
|                                  | δ(OMe)         | t-Butyls            |                    | Hydride          |                    | δ                 | <sup>2</sup> J(PP) |
|                                  |                | δ(Bu <sup>t</sup> ) | <sup>3</sup> J(PH) | δ(H)             | <sup>2</sup> J(PH) |                   |                    |
| (1)                              | 3.77 (s)       | 1.37 (t)            | 14.2 <sup>c</sup>  | -47.8 (t)        | 12                 | 70.0              |                    |
| (2) L = CO                       | 3.78 (s)       | 1.45 (t)            | 13.2 <sup>c</sup>  | -7.07 (t)        | 15                 |                   |                    |
|                                  |                | 1.42 (t)            | 15.2 <sup>c</sup>  |                  |                    |                   |                    |
| L = py                           | 3.70 (s)       | 1.40 (t)            | 13.8 <sup>c</sup>  | -22.85 (t)       | br                 | 56.0 <sup>d</sup> |                    |
| (4) <sup>e</sup>                 | 3.86 (s)       | 1.05 (t)            | 13.9 <sup>c</sup>  |                  |                    |                   |                    |
|                                  |                | 1.75 (t)            | 14.4 <sup>c</sup>  |                  |                    |                   |                    |
| (10) <sup>e</sup> X = OMe, Y = H | 3.77 (s)       | 1.39 (d)            | 10.3               | -17.58 (dd)      | 10.0               | 77.2              | 265                |
|                                  |                | 1.44 (d)            | 10.5               | 12.0             | 78.15              |                   |                    |
| X = H, Y = OMe                   | 3.47 (s)       | 1.41 (d)            | 10.5               | -18.1 (dd)       | 12.0               | 74.95             | 289                |
|                                  |                | 3.03 (s)            | 1.46 (d)           | 10.4             | 13.0               | 68.65             |                    |
|                                  |                | 1.64 (d)            | 11.0               |                  |                    | 64.5              |                    |
| (8) <sup>f</sup>                 | 3.78 (s)       | 1.64 (d)            | 16.0               | CMe <sub>2</sub> |                    | 53.7              | 331                |
|                                  |                | 1.35 (d)            | 15.5               | 1.67 (d)         | 15.5               |                   |                    |
|                                  |                | 1.16 (d)            | 14.0               | 0.82             | 14.0               |                   |                    |
| (7) L = py                       | 3.72 (s)       | 1.39 (d)            | 13.5               | 1.58 (d)         | 16.4               |                   |                    |
|                                  |                | 3.69 (s)            | 1.08 (d)           | 14.0             | 0.89 (d)           |                   |                    |
|                                  |                | 0.97 (d)            | 12.8               |                  |                    |                   |                    |
| L = CO                           | 3.80 (s)       | 1.55 (d)            | 16.1               | 1.61 (d)         | 16.8               | 58.8              | 300                |
| L = PMe <sub>2</sub> Ph          | 3.78 (s)       | 1.45 (d)            | 14.4               | 0.82 (d)         | 17.1               | -8.1              |                    |
|                                  |                | 3.53 (s)            | 1.84 (d)           | 11.2             | 2.18 (d)           | 17.3              | g                  |
|                                  |                | 3.30 (s)            | 9.3                | 1.25 (d)         | 15.2               |                   |                    |
| L = MeNC <sup>d</sup>            | 3.37 (s)       | 1.70 (d)            | 14.5               |                  |                    |                   |                    |
|                                  |                | 3.35 (s)            | 1.67 (d)           | 13.7             | 1.85 (d)           | 16.1              | 54.9               |
|                                  |                | 1.64 (d)            | 15.1               | 1.15 (d)         | 18.3               | -10.9             |                    |
|                                  |                | 1.48 (d)            | 12.9               |                  |                    |                   |                    |

<sup>a</sup> At 34 °C and 60 MHz, unless stated otherwise; δ ± 0.02 p.p.m.; J ± 0.2 Hz. <sup>b</sup> At 25 °C and 36.43 MHz, shifts relative to 85% H<sub>3</sub>PO<sub>4</sub>; δ ± 0.05 p.p.m., J ± 2 Hz. <sup>c</sup> [<sup>3</sup>J(PH) + <sup>5</sup>J(PH)]. <sup>d</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>e</sup> At 25 °C and 90 MHz. <sup>f</sup> Proton spectrum at 220 MHz and 21 °C. <sup>g</sup> See text for <sup>31</sup>P data. Proton spectrum at 34 °C in C<sub>6</sub>H<sub>6</sub>.

mononuclear iridium(II) complexes had been reported,<sup>5,6</sup> although several examples of diamagnetic species of type  $[\{\text{Ir}(\text{CO})_2\text{X}_2\}_n]$  ( $\text{X} = \text{halide}$ ) were known: these are

When nitrogen monoxide was bubbled through a solution of the iridium(II) complex (3) the solution turned brown and brown crystalline

TABLE 3



Carbon-13 n.m.r. data <sup>a</sup> for  $\text{PBu}^t_2[\text{C}_6\text{H}_3(\text{OMe})_{2-2,6}]$ ,  $[\text{Pt}\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBu}^t_2-2)\}_2]$ , and  $[\text{Ir}\{\text{CH}_2\text{CMe}_2\text{PBu}^t\text{C}_6\text{H}_3(\text{OMe}-6)\}\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBu}^t_2-2)\}]$  with the aryl carbons numbered as in A, B, and C respectively. Shifts (p.p.m.) relative to  $\text{SiMe}_4$  were recorded in  $\text{C}_6\text{D}_6$  at 25 °C and 22.62 MHz

|  | Aliphatic carbons |                                      |                                      | Aromatic carbons        |                                  |                                  |
|--|-------------------|--------------------------------------|--------------------------------------|-------------------------|----------------------------------|----------------------------------|
|  | Shift (p.p.m.)    | $J$ (Hz)                             | Assignment                           | Shift (p.p.m.)          | $J$ (Hz)                         | Assignment                       |
| $\text{PBu}^t_2[\text{C}_6\text{H}_3(\text{OMe})_{2-2,6}]$ (A)               | 30.7 (d)          | $^2J$ 17                             | $\text{C}(\text{CH}_3)_3$            | 103.3 (s), 104.35 (s)   |                                  | $\text{C}^4, \text{C}^6$         |
|  | 32.65 (d)         | $^1J$ 25                             | $\text{C}(\text{CH}_3)_3$            | 112.5 $^1J$ ca. 25      |                                  | $\text{C}^2$                     |
|  | 53.85 (s),        |                                      | $\text{OCH}_3$                       | 131.0 (s)               |                                  | $\text{C}^5$                     |
|  | 55.95 (s)         |                                      |                                      | 162.05 (d) $^2J$ 4      |                                  | $\text{C}^1, \text{C}^3$         |
|  |                   |                                      | 165.25 (d) $^2J$ 21                  |                         |                                  |                                  |
| $[\text{Pt}\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBu}^t_2-2)\}_2]$ (B) | 30.15 (s)         |                                      | $\text{C}(\text{CH}_3)_3$            | 95.85 (s), 111.7 (s)    |                                  | $\text{C}^4, \text{C}^6$         |
|  | 38.25 (t)         | $^1J + ^3J = 22$                     | $\text{C}(\text{CH}_3)_3$            | 133.2                   |                                  | $\text{C}^5$                     |
|  | 53.8 (s)          |                                      | $\text{OCH}_3$                       | 162.5 (s)               |                                  | $\text{C}^1$                     |
| (8) (C)  | -7.0              | $^2J$ 23                             | $\text{Ir}-\text{CH}_2$              | 184.2 (d) $^2J$ 7       |                                  | $\text{C}^3$                     |
|  | 23.0 (s)          |                                      | $\text{IrCH}_2\text{C}(\text{CH}_3)$ | 96.4 (s)                |                                  | $\text{C}^5, \text{C}^{6'}$      |
|  | 28.8 (s)          |                                      | $\text{IrCH}_2\text{C}(\text{CH}_3)$ | $\{103.5 (d) ^b ^1J 40$ |                                  | $\text{C}^2$ and $\text{C}^{2'}$ |
|  | 28.8 (s)          |                                      | $\text{C}(\text{CH}_3)_3$            | $\{104.0 (d) ^1J 37$    |                                  |                                  |
|  |                   |                                      |                                      | or                      |                                  |                                  |
|  |                   |                                      |                                      | $\{102.8 (d) ^1J 14$    |                                  |                                  |
|  |                   |                                      |                                      | $\{104.5 (d) ^1J 10$    |                                  |                                  |
|  | 30.35 (s)         |                                      | $\text{C}(\text{CH}_3)_3$            |                         |                                  |                                  |
|  | 34.9 (d)          | $^1J$ 19                             | $\text{C}(\text{CH}_3)_3$            | 114.3 (s), 114.6 (s)    |                                  | $\text{C}^4$ and $\text{C}^{4'}$ |
|  | 35.7 (d)          | $^1J$ 19                             |                                      |                         |                                  |                                  |
| 46.15 (d)  | $^1J$ 21          | or                                   | 133.1 (s), 133.3 (s)                 |                         | $\text{C}^5$ and $\text{C}^{5'}$ |                                  |
| 61.3 (d)   | $^1J$ 24          | $\text{CH}_2\text{C}(\text{CH}_3)_2$ | 162.9 (s)                            |                         | $\text{C}^1$ and $\text{C}^{1'}$ |                                  |
| 53.7, 53.95  |                   | $\text{OCH}_3$                       | 184.9 (dd) $^2J$ 16,                 |                         | $\text{C}^3$ and $\text{C}^{3'}$ |                                  |
|  |                   |                                      | $^4J$ 6                              |                         |                                  |                                  |
|  |                   |                                      | 186.6 (dd) $^2J$ 18,                 |                         |                                  |                                  |

<sup>a</sup> Many of the resonances due to aromatic carbons could not be assigned unambiguously, e.g. we could not distinguish between corresponding carbons in the two aromatic rings in C.  $J$  values ( $\pm 3$  Hz) are for couplings between  $^{13}\text{C}$  and  $^{31}\text{P}$ . <sup>b</sup> These pairs of doublets were close together and we could not distinguish between the two interpretations.

probably iridium(II) species with metal-metal bonds. The nitrosyl complex  $[\text{IrBr}_3(\text{NO})(\text{PPh}_3)_2]$  is paramagnetic and may be regarded as containing  $\text{Ir}^{\text{II}}$  if the nitrosyl ligand is assigned a positive charge. There is evidence of transient iridium(II) species in some oxidative-addition reactions of iridium(I) to iridium(III) complexes,<sup>7,8</sup> and in the decomposition of hydroperoxides catalysed by iridium(I) complexes.<sup>9</sup>

We also followed spectrophotometrically the conversion of the purple hydrido-iridium(III) complex (1) into the red iridium(II) complex (3) in benzene. The conversion shows a well defined isosbestic point at 547 nm. Species (1) was stable when oxygen was rigorously excluded.

<sup>5</sup> W. P. Griffith, 'The Chemistry of the Rarer Platinum Metals,' Interscience, London, 1967.

<sup>6</sup> S. E. Livingstone in 'Comprehensive Inorganic Chemistry,' Pergamon, Oxford, 1973, vol. 3, p. 1263.

<sup>7</sup> J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1972, **94**, 4043.

$[\text{Ir}(\text{NO})\{\text{OC}_6\text{H}_3(\text{OMe}-3)(\text{PBu}^t_2-2)\}_2]$  (4) formed. The i.r. spectrum shows a band at  $1745 \text{ cm}^{-1}$  due to  $\nu(\text{N}\equiv\text{O}^+)$ .<sup>10</sup> This nitrosyl complex is very stable; for example in deuteriochloroform a solution of the complex was unchanged after 7 d (as judged from the  $^1\text{H}$  n.m.r. pattern). As described below, the iridium(II) complex (3) reacts with a number of oxidizing agents, e.g.  $\text{Cl}_2$ ,  $\text{FeCl}_3$ ,  $\text{H}_2\text{O}_2$ , and  $\text{O}_2$ , but the products are unstable and we were unable to isolate them in a solid state. When a red benzene solution of complex (3) was treated with  $\text{Cl}_2-\text{CCl}_4$  a deep green solution formed immediately. Similarly, treatment with an  $\text{FeCl}_3$  solution in ethanol gave a deep green solution. Addition of hydrogen peroxide to a benzene-ethanol solution complex (3) gave a purple

<sup>8</sup> J. A. Labinger, A. V. Kramer, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1973, **95**, 7908.

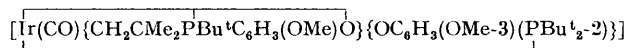
<sup>9</sup> B. L. Booth, R. N. Haszeldine, and G. R. Neuss, *J.C.S. Perkin I*, 1975, 209.

<sup>10</sup> J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

solution. When dioxygen was bubbled through a chloroform solution of the red iridium(II) species a purple solution was formed (no colour change being observed with benzene as solvent). The red colour re-formed when the chloroform solution was degassed with argon. The interconversion of the red-purple solutions was repeated a number of times and also followed spectrophotometrically. We suggest that the purple species is a dioxygen adduct, and formulate it with end-on bonded dioxygen as in (5) since molecular models suggest that the very bulky t-butyl groups will prevent side-on or  $\pi$ -bonded dioxygen. The analogous

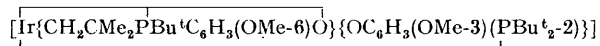
iridium(II) complex  $[\text{Ir}\{\text{OC}_6\text{H}_4(\text{PBu}^t_2)_2\}_2]$  did not show reversible uptake of dioxygen to a significant extent, *i.e.* there was no colour change on bubbling dioxygen through its solution. Thus the additional methoxy-groups increase the stability of the dioxygen adduct relative to the four-co-ordinate iridium(II) complex. The dioxygen adduct may be an iridium(III) hyperoxide, analogous to the well known cobalt(III) hyperoxides, formed by the addition of dioxygen to some planar cobalt(II) complexes.<sup>11</sup>

When carbon monoxide was bubbled through a benzene solution of complex (3) a pale green solution was produced which rapidly became deep blue when exposed to air. The blue colour gradually faded over several hours and passed through a pale red stage, eventually becoming almost colourless. The changes were followed by i.r. spectroscopy. The green solution shows a strong band due to  $\nu(\text{C}=\text{O})$  at  $2\ 050\ \text{cm}^{-1}$ , the blue solution several bands at  $1\ 980\text{--}2\ 050\ \text{cm}^{-1}$ , and the final pink solution a strong band at  $1\ 996\ \text{cm}^{-1}$ . From this pink solution the colourless six-co-ordinate carbonyl complex



(7; L = CO), containing a metallated t-butyl group, was isolated. We suggest that the green species was an iridium(II) carbonyl complex (6) which in air was converted *via* unknown intermediate stages into (7).

*A C-Metallated Iridium(III) Complex.*—A benzene solution of complex (3) when exposed to the air gradually turns purple over 14 h and a purple crystalline material was isolated from this solution. The structure

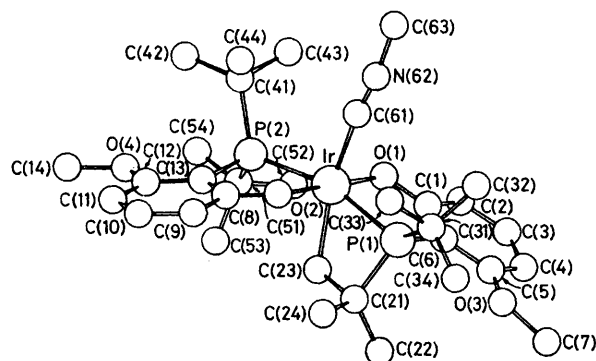


(8) was assigned on the basis of microanalytical and molecular-weight measurements,  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{13}\text{C}$  n.m.r. data, and from the single-crystal X-ray structural determination of the methyl isocyanide adduct (see below). The 60-MHz  $^1\text{H}$  n.m.r. spectrum of this C-metallated species is complicated in the  $\delta$  0.5–2 p.p.m. region, but at 220 MHz the spectrum shows three t-butyl doublets at 1.64, 1.35, and 1.16 p.p.m. [ $^3J(\text{PH})$

<sup>11</sup> B. M. Hoffmann, T. Szymanski, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 673.

<sup>12</sup> J. B. Stothers in 'Carbon-13 N.M.R. Spectroscopy,' A series of monographs, vol. 23, Academic Press, New York, London, 1972.

16.0, 15.5, and 14.4 Hz respectively] and two doublets having one-third the intensity due to the geminal methyl groups at 1.58 and 0.89 p.p.m. [ $^3J(\text{PH})$  16.4 and 16.2 Hz respectively]. There is also a complex multiplet of low intensity in the 2–0.5 p.p.m. region which we assign to the methylene group attached to the iridium. The  $^{31}\text{P}$  n.m.r. spectrum shows an AB pattern (Table 2). The  $^{13}\text{C}$  n.m.r. spectral data with possible assignments are shown in Table 3, data for the free phosphine  $\text{PBu}^t_2$ - $[\text{C}_6\text{H}_3(\text{OMe})_2$ -2,6] and *trans*- $[\text{Pt}\{\text{OC}_6\text{H}_3(\text{OMe-3})(\text{PBu}^t_2)_2\}_2]$  being given for comparison. A feature is the high-field doublet of the metallated carbon,  $\text{CH}_2\text{CMe}_2$ . The other assignments are based on published data,<sup>12,13</sup> by



ORTEP drawing of the molecular structure of complex (7; L = MeNC). The iridium, nitrogen, phosphorus, and oxygen atoms are indicated; the other numbered atoms are all carbons. See Tables 4, 5, and the Experimental section for bond lengths, angles, and other data

comparison with chemical shifts and coupling constants for the other two compounds (Table 3), and from the relative intensities and coupling constants. Surprisingly, two of the quaternary t-butyl carbons resonate at relatively low field, *viz.*  $\delta$  46.15 and 61.3 p.p.m.

The purple cyclometallated complex (8) readily reacts with small donor ligands such as pyridine, carbon monoxide, dimethyl(phenyl)phosphine, or methyl isocyanide to give six-co-ordinate species of configuration (7). The pyridine adduct (7; L = pyridine) forms white prisms which on heating to *ca.* 230 °C evolve pyridine and reform the five-co-ordinate complex (8). The carbon monoxide adduct was readily prepared and shown to be identical with the product obtained from the green iridium(II) carbonyl (6) by aerial oxidation. The structure of the methyl isocyanide adduct has been determined by single-crystal X-ray diffraction. We first examined the carbonyl complex (7; L = CO) but found it to contain two molecules per asymmetric unit and we therefore turned our attention to the methyl isocyanide adduct. The atomic co-ordinates of the non-hydrogen atoms are given in Table 4, the molecular structure and atom numbering are shown in the Figure, and principal bond lengths and angles are given in Table 5.

<sup>13</sup> B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135 and refs. therein.

The analysis confirms the formation of a four-membered IrPC<sub>2</sub> ring by internal metallation of a *t*-butyl

TABLE 4

Fractional co-ordinates *x*, *y*, *z* with estimated standard deviations in parentheses for complex (7; L = MeNC)

|       |              |              |              |
|-------|--------------|--------------|--------------|
| Ir    | 0.426 79(2)  | 0.278 03(2)  | 0.371 69(2)  |
| P(1)  | 0.590 43(15) | 0.232 83(14) | 0.427 98(14) |
| P(2)  | 0.258 65(15) | 0.292 10(13) | 0.283 42(14) |
| O(1)  | 0.499 6(5)   | 0.367 1(4)   | 0.317 7(4)   |
| O(2)  | 0.355 8(4)   | 0.188 7(4)   | 0.425 7(4)   |
| C(1)  | 0.599 1(7)   | 0.361 5(6)   | 0.326 7(5)   |
| C(2)  | 0.646 0(9)   | 0.420 9(7)   | 0.283 3(6)   |
| C(3)  | 0.749 1(10)  | 0.417 2(9)   | 0.291 1(7)   |
| C(4)  | 0.810 6(9)   | 0.357 7(10)  | 0.338 1(9)   |
| C(5)  | 0.764 4(7)   | 0.300 8(7)   | 0.381 5(7)   |
| C(6)  | 0.661 8(7)   | 0.302 2(6)   | 0.378 2(6)   |
| O(3)  | 0.820 1(6)   | 0.239 6(7)   | 0.430 9(6)   |
| C(7)  | 0.922 1(10)  | 0.229 7(15)  | 0.429 7(12)  |
| C(8)  | 0.266 9(6)   | 0.159 3(5)   | 0.384 1(6)   |
| C(9)  | 0.231 8(7)   | 0.085 7(6)   | 0.415 8(7)   |
| C(10) | 0.138 0(8)   | 0.052 9(7)   | 0.376 7(8)   |
| C(11) | 0.076 3(8)   | 0.088 4(7)   | 0.306 1(9)   |
| C(12) | 0.111 5(7)   | 0.158 7(7)   | 0.274 7(8)   |
| C(13) | 0.207 3(7)   | 0.195 9(6)   | 0.312 3(7)   |
| O(4)  | 0.057 4(6)   | 0.198 0(6)   | 0.203 7(7)   |
| C(14) | -0.040 5(12) | 0.165 9(13)  | 0.164 7(13)  |
| C(21) | 0.567 9(8)   | 0.136 8(6)   | 0.366 8(6)   |
| C(22) | 0.648 9(8)   | 0.107 8(8)   | 0.325 2(9)   |
| C(23) | 0.472 1(7)   | 0.178 0(6)   | 0.302 1(6)   |
| C(24) | 0.531 3(9)   | 0.063 4(6)   | 0.410 4(7)   |
| C(31) | 0.647 5(7)   | 0.225 2(7)   | 0.541 7(6)   |
| C(32) | 0.687 3(8)   | 0.311 3(8)   | 0.571 6(7)   |
| C(33) | 0.562 2(8)   | 0.202 4(7)   | 0.582 3(7)   |
| C(34) | 0.733 3(8)   | 0.160 7(9)   | 0.567 5(7)   |
| C(41) | 0.177 2(7)   | 0.377 0(6)   | 0.312 5(7)   |
| C(42) | 0.233 6(10)  | 0.460 4(7)   | 0.313 0(8)   |
| C(43) | 0.065 4(9)   | 0.383 1(9)   | 0.265 1(9)   |
| C(44) | 0.172 8(8)   | 0.356 6(8)   | 0.403 0(8)   |
| C(51) | 0.251 5(8)   | 0.297 2(7)   | 0.167 1(7)   |
| C(52) | 0.338 7(8)   | 0.351 5(9)   | 0.155 5(7)   |
| C(53) | 0.262 8(12)  | 0.209 5(9)   | 0.136 6(8)   |
| C(54) | 0.152 5(8)   | 0.333 0(10)  | 0.111 5(8)   |
| C(61) | 0.417 1(7)   | 0.361 1(6)   | 0.457 7(6)   |
| N(62) | 0.420 9(7)   | 0.406 4(5)   | 0.511 8(6)   |
| C(63) | 0.415 6(12)  | 0.461 0(8)   | 0.578 1(8)   |

group, and shows that the resulting tridentate ligand occupies *facial* positions in the octahedral complex. Four-membered MPC<sub>2</sub> rings of this type have been characterized crystallographically.<sup>14-16</sup>

In the present complex the strain in the four-membered ring is evident in the 67° angle at the metal and the angles of 92° at P and 91° at C(21), although the angle at C(23) of 104° is only slightly less than normal. The Ir-P(1) bond length [2.291(2) Å] is substantially less than Ir-P(2) [2.390(2) Å] and is presumably compressed as a result of ring strain, while the opposite bond in the ring [C(21)-C(23) 1.606(13) Å] is significantly lengthened from its normal value. There is a substantial departure from planarity in this ring, with an Ir-P(1)-C(21)-C(23) torsion angle of 20° relieving the eclipsed interaction of the two methyl groups on C(21) with the *t*-butyl and phenyl groups on P(1). There is also an associated loss of planarity in the fused five-membered chelate ring; in iridium (II) complexes of type (3) the chelate rings are quite accurately planar.<sup>1</sup> The

<sup>14</sup> G. Perego, G. del Piero, M. Cesari, M. G. Clerici, and E. Perotti, *J. Organometallic Chem.*, 1973, **54**, C51-C52.

<sup>15</sup> R. Countryman and W. S. McDonald, *Acta Cryst.*, 1977, **B33**, 3580.

methyl isocyanide ligand departs slightly from linearity, and the Ir-C(61) bond length [1.99(1) Å] is probably substantially lengthened by the *trans* influence of the Ir-C(23) bond. The <sup>1</sup>H and <sup>31</sup>P n.m.r. data and i.r. data for this methyl isocyanide adduct (7; L = MeNC) are given in Table 2. Analytical and spectroscopic data for the corresponding carbon monoxide and pyridine adducts are given in Tables 1 and 2 and clearly confirm the assigned structures.

TABLE 5

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

|                       |           |                    |           |
|-----------------------|-----------|--------------------|-----------|
| Ir-P(1)               | 2.291(2)  | Ir-O(2)            | 2.050(6)  |
| Ir-O(1)               | 2.062(7)  | Ir-C(61)           | 1.987(10) |
| Ir-C(23)              | 2.155(10) | P(2)-C(13)         | 1.805(10) |
| P(1)-C(6)             | 1.802(16) | P(2)-C(41)         | 1.886(11) |
| P(1)-C(21)            | 1.832(11) | P(2)-C(51)         | 1.921(11) |
| P(1)-C(31)            | 1.868(10) | O(2)-C(8)          | 1.316(10) |
| O(1)-C(1)             | 1.315(11) | O(4)-C(12)         | 1.382(15) |
| O(3)-C(5)             | 1.380(14) | O(4)-C(14)         | 1.416(19) |
| O(3)-C(7)             | 1.388(17) | C(61)-N(62)        | 1.151(14) |
| C(21)-C(23)           | 1.606(13) | N(62)-C(63)        | 1.426(17) |
| C-C(Bu <sup>t</sup> ) | 1.504(19) | C-C (benzene ring) | 1.364(18) |
|                       | 1.559(18) |                    | 1.434(15) |
|                       | 2.390(2)  |                    |           |
| Ir-P(2)               |           | P(2)-Ir-O(2)       | 82.2(2)   |
| P(1)-Ir-O(1)          | 83.4(2)   | P(2)-Ir-C(23)      | 95.1(2)   |
| P(1)-Ir-C(23)         | 67.3(2)   | O(2)-Ir-C(23)      | 86.6(3)   |
| O(1)-Ir-C(23)         | 93.0(3)   | P(2)-Ir-C(61)      | 99.3(2)   |
| P(1)-Ir-C(61)         | 98.2(2)   | O(2)-Ir-C(61)      | 91.8(3)   |
| O(1)-Ir-C(61)         | 88.5(3)   | O(1)-Ir-O(2)       | 179.4(2)  |
| P(1)-Ir-P(2)          | 160.4(1)  | C(61)-N(62)-C(63)  | 174.6(11) |
| C(23)-Ir-C(61)        | 165.1(3)  | Ir-O(2)-C(8)       | 118.8(6)  |
| Ir-O(1)-C(1)          | 118.9(5)  | O(2)-C(8)-C(13)    | 124.0(8)  |
| O(1)-C(1)-C(6)        | 123.8(9)  | C(8)-C(13)-P(2)    | 114.3(7)  |
| C(1)-C(6)-P(1)        | 112.9(7)  | C(13)-P(2)-Ir      | 97.0(3)   |
| C(6)-P(1)-Ir          | 100.6(3)  | C(5)-O(3)-C(7)     | 117.9(13) |
| Ir-P(1)-C(21)         | 91.5(3)   | C(12)-O(4)-C(14)   | 117.6(12) |
| P(1)-C(21)-C(23)      | 91.4(6)   |                    |           |
| C(21)-C(23)-Ir        | 103.6(5)  |                    |           |

When PMe<sub>2</sub>Ph was added to a benzene solution of the co-ordinatively unsaturated cyclometallated complex (8) a colourless solution formed and the adduct (7; L = PMe<sub>2</sub>Ph) was isolated as white needles. This behaviour contrasts with that of the five-co-ordinate hydride (1) for which there was no apparent reaction with PMe<sub>2</sub>Ph under similar conditions. The cause of this difference in affinity is probably two-fold: (i) the *trans*-bond-weakening effect of hydride is somewhat greater than that of carbon; and (ii) the disruption from planarity of the two five-membered chelate rings in (8) due to the presence of the four-membered ring 'exposes' the sixth co-ordination site which can thus accommodate a relatively large ligand such as PMe<sub>2</sub>Ph. We have shown previously that the steric effect of a ligand L controls its affinity for five-co-ordinate iridium hydrides of the type [IrHCl<sub>2</sub>(PBU<sup>t</sup><sub>2</sub>R)<sub>2</sub>] (R = alkyl).<sup>17</sup> However, the adduct (7; L = PMe<sub>2</sub>Ph) was less stable than the corresponding adducts with CO, MeNC, or pyridine and dissociated at ca. 140 °C to give the free phosphine and the purple five-co-ordinate complex (8). Moreover, the <sup>31</sup>P n.m.r. spectrum of (7; L = PMe<sub>2</sub>Ph) in C<sub>6</sub>D<sub>6</sub> at 300 K shows an

<sup>16</sup> R. J. McKinney, C. B. Knobler, B. T. Huie, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1977, **99**, 2988.

<sup>17</sup> B. L. Shaw and R. E. Steinbank, *J.C.S. Dalton*, 1972, 2108.

AB pattern with  $\delta_A$  49.1,  $\delta_B = -19.2$  p.p.m., and  $^2J$ -( $P_A P_B$ ) 346 Hz together with a singlet at  $\delta = -47.0$  p.p.m., *i.e.* the P of  $PMe_2Ph$  is apparently not coupled to the other phosphorus nuclei. The chemical shift for free  $PMe_2Ph$  in this solvent is  $-46.9$  p.p.m.<sup>18</sup> The absence of coupling is probably due to rapid chemical exchange between free and complexed  $PMe_2Ph$  since at 233 K in a mixture of toluene- $C_6D_6$  (4:1) an ABC pattern is obtained for which  $J(AC)$  and  $J(BC)$  can be observed although they are small (*i.e.* these are *cis* couplings) whereas  $|J(AB)|$  is a *trans* coupling and is large:  $\delta_A$  46.6,  $\delta_B = -20.5$ ,  $\delta_C = -46.6$  p.p.m.;  $J(AC)$  17,  $J(BC)$  7.3, and  $J(AB)$  343 Hz.

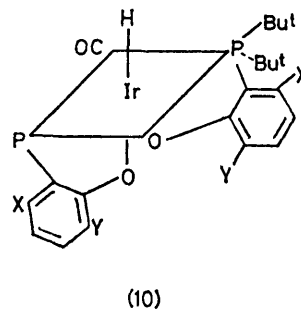
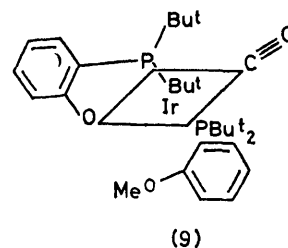
The  $^1H$  n.m.r. spectrum at *ca.* 300 K shows resonances at 3.53 and 3.30 p.p.m. due to  $OCH_3$ , three *t*-butyl doublet resonances at 1.64, 1.53, and 0.9 p.p.m. [ $^3J(PH)$  13.6, 14.1, and 12.5 Hz], and four methyl doublets at 1.27, 1.23, 1.19, and 0.98 p.p.m. [ $^3J(PH)$  13.9, 12.5, 13.4, and 14.9 Hz respectively]. Two methyl signals are due to the non-equivalent  $PMe_2Ph$  methyls and the other two to the non-equivalent methyls of the metallated *t*-butyl group. At 223 K the  $^1H$  n.m.r. spectrum is considerably broadened. The broadening may be in part due to restricted rotation around some bonds in this crowded molecule, but is also in part due to small couplings to remote phosphorus nuclei. Some of these couplings are effectively removed at room temperature due to rapid  $PMe_2Ph$  exchange.

We have also investigated the action of the very bulky ligand  $PBu_2^t[C_6H_3(OMe)_2-2,6]$  with a solution of an iridium carbonyl chloride. We have shown previously that when  $PBu_2^t(C_6H_4OMe-2)$  is heated under reflux with the yellow solution formed by passing carbon monoxide through a boiling 2-methoxyethanol solution of sodium chloroiridate the bright yellow iridium(I) complex

$[Ir(CO)\{OC_6H_4(PBu_2^t-2)\}\{PBu_2^t(C_6H_4OMe-2)\}]$ , configuration (9), is formed.<sup>2</sup> We now find that when  $PBu_2^t[C_6H_3(OMe)_2-2,6]$  is heated with the 2-methoxyethanol solution of carbonylated  $Na_3[IrCl_6]$  both phosphine ligands are demethylated and the yellow iridium-

(III) carbonyl hydride  $[IrH(CO)\{OC_6H_3(OMe-3)(PBu_2^t-2)\}_2]$ , configuration (10), is formed. This complex is much more stable than its isomer of configuration (2;  $L = CO$ ) and shows no tendency to lose carbon monoxide on heating. The assigned structure follows from the micro-analytical and molecular-weight (Table 1) and i.r. and n.m.r. data (Table 2). The i.r. spectrum shows a band at  $2\ 230\ cm^{-1}$  due to  $\nu(Ir-H)$ , a high value typical of hydrogen *trans* to a ligand donor atom of high electronegativity (*i.e.* oxygen). The band due to  $\nu(C=O)$  is at  $1\ 990\ cm^{-1}$  in Nujol and  $1\ 988\ cm^{-1}$  in benzene. The  $^{31}P$  n.m.r. spectrum shows a strongly coupled AB pattern characteristic of *trans*-bonded, non-equivalent, P-donor atoms. The  $^1H$  n.m.r. spectrum shows a double doublet hydride resonance at  $-17.6$  p.p.m. [ $^2J(PH)$  10.0 and 12.0

Hz] and two signals due to the  $OCH_3$  groups. Two doublets at 1.39 and 1.44 p.p.m. [ $^3J(PH)$  10.25 and 10.5 Hz respectively] are due to two *t*-butyl groups, but there is also a complex multiplet in this region suggesting that the pattern of the other two *t*-butyls is complex due to restricted rotation caused by steric interactions with other groups (probably  $OCH_3$ ) in this extremely crowded molecule. We have not investigated the  $^1H$  n.m.r. pattern at higher temperatures, but the other evidence discussed above is overwhelmingly in favour of configuration (10). We have similarly made an isomeric



complex of configuration (10;  $X = H$ ,  $Y = OMe$ ) from the ligand  $PBu_2^t[C_6H_3(OMe)_2-2,3]$ . Characterizing data for this complex are given in Tables 1 and 2, and are similar to those for the isomer described above, *i.e.* (10;  $X = OMe$ ,  $Y = H$ ). In this case, however, the four non-equivalent *t*-butyl groups each give a doublet pattern, presumably because the methoxy-groups are too far away to interfere with the free rotation of the *t*-butyl groups. Both these complexes of configuration (10) are unaffected by treatment with either  $Na[BH_4]$  in ethanol or by sodium methoxide in boiling methanol.

We also studied the action of  $PBu_2^t[C_6H_3(OMe)_2-2,3]$  on iridium trichloride in boiling propan-2-ol for 3 d. A purple solid product was obtained but we were unable to isolate a pure complex from it. However, the  $^1H$  n.m.r. spectrum of the crude product suggested the presence of a hydride of configuration [1;  $P-O = OC_6H_3(OMe-6)(PBu_2^t-2)$ ] with a high-field 1:2:1 triplet at  $\delta = -47.7$  p.p.m. [ $^2J(PH) = 11.5$  Hz] and two 1:2:1 resonances at 1.63 and 1.62 p.p.m. [ $^3J(PH) + ^5J(PH)$  13.8 and 14.1 Hz respectively]. When a chloroform solution of this purple product was exposed to the air it gradually turned red (over 5 h) but some metal was also deposited.

<sup>18</sup> M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 19.

Possibly an iridium(II) species was formed but the oxidation goes much more slowly than with the corresponding five-co-ordinate hydride (1) formed from  $\text{PBUt}_2[\text{C}_6\text{H}_3(\text{OMe})_2]_2$ .

#### EXPERIMENTAL

Melting points were determined in a Kofler hot-stage apparatus and are corrected. The general techniques and instruments used were the same as those described previously.<sup>2</sup>

*Bis[2-(di-t-butylphosphino)-3-methoxyphenoxo-OP]-hydrido-iridium(III)* (1).—*Method (a)*. (2,6-Dimethoxyphenyl)-di-t-butylphosphine (3.39 g, 12.0 mmol) was added to a warm suspension of hydrated iridium(III) chloride [1.10 g, 3.0 mmol in propan-2-ol (20 cm<sup>3</sup>)]. The resulting green slurry was heated under reflux for 66 h. The dark purple solution was then cooled at ca. -15 °C giving the required *product* (1) (1.07 g, 1.48 mmol, 49%) as purple prisms with some metallic impurity (very slight amount).

*Method (b)*. A solution of sodium tetrahydroborate (0.089 g, 2.39 mmol) in ethanol (10 cm<sup>3</sup>) was added to a stirred solution of *trans*-bis[2-(di-t-butylphosphino)-3-methoxyphenoxy-OP]iridium(II) (0.157 g, 0.239 mmol) in benzene (20 cm<sup>3</sup>). Evaporation of the solvent gave the required *product* (0.118 g, 0.175 mmol, 75%) as purple prisms.

*trans-Bis[2-(di-t-butylphosphino)-3-methoxyphenoxo-OP]-iridium(II)* (3).—A solution of (1) (0.493 g, 0.680 mmol) in benzene (20 cm<sup>3</sup>)-methanol (10 cm<sup>3</sup>) was left open to the atmosphere for 0.5 h. The resulting red solution was reduced in volume to ca. 10 cm<sup>3</sup> giving the required *product* (3) (0.372 g, 0.421 mmol, 78%) as red prisms.

*Bis[2-(di-t-butylphosphino)-3-methoxyphenoxo-OP]-nitrosyliridium*.—Nitrogen monoxide was bubbled through a solution of complex (3) (0.165 g, 0.227 mmol) in benzene for 5 min. Evaporation of the resulting brown solution to dryness and addition of methanol gave the *product* (0.146 g, 0.195 mmol, 84%) as brown prisms.

[2-(Di-t-butylphosphino)-3-methoxyphenoxo-OP]{2-[(2-hydroxy-6-methoxyphenyl)-t-butylphosphino]-2-methylpropanato(2-)-C<sup>1</sup>PO<sup>2</sup>}iridium(III).—A solution of complex (3) (0.317 g, 0.437 mmol) in benzene (15 cm<sup>3</sup>) was left open to the atmosphere for 20 h. Evaporation of the purple solution gave the *product* (8) (0.276 g, 0.381 mmol, 88%) as purple prisms.

[2-(Di-t-butylphosphino)-3-methoxyphenoxo-OP]{2-[(2-hydroxy-6-methoxyphenyl)-t-butylphosphino]-2-methylpropanato(2-)-C<sup>1</sup>PO<sup>2</sup>}pyridineiridium(III) (7; L = py).—Pyridine (0.148 g, 1.75 mmol) was added to a solution of complex (8) (0.109 g, 0.150 mmol) in benzene. The resulting solution was evaporated to dryness giving the *product* (7; L = py) (0.074 g, 0.092 mmol, 65%) as white prisms from benzene-methanol.

*Carbon Monoxide Adduct* (7; L = CO).—Carbon monoxide was bubbled through a solution of complex (8) (0.048 g, 0.066 mmol) in benzene (5 cm<sup>3</sup>) for 5 min. Evaporation of the resulting colourless solution gave the *product* (7; L =

CO) (0.039 g, 0.052 mmol, 79%) as white needles from dichloromethane-methanol.

*Dimethylphenylphosphine Adduct* (7; L = PMe<sub>2</sub>Ph).—Dimethylphenylphosphine (34.3 μl, 0.239 mmol) was added to a solution of complex (8) (0.158 g, 0.217 mmol) in benzene (15 cm<sup>3</sup>). The pale yellow solution was evaporated to dryness giving the *product* (7; L = PMe<sub>2</sub>Ph) (0.151 g, 0.181 mmol, 85%) as yellow needles from benzene-methanol.

*Methyl Isocyanide Adduct* (7; L = MeNC).—Methyl isocyanide (0.147 g, 1.75 mmol) was added to a solution of complex (8) (0.126 g, 0.174 mmol) in benzene (10 cm<sup>3</sup>). The resulting colourless solution was evaporated under reduced pressure to dryness giving the *product* (7; L = MeNC) (0.110 g, 0.144 mmol, 81%) as white needles from benzene-methanol.

*Carbonylbis[2-(di-t-butylphosphino)-3-methoxyphenoxo-OP]hydrido-iridium(III)* (6).—Carbon monoxide was bubbled through a boiling solution of sodium chloroiridate (0.722 g, 1.26 mmol) in 2-methoxyethanol (25 cm<sup>3</sup>) for 4 h. (2,6-Dimethoxyphenyl)di-t-butylphosphine (0.780 g, 2.77 mmol) was added to the resulting yellow solution and heating under reflux was continued for 1 h. The bright yellow solution was cooled at ca. -15 °C giving the *product* (6) (0.588 g, 0.778 mmol, 64%) as yellow prisms. *Carbonylbis[2-(di-t-butylphosphino)-6-methoxyphenoxo]hydrido-iridium(III)* was prepared in an analogous manner giving the *product* (0.637 g, 0.841 mmol, 61%) as yellow prisms.

*X-Ray Structural Determination*.—*Crystal data*. (7; L = CO), C<sub>31</sub>H<sub>47</sub>O<sub>5</sub>P<sub>2</sub>Ir, *M* = 754, Triclinic, space group *P1* or *P1̄*, *a* = 20.126(2), *b* = 19.975(5), *c* = 8.662(2) Å, α = 95.24(4), β = 93.10(5), γ = 103.92(1)°, *U* = 3 355 Å<sup>3</sup>, *D<sub>m</sub>* = 1.47 g cm<sup>-3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.473 g cm<sup>-3</sup>, *F*(000) = 1 520. (7; L = MeNC), C<sub>32</sub>H<sub>50</sub>IrNO<sub>4</sub>P<sub>2</sub>, *M* = 767, Monoclinic, space group *P2<sub>1</sub>/c*, *a* = 13.471(2), *b* = 16.043(3), *c* = 16.690(3) Å, β = 104.22(1)°, *U* = 3 496 Å<sup>3</sup>, *D<sub>m</sub>* = 1.47 g cm<sup>-3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.457 g cm<sup>-3</sup>, *F*(000) = 1 552.

Measurements were made on a Nonius CAD-4 diffractometer using monochromatized Cu-K<sub>α</sub> radiation (λ 1.541 8 Å). The cell dimensions were determined by a least-squares fit of sin θ values for 44 reflections centred using the program SETANG. Intensities were recorded in the θ—2θ scan mode. Of 6 609 independent reflections having θ < 70°, the 4 683 having *I* > 3σ(*I*) were used in the structure analysis. Solution by means of Patterson and difference syntheses followed by least-squares refinement of co-ordinates and anisotropic vibration parameters for the non-hydrogen atoms gave *R* 0.054. The hydrogen atoms were then located on a difference map; they were included with isotropic temperature factors equivalent to those of the carbons to which they are attached, but were not refined. The final value of *R* was 0.049; Σw(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup> was minimized, with the standard deviations from counting statistics modified to σ<sup>2</sup>(*I*) = σ<sub>c</sub><sup>2</sup>(*I*) + (0.051)<sup>2</sup> and *w*<sup>-1</sup> = σ<sup>2</sup>(*F*) = σ<sub>c</sub><sup>2</sup>(*F*) + 0.25(0.05*F*)<sup>2</sup>. Calculations used the 'X-RAY '72' programs and atomic scattering factors were taken from ref. 19.\*

We thank I.C.I. Ltd. for the award of a Fellowship (to H. D. E.), and the S.R.C. for support.

[7/1324 Received, 22nd July, 1977]

\* Observed and calculated structure-factor amplitudes, anisotropic thermal parameters, and hydrogen-atom co-ordinates are listed in Supplementary Publication No. SUP 22254 (34 pp.). For details see Notice to Authors No. 7, *J.C.S. Dalton* 1977, Index issue.

<sup>19</sup> 'International Tables for X-Ray Crystallography,' vol. IV, 1974, Kynoch Press, Birmingham.