Preparation and Characterisation of a Series of Cationic Monometallated, and Neutral and Cationic Tridentate Dimetallated, Tri-*o*-tolyl Phosphite Iridium(III) Complexes

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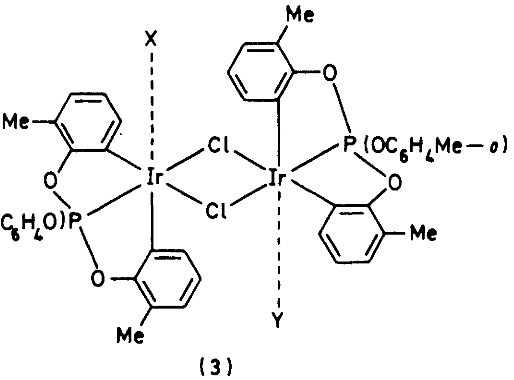
Stoicheiometric additions of $P(OC_6H_4Me\text{-}o)_3$ to $[\{IrCl(cod)\}_2]$ (cod = cyclo-octa-1,5-diene) in various solvents have given the internally metallated complexes $[Ir(P{-}C)(cod)\{P(OC_6H_4Me\text{-}o)_3\}]$ [$P{-}C = P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2$], $[IrCl(P{-}C)_2\{P(OC_6H_4Me\text{-}o)_3\}]$, and a complex analysing for $[Ir_2Cl_2\{P(OC_6H_4Me\text{-}o)_3\}_3]$. Chemical attempts to fully characterise the last product afforded the dimers $[Ir_2Cl_2(P{-}C_2)_2L(L')]$ [$P{-}C_2 = P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)$; $L = P(OC_6H_4Me\text{-}o)_3$, L' = MeCN; $L = L'$ = MeCN, EtOH, Pr^nOH, CO, or $SbPh_3$]. Bridge fission of $[Ir_2Cl_2(P{-}C_2)_2(CO)_2]$ with 4-methylpyridine gives $[IrCl(P{-}C_2)(CO)(4Me\text{-}py)]$. The complex $[Ir_2Cl_2\{P(OC_6H_4Me\text{-}o)_3\}_3]$ is an excellent precursor for the preparation of: (*i*) $[IrCl(P{-}C_2)L_2]$ [L = 4Me-py, py, $PMePh_2$, PMe_2Ph, $AsMe_2Ph$, $P[(OCH_2)_3CMe]$, or PEt_3; L_2 = 2,2′-bipyridyl] from ethanol {addition of $Na[BPh_4]$ to the mother liquors of these reactions gives the salts $[IrCl(P{-}C)L_3][BPh_4]$}; and (*ii*) the salts $[Ir(P{-}C_2)(NCMe)_3]A$ ($A = PF_6$ or BPh_4) from EtOH–MeCN mixtures. Further substitution of this salt produces $[Ir(P{-}C_2)(NCMe)L_2]A$ ($L_2 = Ph_2PCH_2CH_2PPh_2$; $L = PMePh_2$ or PMe_2Ph). Relevant aspects of the *X*-ray crystallographic determination of $[IrCl(P{-}C_2)(4Me\text{-}py)_2]$ are briefly discussed together with i.r. and ^1H n.m.r. data for all the complexes prepared.

THE complex $[Pt\{(CH_2C_6H_4)PBu^t(C_6H_4CH_2)\}\{PBu^t(C_6H_4Me\text{-}o)_2\}]$ is the only example [1] to date of a complex containing a dimetallated, tridentate, tertiary phosphorus ligand and this was prepared by heating $[PtMe\{CH_2C_6H_4PBu^t(C_6H_4Me\text{-}o)\}\{PBu^t(C_6H_4Me\text{-}o)_2\}]$. In fact, very bulky ligands of the above type readily undergo internal metallation through ligand loss enhanced by interligand non-bonded repulsions.[2] On the other hand, cyclometallation reactions involving $P(OPh)_3$ can be related to both its ability to form five-membered rings and to electronic factors. The much greater size of tri-*o*-tolyl phosphite, coupled with its similar properties to $P(OPh)_3$ may greatly enhance its ability to form internally metal–carbon-bonded species. Thus, this, together with the ease with which iridium(I) complexes undergo oxidative additions, has prompted us to investigate the reactions of $[\{IrCl(cod)\}_2]$ (cod = cyclo-octa-1,5-diene) with various mol equivalents of $P(OC_6H_4Me\text{-}o)_3$ per iridium atom in higher-boiling solvents as a possible route to multiply metallated iridium(III) complexes. The results of this investigation are now presented and for convenience the various reactions have been outlined in the Scheme. A communication on this work has already appeared.[3]

RESULTS AND DISCUSSION

Preparation of Metallated Complexes.—(*i*) *Monometallated complexes.* Treatment of a suspension of $[\{IrCl(cod)\}_2]$ in ethanol with 3 mol equivalents of $P(OC_6H_4Me\text{-}o)_3$ per dimer effected immediate conversion into $[Ir(P{-}C)(cod)\{P(OC_6H_4Me\text{-}o)_3\}]$ [1; $P{-}C = P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2$]. No intermediate cation of the type $[Ir(cod)\{P(OC_6H_4Me\text{-}o)_3\}_3]^+$ was detected in the reaction solution in contrast to similar reactions of $P(OPh)_3$ which produced [4] $[Ir(cod)\{P(OPh)_3\}_3]^+$ under the same conditions. When the above reaction of $P(OC_6H_4Me\text{-}o)_3$ was performed in refluxing solvents (*e.g.* ethanol, acetone, or benzene) the complex $[IrCl(P{-}C)_2\{P(OC_6H_4Me\text{-}o)_3\}]$ (2), analogous to the known [5] $[IrCl\{P(OC_6H_4)(OPh)_2\}\{P(OPh)_3\}]$, was formed.

(*ii*) *Dimetallated complexes.* The reaction of $[\{IrCl(cod)\}_2]$ with 3 mol equivalents of $P(OC_6H_4Me\text{-}o)_3$ per dimer in boiling xylene for 12 h gave an oil which was converted into a yellow powder (95%) on trituration under light petroleum. This powder analysed approximately for $[Ir_2Cl_2\{P(OC_6H_4Me\text{-}o)_3\}_3]$ and was shown to contain the basic structural unit (3) from chemical evidence. We hence assign $[Ir_2Cl_2\{P(OC_6H_4Me\text{-}o)_3\}_3]$ as (3a) [*i.e.* 3; $X = P(OC_6H_4Me\text{-}o)_3$, Y = a free co-ordination site], but this assignment must be regarded as tentative since attempts to bond dimethyl sulphoxide, dimethylformamide, and MeCN at the free co-ordination



(3)

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[2] M. I. Bruce, *Angew. Chem. Internat. Edn.*, 1977, **16**, 73.

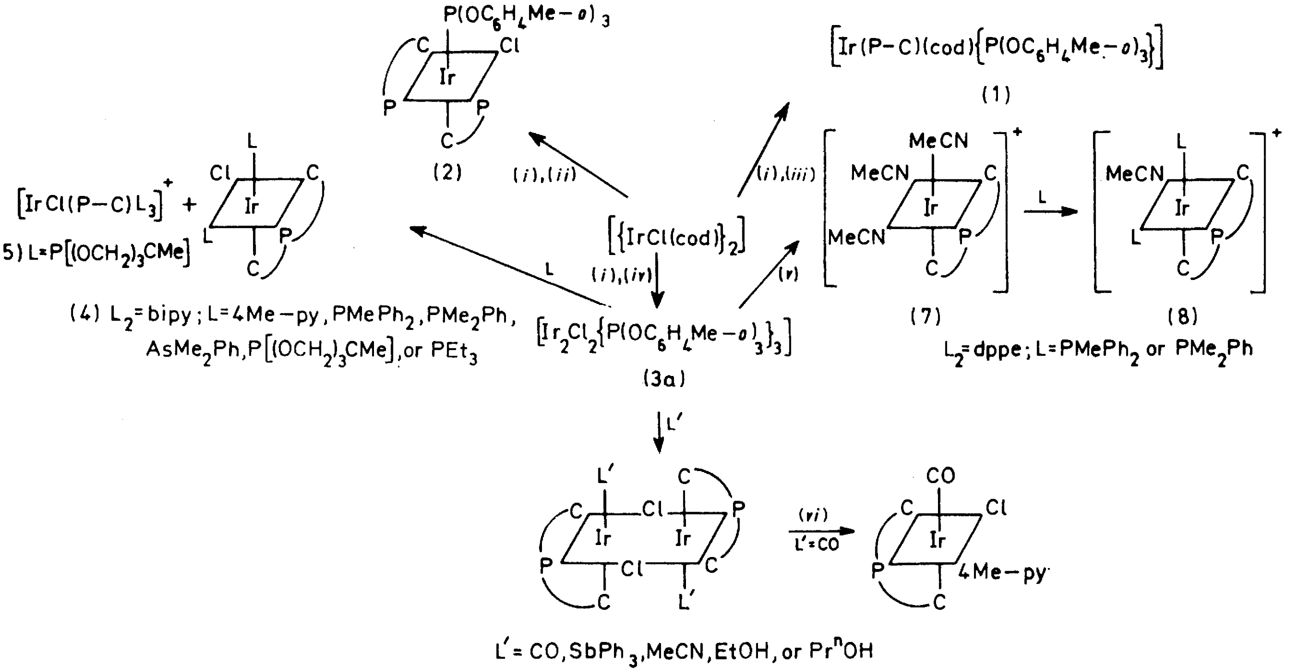
[3] M. J. Nolte, E. van der Stok, and E. Singleton, *J. Organometallic Chem.*, 1976, **105**, C13.

[4] L. M. Haines and E. Singleton, *J. Organometallic Chem.*, 1970, **25**, C83.

[5] E. W. Ainscough, S. D. Robinson, and J. J. Levison, *J. Chem. Soc.* (*A*), 1971, 3413.

site failed. However, in refluxing MeCN the products $[Ir_2Cl_2\{P(OC_6H_4Me\text{-}o)_3\}_3]\cdot MeCN$ and (3; X = Y = MeCN) were obtained. For the former product the acetonitrile could be simply solvent of crystallisation which may account for its low ν(CN) at 2 260 cm^{-1}. In comparison, other observed ν(CN) for bonded MeCN ligands occurred at ⩾2 290 cm^{-1} (see Table 1).

Reactions of the Dimetallated Complex.—(*i*) *Dimeric products.* When (3a) was boiled in the alcohols ROH (R = Et or Pr^n) for 8—12 h the insoluble complex (3; X = Y = ROH) precipitated slowly from the reaction solutions. The i.r. spectra of these complexes contained a ν(OH) band at 3 440 cm^{-1} and the presence of the alcohol molecules was further confirmed by recording the ^1H n.m.r. spectrum of the CD_2Cl_2 filtrate from the reaction which converted (3; X = Y = ROH) into (3; X = Y = $SbPh_3$) (see below). These spectra contained the characteristic resonances of the free alcohols.



SCHEME Reaction of $[\{IrCl(cod)\}_2]$ with $P(OC_6H_4Me\text{-}o)_3$; P–C = $P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2$, P–$C_2$ = $P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)$. (*i*) $P(OC_6H_4Me\text{-}o)_3$; (*ii*) Refluxing Me_2CO; (*iii*) EtOH; (*iv*) refluxing xylene; (*v*) MeCN–EtOH; (*vi*) 4Me-py

Treatment of a solution of (3a) in boiling benzene with CO or $SbPh_3$ gave very insoluble white complexes of stoicheiometry $[\{IrCl(L)[P(OC_6H_4Me\text{-}o)_3]\}_n]$ (L = CO or $SbPh_3$) in 90—95% yield. The i.r. spectrum of the carbonyl complex contained a single ν(CO) band at 2 075 cm^{-1} characteristic of an iridium(III) carbonyl vibration. The complex reacted further with 1 mol equivalent of 4-methylpyridine to give a soluble monomer of formula $[IrCl(CO)(4Me\text{-}py)\{P(OC_6H_4Me\text{-}o)_3\}]$ [ν(CO) at 2 045 cm^{-1}, 80% yield] in a typical halogen bridge-splitting reaction (*n* = 2). From this and the high i.r. carbonyl frequency the dimeric structure (3; X = Y = CO) is inferred for this complex and to (3; X = Y = $SbPh_3$) by analogy.

(*ii*) *Neutral monomeric complexes.* When a boiling ethanol solution of (3a) was treated with an excess of a series of neutral ligands the monomeric products $[IrCl(P\text{–}C_2)L_2]$ {4; L = 4Me-py, py, $PMePh_2$, PMe_2Ph, PPh_3, $AsMe_2Ph$, $P[(OCH_2)_3CMe]$, or PEt_3; L_2 = 2,2′-bipyridyl (bipy)} were formed as air-stable crystalline complexes in yields of 30—60%. These complexes are white, as are all the complexes fully characterised in this paper, and this seems to preclude their formulation as square-planar iridium(I) species. Hence this provides further evidence for an iridium(III) oxidation state, suggesting that the single $P(OC_6H_4Me\text{-}o)_3$ ligand in these complexes is bonding as a tridentate dimetallated group. In order to confirm this the structure of (4; L = 4Me-py) was determined crystallographically[3] (Figure). Relevant bond lengths observed were Ir–Cl 2.44, Ir–P 2.14, Ir–C (mean) 2.05, and Ir–N (mean) 2.16 Å. The long Ir–Cl bond, similar in length to that found[6] for Ir–Cl *trans* to a phosphite phosphorus atom (2.42 Å) in $[IrCl\{P(OC_6H_4)(OPh)_2\}_2\{P(OPh)_3\}]$, has been explained in terms of the strong crystallographic *trans* influence of phosphites. However, complexes (4) form from reactions involving an excess of donor ligands so there seems to be no correlation of this structural *trans* influence with bond weakening and a corresponding kinetic *trans* effect.

The strain related to dimetallation can be seen with the variations in the angles found for the $P(OC_6H_4Me\text{-}o)_3$ ligand. For example, the metallated Ir–P–O angles average 110° whereas the unmetallated Ir–P–O angle is 125°. The metallated C–O–P angles average 112.3° and

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[6] J. M. Guss and R. Mason, *J.C.S. Dalton*, 1972, 2193.

TABLE 1

Infrared [a] and physical [b] data for the iridium complexes

Complex	M.p. (θ_c/°C)	M [c]	Analysis (%) C	H	Cl	Other elements	ν/cm^{-1}
(1) $[Ir\{P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2\}(cod)\{P(OC_6H_4Me\text{-}o)_3\}]$	165—166	1 042 (1 004) [d]	59.4 (59.8)	5.2 (5.3)			
(2) $[IrCl\{P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2\}_2\{P(OC_6H_4Me\text{-}o)_3\}]$	230—255	1 309 (1 282)	59.0 (59.0)	4.85 (4.8)	2.75 (2.75)		
(3a) $[Ir_2Cl_2\{P(OC_6H_4Me\text{-}o)_3\}_3]$	122—124	1 204 (1 508)	50.85 (50.15)	4.15 (3.95)	4.8 (4.7)	O 10.15 (9.55) P 6.55 (6.15) Ir 24.8 (25.5)	
(4) $[IrCl\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}L_2]$							
L = py	198—205	786 (736)	50.5 (50.55)	4.0 (3.95)	5.2 (4.8)	N 3.8 (3.8)	1 610 ν(CN)
4Me-py	275—280	820 (764)	51.75 (51.85)	4.4 (4.35)	4.7 (4.65	N 3.55(3.75), O 6.35 (6.3)	1 620 ν(CN)
$PMePh_2$	210—245		57.35 (57.7)	4.6 (4.65)	3.5 (3.6)		
PMe_2Ph	245—255		52.05 (52.9)	4.75 (4.85)	6.05 (4.15)		
$AsMe_2Ph$	214—216		46.6 (47.15)	4.3 (4.35)	4.0 (3.75)		
$P[(OCH_2)_3CMe]$	>300		42.2 (42.6)	4.2 (4.25)	4.2 (4.05)		
PEt_3	205—212		49.05 (48.65)	5.95 (6.05)	4.15 (4.35)	N 3.85 (3.8), O 7.0 (6.55)	1 620 ν(CN)
L_2 = bipy	>300		50.5 (50.75)	3.75 (3.7)	5.1(4.85)		
$[IrCl\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(CO)(4Me\text{-}py)]$	187—200	692 (699)	48.4 (48.1)	3.9 (3.75)	5.45 (5.05)	N 2.3 (2.0)	2 045 [e] ν(CO) 1 620 ν(CN)
(5) $[IrCl\{P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2\}\{P[(OCH_2)_3CMe]\}_3]\text{-}[BPh_4]$	152—158		53.65 (63.65)	5.0 (5.05)	2.45 (2.45)		
(7) $[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)_3]A$							
A = BPh_4	180		61.65 (62.2)	4.95 (4.9)		N 2.3 (2.0)	2 290, 2 310 ν(CN)
PF_6	230—240		39.7 (40.0)	3.4 (3.5)		N 5.1 (5.2)	2 320, 2 340 ν(CN)
(8) $[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)L_2]A$							
L = $PMePh_2$, A = BPh_4	75—95		67.6 (67.25)	5.4 (5.25)		N 0.9 (1.05)	2 310, 2 330 ν(CN)
L = $PMePh_2$, A = PF_6	198—200		51.95 (52.1)	3.95 (4.3)		N 1.2 (1.25)	2 315, 2 340 ν(CN)
L = PMe_2Ph, A = BPh_4	165—173		63.65 (64.2)	5.25 (5.45)		N 1.15 (1.2)	2 315 ν(CN)
L = PMe_2Ph, A = PF_6	210—218		46.9 (46.6)	4.3 (4.4)		N 1.1 (1.4)	2 310, 2 335 ν(CN)
L_2 = dppe, A = BPh_4	210—225		67.65 (67.35)	5.2 (5.1)		N 1.05 (1.1)	2 300, 2 320 ν(CN)
L_2 = bipy, A = BPh_4	200—210		63.95 (64.65)	4.75 (4.75)		N 4.0 (3.95)	2 300, 2 330 ν(CN)
$[\{IrCl[P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)]L\}_2]$							
L = CO	248—251		43.2 (43.6)	3.15 (3.15)	6.2 (5.85)		2 076 ν(CO)
MeCN	180—185		44.9 (44.6)	3.8 (3.6)	5.65 (5.75)	N 2.2 (2.25)	2 300 ν(CN)
EtOH	232—237		43.5 (44.25)	4.2 (4.05)	6.1 (5.7)		3 440 ν(OH)
PrOH	230—240		44.5 (45.2)	4.0 (4.25)	5.5 (5.55)		3 440 ν(OH)
$SbPh_3$	275—283		50.55 (50.3)	3.75 (3.7)	4.2 (3.8)		
$[Ir_2Cl_2\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}_2\{P(OC_6H_4Me\text{-}o)_3\}\text{-}(NCMe)]$	135—140		50.3 (50.4)	4.0 (4.05)	1.2 (0.9)	N 5.05 (4.6)	2 260 ν(CN)

[a] In Nujol. [b] Calculated values are given in parentheses. [c] In CH_2Cl_2, vaporimetrically unless otherwise stated. [d] In $CHCl_3$. [e] In CH_2Cl_2.

the unmetallated C–O–P angle is 127.8°. It appears that chelate-ring closure pulls the phosphorus *ca.* 10° towards the metal–carbon bond (*cf.* Cl–Ir–P 80°, Figure) and 0.30 Å out of the plane defined by Ir, O(2), C(4), and C(3). In forming a *facial* dichelated product the phosphorus is also pulled 11° towards the other metal–carbon bond [*cf.* C(3)–Ir–P 79°], 0.21 Å out of the plane defined by Ir, O(1), C(2), and C(1). These two planes are approximately perpendicular (89°), with the effect that the formation of the second ring causes very little extra intramolecular strain on the first ring. The Ir–P bond is tilted towards C(1) and C(3) in the plane C(1)–C(3)–Ir, 14° away from the normal. With trichelation, however, metallation of the third arene group *via* an *o*-phenyl carbon atom would require significant and excessive distortion of the third chelate ring. The position of a new metal–carbon bond is limited geometrically to one of the two positions *trans* to an existent one, and distortions in opposite directions would be required. Because of this it seems unlikely that trimetallation will be effected in aryl phosphites *via* *o*-aryl metal–carbon bonds. From a model of this complex, however, it is possible to metallate the non-bonded arene group *via* the *o*-methyl group, causing very little extra strain in the metallated rings and forming a fairly strain-free six-membered ring. Attempts in this direction are at present under way.

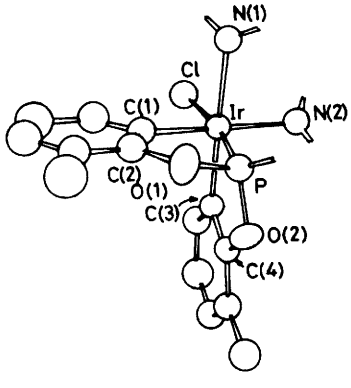


FIGURE Crystal structure of (4; L = 4Me-py)

From the mother liquors of {4; L = $P[(OCH_2)_3CMe]$ or py} the salts $[IrCl(P\text{–}C)L_3][BPh_4]$ (5) were obtained in fairly low yield with $Na[BPh_4]$, as highly soluble, stable, white powders. Complexes {4; L = $P[(OCH_2)_3CMe]$ or py} were not converted into (5) on refluxing in ethanol over extended periods, so the formation of these salts *via* their neutral counterparts through interaction with the alcohol solvent seems unlikely. However, we cannot rule out at this stage a rapid conversion of some of [3;

TABLE 2

Hydrogen-1 n.m.r. data [a] of the iridium complexes

Complex	Tolyl methyl resonances [b]	Other methyl resonances [b]	Other resonances [b]	Comments
(1)	7.59 (1, s), 8.04 (5, m)		5.2 (cod), 6.92 (cod), 8.8 (cod)	
(2)	7.49 (1, s), 7.66 (1, s), 7.77 (3, s), 7.93 (1, s), 8.21 (1, s), 8.56 (1, s)			
(3a)	8 (bm)			
(4)				
L = py	7.75 (1, s), 7.86 (2, s)			
4Me-py	7.74 (1, s), 7.86 (1, s)			4Me-py methyl protons overlap tolyl methyl protons, at τ 7.74
$PMePh_2$	7.65 (1, s), 7.83 (1, s), 7.97 (1, s), 8.13 (2, s)			Unable to distinguish between tolyl methyl and other methyl protons
PMe_2Ph	7.58 (1, s), 7.93 (2, s)	8.59 (2, d, J 9) 8.63 (2, d, J 9)		
$AsMe_2Ph$	7.77 (1, s), 7.93 (2, s)	8.74 (2, s), 8.87 (2, s)		
$P[(OCH_2)_3CMe]$	7.51 (1, s), 7.84 (2, s)	9.37 (2, s)	6.02 (4, m, CH_2, J 5)	
PEt_3	7.59 (1, s), 7.96 (2, s)	9.05 [6, qa, J(P–H) 14, J(H–H) 7]	8.22 [4, qb, CH_2, J(P–H) 7, J(H–H) 7]	
$[IrCl\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(CO)(4Me\text{-}py)]$	7.71 (1, s), 7.78 (1, s)			4Me-py methyl protons overlap tolyl methyl protons at τ 7.71
(5)	7.8 (bm)	9.5 (m), 9.7 (m)	5.95 (m, CH_2), 6.1 (m, CH_2)	
(7)				
A = BPh_4	7.54 (1, s), 7.74 (2, s)	8.21 (1, m [c]), 8.45 (2, s)		
PF_6	7.28 (1, s), 7.48 (1, s), 7.71 (2, s), 7.78 (2, s)			Unable to distinguish between MeCN and tolyl methyl protons
(8)				
L = $PMePh_2$, A = BPh_4	7.67 (1, s), 8.01 (2, s)	8.12 (2, d, PMe, J 8) 8.39 (1, m,[c] MeCN)		
L = $PMePh_2$, A = PF_6	7.63 (1, s), 8.02 (3, s)	7.94 (1, s, PMe) 7.44 (1, s, MeCN)		The doublet for $PMePh_2$ is partly obscured by one tolyl peak at τ 8.02
L = PMe_2Ph, A = BPh_4	7.54 (1, s), 7.89 (2, s)	8.47 (2, d, PMe, J 8) 8.8 (2, d, PMe, J 8) 8.66 (1, s, MeCN)		
L = PMe_2Ph, A = PF_6	7.51 (1, s), 7.91 (2, s)	8.44 (2, d, PMe, J 9) 8.62 (2, d, PMe, J 9) 7.62 (1, m,[c] MeCN)		
L_2 = dppe, A = BPh_4	8.03 (6, s,) 8.56 (3, s)	8.47 (3, m [c])	7.02 (2, bm, CH_2) 7.18 (2, bm, CH_2)	

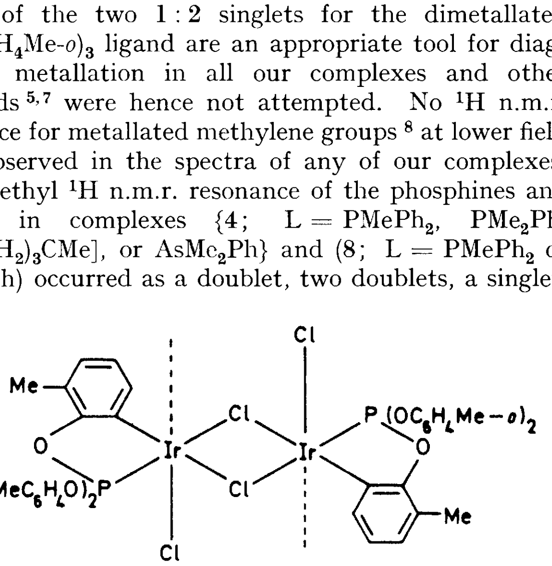
[a] In CD_2Cl_2. [b] Resonances in τ; J in Hz = separation of outer peaks. s = Singlet, d = 1 : 1 doublet, m = multiplet, bm = broad unresolved multiplet, qa = 1 : 2 : 2 : 2 : 1 quintet, qb = 1 : 4 : 6 : 4 : 1 quintet; figures in parentheses refer to relative peak intensities. Assignments in parentheses are only given when ambiguity may arise. [c] A small splitting is observed with $1 < J < 2$ due to J(P–H) coupling, indicative of co-ordinated MeCN.

$X = P(OC_6H_4Me\text{-}o)_3$, Y = a free co-ordination site] in the ethanol solution prior to the formation of (4) with these ligands. It seems more likely though that (5) is formed from some by-product of (3a), possibly containing the monometallated basic unit (6) related to (3).

(*iii*) *Cationic salts.* When (3a) was heated under reflux in ethanol–acetonitrile (1 : 1) it was rapidly converted into the cation $[Ir(P–C_2)(NCMe)_3]^+$. This was isolated as the $[PF_6]^-$ or $[BPh_4]^-$ salt on addition of the respective counter anion to the resulting ethanol solution obtained after removal of the MeCN. Attempts to extend the range of salts produced the series of disubstituted cations $[Ir(P–C_2)L_2(NCMe)]^+$. Thus treatment of $[Ir(P–C_2)(NCMe)_3]A$ (7; A = PF_6 or BPh_4) with an excess of L (or L_2) in various boiling organic solvents gave the salts $[Ir(P–C_2)L_2(NCMe)]A$ [8; L = PMe_2Ph or $PMePh_2$, A = PF_6 or BPh_4, $L_2 = Ph_2PCH_2CH_2PPh_2$(dppe) or bipy, A = BPh_4].

Physical Data for the Complexes.—Microanalytical, molecular-weight, and i.r. data for all the complexes prepared are given in Table 1. The ^1H n.m.r. spectral data are collected in Table 2.

The ν(CN) in the i.r. spectra of (7) and (8) appeared as weak bands in the 2 290—2 340 cm^{-1} region. The ^1H n.m.r. spectra of all the dimetallated complexes always contained two singlets in the τ 7—9 region for the methyl protons of the *o*-tolyl groups. The intensity ratio of 1 : 2 between the low-field and the high-field singlet [except for (8; L_2 = dppe)] is hence accounted for by the one unmetallated 'OC_6H_4Me' and the two equivalent metallated 'OC_6H_3Me' groups. In contrast, the methyl of the unmetallated *o*-tolyl group for (8; L_2 = dppe) resonates at higher field than the metallated, giving ratios of 2 : 1 between the low- and high-field singlets. When a model of this complex was constructed it became apparent that the unmetallated *o*-tolyl methyl was sandwiched between phenyl rings on the dppe ligand, and hence the upfield chemical shift for this methyl probably results from anisotropic shielding effects. The resonances of the two 1 : 2 singlets for the dimetallated $P(OC_6H_4Me\text{-}o)_3$ ligand are an appropriate tool for diagnosing metallation in all our complexes and other methods [5,7] were hence not attempted. No ^1H n.m.r. evidence for metallated methylene groups [8] at lower field was observed in the spectra of any of our complexes. The methyl ^1H n.m.r. resonance of the phosphines and arsine in complexes {4; L = $PMePh_2$, PMe_2Ph, $P[(OCH_2)_3CMe]$, or $AsMe_2Ph$} and (8; L = $PMePh_2$ or PMe_2Ph) occurred as a doublet, two doublets, a singlet, two singlets, and a doublet and two doublets respectively for the expected ' all-*cis* ' configuration [J(P–P) 0 and no plane of symmetry along the Ir–L bond]. On this evidence complexes (4) and (8) were assigned the stereochemistries given in the Scheme. For {4; L = $P[(OCH_2)_3CMe]$} the methylene hydrogens appeared as a three-line resonance centred at τ 6.02. The salts (7; A = PF_6 or BPh_4) showed, apart from the two 1 : 2 tolyl singlets, two additional resonances indicative of the two equivalent and one unique MeCN groups in an apparently non-exchanging system in solution. A distinct upfield shift for the MeCN resonance occurs from (7; A = PF_6) to (7; A = BPh_4) due to the near-neighbour anisotropic shielding of the methyl protons by the phenyl rings on the $[BPh_4]^-$ anion. This has recently been shown [9] to be an excellent diagnostic tool for MeCN resonances contained in complex or overlapping resonance spectra.



(6)

The monometallated complexes (1) and (5) gave complicated ^1H n.m.r. data and were assigned as such simply on iridium oxidation-state stabilities, iridium(II) species being most unlikely. For (2), six well resolved singlets of intensity *ca.* 1 : 1 : 3 : 1 : 1 : 1 were observed which we were unable to analyse, but these could be consistent with a structure similar to that proposed for the corresponding triphenyl phosphite complex.[5]

Although numerous complexes of PEt_nPh_{3-n} (n = 1—3) have been reported,[10-16] surprisingly little explanation has been given for the ethyl region of their ^1H n.m.r. spectra. Complex (4; L = PEt_3) shows a well resolved 1 : 4 : 6 : 4 : 1 quintet for the methylene protons and a well resolved 1 : 2 : 2 : 2 : 1 double triplet for the methyl protons of the PEt_3 ligand. Similar resonances were also observed [11] for the colourless *fac*-$[IrCl_3(PEt_3)_3]$ (prepared by us in high yield from $[\{IrCl(cod)\}_2]$ and PEt_3 in ethanol containing a few drops of concentrated HCl) in which all PEt_3 ligands are mutually *cis*. Thus a quintet for the methyl protons as such is not characteristic of mutually *trans*-ligand geometry as has been stated implicitly before.[10,13,14,16] The 1 : 2 : 2 : 2 : 1 double triplet observed in the ^1H n.m.r. spectra of (4; L = PEt_3) is consistent with coupling of the methyl protons on the ethyl group on the PEt_3 ligand with the two methylene protons and with one ^{31}P nucleus to give the required methyl pattern. Coupling constants observed were J(H–H) 7 and $J(P\text{–}H_{CH_3})$ 14 Hz, both values being the same as those found [13] for *mer*-$[RhCl_3(PEt_3)_3]$. The spectrum of the ethyl methylenes in (4; L = PEt_3) arise from couplings with the methyl protons on the ethyl group to give a 1 : 3 : 3 : 1 quartet which is further split by one ^{31}P nucleus into a 1 : 4 : 6 : 4 : 1 quintet [J(H–H) 7 and $J(P\text{–}H_{CH_2})$ 7 Hz]. The larger J(P–H) for the more remote methyl protons has been observed previously.[17] In a series of complexes containing *trans*-PEt_3 ligands [12,18] the methyl protons were observed as a 1 : 4 : 6 : 4 : 1 quintet due to their coupling with two methylene protons and two ^{31}P nuclei (virtual coupling). The methylene proton resonances in this series however were reported [10,12,14,18] to be poorly resolved or too complex for analysis. Thus it now appears that in ideal cases a methyl quintet of 1 : 4 : 6 : 4 : 1 is indicative of *trans*-PEt_3 ligands and a methyl double triplet of 1 : 2 : 2 : 2 : 1 together with a 1 : 4 : 6 : 4 : 1 methylene quintet are indicative of *cis*-PEt_3 groups. For a *mer* configuration a combination of one 1 : 2 : 2 : 2 : 1 and two 1 : 4 : 6 : 4 : 1 quintets would give a 3 : 10 : 14 : 10 : 3 methyl multiplet which could well fit the spectra observed for *mer*-$[RhCl_3(PEt_3)_3]$ [13] and $[PtI(PEt_3)_3][PF_6]$.[18]

EXPERIMENTAL

Except for $P[(OCH_2)_3CMe]$,[19] phosphines and phosphites were obtained commercially and were not further purified. It was not found necessary to perform the reactions under

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nitrogen. Melting points were determined on a Kofler hot-stage and are not corrected. The ^{1}H n.m.r. spectra were recorded with Varian A-60A, HA100, and XL100 instruments and the i.r. spectra with a Perkin-Elmer 457 grating spectrometer. Molecular weights were determined on a Mechrolab vapour-pressure osmometer in $CHCl_3$ and CH_2Cl_2. Calculations of percentage yields are based on the assumed stoicheiometry of $[Ir_2Cl_2\{P(OC_6H_4Me\text{-}o)_3\}_3]$ for (3a).

$[Ir\{P(OC_6H_3Me)(OC_6H_4Me\text{-}o)_2\}(cod)\{P(OC_6H_4Me\text{-}o)_3\}]$ (1).—To a suspension of $[\{IrCl(cod)\}_2]$ (0.74 g) in ethanol (30 cm^3) was added $P(OC_6H_4Me\text{-}o)_3$ (2.4 g). The mixture was stirred for 3 h and then filtered. Recrystallisation of the resulting precipitate from dichloromethane–ethanol gave the product as white *prisms* (1.1 g, 50%).

$[IrCl\{P(OC_6H_3Me)(OC_6H_4Me\text{-}o)_2\}_2\{P(OC_6H_4Me\text{-}o)_3\}]$ (2).—Treatment of $[\{IrCl(cod)\}_2]$ (0.57 g) with $P(OC_6H_4Me\text{-}o)_3$ in refluxing benzene (40 cm^3) for 6 h gave a light yellow solution, which when concentrated produced a precipitate on addition (20 cm^3) of light petroleum (b.p. 60—80 °C). Recrystallisation from dichloromethane–ethanol gave the product as white *prisms* (0.75 g, 34%).

$[Ir_2Cl_2\{P(OC_6H_4Me\text{-}o)_3\}_3]$ (3a).—A mixture of $[\{IrCl(cod)\}_2]$ (4.14 g) and $P(OC_6H_4Me\text{-}o)_3$ (6.15 g) was heated under reflux in xylene (70 cm^3) for 12 h. Removal of the solvent under reduced pressure gave a pale yellow oil which produced a pale yellow *powder* (7.5 g, 81%) on triturating under light petroleum (30 cm^3).

$[IrCl\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(PEt_3)_2]$ (4).—Excess of PEt_3 (0.42 g) was added to a suspension of (3a) (0.88 g) in ethanol (60 cm^3) and the mixture was heated under reflux for 2 h. The precipitate formed by water addition to the concentrated solution gave white *prisms* (0.5 g, 52%) after recrystallisation from dichloromethane–ethanol. Similarly prepared were $[IrCl\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}L_2]$ {4; L = py, 4Me-py, $PMePh_2$, PMe_2Ph, $AsMe_2Ph$, or $P[(OCH_2)_3CMe]$; L_2 = bipy} in yields varying from 30 to 50% as white *crystals* except for (4; L_2 = bipy) which formed yellow *microcrystals*.

To the mother liquors from {4; L = $P[(OCH_2)_3CMe]$} was added a saturated solution of $Na[BPh_4]$ in ethanol (10 cm^3) to give a white *powder* of $[IrCl\{P(OC_6H_3Me\text{-}o)(OC_6H_4Me\text{-}o)_2\}\{P[(OCH_2)_3CMe]\}_3][BPh_4]$ (5).

$[\{IrCl[P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](CO)\}_2]$.— Carbon monoxide gas was passed through a boiling solution of (3a) (0.61 g) in benzene (20 cm^3) for 2 h. The solvent was then evaporated, and ethanol (10 cm^3) added to yield white *prisms* (0.46 g, 94%).

$[\{IrCl[P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](NCMe)\}_2]$.— Complex (3a) (0.32 g)was heated under reflux in acetonitrile (20 cm^3) for 1.5 h. Ethanol was then added and evaporating the solution under reduced pressure gave the product as white microcrystals (0.8 g). Evaporating the mother liquor of the above reaction to low volume produced $[Ir_2Cl_2\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}_2\{P(OC_6H_4Me\text{-}o)_3\}(NCMe)]$ as white *microcrystals* (0.8 g).

$[\{IrCl[P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](HOR)\}_2]$ (R = Et *or* Pr^n).—Complex (3a) was heated under reflux in ROH (50 cm^3) for 12 h during which time the product was deposited from the boiling solution as white *microcrystals* (24%, R = Et; 17%, R = Pr^n).

$[\{IrCl[P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](SbPh_3)\}_2]$.—Addition of $SbPh_3$ (0.05 g) to a suspension of $[\{IrCl[P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](HOEt)\}_2]$ (0.08 g) in dichloromethane produced a clear solution which after 2 min gave a precipitate of the required product as a white *powder* (0.06 g, 48%).

$[IrCl\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(CO)(4Me\text{-}py)]$.— 4-Methylpyridine (0.05 cm^3) was added to a suspension of $[\{IrCl[P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](CO)\}_2]$ (0.21 g) in dichloromethane (15 cm^3). On refluxing for 2 h a clear solution was formed which deposited the required product as white *prisms* (0.19 g, 78%) on addition (15 cm^3) of light petroleum to the concentrated solution.

$[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)_3][BPh_4]$ (7).—Complex (3a) (0.75 g) was dissolved in acetonitrile (10 cm^3), a saturated solution of $Na[BPh_4]$ in ethanol (10 cm^3) was added, and the solution was heated under reflux for 1 h. Removal of the acetonitrile under reduced pressure, followed by addition (10 cm^3) of water, gave the product as a cream *powder* (0.37 g, 33%). Similarly prepared was $[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)_3][PF_6]$ (35%) using $[NH_4][PF_6]$.

$[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)(PMePh_2)_2][BPh_4]$ (8).—Methyldiphenylphosphine was added to $[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)_3][BPh_4]$ (0.09 g) in acetone (30 cm^3) and heated under reflux for 2 h. The solution was reduced in volume, and light petroleum was added (10 cm^3) to yield the product as white *prisms* (0.08 g, 65%). Similarly prepared were $[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)(PMePh_2)_2][PF_6]$, $[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)(PMe_2Ph)_2][BPh_4]$, and $[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)(PMe_2Ph)_2][PF_6]$ (the solvent 2-methoxyethanol was used in this reaction).

$[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)(bipy)][BPh_4]$.—Addition of 2,2′-bipyridine (0.03 g) to a solution of $[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)_3][BPh_4]$ (0.16 g) in dichloromethane (15 cm^3) gave an immediate yellow solution which on addition (10 cm^3) of ethanol and boiling off the dichloromethane gave the product as yellow *microcrystals* (0.14 g, 81%). Similarly prepared as white *needles* was $[Ir\{P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)\}(NCMe)(dppe)][BPh_4]$.

[7/1126 *Received, 28th June,* 1977]