The Iridium(I) Cation, $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ and Its Substitution Reactions

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Reaction of $IrCl(CO)(PPh_3)_2$ with silver perchlorate in various solvents gives $[Ir(CO)(solvent)(PPh_3)_2]ClO_4$. Crystalline salts have been isolated where solvent = acetonitrile, benzonitrile, and dimethyl sulphoxide. $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ readily undergoes substitution reactions with carbon monoxide, phosphines, and isocyanides and the following cations have been characterised: $[Ir(CO)_3(PPh_3)_2]^+$, $[Ir(CO)(PPh_3)_3]^+$, $[Ir(CO)(PPh_2Me)_3]^+$, $[Ir(CO)(PPh_2Et)_3]^+$, $[Ir(PPh_2Me)_4]^+$, $[Ir(CO)(Ph_2PCH{=}CHPPh_2)_2]^+$, $[Ir(CO)(p\text{-tolylisocyanide})(PPh_3)_2]^+$, and $[Ir(p\text{-tolylisocyanide})_3(PPh_3)_2]^+$.

FOUR-CO-ORDINATE iridium(I) cations undergo oxidative addition reactions,[1] and the facility with which they do so shows a marked ligand dependence. An illustration is provided by $[IrCl(NO)(PPh_3)_2]^+$ and $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ which exhibit quite different reactivity towards oxygen and hydrogen.[2] To help evaluate the role of the ligands we have sought preparative routes to $[IrL_4]^+$ systems where L_4 is a combination of various neutral donor molecules. We describe here the preparation and characterisation of a series of cations involving carbon monoxide, nitriles, dimethyl sulphoxide (dmso), phosphines, and isocyanides. Oxidative addition reactions of these cations will be described separately. Some of these results have been the subject of a preliminary communication.[3]

$IrCl(CO)(PPh_3)_2$ reacts with silver ions in donor solvents to give the cations $[Ir(CO)(solvent)(PPh_3)_2]^+$ and to precipitate silver chloride.

$$AgY + IrCl(CO)(PPh_3)_2 \xrightarrow{\text{solvent}} [Ir(CO)(solvent)(PPh_3)_2]Y + AgCl$$
$$(Y = ClO_4,\ BF_4)$$

Bright yellow, crystalline salts have been isolated, in high yield, from acetonitrile, benzonitrile, and dimethyl sulphoxide. Reaction also proceeds in tetrahydrofuran,

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[1] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, 7, 53.

[2] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1973, 1014.

[3] G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 758.

dimethylformamide, acetone, and ethanol containing triphenylphosphine oxide or diphenyl sulphoxide but from these solvents pure products could not be obtained. By using benzene as solvent, Peone and Vaska [4] isolated the perchlorato-compound $Ir(OClO_3)(CO)(PPh_3)_2$. All the cations show a strong carbonyl stretching frequency in the i.r. region 1970—2000 cm^{-1}, typical of four-co-ordinate iridium(I) (see Table).

Infrared data for the iridium(I) cations [a]

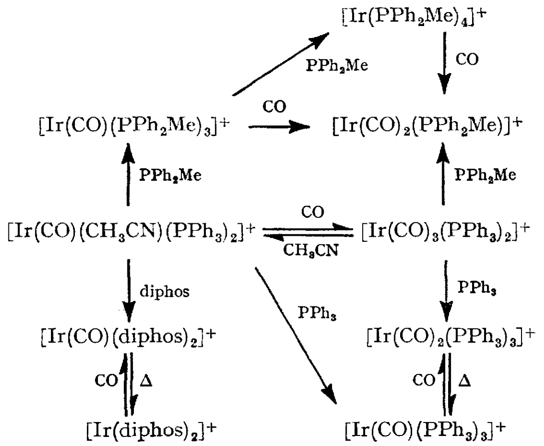
Compound	Colour	ν(CO)	Other frequencies
$[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ [b]	Yellow	1975vs	ν(CN) 2290w
$[Ir(CO)(C_6H_5CN)(PPh_3)_2]ClO_4$	Yellow	2000vs	ν(CN) 2250w
$[Ir(CO)(dmso)(PPh_3)_2]ClO_4$	Yellow	1965vs, 1985sh	ν(SO) 920s
$[Ir(CO)(PPh_3]ClO_4$	Yellow-orange	1995s	
$[Ir(CO)(PMePh_2)_3]ClO_4$	Orange	2000s	
$[Ir(Ph_2PCH{:}CHPPh_2)_2]ClO_4$	Orange		560s (diphos)
$[Ir(CO)(tic)(PPh_3)_2]ClO_4$ [c]	Orange	2030vs	ν(NC) 2180s; 820(*p*-tolyl)
$[Ir(tic)_3(PPh_3)_2]ClO_4$	Orange		ν(NC) 2115vs; 820(*p*-tolyl)
$[Ir(PMePh_2)_4]ClO_4$ [b]	Red		δ(PMe) 800vs
$[Ir(CO)_2(PMePh_2)_3]ClO_4$ [b]	Colourless	1950vs,br, 2000s	δ(PMe) 885vs
$[Ir(CO)_2(PEtPh_2)_3]ClO_4$	Very pale yellow	1945vs, 1995s	
$[Ir(CO)(Ph_2PCH{=}CHPPh_2)_2]ClO_4$	Cream	1970vs	560s (diphos)

[a] In cm^{-1}, for Nujol mulls. [b] The BF_4 and PF_6 salts gave similar spectra. [c] tic = *p*-tolyl isocyanide.

In the acetonitrile cation, the weak carbon–nitrogen stretching frequency rises slightly upon co-ordination (from 2250 in the free ligand to 2290 cm^{-1} in the complex) in common with almost all acetonitrile complexes.[5] Significant π-backbonding has been claimed in ruthenium(III) pentammine–nitrile complexes where ν(CN) decreases upon co-ordination,[6] but from Mössbauer studies on iron(II) complexes it has been deduced that nitriles are considerably poorer σ-donors and/or π-acceptors than isocyanides or carbon monoxide.[7] The stability of $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ suggests that the *trans*-combination of CO and CH_3CN is a favourable bonding situation in this cationic d^8 complex and the nitrile is probably behaving as a good σ-donor. The rise in ν(CN) upon co-ordination is in keeping with little π-backbonding to the nitrile. The ^1H n.m.r. spectrum of $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ shows the methyl protons as a singlet at τ 9·40 upfield from free acetonitrile (τ 8·00). The methyl singlet of $[Ir(CO)(DMSO)(PPh_3)_2]^+$ also appears slightly upfield from free dimethyl sulphoxide. These upfield positions probably result from the proximity of the phenyl rings of the adjacent triphenylphosphine ligands.

In $[Ir(CO)(dmso)(PPh_3)_2]^+$ a strong i.r. absorption at 920 cm^{-1} due to ν(SO) is indicative of an *O*-bound sulphoxide. The ν(SO) for free sulphoxide (1055 cm^{-1}) is raised when sulphur co-ordinates to a metal but lowered when oxygen is the donor atom.[8] Co-ordination of the ' harder ' donor atom must result from the dimethyl sulphoxide being positioned *trans* to the strongly π-acid CO ligand and to the presence of a positive charge, although convincing evidence for steric control of linkage isomerism in cationic palladium(II) complexes has been presented.[9]

Substitution Reactions of $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$.—Co-ordinatively unsaturated complexes are kinetically labile because an associative mechanism provides a low energy pathway for substitution. A positive charge might also be expected to enhance donor interaction and it is therefore not surprising to find that $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ is the precursor of a wide range of iridium(I) cations most of which remain four-co-ordinate. The substitution reactions we have studied are indicated in the Scheme.



diphos = *cis*-1,2-bis(diphenylphosphino)ethene

SCHEME Substitution reactions of $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$

With carbon monoxide. Yellow solutions of $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ are immediately decolourised by carbon monoxide producing a quantitative yield of the known cation $[Ir(CO)_3(PPh_3)_2]^+$ (refs. 10 and 11).

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[4] J. Peone, jun., and L. Vaska, *Angew. Chem. Internat. Edn.*, 1971, **10**, 511.

[5] R. A. Walton, *Quart. Rev.*, 1965, **19**, 126.

[6] R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 1970, **9**, 227.

[7] G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefanine, *J. Chem. Soc.* (*A*), 1970, 2146.

[8] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.

[9] J. H. Price, R. F. Schramm, and B. B. Wayland, *Chem. Comm.*, 1970, 1377.

[10] L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 1965, 6974.

[11] M. J. Church, M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 2909.

The reaction is reversed by passing a stream of nitrogen through a refluxing acetonitrile solution of the tricarbonyl cation. Substitution of carbon monoxide by a nitrile is uncommon and is testimony to the exceptional stability of $[\mathrm{Ir(CO)(CH_3CN)(PPh_3)_2}]^+$. No evidence for the four-co-ordinate dicarbonyl species $[\mathrm{Ir(CO)_2(PPh_3)_2}]^+$ was obtained in either the forward or the back reaction but the red cations $[\mathrm{Ir(CO)_2L_2}]^+$ have been reported where L is the basic and bulky phosphines $\mathrm{P(cyclohexyl)_3}$ or $\mathrm{P(isopropyl)_3}$.[11]

The action of tertiary phosphines on $[\mathrm{Ir(CO)_3(PPh_3)_2}]^+$ causes rapid loss of one carbonyl ligand and formation of $[\mathrm{Ir(CO)_2L_3}]^+$ cations. We have prepared perchlorate salts with $\mathrm{L = PPh_3}$, $\mathrm{PPh_2Me}$, and $\mathrm{PPh_2Et}$. The cations with $\mathrm{L = PPh_3}$,[10] $\mathrm{PPh_2Me}$,[11] and $\mathrm{PPhMe_2}$[12] have been previously described. A preparative feature of these cations which is worth noting, is the nonstoicheiometric inclusion of dichloromethane in the crystals. Elemental analysis and ^{1}H n.m.r. spectra confirmed 0·6—0·7 mol in $[\mathrm{Ir(CO)_2(PPh_2CH_3)_3}]\mathrm{ClO_4}$ and 0·6—0·8 mol in $[\mathrm{Ir(CO)_3(PPh_3)_2}]\mathrm{ClO_4}$. The appearance of a weak band in the i.r. spectrum of $[\mathrm{Ir(CO)_3(PPh_3)_2}]\mathrm{ClO_4,CH_2Cl_2}$ at 1265 cm^{-1} is probably associated with a δ(C–H) bending mode of $\mathrm{CH_2Cl_2}$. Nonstoicheiometric solvation by chloroform has been observed in $\mathrm{RhCl_2(py)_2[P(\mathit{o}\text{-}C_6H_4Me)_2(\mathit{o}\text{-}C_6H_4CH_2)],0{\cdot}61CHCl_3}$ and confirmed by an *X*-ray single crystal study.[13] In the ^{1}H n.m.r. spectrum of $[\mathrm{Ir(CO)_2(PPh_2Me)_3}]^+$ the methyl resonance approximates a triplet at τ 8·0 indicating, perhaps, fast phosphine exchange or rapid interconversion of two configurations. The spectrum of $[\mathrm{Ir(CO)_2\{PPh(CH_3)_2\}_3}]^+$ has been discussed by Deeming and Shaw.[12]

With triphenylphosphine. Acetonitrile is displaced from $[\mathrm{Ir(CO)(CH_3CN)(PPh_3)_2}]^+$ by triphenylphosphine to give orange $[\mathrm{Ir(CO)(PPh_3)_3}]^+$. The same cation has been produced by the action of triphenylphosphine upon the perchlorato-compound, $\mathrm{Ir(OClO_3)(CO)(PPh_3)_2}$.[4] The increase in ν(CO) compared with that of the acetonitrile cation (see Table) probably reflects better competition by triphenylphosphine for the π-electron density or the iridium.

Triphenylarsine causes a slight orange colouration when added to a yellow solution of $[\mathrm{Ir(CO)(CH_3CN)(PPh_3)_2}]^+$ but even in refluxing ethanol with a large excess of triphenylarsine, the starting material can be recovered unchanged. Triphenylstibine also fails to displace the acetonitrile. The bulk of the arsine and stibine donors is probably responsible for this since any distortion of four-co-ordinate iridium(I) from its preferred planar geometry necessary to accommodate the heavier Group V donors may not be adequately compensated by the strength of the Ir–As or Ir–Sb bond. The crystal structure of $\mathrm{RhCl(PPh_3)_3}$ shows considerable distortion from planarity towards tetrahedral in order to minimise intramolecular non-bonding interactions[14] and although they have been prepared, $\mathrm{IrCl(AsPh_3)_3}$ and $\mathrm{IrCl(SbPh_3)_3}$ are not as stable as $\mathrm{IrCl(PPh_3)_3}$.[15]

With carbon monoxide $[\mathrm{Ir(CO)(PPh_3)_3}]^+$ decolourises giving $[\mathrm{Ir(CO)_2(PPh_3)_3}]^+$ and the reaction can be reversed by extended heating with triphenylphosphine in ethanol under reflux.

Alkyl-substituted phenylphosphines. Methyldiphenylphosphine and ethyldiphenylphosphine rapidly displace acetonitrile and triphenylphosphine from $[\mathrm{Ir(CO)(CH_3CN)(PPh_3)_2}]^+$ to give bright orange-red $[\mathrm{Ir(CO)(PPh_2CH_3)_3}]^+$ and $[\mathrm{Ir(CO)(PPh_2C_2H_5)_3}]^+$ respectively, the latter proving very difficult to crystallise. An attempt to prepare $[\mathrm{Ir(CO)(PPh_2CH_3)(PPh_3)_2}]^+$ by addition of one equivalent of $\mathrm{PPh_2Me}$ produced, instead, a mixture of starting material and some $[\mathrm{Ir(CO)L_3}]^+$ species where $\mathrm{L = PPh_2Me}$ or $\mathrm{PPh_3}$. The ^{1}H n.m.r. spectrum of $[\mathrm{Ir(CO)(PPh_2CH_3)_3}]\mathrm{ClO_4}$ shows a broad multiplet (τ 8·1) which probably results from fast exchange of the labile phosphines and/or distortion from ideal planarity.

With an excess of methyldiphenylphosphine. Unlike the triphenylphosphine analogue, treatment of $[\mathrm{Ir(CO)(PPh_2Me)_3}]^+$ with an excess of tertiary phosphine in ethanol under reflux effects displacement of the remaining carbon monoxide ligand to give the deep red tetrakis(methyldiphenylphosphine) cation $[\mathrm{Ir(PPh_2CH_3)_4}]^+$ isolated as the perchlorate, tetrafluoroborate, hexafluorophosphate, and tetraphenylborate salts. A similar red colour was produced using ethyldiphenylphosphine indicating the formation of $[\mathrm{Ir(PPh_2Et)_4}]^+$ but a crystalline solid could not be obtained. The formation of $[\mathrm{Ir(PPh_2Me)_4}]^+$ was also observed in the reaction of other low valent iridium cations with an excess of methyldiphenylphosphine, *e.g.*, $[\mathrm{Ir(NO)_2(PPh_3)_2}]^+$ (ref. 16) where nitric oxide gas is given off, $[\mathrm{IrCl(NO)(PPh_3)_2}]^+$ (ref. 2), and $[\mathrm{Ir(CO)_3(PPh_3)_2}]^+$. The red salts are 1 : 1 electrolytes in nitrobenzene, and occlude approximately 0·5 mol of cyclohexane as solvate when recrystallised from dichloromethane–ethanol–cyclohexane regardless of the accompanying anion. This cyclohexane, detected in the ^{1}H n.m.r. spectrum as a sharp singlet at τ 8·7, can be removed by prolonged pumping under high vacuum or more satisfactorily by recrystallisation from dichloromethane–ethanol.

The methyl protons of the tertiary phosphine ligands appear in the ^{1}H n.m.r. spectrum as a broad singlet at τ 9·6 having the correct integrated ratio with the phenyl protons (a broad singlet at τ 2·6). The position of the methyl signal is considerably higher than in $[\mathrm{Ir(CO)(PPh_2Me)_3}]^+$ (τ 8·1) or $[\mathrm{Ir(CO)_2(PPh_2CH_3)_3}]^+$ (τ 8·0) and this may indicate some sort of interaction of the methyl groups with the iridium atom. The uncharged, related ruthenium compound $\mathrm{Ru(Me_2PCH_2CH_2PMe_2)_2}$

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[12] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 2705.

[13] R. Mason and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1970, 1601.

[14] P. B. Hitchcock, M. McPartlin, and R. Mason, *Chem. Comm.*, 1969, 1367.

[15] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

[16] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1972, 1243.

exists in the solid state as a ruthenium(II) hydride formed by insertion of the ruthenium into a C–H bond of a phosphine methyl group.[17]

Significantly, the five-co-ordinate species $[Ir(CO)(PPh_2CH_3)_4]^+$ does not appear to exist. The reaction of $[Ir(PPh_2CH_3)_4]^+$ with carbon monoxide results in the displacement of tertiary phosphine by CO giving $[Ir(CO)_2(PPh_2Me)_3]^+$, probably *via* $[Ir(CO)(PPh_2Me)_3]^+$, with no trace of a five-co-ordinate monocarbonyl. This contrasts with $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ which takes up carbon monoxide reversibly.[18] $[Ir(CO)(PPhMe_2)_4]^+$ is also known.[12] It is probable that steric factors are the major controlling influence here, and the available *X*-ray crystal structure data support this conclusion. $[Ir(PPh_2Me)_4]^+$ and $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ differ only in that the methyl groups of the former are linked in the latter making its ligand structure both more rigid but less bulky. $[Rh(Ph_2PCH_2CH_2PPh_2)_2]ClO_4$ has an almost perfectly square planar geometry [19] and the tendency for this d^8 system to achieve planarity is reflected in the large distortions of the ethane bridges. The same geometry is likely to occur in $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ but in $[Ir(PPh_2Me)_4]^+$, however, the less efficient packing of the PPh_2Me ligands prevent planarity and shield the metal atom from incoming ligands. A single crystal *X*-ray study confirms this [3] indicating that in $[Ir(PPh_2Me)_4]^+$ significant distortion of the geometry from planar towards tetrahedral takes place (P–Ir–P = 150° rather than 180°).

With bidentate phosphines. The ligand $Ph_2PCH{=}CHPPh_2$ (diphos) immediately displaces acetonitrile and triphenylphosphine from $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ to form five-co-ordinate $[Ir(CO)(diphos)_2]^+$ isolated as cream crystals of the perchlorate salt. When heated in the solid or in solution this cation readily loses carbon monoxide to form orange, co-ordinatively unsaturated $[Ir(diphos)_2]^+$, a reaction which parallels that of $[Ir(CO)(Ph_2PCH_2CH_2PPh_2)_2]^+$ (ref. 18). This latter cation can also be prepared from $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ in excellent yield.

With p-*tolyl isocyanide*(*tic*). Iridium(I) complex cations with isocyanide ligands which have been reported include $[Ir(tic)_4]^+$, $[Ir(CO)(tic)_3]^+$ (ref. 20), $[Ir(tic)_2(PPh_3)_2]^+$, and $[Ir(tic)_3(PPh_3)_2]^+$ (ref. 21). Acetonitrile is readily displaced from $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ by *p*-tolyl isocyanide but a mixture of products results regardless of solvent or reagent concentration. However, under controlled conditions reasonable yields of the bright orange-red cations $[Ir(CO)(tic)(PPh_3)_2]^+$ and $[Ir(tic)_3(PPh_3)_2]^+$ are produced using one and three equivalents of *p*-tolyl isocyanide respectively. ν(CN) for $[Ir(CO)(tic)(PPh_3)_2]^+$ is higher than for $[Ir(tic)_3(PPh_3)_2]^+$ (see Table), in keeping with the idea of isocyanides being poorer π-acceptors than carbon monoxide although their σ-donor capacity may well be greater.

EXPERIMENTAL

I.r. spectra (400—400 cm^{-1}) were measured on a Shimadzu IR27G spectrometer calibrated with Polystyrene. M.p.s were measured on a Reichert hot-stage apparatus, conductivities with a Philips PR9501 meter, and ^1H n.m.r. spectra with a Varian T60. Kiesel-gel S (Riedel de Haën) was used for column chromatography. All reactions involving heating under reflux were carried out in a nitrogen atmosphere (<10 p.p.m. oxygen) but subsequent manipulation, unless otherwise specified, was open to the air.

Carbonyl(*acetonitrile*)*bis*(*triphenylphosphine*)*iridium*(I) *Perchlorate and Tetrafluoroborate.*—A mixture of $IrCl(CO)(PPh_3)_2$ (500 mg) and silver perchlorate (135 mg) in acetonitrile (20 ml) was stirred until the complex was dissolved. The solvent was removed at reduced pressure, the product extracted with dichloromethane, filtered, and chromatographed on a silica gel column, eluting with acetone–dichloromethane (1 : 25). The solvents were removed at reduced pressure and the product crystallised from dichloromethane–ethanol–cyclohexane as bright yellow prisms (510 mg, 90%). m.p. 173—178°. ^1H N.m.r. ($CDCl_3$) shows τ 9·40 (s, CH_3) and τ 2·5 (m, Ph) with integrated ratio 3.1 : 30, required 3 : 30 (Found: C, 53·3; H, 3·85; N, 1·45. $C_{39}H_{33}ClIrNO_5P_2$ requires C, 52·9; H, 3·75; N, 1·6%).

The tetrafluoroborate salt was prepared similarly from $AgBF_4$. M.p. 153—156° (Found: C, 53·55; H, 3·95; N, 1·5. $C_{39}H_{33}BF_4IrNOP_2$ requires C, 53·65; H, 3·8; N, 1·6%).

Carbonyl(*benzonitrile*)*bis*(*triphenylphosphine*)*iridium*(I) *Perchlorate.*—This was prepared as above using benzonitrile as solvent. M.p. 164—166° (Found: C, 55·8; H, 3·7; N, 1·45. $C_{44}H_{35}ClIrNO_5P_2$ requires C, 55·8; H, 3·7; N, 1·5%).

Carbonyl(*dimethyl sulphoxide*)*bis*(*triphenylphosphine*)*iridium*(I) *Perchlorate.*—This was prepared as above using dimethyl sulphoxide as solvent. M.p. 181—183°. ^1H N.m.r. ($CDCl_3$) shows τ 8·18 (s, CH_3) and τ 2·5 (m, Ph) with integrated ratio 6·4 : 30, required 6 : 30 (Found: C, 51·45; H, 4·05. $C_{39}H_{36}ClIrO_6P_2S$ requires C, 50·8; H, 3·95%).

Carbonyltris(*triphenylphosphine*)*iridium*(I) *Perchlorate.*—Triphenylphosphine (50 mg) was added to a dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) and the orange product crystallised by addition of ethanol–cyclohexane (120 mg, 95%). M.p. 167—169° (Found: C, 60·5; H, 4·45; P, 8·4. $C_{55}H_{45}ClIrO_5P_3$ requires C, 59·7; H, 4·1; P, 8·4%).

Carbonyltris(*methyldiphenylphosphine*)*iridium*(I) *Perchlorate.*—Methyldiphenylphosphine (200 mg) was added to a dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) and the solution was immediately passed down a short silica gel column. The excess of tertiary

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[17] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843.

[18] L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, 1966, **88**, 5324.

[19] M. C. Hall, B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc.* (*A*), 1970, 2539.

[20] L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley–Interscience, London, 1969, p. 146.

[21] J. W. Dart, M. K. Lloyd, J. A. McCleverty, and R. Mason, *Chem. Comm.*, 1971, 1197.

phosphines was eluted first with dichloromethane and the product was eluted with acetone–dichloromethane (1 : 20). The solvents were removed at reduced pressure and the product crystallised as orange prisms by addition of ethanol–cyclohexane, maintaining an oxygen-free nitrogen atmosphere during crystallisation (85 mg, 83%). M.p. 155—157°. ^{1}H N.m.r. ($CDCl_3$) shows τ 8·1 (m, CH_3) and τ 2·6 (m, Ph) with integrated ratio 3·1 : 10, required 3 : 10. The ethyldiphenylphosphine complex $[Ir(CO)(PEtPh_2)_3]ClO_4$ was prepared in a similar manner but was not isolated as a crystalline solid (Found: C, 52·25; H, 4·35; P, 9·85. $C_{40}H_{39}ClIrO_5P_3$ requires C, 52·2; H, 4·25; P, 10·1%).

Tetrakis(*methyldiphenylphosphine*)*iridium*(I) *Perchlorate, Tetrafluoroborate, Hexafluorophosphate, and Tetraphenylborate*.—A solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO$ (200 mg) and methyldiphenylphosphine (600 mg) in ethanol (30 ml) was heated under reflux for 2 h. On cooling, red crystals of the product formed and these were washed with ethanol (200 mg, 80%). M.p. 172—174°. ^{1}H N.m.r. ($CDCl_3$) shows τ 9·67 (broad s, CH_3) and τ 2·6 (broad s, Ph) with integrated ratio 2·9 : 10, required 3 : 10. When recrystallised from dichloromethane–ethanol–cyclohexane a 0·5 cyclohexane solvate (τ 8·76, s) is formed showing integrated ratio $CH_3 : C_6H_{12} :$ Ph as 40 : 5·5 : 11, required 40 : 6 : 12. $\Lambda_M = 24·0\ \Omega^{-1}\ cm^2\ mol^{-1}$ in nitrobenzene at 25° (10^{-3}M) (Found: C, 56·9; H, 5·0; P, 10·0. $C_{52}H_{52}ClIrO_4P_4$ requires C, 57·2; H, 4·8; P, 11·35%).

The tetrafluoroborate salt was prepared similarly. M.p. 167—169°. A red material, presumably, the ethyldiphenylphosphine analogue, $[Ir(PEtPh_2)_4]BF_4$, was prepared in the same way but a crystalline product could not be isolated and no analytical data were obtained (Found: C, 57·75; H, 5·35. $C_{52}H_{52}BF_4IrP_4$ requires C, 57·85; H, 4·85%).

The hexafluorophosphate salt was prepared by adding methyldiphenylphosphine (300 mg) to a dichloromethane solution of $[Ir(NO)_2(PPh_3)_2]PF_6$ (100 mg) and crystallising the product by addition of ethanol–cyclohexane. The red solid was recrystallised from dichloromethane–ethanol as red crystals (60 mg, 50%). M.p. 167—169° (Found: C, 54·6; H, 5·1; P, 12·3. $C_{52}H_{52}F_6IrP_5$ requires C, 54·9; H, 4·6; P, 13·6%).

The tetraphenylborate salt was obtained as red crystals by recrystallising $[Ir(PMePh_2)_4]ClO_4$ (100 mg) from dichloromethane–ethanol in the presence of $NaBPh_4$ (300 mg). M.p. 175—176° (Found: C, 69·6; H, 5·6; P, 9·15. $C_{76}H_{72}BIrP_4$ requires C, 69·55; H, 5·55; P, 9·45%).

Bis[cis-1,2-*bis*(*diphenylphosphino*)*ethene*]*iridium*(I) *Perchlorate* $[Ir(Ph_2PCH{=}CHPPh_2)_2]ClO_4$.—*cis*-1,2-Bis(diphenylphosphino)ethene (120 mg) was added to an ethanol suspension of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) and the solution heated under reflux with a nitrogen through-flow for 10 min. On cooling and after addition of cyclohexane an orange solid was deposited. Recrystallisation was done under a nitrogen atmosphere from dichloromethane–ethanol (80 mg, 70%). M.p. 270—273°. The known $[Ir(Ph_2PCH_2CH_2PPh_2)_2]BF_4$ was prepared in a similar manner from bis(diphenylphosphino)ethane and its m.p. found close to the literature [18] value (270°) (Found: C, 57·2; H, 4·35; P, 11·5. $C_{52}H_{44}ClIrO_4P_4$ requires C, 57·6; H, 4·1; P, 11·4%).

Carbonylbis[cis-1,2-*bis*(*diphenylphosphino*)*ethene*]*iridium*(I) *Perchlorate*.—*cis*-1,2-Bis(diphenylphosphino)ethene (120 mg) was added to an ethanol–dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) and a brief stream of carbon monoxide was passed through the solution. Crystallisation was effected from cyclohexane to give cream crystals (90 mg, 75%). M.p. 278—280° (with some loss of CO during the heating period) (Found: C, 57·05; H, 4·1; P, 10·9. $C_{53}H_{44}ClIrO_5P_4$ requires C, 57·25; H, 4·0; P, 11·15%).

Carbonyl(p-*tolyl isocyanide*)*bis*(*triphenylphosphine*)*iridium*(I) *Perchlorate*.—*p*-Tolyl isocyanide (75 mg) was added to a dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (500 mg) and the concentrated solution passed down a silica gel column eluting with dichloromethane. The orange fraction was collected, rechromatographed, and the last five-sixths of the orange fraction collected. Crystallisation was effected from ethanol–cyclohexane to yield orange prisms (260 mg, 50%). M.p. 174—176°. ^{1}H N.m.r. ($CDCl_3$) shows τ 7·78 (s, CH_3) and τ 2·5 (m, Ph) with integrated ratio found 4 : 34, required 3 : 34 (Found: C, 56·05; H, 4·2; N, 1·1. $C_{45}H_{37}ClIrNO_5P_2$ requires C, 56·25; H, 3·9; N, 1·45%).

Tris(p-*tolyl isocyanide*)*bis*(*triphenylphosphine*)*iridium*(I) *Perchlorate*.—*p*-Tolyl isocyanide (225 mg) was added to a dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (500 mg) and the concentrated solution passed down a silica gel column eluting with dichloromethane. The orange fraction was collected, rechromatographed, and the first three-quarters of the orange fraction collected. n-Hexane was added to precipitate the orange product (240 mg, 45%). M.p. 99—101° (Found: C, 60·05; H, 5·5; N, 3·95. $C_{60}H_{51}ClIrN_3O_4P_2$ requires C, 61·25; H, 4·4; N, 3·6%).

Tricarbonylbis(*triphenylphosphine*)*iridium*(I) *Perchlorate*.—A brief stream of carbon monoxide was passed through a dichloromethane–ethanol solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) and the solvents were concentrated at reduced pressure to yield colourless crystals (100 mg, 90%). M.p. 160—162°. Approximately 0·65 mol of dichloromethane solvate was detected in the ^{1}H n.m.r. spectrum ($CDCl_3$) which shows τ 4·70 (s, CH_2Cl_2) and τ 2·4 (m, Ph) with integrated ratio 1·15 : 30 (Found: C, 49·45; H, 3·35. $C_{39}H_{30}ClIrO_7P_2,0·65CH_2Cl_2$ requires C, 49·9; H, 3·3%).

Dicarbonyltris(*methyldiphenylphosphine*)*iridium*(I) *Perchlorate and Tetrafluoroborate*.—*Method* 1. A dichloromethane solution of $[Ir(PCH_3Ph_2)_4]ClO_4$ (100 mg) was stirred under carbon monoxide (2 atm) until colourless (15 min). A white solid was precipitated with n-hexane and this was recrystallised from dichloromethane–ethanol–cyclohexane to give colourless needles (60 mg, 85%). M.p. 138—141° dec. The same method was used to prepare the BF_4^- salt. M.p. 78—79°.

Method 2. Methyldiphenylphosphine (300 mg) was added to a dichloromethane solution of $[Ir(CO)_3(PPh_3)_2]ClO_4$ (100 mg). A white solid was precipitated with n-hexane and this was recrystallised from dichloromethane–ethanol–cyclohexane (95 mg, 90%). ^{1}H N.m.r. of the perchlorate salt revealed 0·6 mol dichloromethane solvate: τ 8·0 (broad t, CH_3), τ 4·74 (s, CH_2Cl_2), and τ 2·7 (m, Ph) with integrated ratio 9 : 1·4 : 30 (Found for perchlorate: C, 50·0; H, 4·4; P, 9·2. $C_{41}H_{39}ClIrO_4P_3,0·6CH_2Cl_2$ requires C, 50·0; H, 4·05; P, 9·3. Found for tetrafluoroborate: C, 53·45; H, 4·55; P, 10·0. $C_{41}H_{39}BF_4IrO_2P_3$ requires C, 52·65; H, 4·2; P, 9·95%).

Dicarbonyltris(*ethyldiphenylphosphine*)*iridium*(I) *Perchlorate*.—This was prepared by method 2 above using ethyldiphenylphosphine (300 mg) and obtained as very pale yellow crystals. M.p. 149—151°. ^{1}H N.m.r. ($CDCl_3$) shows τ 9·1 (broad m, CH_3), τ 7·6 (broad s, CH_2), and τ 2·6 (m, Ph) with integrated ratio 3 : 2 : 10, required 3 : 2 : 10 (Found: C, 53·3; H, 4·6. $C_{44}H_{45}ClIrO_6P_3$ requires C, 53·35; H, 4·6%).

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