Members of the Series $IrX(CO)(PPh_3)_2$ with Various Anionic Ligands and Their Dioxygen Complexes

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Acetonitrile is displaced from $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ by the co-ordinating anions, F^-, OH^-, NCO^-, NCS^-, O_2CH^-, $O_2CCF_3^-$, SH^-, $C{\equiv}CPh^-$, *p*-toluenesulphinate, and CN^- to yield four-co-ordinate analogues of $IrCl(CO)(PPh_3)_2$, except for the cyanide which is five-co-ordinate, $IrCN(CO)(PPh_3)_3$. The comparative uptake of dioxygen by these compounds to form dioxygen complexes has been studied. The sulphinate, Ir(*p*-toluenesulphinate)$(CO)(PPh_3)_2$ is *O*-bound but upon further co-ordination of CO or O_2 the sulphinate changes to *S*-bound although addition of methyl iodide produces an *O*-bound iridium(III) compound.

REPLACEMENT of chloride by other anions in $IrCl(CO)(PPh_3)_2$ can sometimes be brought about by direct reaction with an excess of the replacing anion. Successful preparations of $IrX(CO)(PPh_3)_2$ for X = Br, I, NCO, NCS, and N_3 have been achieved by this route.[1] $Ir(Ph)(CO)(PPh_3)_2$ results from reaction of $IrCl(CO)(PPh_3)_2$ with LiPh.[2] Other analogues, where $X = GeR_3$ [3] or $C{\equiv}CR$,[4] result from favourable addition–elimination sequences, and for $X = CS_2H$ [5] by iridium–hydride addition to CS_2 and $X = SC_6F_5$ [6] by using $TlSC_6F_5$. The acetonitrile cation, $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$, which is itself easily prepared in high yield,[7,8] provides a convenient high yield route to a series of $IrX(CO)(PPh_3)_2$ compounds. Few limits are imposed upon the scope of this reaction and anions with as diverse bonding requirements as F^- and CN^- can be used to displace acetonitrile.

$IrX(CO)(PPh_3)_2$ *Compounds*.—Lithium halides in ethanol almost quantitatively convert $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ to $IrX(CO)(PPh_3)_2$ for X = Cl, Br, and I. Ammonium thiocyanate and sodium cyanate were used to prepare $Ir(NCS)(CO)(PPh_3)_2$ and $Ir(NCO)(CO)(PPh_3)_2$ respectively. These anions are reported to be *N*-bound [9] giving the first indication of a trend favouring 'hard' anions *trans* to the carbonyl group. *p*-Toluenesulphinate (pts) ions give $Ir(pts)(CO)(PPh_3)_2$ whose sulphur–oxygen stretching frequencies identify oxygen as the donor atom rather than the 'softer' sulphur atom (see later discussion). Hydroxide ions also co-ordinate to $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ giving $Ir(OH)(CO)(PPh_3)_2$ which is isoelectronic with $[Ir(OH)(NO)(PPh_3)_2]^+$ (ref. 10). Unlike the nitrosyl cation, however, no exchange of hydroxide for alkoxide occurs in $Ir(OH)(CO)(PPh_3)_2$ and attempts to add sodium ethoxide to $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ resulted in hydroxide formation, probably because of the difficulty of removing all traces of water from the reagents and solvents. The rhodium analogue $Rh(OH)(CO)(PPh_3)_2$ has been reported resulting from the reaction of $RhCl(CO)(PPh_3)_2$ with sodium alkoxides.[11] Fluoride ions co-ordinate to $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ giving $IrF(CO)(PPh_3)_2$. A medium intensity band in the i.r. spectrum at 485 cm^{-1}, absent in all other $IrX(CO)(PPh_3)_2$ compounds, is assigned to the iridium–fluorine stretching frequency. This fluoride has also been prepared by reaction of $IrCl(CO)(PPh_3)_2$ with ammonium fluoride and silver carbonate in aqueous methanol.[12] $RhF(CO)(PPh_3)_2$ is also known.[13]

Formato-, trifluoroacetato-, phenylethynyl-, and thiolo-complexes $Ir(O_2CH)(CO)(PPh_3)_2$, $Ir(O_2CCF_3)(CO)(PPh_3)_2$, $Ir(C{\equiv}CPh)(CO)(PPh_3)_2$, and $Ir(SH)(CO)(PPh_3)_2$ were prepared by similar reactions of $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ with a source of the appropriate anion. The thiolo-complex was also prepared directly from H_2S on the acetonitrile cation and like most thiolo-complexes no ν(SH) frequency was observed in the i.r. spectrum.[10] Neither the trifluoroacetate nor the formate complex was

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

[11] G. Gregorio, G. Pregaglia, and R. Ugo, *Inorg. Chim. Acta*, 1969, **3**, 89.

[12] L. Vaska and J. Peone, jun., *Chem. Comm.*, 1971, 418.

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found to decarboxylate upon heating under reflux in toluene.

All the compounds crystallise beautifully as lemon yellow solids and their structures, like $IrCl(CO)\{P(o\text{-}tolyl)_3\}_2$,[14] are undoubtedly *trans*-square-planar. The variation of their carbonyl stretching frequencies (see Table 2) must reflect the transmission of the electronic features of the *trans* anionic group (X) through the metal centre of the carbonyl ligand.

The most significant feature of the ν(CO) values is that π-back-bonding into antibonding orbitals of the carbonyl ligand appears to be greatest [as judged by the lowest ν(CO)] when hydroxide is the *trans*-ligand. This supports the idea that oxygen can function as a $p\pi$ donor in this situation. When the complex is given a choice of a ' hard ' or a ' soft ' anionic donor atom as in $Ir(pts)(CO)(PPh_3)_2$ or $Ir(NCS)(CO)(PPh_3)_2$ it chooses the ' hard ' donor. A possible explanation lies in the $p\pi$ donor ability of the ' hard ' ligands since under conditions of $p\pi$ donation and σ acceptance, not only does the carbonyl ligand become more strongly bound, but the anion must also become more strongly bound.

No successful synthesis of the four-co-ordinate hydride $IrH(CO)(PPh_3)_2$ has been reported although many attempts have been made.[15] It has, however, been detected kinetically as an intermediate in the addition of substituted silanes to $IrH(CO)(PPh_3)_2$ [16] and as the active catalyst derived from $IrH_3(CO)(PPh_4)_2$.[17] Introduction of a hydride source, in the form of hydrazine hydrate, to $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ produced a 50% yield of $IrH(CO)(PPh_3)_3$ perhaps indicating that $IrH(CO)(PPh_3)_2$ is unstable with respect to disproportionation. In a similar reaction with sodium borohydride, $IrH_3(CO)(PPh_3)_2$ [18] was isolated.

No cyanide analogue of $IrCl(CO)(PPh_3)_2$ is known and attempts to prepare it by a replacement reaction leads to destruction of the complex. Introduction of cyanide ions to $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$ also leads to intractable products but when an excess of triphenylphosphine is present, a high yield of pale yellow crystals having a cyanide stretching frequency at 2120 cm^{-1} and ν(CO) at 1975 cm^{-1} is obtained. Elemental analysis confirms the formulation $Ir(CN)(CO)(PPh_3)_3$. Five-co-ordination in this product was unexpected since the hydride $IrH(CO)(PPh_3)_3$ is the only other member of this iridium(I) series which chooses to co-ordinate three triphenylphosphine ligands. The stereochemistry is probably like $IrH(CO)(PPh_3)_3$ with equatorial phosphines.[19]

Dioxygen Complexes.—Replacement of chloride by iodide in $Ir(O_2)Cl(CO)(PPh_3)_2$ to give $Ir(O_2)I(CO)(PPh_3)_2$ not only makes dioxygen co-ordination irreversible but causes a marked increase in the length of the O–O bond.[20] This is attributed to the lower electronegativity of iodine permitting greater charge transfer from iridium to dioxygen and hence stronger co-ordination. Subsequent kinetic investigations [21] have confirmed that the rates of oxygenation and deoxygenation of a series of iridium complexes increase and decrease, respectively, with increasing electron-releasing tendency of the anionic group X in $IrX(CO)(PPh_3)_2$. To further test the truth of these trends the affinity of the present complexes towards dioxygen was tested.

Without exception, dioxygen complexes were isolated from all $IrX(CO)(PPh_3)_2$ complexes as well as from the five-co-ordinate cyanide complex (see Table 1). For X = SH, C≡CPh, pts, and O_2CH, dioxygen complexes formed rapidly when solutions were left standing in the air. For X = NCS, NCO, and O_2CCF_3, suitable reaction conditions were to stir an ethanol suspension of the complex under a dioxygen pressure (2—3 atm). The ready reversibility of dioxygen uptake by the thiocyanate complex probably accounts for the report [22] that $Ir(O_2)(NCS)(CO)(PPh_3)_2$ does not form. In ethanol suspension $Ir(OH)(CO)(PPh_3)_2$ produced the ethoxide dioxygen complex $Ir(O_2)(OEt)(CO)(PPh_3)_2$. The formation of the fluoride and cyanide dioxygen complexes was accompanied by decomposition and gave very low yields. This prevented the isolation of pure samples for analysis of the fluoride and cyanide compounds but in view of their i.r. spectra all showing ν(CO) close to 2000 cm^{-1} and $\nu(IrO_2)$ close to 840 cm^{-1} there can be no doubt of their composition. As far as possible, the reversibility of dioxygen uptake [in the sense that the dioxygen can be

TABLE 1

Dioxygen complexes $Ir(O_2)X(CO)(PPh_3)_2$

Compound	I.r. spectra [a] ν(CO)	I.r. spectra [a] $\nu(IrO_2)$	Reversibility	Forward rate
$Ir(O_2)Cl(CO)(PPh_3)_2$	2005vs	855s	Rev.	Slow
$Ir(O_2)(NCS)(CO)(PPh_3)_2$	2015vs	855s	Rev.	Slow
$Ir(O_2)(NCO)(CO)(PPh_3)_2$	2005vs	855s	Rev.	Slow
$Ir(O_2)(O_2CCF_3)(CO)(PPh_3)_2$	2020vs	860s	Rev.	Very fast
$Ir(O_2)I(CO)(PPh_3)_2$	2005vs	850s	Irrev.	Mod. fast
$Ir(O_2)(SH)(CO)(PPh_3)_2$	1990vs	845s	Irrev.	Fast
$Ir(O_2)(O_2CH)(CO)(PPh_3)_2$	2010vs	855s	Irrev.	Fast
$Ir(O_2)(C{\equiv}CPh)(CO)(PPh_3)_2$	1990vs	835s	Irrev.	Very fast
$Ir(O_2)(pts)(CO)(PPh_3)_2$	2025vs	835s	Irrev	Mod. fast
$Ir(O_2)(OEt)(CO)(PPh_3)_2$	2000s	835m		Slow
$Ir(O_2)F(CO)(PPh_3)_2$	2005vs	850m		Slow
$Ir(O_2)(CN)(CO)(PPh_3)_2$	2010vs	840s		Slow

[a] In cm^{-1}, from Nujol mulls.

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TABLE 2

Infrared data for iridium complexes [a]

Compound	Colour	ν(CO)	Other frequencies	ν(CO) [b]
$\mathrm{IrF(CO)(PPh_3)_2}$	Yellow	1945vs, 1960vs	ν(IrF) 485m	1955s
$\mathrm{Ir(OH)(CO)(PPh_3)_2}$	Yellow	1930vs, 1950w	ν(OH) 3580m	1935s
$\mathrm{Ir(NCO)(CO)(PPh_3)_2}$	Yellow	1965vs	ν(NC) 2240vs	1962s
$\mathrm{Ir(NCS)(CO)(PPh_3)_2}$	Yellow	1970vs	ν(NC) 2080vs	1970s
$\mathrm{Ir(SH)(CO)(PPh_3)_2}$	Yellow	1945vs		1960s
$\mathrm{Ir(pts)(CO)(PPh_3)_2}$	Yellow	1955vs	ν(SO) 1085s, 840vs, 855s; 815m (*p*-tolyl); $\delta(\mathrm{SO_2})$ 640m	1963s
$\mathrm{Ir(C{\equiv}CPh)(CO)(PPh_3)_2}$	Yellow-orange	1955vs	ν(CC) 2115m	1958s
$\mathrm{Ir(O_2CCF_3)(CO)(PPh_3)_2}$	Yellow	1970vs, 1944w	1695s, 1180vs, 1190sh, 1140s, 780m ($\mathrm{CF_3CO_2}$)	1965s
$\mathrm{Ir(O_2CH)(CO)(PPh_3)_2}$	Yellow	1955vs	ν(C=O) 1635vs; ν(C–O) 1285vs	
$\mathrm{Ir(CN)(CO)(PPh_3)_3}$	Pale yellow	1975vs	ν(NC) 2120m	
$\mathrm{Ir(O_2)(NCS)(CO)(PPh_3)_2}$	Orange-brown	2015vs	$\nu(\mathrm{IrO_2})$ 855s; ν(NC) 2090s	
$\mathrm{Ir(O_2)(NCO)(CO)(PPh_3)_2}$	Very pale brown	2005vs	$\nu(\mathrm{IrO_2})$ 855s; ν(NC) 2240vs	
$\mathrm{Ir(O_2)(CF_3CO_2)(CO)(PPh_3)_2}$	Orange-brown	2020vs	$\nu(\mathrm{IrO_2})$ 860s; 1710s, 1180vs, 1195sh, 1045s, 780m ($\mathrm{CF_3CO_2}$)	
$\mathrm{Ir(O_2)(SH)(CO)(PPh_3)_2}$	Orange-brown	1990vs	$\nu(\mathrm{IrO_2})$ 855s	
$\mathrm{Ir(O_2)(C{\equiv}CPh)(CO)(PPh_3)_2}$	Orange-brown	1990vs	$\nu(\mathrm{IrO_2})$ 835s; ν(C≡C) 2125m	
$\mathrm{Ir(O_2)(pts)(CO)(PPh_3)_2}$	Orange-brown	2025vs	$\nu(\mathrm{IrO_2})$ 835s; ν(SO) 1210vs, 1190vs, 1050s; $\delta(\mathrm{SO})_2$ 645s	
$\mathrm{Ir(O_2)(OEt)(CO)(PPh_3)_2}$	Orange-brown	2000vs	$\nu(\mathrm{IrO_2})$ 835m; 1045m, 850m (EOt)	
$\mathrm{Ir(O_2)F(CO)(PPh_3)_2}$	Orange-brown	2005vs	$\nu(\mathrm{IrO_2})$ 850m	
$\mathrm{Ir(O_2)(CN)(CO)(PPh_3)_2}$	Orange-brown	2010vs	$\nu(\mathrm{IrO_2})$ 840s; ν(CN) 2140m	
$\mathrm{Ir(pts)(SO_4)(CO)(PPh_3)_2}$	Colourless	2055vs	1300vs, 1240s, 1170vs, 890s, 860s, 660vs, 580vs, 555s ($\mathrm{SO_4}$); 1190sh, 1060s; $\delta(\mathrm{SO_2})$ 640s	
$\mathrm{Ir(pts)(CO)_2(PPh_3)_2}$	Very pale yellow	1940vs,br, 2000vs	ν(SO) 1155s, 1140s, 1020s, 1010s; 810m (*p*-tolyl); $\delta(\mathrm{SO_2})$ 640s	
$\mathrm{Ir(CH_3)I(pts)(CO)(PPh_3)_2}$	Colourless	2040vs	ν(SO) 1075sh,br, 870s,br; 810m (*p*-tolyl); $\delta(\mathrm{SO_2})$ 640m	
$\mathrm{IrH(O_2CCF_3)_2(CO)(PPh_3)_2}$	Colourless		ν(IrH) 2245m; δ(IrH) 845m, 800m; 1700s, 1675vs, 1180vs, 1195sh, 1145vs, 780s ($\mathrm{CF_3CO_2}$)	
$\mathrm{IrFI_2(CO)(PPh_3)_2}$	Orange	2055vs		
$\mathrm{[IrH(CN)(CO)(PPh_3)_3]ClO_4}$	Colourless	2055vs	ν(IrH), ν(CN) 2150m,br, 2140sh; δ(IrH) 820m,br, 795m	

[a] In $\mathrm{cm^{-1}}$ from Nujol mulls. [b] In $\mathrm{CH_2Cl_2}$ solution.

removed to return the four-co-ordinate complex $\mathrm{IrX(CO)(PPh_3)_2}$] was tested by boiling a benzene solution of the *dioxygen* complex with a nitrogen through-flow. Also, estimations of the speed of dioxygen uptake were gained from handling experience and graded slow, moderately fast, fast, and very fast (see Table 1). Naturally, a detailed analysis of the influence of the anion cannot be sustained on these limited qualitative data, but one feature warrants comment. Although most of the complexes which were formed rapidly were formed irreversibly, $\mathrm{Ir(O_2)(O_2CCF_3)(CO)(PPh_3)_2}$ is a notable exception. In solution $\mathrm{Ir(O_2CCF_3)(CO)(PPh_3)_2}$ rapidly takes up dioxygen from the air but to achieve complete conversion to $\mathrm{Ir(O_2)(O_2CCF_3)(CO)(PPh_3)_2}$ dioxygen pressures were required. Once isolated as a pure solid, $\mathrm{Ir(O_2)(O_2CCF_3)(CO)(PPh_3)_2}$ rapidly loses approximately 30% of its dioxygen upon dissolution in dichloromethane at room temperature. Solid $\mathrm{Ir(O_2CCF_3)(CO)(PPh_3)_2}$, when heated to 100° in air, was found to be changed almost completely to its dioxygen adduct. In general, the 'softer' anions such as $\mathrm{SH^-}$, $\mathrm{C{\equiv}CPh^-}$, $\mathrm{O_2CH^-}$, $\mathrm{I^-}$, and pts enhance the thermodynamic stability of the dioxygen adduct (dioxygen is bound irreversibly) but even without quantitative rate data, it is evident that the kinetic picture can follow a different pattern.

Isomerism in Iridium Sulphinates.—A criterion for distinguishing between the sulphur and oxygen modes of sulphinate bonding, $\mathrm{M{-}SO_2{-}R}$ and M–O–SO–R, is based on the observation that the asymmetric and symmetric sulphur–oxygen stretching frequencies for organic sulphones $\mathrm{R'{-}SO_2{-}R}$ occur at considerably higher frequencies than for the corresponding sulphinate esters R′–O–SO–R. In metal sulphinates the metal takes the place of the R′ group leading to the hypothesis that *S*-sulphinates will absorb at higher wavenumbers than *O*-sulphinates and this prediction has proved true where n.m.r. [23] or crystal structure [24] confirmation is available. Sulphinate complexes of the transition metals have usually been found to be *S*-bound [23] although some *S*- and *O*-bound bridged dimers of platinum have been reported [25] and the crystal structure of $\mathrm{Cu(pts)_2,4H_2O}$ has shown it to contain monodentate *O*-bound sulphinate.[24] The ν(SO) positions in the i.r. spectra for $\mathrm{Ir(pts)(CO)(PPh_3)_2}$ at 1085 and 840 $\mathrm{cm^{-1}}$ require *O*-bound sulphinate. Values for *O*- and *S*-bound mercury sulphinates are 1048 and 838, and 1175 and 1049 $\mathrm{cm^{-1}}$ respectively.[26] These bands persist in solution spectra ($\mathrm{CH_2Cl_2}$, $\mathrm{CH_2Br_2}$, $\mathrm{C_6H_6}$) and in solvents where the 1200 $\mathrm{cm^{-1}}$ region was available, no absorptions were found that

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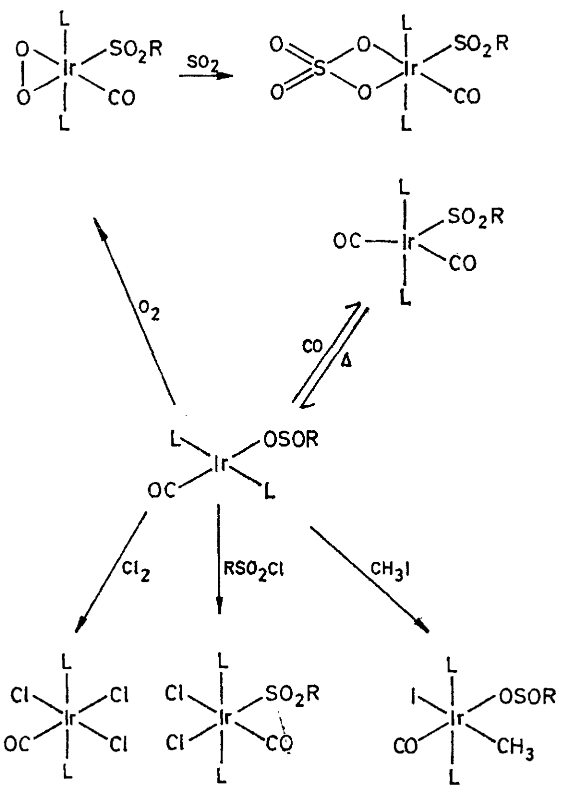
might suggest the presence of *S*-bound sulphinate.[27] The possibility of a bridging situation existing in a dimer or a polymer can be discounted in view of the similarity of the i.r. spectrum [particularly the single ν(CO)] with other $IrX(CO)(PPh_3)_2$ complexes, its normal solubility and its monomeric behaviour under the conditions of an osmometric molecular weight determination in benzene (*M*, found 890, calc. 899). The possibility of a formally five-co-ordinate complex where both oxygen atoms of the sulphinate are bound equally or unequally to the iridium can also be dismissed because the bright yellow colour is typical of four-co-ordinate iridium(I) and the ν(SO) bands are very similar to those for $Ir(CH_3)I(pts)(CO)(PPh_3)_2$ (see later) where the sulphinate group must be monodentate.

Application of ' hard ' and ' soft ' acid–base theory would predict that *O*-bound sulphinates are more likely to exist in high oxidation state complexes.[23] Yet, for the few known iridium(III) sulphinates only *S*-bound groups have been reported, these examples having been derived from oxidative additions of aryl and alkyl sulphonyl halides to $IrCl(CO)(PPh_3)_2$.[28]

To investigate whether *S*-bound sulphinates in iridium(III) complexes are the rule or the exception, a number of oxidative addition reactions were carried out on $Ir(pts)(CO)(PPh_3)_2$ (see Scheme). Upon irreversible uptake of dioxygen, ν(SO) bands in the i.r. spectrum of $Ir(O_2)(pts)(CO)(PPh_3)_2$ require an *S*-bound group.[27] When this product is treated with sulphur dioxide converting bound dioxygen to bidentate sulphate in $Ir(SO_4)(pts)(CO)(PPh_3)_2$, the Ir–S linkage persists. Similarly in the five-co-ordinate carbon monoxide adduct, $Ir(pts)(CO)_2(PPh_3)_2$, the sulphinate switches from *O*- to *S*-bound. This last isomerisation is fast and reversible. Chatt and Mingos, in their study of platinum *S*-sulphinates,[25] concluded that *S*-sulphinates can exert a strong *trans* influence comparable to that of phosphines and should therefore be viewed as good σ-donors but relatively poor π-acceptors. The operation of this strong inductive release in $Ir(O_2)(pts)(CO)(PPh_3)_2$ and $Ir(pts)(CO)_2(PPh_3)_2$ must best satisfy the bonding requirements of the electron accepting dioxygen and carbonyl ligands.

An exception is provided by the methyl iodide adduct of $Ir(pts)(CO)(PPh_3)_2$ the i.r. spectrum of which (see Table 2) requires *O*-bound sulphinate. This may result from sulphinate bonding *trans* to carbon monoxide but the influence of steric factors cannot be ignored and the larger methyl and iodide groups may force the sulphinate group to adopt a mode of co-ordination where non-bonding contracts are minimised. Presumably *O*-sulphinates are less bulky donors than *S*-sulphinates. Steric factors can control *S*- or *O*-co-ordination of sulphoxides in palladium complexes.[29]

Chlorine cleaves the sulphinate group from $Ir(pts)(CO)(PPh_3)_2$ the products being *p*-tolylsulphonyl chloride, $IrCl(CO)(PPh_3)_2$, and $IrCl(CO)(PPh_3)_2$. An attempt to prepare a bis(sulphinato)-complex by addition of *p*-tolylsulphonyl chloride to $Ir(pts)(CO)(PPh_3)_2$ gave instead $IrCl_2(pts)(CO)(PPh_3)_2$. An oxidative addition–reductive elimination sequence with loss of di-*p*-tolyl disulphone may be responsible. No successful desulphonylation to give aryl complexes as has been observed for $IrCl_2(pts)(CO)(PPh_3)_2$ [28] was found for the sulphinate complexes described herein.



(L = PPh$_3$, R = *p*-tolyl)

SCHEME Reactions of $Ir(pts)(CO)(PPh_3)_3$

Other Oxidative Additions.—In the preparation of $Ir(O_2CCF_3)(CO)(PPh_3)_2$, excess CF_3CO_2H was found to add rapidly producing $IrH(O_2CCF_3)_2(CO)(PPh_3)_2$. Similar additions have been reported.[30] The addition was reversible and no decarboxylation to give trifluoromethyl complexes was observed. Perchloric acid was found to protonate the five-co-ordinate $Ir(CN)(CO)(PPh_3)_3$ giving $[IrH(CN)(CO)(PPh_3)_3]ClO_4$, demonstrating the basic nature of the metal centre, a reaction analogous to protonation of $IrH(CO)(PPh_3)_3$ giving $[IrH_2(CO)(PPh_3)_3]^+$ (ref. 18). The high field ^1H n.m.r. of $[IrH(CN)(CO)(PPh_3)_2]^+$ reveals a widely separated pair of

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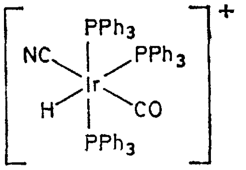
triplets consistent only with the structure depicted below.



$IrF(CO)(PPh_3)_2$ was found to add iodine cleanly without cleavage of the fluoride ligand to give the orange crystalline compound $IrFI_2(CO)(PPh_3)_2$. Reaction of $IrF(CO)(PPh_3)_2$ with carbon monoxide resulted in displacement of fluoride ion and production of $[Ir(CO)_3(PPh_3)_2]^+$.

EXPERIMENTAL

I.r. spectra (4000—400 cm^{-1}) were measured on a Shimadzu IR27G spectrometer calibrated with Polystyrene. M.p.s were measured on a Reichert hot-stage apparatus and ^1H n.m.r. spectra with a Varian A60 or T60. Molecular weight determinations were made with a Hewlett–Packard 302 osmometer.

Anion Additions to $[Ir(CO)(CH_3CN)(PPh_3)_2]^+$.—(*a*) N-*Cyanatocarbonylbis(triphenylphosphine)iridium*(I). A dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) was added to an ethanol suspension of sodium cyanate (20 mg) and the mixture stirred for 30 min. The solvents were partially stripped under reduced pressure and the product recrystallised from dichloromethane–ethanol as yellow crystals (65 mg, 75%). M.p. >250° dec. (Found: C, 58·15; H, 4·05; N, 1·4. $C_{38}H_{30}IrNO_2P_2$ requires C, 58·05; H, 3·85; N, 1·8%).

(*b*) N-*Thiocyanatocarbonylbis(triphenylphosphine)iridium*(I). A dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) was added to an ethanol solution of ammonium thiocyanate (15 mg) and the solvents stripped to a small volume under reduced pressure. The product was recrystallised from dichloromethane–ethanol as yellow crystals (85 mg, 95%). M.p. 209—210° (Found: C, 56·9; H, 3·9; N, 1·8. $C_{38}H_{30}IrNOP_2S$ requires C, 56·85; H, 3·75; N, 1·75%).

(*c*) (O-p-*Toluenesulphinato*)*carbonylbis(triphenylphosphine)iridium*(I). A dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) was added to an ethanol suspension of sodium *p*-toluenesulphinate tetrahydrate (35 mg) and the mixture stirred for 30 min under a nitrogen atmosphere. The solvents were stripped under reduced pressure and the product recrystallised from dichloromethane–ethanol as yellow crystals (75 mg, 75%). M.p. 172—173° (*M*, found 890, required 899) (Found: C, 58·6; H, 4·2. $C_{44}H_{37}IrO_3P_2S$ requires C, 58·75; H, 4·15%).

(*d*) *Hydroxocarbonylbis(triphenylphosphine)iridium*(I). A dilute ethanolic solution of potassium hydroxide was added to a dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) and the solvents stripped under reduced pressure. The product was recrystallised from benzene–ethanol as yellow crystals (75 mg, 85%). M.p. 177—179°. ^1H N.m.r. ($CDCl_3$) shows τ 8·3 (v. broad s, OH) and τ 2·6 (m, Ph) with integrated ratio 0·9 : 30, required 1 : 30). The OH signal disappeared on addition of D_2O (Found: C, 58·35; H, 4·1; P, 8·35. $C_{37}H_{31}IrO_2P_2$ requires C, 58·35; H, 4·15; P, 8·15%).

(*e*) *Fluorocarbonylbis(triphenylphosphine)iridium*(I). A dichloromethane–ethanol solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) was added to an ethanol solution of conc. (40%) aqueous hydrofluoric acid (0·04 ml) containing diethylamine (70 mg) and the solvents stripped to a small volume at reduced pressure. The product was recrystallised from dichloromethane–ethanol as yellow crystals (65 mg, 75%). M.p. 208—211°. Fluorine analysis was found to be unreliable in the presence of phosphorus (Found: C, 58·05; H, 4·05; P, 8·15. $C_{37}H_{30}FIrOP_2$ requires C, 58·15; H, 3·95; P, 8·1%).

(*f*) (*Trifluoroacetato*)*carbonylbis(triphenylphosphine)iridium*(I). Under a nitrogen atmosphere a dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) was added to an ethanol solution of trifluoroacetic acid (14 mg) containing diethylamine (50 mg) and the solvents stripped to a small volume at reduced pressure. The product was recrystallised from dichloromethane–ethanol as yellow crystals maintaining an oxygen-free atmosphere throughout (85 mg, 90%). M.p. 182—184° (Found: C, 54·65; H, 3·7. $C_{39}H_{30}F_3IrO_3P_2$ requires C, 54·6; H, 3·55%).

(*g*) (*Phenylethynyl*)*carbonylbis(triphenylphosphine)iridium*(I). An oxygen-free nitrogen atmosphere was maintained throughout this preparation. To a dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) was added phenylacetylene (50 mg) and diethylamine (100 mg). The resulting solution was passed down a short silica gel column and the yellow-orange fraction eluted with dichloromethane. An orange precipitate was obtained on addition of n-hexane (65 mg, 75%). M.p. 115—118° (Found: C, 64·0; H, 4·45. $C_{45}H_{35}IrOP_2$ requires C, 63·9; H, 4·15%).

(*h*) *Formatocarbonylbis(triphenylphosphine)iridium*(I). A nitrogen atmosphere was maintained throughout this preparation. A dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) was added to an ethanol solution of conc. (95%) aqueous formic acid (0·03 ml) containing *p*-toluidine (100 mg) and the solvents stripped under reduced pressure. The product was recrystallised from dichloromethane–ethanol as yellow crystals (65 mg, 70%). M.p. 152—154° (Found: C, 57·45; H, 4·05. $C_{38}H_{31}IrO_3P_2$ requires C, 57·8; H, 3·95%).

(*i*) *Thiolocarbonylbis(triphenylphosphine)iridium*(I). A nitrogen atmosphere was maintained throughout this preparation. An aqueous ethanol solution of sodium sulphide (50 mg) was added to a dichloromethane solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) and the solvents stripped at reduced pressure. The product was recrystallised as yellow crystals from dichloromethane–ethanol (75 mg, 85%). M.p. 205—206°. The same product was isolated in lower yield by briefly treating a solution of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ with hydrogen sulphide (Found: C, 56·85; H, 4·15; P, 7·8. $C_{37}H_{31}IrOP_2S$ requires C, 57·15; H, 4·0; P, 7·95%).

(*j*) *Cyanocarbonyltris(triphenylphosphine)iridium*(I). An ethanol suspension of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (250 mg), triphenylphosphine (100 mg) and sodium cyanide (16 mg) was stirred until the suspension changed to a pale yellow colour. The product was recrystallised from dichloromethane–ethanol as pale yellow crystals. M.p. 165—168° (Found: C, 65·0; H, 4·45; N, 1·4. $C_{56}H_{45}IrNOP_3$ requires C, 65·15; H, 4·4; N, 1·35%).

(*k*) *Hydridocarbonyltris(triphenylphosphine)iridium*(I). An ethanol suspension of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ and hydrazine hydrate (0·3 ml) was stirred for 30 min. The pale yellow solid was filtered off and identified by comparison of its i.r. spectrum with that of an authentic sample.[18]

(*l*) *Trihydridocarbonylbis(triphenylphosphine)iridium*(III). An ethanol suspension of $[Ir(CO)(CH_3CN)(PPh_3)_2]ClO_4$ (100 mg) and sodium borohydride (50 mg) was stirred in ethanol until colourless. The product was recrystallised from dichloromethane–ethanol as colourless crystals (85 mg, 95%). M.p. 149—151° dec. (Found: C, 59·05; H, 4·7. $C_{37}H_{33}IrOP_2$ requires C, 59·45; H, 4·45%).

Dioxygen Adducts, $Ir(O_2)X(CO)(PPh_3)_2$.—*Method* 1. A dichloromethane–ethanol solution of $IrX(CO)(PPh_3)_2$ was stirred under dioxygen (2 atm) for 30 min and the solvents removed at reduced pressure. The product was recrystallised from dichloromethane.

Method 2. An ethanol suspension of $IrX(CO)(PPh_3)_2$ was stirred under dioxygen (3 atm) until the yellow solids changed to pale orange-brown solids.

(*a*) *(Dioxygen)cyanatocarbonylbis(triphenylphosphine)iridium*(III). This was prepared in good yield by method 1 and isolated as an almost colourless crystalline solid with 0·8 mol of dichloromethane solvate. M.p. 240—244° (Found: C, 52·7; H, 3·8; H, 1·5. $C_{38}H_{30}IrNO_4P_2,0{\cdot}8CH_2Cl_2$ requires C, 52·55; H, 3·6; N, 1·6%).

(*b*) *(Dioxygen)thiocyanatocarbonylbis(triphenylphosphine)iridium*(III). This was prepared in good yield by method 1 and isolated as an orange-brown crystalline solid with 0·7 mol of dichloromethane solvate. M.p. 185—187° (Found: C, 51·85; H, 3·75; N, 1·5. $C_{38}H_{30}IrNO_3P_2S,0{\cdot}7CH_2Cl_2$ requires C, 51·95; H, 3·55; N, 1·55%).

(*c*) *(Dioxygen)*(S-p-*toluenesulphinato)carbonylbis(triphenylphosphine)iridium*(III). This was prepared in good yield by method 1 and isolated as orange-brown crystals. M.p. 153—155°. Recrystallisation from benzene–cyclohexane gave a benzene solvate. M.p. 160—162° (Found: C, 55·5; H, 4·30. $C_{44}H_{37}IrO_5P_2S$ requires C, 56·7; H, 4·0. Found for benzene solvate: C, 59·7; H, 4·4. $C_{44}H_{37}IrO_5P_2S,C_6H_6$ requires C, 59·45; H, 4·3%).

(*d*) *(Dioxygen)thiolocarbonylbis(triphenylphosphine)iridium*(III). This was prepared in good yield by method 1 and isolated as orange-brown crystals. M.p. 178—180° (Found: 54·15; H, 3·9. $C_{37}H_{31}IrO_3P_2S$ requires C, 54·85; H, 3·85%).

(*e*) *(Dioxygen)(phenylethynyl)carbonylbis(triphenylphosphine)iridium*(III). This was prepared by method 1 in good yield and isolated as orange-brown crystals. M.p. 177—178° (Found: C, 62·2; H, 4·1. $C_{45}H_{35}IrO_3P_2$ requires C, 61·55; H, 4·0%).

(*f*) *(Dioxygen)(trifluoroacetato)carbonylbis(triphenylphosphine)iridium*(III). This was prepared in high yield by method 2 and isolated as orange-brown crystals. M.p. 173—174°. The same product was isolated by heating a sample of $Ir(O_2CCF_3)(CO)(PPh_3)_2$ in air to 100° for 2 h (Found: C, 52·6; H, 3·9. $C_{39}H_{30}F_3IrO_5P_2$ requires C, 52·65; H, 3·4%).

(*g*) *(Dioxygen)formato(carbonyl)bis(triphenylphosphine)iridium*(III). This was prepared in good yield by method 1 as orange-brown crystals. M.p. 145—147° (Found: C, 55·3; H, 3·8. $C_{38}H_{31}IrO_5P_2$ requires C, 55·55; H, 3·8%).

(*h*) *(Dioxygen)ethoxo(carbonyl)bis(triphenylphosphine)iridium*(III). This was prepared from $Ir(OH)(CO)(PPh_3)_2$ by method 2 and isolated as pale orange-brown crystals. M.p. 138—140° (Found: C, 56·4; H, 4·4. $C_{39}H_{35}IrO_4P_2$ requires C, 57·0; H, 4·3%).

(*i*) *(Dioxygen)fluoro(carbonyl)bis(triphenylphosphine)iridium*(III). This was prepared as a pale orange-brown solid in low yield by method 2 (2 h reaction time) and identified by its i.r. spectrum (Table 2).

(*j*) *(Dioxygen)cyano(carbonyl)bis(triphenylphosphine)iridium*(III). This was prepared by method 2 as a pale orange-brown solid in low yield (16 h reaction time) and identified by its i.r. spectrum (Table 2).

Reactions Involving $Ir(pts)(CO)(PPh_3)_2$.—(*a*) (S-p-*Toluenesulphinato)dicarbonylbis(triphenylphosphine)iridium*(I). An n-hexane suspension of $Ir(pts)(CO)(PPh_3)_2$ was stirred under carbon monoxide (3 atm) for 5 h. The microcrystalline pale yellow solid was filtered off. M.p. 113—115° (Found: C, 57·4; H, 4·1. $C_{45}H_{37}IrO_4P_2S$ requires C, 58·25; H, 4·0%).

(*b*) *Sulphato*(S-p-*toluenesulphinato)carbonylbis(triphenylphosphine)iridium*(III). A stream of sulphur dioxide was passed briefly through a dichloromethane solution of $Ir(O_2)(pts)(CO)(PPh_3)_2$ and the colourless product precipitated with n-hexane. M.p. 185—187° (Found: C, 53·05; H, 4·2. $C_{44}H_{37}IrO_7P_2S_2$ requires C, 53·05; H, 3·7%).

(*c*) *Iodomethyl*(O-p-*toluenesulphinato)carbonylbis(triphenylphosphine)iridium*(III). Methyl iodide (1 ml) was added to a dichloromethane solution of $Ir(pts)(CO)(PPh_3)_2$ (100 mg) and after 5 min ethanol was added. Upon partial removal of the solvents at reduced pressure, off-white crystals were deposited and these were recrystallised from dichloromethane–ethanol (70 mg, 60%). M.p. 148—149° (Found: C, 51·65; H, 4·3. $C_{45}H_{40}IIrO_3P_2S$ requires C, 51·9; H, 3·9%).

(*d*) *Chlorine and* p-*toluenesulphonyl chloride* additions to $Ir(pts)(CO)(PPh_3)_2$ were done in dichloromethane–ethanol solution and the products (see text) were identified by their i.r. spectra.

Other Reactions.—Hydrido(cyano)carbonyltris(triphenylphosphine)iridium(III) *Perchlorate*. An ethanol solution of conc. (70%) aqueous perchloric acid (0·1 ml) was added to a dichloromethane solution of $Ir(CN)(CO)(PPh_3)_3$ (100 mg) and the solvents stripped to a small volume at reduced pressure. On standing, colourless crystals were deposited (80 mg, 70%). M.p. 194—196°. ^1H N.m.r. ($CDCl_3$) shows τ 21·7 [t, IrH, J(HP) 16 Hz], τ 19·9 [t, IrH, J(HP) 16 Hz], and τ 2·7 (m, Ph) (Found: C, 60·6; H, 4·4; N, 1·3; P, 8·0. $C_{56}H_{46}ClIrNO_5P_3$ requires C, 59·35; H, 4·1; N, 1·25; P, 8·2%).

Hydridobis(trifluoroacetato)carbonylbis(triphenylphosphine)iridium(III). Trifluoroacetic acid (0·1 ml) was added to a dichloromethane solution of $Ir(O_2CCF_3)(CO)(PPh_3)_2$ (100 mg) and the almost colourless product crystallised by addition of ethanol. M.p. 165—166° (Found: C, 50·8; H, 3·6. $C_{41}H_{31}F_6IrO_5P_2$ requires C, 50·65; H, 3·2%).

Fluorodi-iodocarbonylbis(triphenylphosphine)iridium(III). A dichloromethane solution of iodine (35 mg) was added to a dichloromethane solution of $IrF(CO)(PPh_3)_2$ (100 mg) and the orange product crystallised by addition of ethanol. M.p. 200—203° (Found: C, 43·7; H, 3·35; I, 24·25. $C_{37}H_{30}FI_2IrOP_2$ requires C, 43·7; H, 2·95; I, 24·95%).

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