Four-co-ordinate Iridium(I) Cations and the Ligand Dependence of Oxygen Uptake: the Crystal Structure of $[Ir(PPh_2CH_3)_4]BF_4$

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Summary Four-co-ordinate iridium(I) cations containing various combinations of the ligands, CO, MeCN, Me_2SO, PPh_3, PPh_2Me, and PPh_2Et are described including an X-ray structural analysis of $[Ir(PPh_2Me)_4]BF_4$: the ability of these cations to co-ordinate oxygen is found to be sensitive to steric factors.

REACTION with oxygen to form 1:1 oxygen complexes is characteristic of four-co-ordinate iridium(I) compounds, both neutral, *e.g.*, $IrCl(CO)(PPh_3)_2$ [1] and cationic, *e.g.*, $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$.[2] The structural studies of Ibers and his co-workers have established that the oxygen ligand is most tightly bound in the charged complex $[Ir(O_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$.[2] In contrast to this result, another iridium(I) cation, $[IrCl(NO)(PPh_3)_2]^+$ shows no interaction with oxygen.[3] This result is surprising, particularly since the uncharged ruthenium analogue $RuCl(NO)(PPh_3)_2$ shows a great affinity for oxygen.[4] To increase the understanding of the factors which are controlling oxygen uptake in these systems we have prepared a wide range of iridium(I) cations and examined their chemistry.

TABLE 1. *I.r. data*[a]

Compound[b]	ν(CO) (cm^{-1})	Other frequencies (cm^{-1})
$[Ir(CO)(MeCN)(PPh_3)_2]^+$	1980vs	ν(CN) 2290w
$[Ir(CO)(Me_2SO)(PPh_3)_2]^+$	1970vs	ν(SO)920s
$[Ir(CO)(PPh_3)_3]^+$	2000s	
$[Ir(CO)(PPh_2Me)_3]^+$	2000s	
$[Ir(CO)(PPh_2Et)_3]^+$	2000s	
$[Ir(PPh_2Me)_4]^+$		
$[Ir(O_2)(CO)(PPh_2Me)_3]^+$	2015s	840m (IrO_2)
$[Ir(O_2)(CO)(PPh_2Et)_3]^+$	2020s	845m (IrO_2)
$[Ir(SO_4)(CO)(PPh_2Me)_3]^+$	2060s	1300s, 1285sh, 1170vs, 860sh, 665vs, 555s (SO_4)
$[Ir(NO_3)_2(CO)(PPh_2Me)_3]^+$	2080s	1510s, 1265vs, 970m, 780w (NO_3)
$[IrH_2(CO)(MeCN)(PPh_3)_2]^+$	2040s	ν(IrH) 2140s, ν(CN) 2250w
$IrF(CO)(PPh_3)_2$	1950vs	
$Ir(OH)(CO)(PPh_3)_2$	1930vs	ν(OH) 3580w
$Ir(CN)(CO)(PPh_3)_3$	1970vs	ν(CN) 2120w

[a] Recorded as Nujol mulls; [b] Satisfactory elemental analyses have been obtained for all new compounds, the cations in association with either ClO_4^- and/or BF_4^- anions.

The cations are prepared by reaction of $IrCl(CO)(PPh_3)_2$ with silver perchlorate (or tetrafluoroborate) in acetonitrile. The resulting acetonitrile co-ordinated salts $[Ir(CO)(MeCN)(PPh_3)_2]Y$, ($Y = ClO_4$, BF_4) crystallise readily and are useful intermediates. Reaction with fluoride, hydroxide, and cyanide produces the unusual compounds, $IrF(CO)(PPh_3)_2$, $Ir(OH)(CO)(PPh_3)_2$, and $Ir(CN)(CO)(PPh_3)_3$, respectively. The cyanide, like the hydride $IrH(CO)(PPh_3)_3$, co-ordinates a third phosphine and is stable in the five-co-ordinate condition. When the preparation of the cations is carried out in dimethyl sulphoxide instead of acetonitrile, a dimethyl sulphoxide co-ordinated cation results $[Ir(CO)(Me_2SO)(PPh_3)_2]^+$. From its i.r. spectrum (see Table 1) the sulphoxide is concluded to be *O*-bound. $[Ir(CO)(MeCN)(PPh_3)_2]^+$ reacts rapidly with phosphines yielding the orange cations $[Ir(CO)L_3]^+$, ($L = PPh_3$, PPh_2Me, and PPh_2Et). In a much slower reaction excess of PPh_2Me eventually displaces the carbon monoxide affording red $[Ir(PPh_2Me)_4]^+$. All of the cations described above react with hydrogen to form colourless dihydrido-iridium(III) cations, but very few form oxygen complexes. In the series $[Ir(CO)L_3]^+$ only the compounds with alkyl-substituted phosphines form crystalline 1:1 oxygen complexes, $[Ir(O_2)(CO)(PPh_2Me)_3]^+$ and $[Ir(O_2)(CO)(PPh_2Et)_3]^+$. These pale brown, almost colourless complexes react with SO_2 and NO_2 forming, respectively, $[Ir(SO_4)(CO)(PPh_2Me)_3]^+$ and $[Ir(NO_3)_2(CO)(PPh_2Me)_3]^+$. Unexpectedly, the red cation, $[Ir(PPh_2Me)_4]^+$ does not react with oxygen; nor does it form a 1:1 adduct with carbon monoxide, but in a slow reaction colourless $[Ir(CO)_2(PPh_2Me)_3]^+$ is produced *via* $[Ir(CO)(PPh_2Me)_3]^+$. The marked change in reactivity between $[Ir(PPh_2Me)_4]^+$ and $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ suggests a structural difference and we have investigated this by X-ray structural analysis of $[Ir(PPh_2Me)_4]BF_4$.

The red crystals are obtained from dichloromethane–ethanol–cyclohexane solution with *ca.* one molecule of cyclohexane per molecule of complex (as suggested by n.m.r. spectroscopy and molecular weight determinations). The cell parameters are $a = 36{\cdot}730(7)$, $b = 22{\cdot}88(2)$, $c = 21{\cdot}633(4)$ Å, $\beta = 121{\cdot}41(1)°$; space group is $C2/c$ with $Z = 12$ for the stoicheiometric formula $[Ir(PPh_2CH_3)_4]BF_4,C_6H_{12}$. The asymmetric volume thus contains the equivalent of 1·5 formula units. Intensity data were collected on a Hilger and Watts automatic four-circle diffractometer with Mo-K_α radiation. The conventional R-factor is 0·115, with refinement continuing.

The analysis has verified the stoicheiometric formula.

TABLE 2. *Bond lengths and bond angles around athe iridium atoms*

Cation on special position	
Ir–P(1)	2·314 Å
Ir–P(2)	2·309
Ir–P(3)	2·325
Ir–P(4)	2·311
P(1)–Ir–P(2)	150·8°
P(3)–Ir–P(4)	151·0
P(1)–Ir–P(3)	93·8
P(1)–Ir–P(4)	93·6
P(2)–Ir–P(3)	93·6
P(2)–Ir–P(4)	93·5
Cation on special position	
Ir–P(1)	2·309 Å
Ir–P(2)	2·320
P(1)–Ir–P(1)	150·6°
P(2)–Ir–P(2)	150·5
P(1)–Ir–P(2)	93·7
P(1)–Ir–P(2)′	93·7

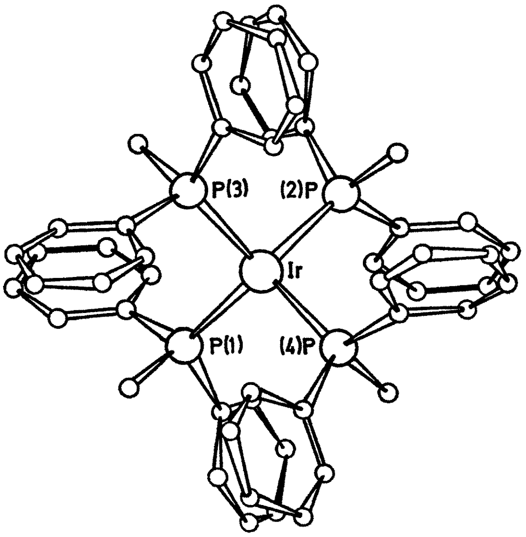
The standard deviations for the bond lengths and angles are 0·006 Å and 0·5°, respectively.

One complex ion occupies a general position in the unit cell but the other is situated on a 2-fold symmetry axis. Although crystallographically independent the ions are similar in geometry as the comparison between bond lengths and angles about the metal atoms shows (Table 2). The similarities extend to the periphery of the ions, differences being slight and undoubtedly a product of "packing forces".

The stereochemistry of the ion on the special position is illustrated in the Figure. The angles subtended at the metal centre (see Table 2) deviate significantly from the values of 90° and 180° defining the expected planar co-ordination and it can be seen that a tetrahedral distortion has been imposed on the basic stereochemistry.

This geometry can be compared with that of the square planar ion $[Rh(Ph_2PCH_2CH_2PPh_2)_2]^+$,[5] assumed to be isostructural with its iridium analogue. The tetrahedral distortion necessitates that approach by additional ligands must be significantly more hindered in $[Ir(PPh_2Me)_4]^+$ than in $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$. Notwithstanding this inertness towards oxygen and carbon monoxide, $[Ir(PPh_2Me)_4]^+$ is oxidised rapidly with hydrogen, hydrogen chloride, and chlorine to *cis*-$[IrH_2(PPh_2Me)_4]^+$, *trans*-$[IrHCl(PPh_2Me)_4]^+$, and $[IrCl_2(PPh_2Me)_4]^+$.

The ability of co-ordinatively unsaturated d^8 complexes to react with oxygen is not related simply to the electron density on the central atom (increased by replacing carbon monoxide by phosphine) but is sensitively dependent on other factors, especially steric effects.



FIGURE

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