Oxygen–Oxygen Distances in Synthetic Oxygen Carriers. The Crystal and Molecular Structure of the Oxygen Adduct of Bis(diphenylethylphosphine)chlorocarbonyliridium(I)

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Summary The crystal structure of dioxygen–bis(diphenylethylphosphine)chlorocarbonyliridium(I) has been shown to consist of *trans*-trigonal bipyramidal molecules with an O–O distance of 1·461 (14) Å.

SYNTHETIC oxygen carriers have been actively investigated since it was shown that $IrCOCl(PPh_3)_2$ reversibly binds O_2.[1,2] Such carriers are interesting because they may provide insight into the action of natural oxygen carriers. Ibers and his co-workers have solved a number of crystal structures in this area.[3–5] Of particular interest are the structures of $O_2,IrCOX(PPh_3)_2$, where X = Cl[3] or I.[4] Both these structures are described as trigonal bipyramidal molecules with *trans*-phosphine ligands, and the O_2 molecule lies in the equatorial plane with its centre as a co-ordination site. In the case of Cl the O–O distance is 1·30(3) Å and this adduct is described as 'reversible', but with $X = I$ the O–O distance is 1·509 (26) Å and described as 'irreversible'.

A simple rationale for these results is that as the halide becomes more electron-releasing the greater is the back donation from the metal to the O_2 antibonding π-MO, and, consequently, the longer the O–O distance. However, the question of the effect of changes in the phosphine ligands on the O–O distance, *i.e.*, whether this distance is relatively insensitive to variations in the *trans*-apical positions, and the effect of the disorder in both $O_2,IrCOX(PPh_3)_2$, $X = Cl$ and I structures on the 'light atom' O–O positions, is not answered by other structure determinations.[5] As a partial answer to these questions, we undertook the crystal structure determination of $O_2,IrCOCl(PPh_2Et)_2$.†

$O_2,IrCOCl(PPh_2Et)_2$ was prepared and crystals grown using standard techniques[1,7] by Prof. C. T. Sears. $M = 692·3$, monoclinic, $P2_1/a$, with Mo-K_α ($\lambda = 0·71068$ Å), $a = 14·772(1)$, $b = 19·604(2)$, $c = 9·929(1)$ Å, $\beta = 101·02(1)°$, $Z = 4$, $D_c = 1·69$ g cm^{-3}, $D_m = 1·67$ g cm^{-3}, $\mu = 52·4$ cm^{-1}. A crystal 0·189 × 0·0796 × 0·389 mm corresponding to the faces of {100}, {010}, and {001} forms was mounted in a capillary with the long direction (c) vertical and used to collect intensity data and make absorption corrections. The transmission coefficient was found to vary between 0·44 and 0·68 for the non-zero data. The crystal was aligned by standard techniques on a Picker FACS-1 diffractometer on-line with an IBM 7040 and equipped with a graphite monochromator. 7059 independent *hkl* intensities were measured to $2\theta \leqslant 60°$ with Mo-K_α radiation of which 3100 were non-zero. The structure was solved by standard heavy atom techniques[8] and refined by full-matrix least-squares with anisotropic temperature factors for Ir, Cl, and P and isotropic factors for all other non-hydrogen atoms to a final R value of 0·050. Anomalous dispersion corrections were made for Ir, P, and Cl.

The general features of the structure are similar to those found for $O_2,IrCOX(PPh_3)_2$ (Figure). However, there is no evidence of disorder in this structure. The most striking difference is the O–O distance of 1·461(14) Å compared to 1·30(3) Å for $IrCOX(PPh_3)_2$ $X = Cl$, the 'reversible' oxygen adduct and 1·509(26) Å for $X = I$, the 'irreversible' oxygen adduct. In fact, the present O–O distance is closer to that of the irreversible than the reversible adduct. Hence, small changes in the phosphine groups bring about pronounced changes in the O–O distances in these molecules. Therefore, correlation of O–O distances between molecules with significantly different ligands or containing chelate ring strain must be made with caution. For example, how much of the O–O distance elongation to 1·625(23) Å in $O_2,[Ir(diphos)_2]^+$ is due to distortions that manifest themselves in the Ir–P distances varying from 2·283(7) to 2·452(9) Å?[5]

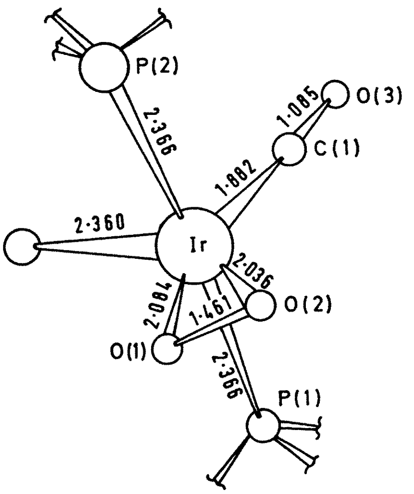

FIGURE. *Molecular structure of* $O_2,IrCOCl(Ph_2Et)_2$. *Estimated standard deviations:* Ir–P ±0·0070, Ir–O ±0·0095, O–O ±0·014, C–O ±0·014, C–C ±0·02, P–C ±0·015 Å. *Angles:* P(2)–Ir–P(1) 174·5(1), Cl–Ir–C 96·6(1)°.

The IrClCO portion of the molecule is planar within experimental error.

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† Prof. E. E. Mercer observed qualitatively that $IrCOCl(PPh_2Et)_2$ reversibly absorbs oxygen.[6]

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