Structure and Bonding in $[Ir(O_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2][PF_6]$ and in $IrBr(CO)(PPh_3)_2C_2(CN)_4$

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THE species of general formula $[Ir(diphos)_2]^+$ and $IrX(CO)(PPh_3)_2$ [diphos = $(Ph_2PCH_2{\cdot}CH_2PPh_2)$ and X is a halogen or pseudohalogen], add simple covalent molecules, often reversibly. The reactions of the chloro-[1] and iodo-complexes[2] with molecular oxygen and the relation of the structures to reversibility have been studied in detail.[2,3] Insight into the nature of the bonding in these molecular oxygen carriers is hindered by the impossibility of determining the hybridization of the oxygen atoms. Yet certain trends are apparent. Thus, as the electronegativity of the substituents on Ir decreases, the strength of bonding of O_2 to Ir increases, as judged by the degree of reversibility, and the O–O bond length increases. The O–O distance is 1·30 Å for X = Cl (reversible) and 1·51 Å for X = I (irreversible), and for the O_2 complex of $[Ir(diphos)_2]^+$ reported here it is extremely long.

Other simple molecules that form complexes with these Ir species include substituted olefins.[4,5] Ethylene and molecular oxygen are isoelectronic, and isoelectronic compounds of the same symmetry should have similar electronic structures. Here we also report on the structure of the tetracyanoethylene (TCNE) complex of $IrBr(CO)(PPh_3)_2$. Comparison of this structure with those containing molecular oxygen shows that both the

O_2 and TCNE ligands have local symmetry C_{2v} with respect to Ir. Thus information gained from this structure should be applicable to molecular oxygen systems, and a bonding scheme is suggested for all these systems. (Earlier bonding schemes do not appear to rationalize all the results reported here.)

X-Ray data for both complexes were collected on a Picker automatic *X*-ray diffractometer in the manner described previously.[6] Details are:

$[Ir(O_2)(diphos)_2][PF_6]$: Monoclinic, $P2_1/n$, $Z = 4$, $a = 17{\cdot}25$, $b = 16{\cdot}35$, $c = 16{\cdot}97$ Å, $\beta = 96{\cdot}6°$. $R = 7{\cdot}3\%$ for 1990 reflections above background. Compound prepared as described previously.[7,8] $IrBr(CO)(PPh_3)_2(TCNE)$: Monoclinic, $P2_1/n$, $Z = 4$, $a = 17{\cdot}66$, $b = 18{\cdot}62$, $c = 11{\cdot}60$ Å, $\beta = 95{\cdot}0°$. $R = 3{\cdot}8\%$ for 2767 reflections above background. Compound prepared in the manner previously described[5] for the chloro-complex.

The overall geometry of the $[Ir(O_2)(diphos)_2]^+$ cation is shown in Figure 1. The Ir–O distance of 1·98 Å is somewhat shorter than the average of 2·06 Å found in the O_2 complexes of $IrX(CO)(PPh_3)_2$. Moreover, the O–O distance of 1·66 ± 0·03 Å is far longer than any reported previously and is about 0·16 Å longer than that expected for oxygen atoms linked by a σ-bond.

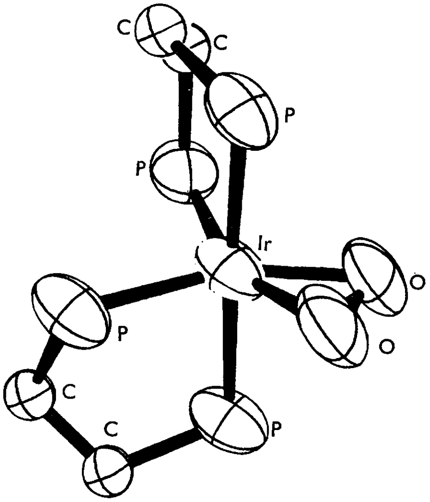

FIGURE 1. *The inner co-ordination sphere about* Ir *in the* $Ir(O_2)(diphos)_2^+$ *cation.*

The inner co-ordination sphere of $IrBr(CO)(PPh_3)_2(TCNE)$ is shown in Figure 2. The co-ordination around Ir is trigonal bipyramidal if TCNE is considered to be a monodentate ligand. The geometry of the TCNE ligand in the complex is shown in Figure 3. To a good approximation it is placed symmetrically with respect to Ir. The two central carbon atoms (C′) are in the equatorial plane and are equidistant from Ir with an Ir–C′ distance of 2·15 Å. None of the four C′–C″–N angles differs significantly from 180°. The dihedral angle between the planes containing C(1)N(1), C(2)N(2) and C(3)N(3),C(4)N(4) is 110°, whereas it is 180° in TCNE itself.[9]

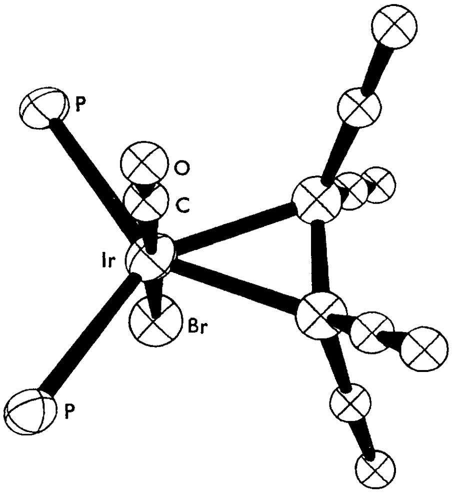

FIGURE 2. *The inner co-ordination sphere about* Ir *in* $IrBr(CO)(PPh_3)_2(TCNE)$.

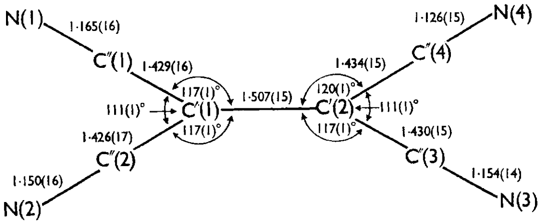

FIGURE 3. *Bond distances and angles in the* TCNE *molecule co-ordinated to* Ir *in* $IrBr(CO)(PPh_3)_2(TCNE)$. *Estimated standard deviations are in parentheses.*

When discussing the nature of the bonding it is more useful to consider bond lengths rather than bond angles, for the angles are often affected by packing. The C′–C′ distance of 1·507 Å is considerably longer than that of 1·339 Å in TCNE itself.[9] The average C′–C″ bond length is 1·430 Å in the TCNE ligand. The shortness of this bond is due to two factors: the hybridization of the carbon atoms[10] (which alters the σ-bond radius) and electron delocalization[11] beyond a two-centre description (which decreases the bond length by forming a partial π-bond between these carbon atoms which are joined nominally by a single σ-bond). The C′–C″ bond length is 1·442 Å in free TCNE, about 0·10 Å shorter than a single bond between two sp^3 hybridized carbon atoms. About 0·08 Å of this shortening may be attributed to the decrease in σ-bond radius derived from one carbon atom being sp hybridized and the other sp^2 hybridized. The additional shortening of 0·02 Å is due to a partial π-bond; a molecular-orbital calculation[12] indicates that the π-bond order is about 0·35. Now if the C′ atoms in the TCNE ligand were sp^3 hybridized, then the π-bond order of the C′–C″ bond would have to be high to account for the observed length, and this seems unlikely in view of the nonplanar geometry of the ligand. Thus we conclude that the carbon atom C′ is not sp^3 hybridized, but is sp^2 hybridized.

Previous models suggested to rationalize the bonding of molecular oxygen and olefins to transition metals have been hampered by a paucity of accurate structural data. Such data on the TCNE complex confirm our earlier proposal that the double σ-bond model for bonding in these complexes is not readily applicable.[2] The model we sketch here seeks to rationalize the salient features of the two precise structures discussed. The model is similar in many ways to the usual π-bonding model and the similarities will be emphasized. However, with the present model one can rationalize the fact that the O–O distance in $[\mathrm{Ir(O_2)(diphos)_2}]^+$ exceeds that of a σ-bond. Essentially, we adopt a three-centre molecular orbital scheme and assume C_{2v} symmetry for these centres. L(1) and L(2) represent oxygen atoms or the central carbon atoms of an olefin. L(1) and L(2) are sp^2 hybridized and the metal is dsp^3 hybridized. The symmetry properties are used to combine the available atomic orbitals of comparable symmetry into molecular orbitals. With three electron pairs available for bonding, the occupied molecular orbitals are:

(1) ψ_1 (symmetry A_1) which is similar to the donation of an electron pair from the π-cloud of the ligand to the vacant dsp^3-orbital of the metal.

(2) ψ_2 (symmetry A_1) which is similar to the σ-bond which would join L(1) and L(2) in the π-bonding model, but with an additional region of electron density centred on the metal. This bonds L(1) and L(2) together, but does not affect the overall binding of the ligand to the metal.

(3) ψ_4 (symmetry B_1) which is similar to the back donation of an electron pair from the filled $d_{x^2-y^2}$ orbital of the metal to an antibonding π^*-orbital of the ligand.

This model incorporates the following features:

(1) As the electronegativity of the substituents on the metal is decreased, the complex should become more stable and the L(1)–L(2) distance should lengthen. This is consistent with the trend noted above.

(2) If sufficient density in the ψ_2 orbital is centred on the metal, then the L(1)–L(2) distance could exceed that for a singly σ-bonded L(1)–L(2) moiety. This occurs in $[\mathrm{Ir(O_2)(diphos)_2}]^+$.

(3) π-bonding substituents on the metal could affect the L(1)–L(2) distance without altering the strength of attachment of the ligand to the metal.

Finally, we call attention to the fact that the phosphorus atoms of the $\mathrm{PPh_3}$ groups are *cis* in the TCNE complex (Figure 2). This is the first indication that the phosphorus atoms, known to be *trans* in the parent complex and in several complexes formed by the addition of one or two ligands, can be *cis* after certain addition reactions. The geometry depicted in Figure 2 differs both from those of the $\mathrm{O_2}$ complexes and that of the $\mathrm{SO_2}$ complex.[13] This again indicates that the energy differences among the various possible five-co-ordinate geometries are very small indeed.

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[1] L. Vaska, *Science*, 1963, **140**, 809.
[2] J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Science*, 1967, **155**, 709; *Inorg. Chem.*, 1967, **6**, 2243.
[3] J. A. Ibers and S. J. La Placa, *Science*, 1964, **145**, 920; S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 2581.
[4] G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, 1965, **87**, 5356.
[5] W. H. Baddley, *J. Amer. Chem. Soc.*, 1966, **88**, 4545.
[6] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.
[7] A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Comm.*, 1966, 589.
[8] L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, 1966, **88**, 5324.
[9] D. A. Bekoe and K. N. Trueblood, private communication.
[10] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, 1959, **5**, 166.
[11] R. S. Mulliken, *Tetrahedron*, 1959, **6**, 68.
[12] B. R. Penfold and W. N. Lipscomb, *Acta Cryst.*, 1961, **14**, 589.
[13] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1966, **5**, 405.