The Preparation and Crystal Structure of μ-Oxido-bis[triphenylphosphinenitrosyliridium(I)]: a Novel Iridium Nitrosyl Compound containing a Bridging Oxygen and a Bent Metal–Metal Bond

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Summary μ-Oxido-bis[triphenylphosphinenitrosyliridium(I)]–C_6H_6 has been prepared by the reaction of *trans*-Ir(CO)Cl$(PPh_3)_2$ and nitrite ion in benzene–aqueous alcohol: its structure contains the first example of a bent iridium–iridium bond and a nitrosyl group π-bonded to an iridium atom.

REACTION between *trans*-Ir(CO)Cl$(PPh_3)_2$ and $NaNO_2$ in benzene and aqueous alcohol (50/50) after some time gives a diamagnetic, orange crystalline compound which is air-stable but which rapidly decomposes in solution if oxygen is present. Elemental analysis and M determination indicated the compound to be dimeric in $CHCl_3$, and two very strong bands in the i.r. spectrum at 1735 and 1758 cm.$^{-1}$ showed that the compound might be $[Ir(NO)(CO)PPh_3]_2$ with bridging carbonyl groups. The monomeric species $Ir(NO)(CO)PPh_3$ has already been reported.[1] On further reaction with an excess of triphenylphosphine in benzene it affords $Ir(NO)(PPh_3)_3$ in high yield, as does our compound.

An X-ray investigation, however, indicated a single atom in one bridge between the two iridium atoms, and that

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the compound is the benzene solvate of μ-oxido-bis[triphenylphosphinenitrosyliridium(I)]. The presence of two NO stretching frequencies and tentative assignment of a band at 725 cm.$^{-1}$ to the asymmetric Ir–O–Ir stretch[2] is in keeping with the crystallographic data. This compound, therefore, represents the first example of an oxygen-bridged iridium system containing a bent metal–metal bond together with the first example of a nitrosyl group π-bonded to an iridium atom. The crystals are monoclinic, space group $C2/c$ (No 15) from the intensity statistics, $a = 12{\cdot}065(3)$, $b = 16{\cdot}953(7)$, $c = 19{\cdot}764(5)$ Å, $\beta = 98{\cdot}98(2)°$, $D_m = 1{\cdot}750$ g./cm.^{3}, with four molecules of $O(IrNOPh_3P)_2 \cdot C_6H_6$, $D_c = 1{\cdot}768$ g./cm.^{3} The structure analysis used 2635 non-zero reflections with $2\theta \leqslant 135°$ for Cu-K_α radiation. The structure was solved by the heavy atom method and refined by least-squares methods. A number of difference Fourier syntheses were calculated at various stages because of the unusual geometry which was observed. The usual R was 0·085 after refinement, with only the iridium and phosphorus atoms having anisotropic thermal parameters.

The distances and angles in μ-oxido-bis(nitrosyltriphenylphosphineiridium) are illustrated in the Figure. The two halves of the molecule are related by a two-fold axis passing through the oxygen bridge. The molecule can be described as two square-planar iridium atoms joined by an oxygen bridge and a bent iridium–iridium bond. Although bent metal-bonds have been previously formulated,[3] examples involving upper-row transition elements are rare. The Ir–Ir distance of 2·555 Å is shorter than the 2·68 Å found in $Ir_4(CO)_{12}$;[4] however, since the bond is not between the nuclear centres, the observed distance would be expected to be shorter.

Evidence supporting the presence of a metal–metal bond is the fact that on treating the complex with mercury(II) chloride, elemental mercury is immediately produced, indicating the presence of a highly reducing system. Generally, d^8 iridium(I) complexes undergo simple oxidative addition reactions with mercury(II) chloride,[5] which in the present case would give rise to an unstable system, namely, an iridium(III) complex with a metal–metal bond.

The dimensions in some pentaco-ordinated iridium compounds have been summarized by Hodgson and Ibers.[6] In the two cases where there is an NO group, the Ir–N–O angle is about 124° and the Ir–N distance is 1·89 and 1·97 Å. Our observation of an Ir–N–O angle of 177° and the Ir–N distance of 1·76 Å suggests that the Ir–N bond has some double bond character. Since the Ir–P distance of 2·31 Å is only slightly shorter than in the pentaco-ordinated species, the decrease in the Ir–N bond distance is not simply due to a change in the Ir radius. The Ir–N distance is comparable to other compounds containing metal–nitrogen multiple bonds.[7] Whether the shortening is related to the oxidation state of the iridium or to a *trans*-effect from the oxido-bridge cannot be resolved at the present time. However, the P $\cdots$ N nonbonded distance of 3·21 Å is close to the value of 3·15 Å found in the other iridium complexes, suggesting that this interaction may be important in determining the mode of attachment of the NO group.

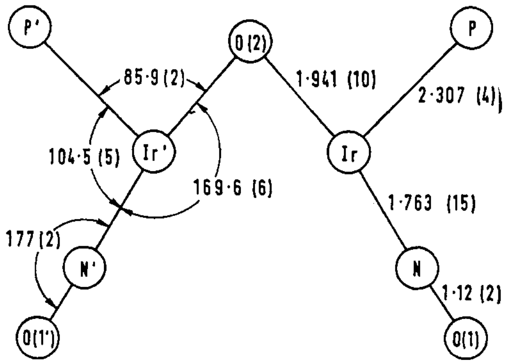

FIGURE. *The distances and angles (with e.s.ds in parentheses) in μ-oxido-bis[triphenylphosphinenitrosyliridium*(I)]. *The primed atoms are related to the unprimed atoms by a two-fold axis through the oxygen atom. The* Ir–O–Ir′ *angle is* 82.3(3)°.

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