Preparation and *X*-Ray Crystal Structure of Tetranitrosylbis(triphenylphosphine)di-iridium

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Summary Tetranitrosylbis(triphenylphosphine)di-iridium, prepared in high yields by a new method, is characterized by a direct iridium–iridium bond and a strongly distorted tetrahedral co-ordination around each metal atom.

In a previous communication, on the basis of analyses and its diamagnetic behaviour, one of us[1] suggested the formula $[Ir(NO)_2(PPh_3)]_2$ (A) for the iridium nitrosyl compound obtained from the reaction of the trihydride $IrH_3(PPh_3)_2$ and NO. Compound (A) was the first isolated iridium nitrosyl compound having a direct intermetallic bond. Recently we have obtained well-formed crystals of (A) in high yield by treating $IrH_3(PPh_3)_2$ with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide in boiling THF under NO for a few minutes, followed by addition of methanol and crystallization. The NO oxidises the triphenylphosphine set free in the reaction. In a nitrogen atmosphere the triphenylphosphine reacts with (A) giving $Ir(NO)(PPh_3)_3$ and the yields are halved.

The iridium atoms reach the inert gas structure if all nitrosyls are three-electron donors, but the i.r. data [ν(NO) 1645 and 1680 cm^{-1}] are not definitive as regards their bonding.

Crystal data: $C_{36}H_{30}Ir_2N_4O_4P_2$, $M = 1029$, triclinic, $a = 15{\cdot}28(2)$, $b = 12{\cdot}50(1)$, $c = 10{\cdot}24(1)$ Å, $\alpha = 66{\cdot}46(8)$, $\beta = 78{\cdot}31(8)$, $\gamma = 82{\cdot}81(8)$, $U = 1755$ Å^3, D_m (by flotation) $= 1{\cdot}94(1)$ g cm^{-3}, $D_c = 1{\cdot}95$ for $Z = 2$, $F(000) = 980$, space group $P\bar{1}$ (No. 2) after refinement.

Three-dimensional *X*-ray data were collected on a Pailred linear diffractometer using a graphite monochromatized Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). Intensities were corrected for Lorentz, polarization, and absorption effects ($\mu =$

81·72 cm^{-1}). The structure was solved by conventional Patterson and Fourier methods on the basis of 3245 independent structure amplitudes having $\sigma(I)/I \leqslant 0{\cdot}20$. Block-matrix least-squares refinements, in which the phenyl rings were treated as rigid bodies of known geometry (D_{6h} symmetry, C–C 1·392 Å) and all the remaining atoms were allowed to vibrate anisotropically, led to R 0·033.

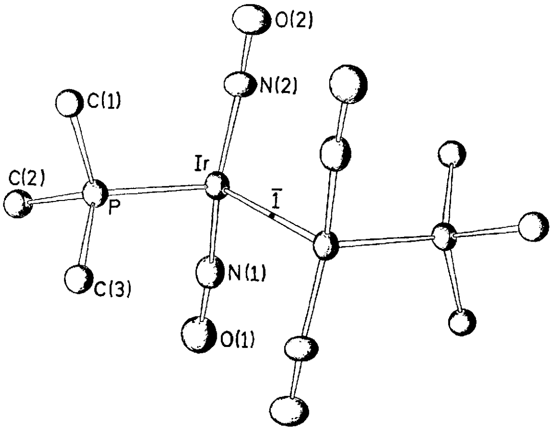

FIGURE. Inner co-ordination in the molecule $[Ir(NO)_2(PPh_3)]_2$. Mean values for bond parameters are: Ir–Ir 2·717, Ir–N 1·787, Ir–P 2·270, N–O 1·19, P–C 1·82 Å; N–Ir–N 156, Ir–Ir–P 105, Ir–Ir–N 95, P–Ir–N 99, Ir–N–O 167°. E.s.d.'s on single interatomic distances are 0·001 for Ir–Ir, 0·003 for Ir–P, and 0·008—0·017 Å for the remaining ones.

The crystal structure derives from the packing of discrete molecules $[Ir(NO)_2(PPh_3)]_2$, in which each iridium atom is bonded to two nitrosyl groups, one phosphine ligand, and the other iridium atom, in a strongly distorted tetrahedral manner (see Figure). Although the asymmetric unit in the cell consists of two half-molecules lying around non-equivalent centres of symmetry, the two centrosymmetrical molecules thus formed display an identical overall geometry, differences in bond parameters being small, even if significant at all. As the same is true for chemically equivalent bond lengths and angles within each molecule, the values reported in the Figure caption are averaged over all the equivalent interactions, and the Figure itself may represent either of the two independent molecules.

No unusual intermolecular contacts are present. The metal–metal bond length compares well with the mean values reported for $Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_9(PPh_3)_3$ (2·73 Å),[2] and for $Ir_4(CO)_{12}$ (2·68 Å).[3] It indicates an essentially single bond, as expected from the noble gas rule when one assumes NO^+ ligands and a formal oxidation state of -2 for the iridium atoms.

The Ir–P distance, 2·27 Å, is short when compared with the corresponding interactions observed in most phosphine complexes of the third transition metals. In particular, it is significantly shorter than the Ir–P distance, 2·339(3) Å, found in the cation $[Ir(NO)_2(PPh_3)_2]^+$ (B).[4] Such a large difference is probably due both to the presence of the positive charge in (B) and to the decrease of the formal oxidation state of the metal in the present molecule.

All the remaining bond parameters are comparable with the corresponding ones in the cation (B), which has a strongly distorted tetrahedral co-ordination.[4,5] The values of the angles N–Ir–N [156 in (A), 154° in (B)] and Ir–N–O [167 in (A), 163° in (B)] are of interest. Such a reproduction of bond lengths and angles in different species, which are packed in different ways, seems to rule out the possibility that these values are determined by intra- and intermolecular steric effects. Further, the possibility that the intermediate Ir–N–O angle results from disorder between linear NO^+ and bent NO^- [5] becomes unlikely. It can be concluded that the effects governing the co-ordination geometry of (A) and (B) are mainly electronic; the large N–Ir–N angle may be qualitatively rationalized in terms of π^* repulsions between the nitrosyl ligands,[5,6] and the NO deviations from linearity are in agreement with the predictions of Kettle[7] and Enemark.[8] However, the extent of the distortions observed in (A) and (B) is unique so far and seems, therefore, to be peculiar both of the nitrosyl ligand and of the nature of its interaction with the third transition metal.

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