Crystal and Molecular Structure of the Oxygen Adduct, $[Pt(O_2)(PPh_3)_2],1{\cdot}5\ C_6H_6$

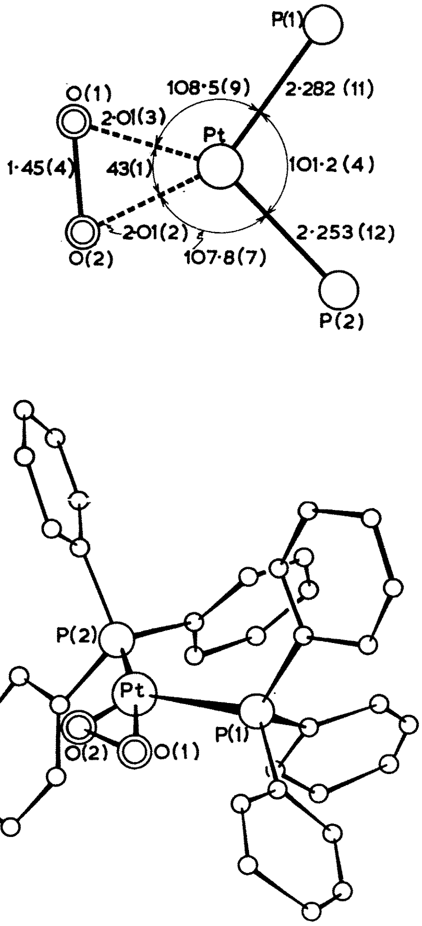
By TOSHIHIDE KASHIWAGI, NORITAKE YASUOKA, NOBUTAMI KASAI,* and MASAO KAKUDO,
(*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-Kami, Suita, Osaka,* 564, *Japan*)
and SHIGETOSHI TAKAHASHI and NOBUE HAGIHARA
(*Institute of Scientific and Industrial Research, Osaka University, Yamada-Kami, Suita, Osaka,* 564, *Japan*)

Summary The molecular structure of $[Pt(O_2)(PPh_3)_2]$ and the co-ordination of the O_2 molecule to the Pt atom have been determined by the *X*-ray structure analysis of $[Pt(O_2)(PPh_3)_2]$, 1·5 C_6H_6.

TETRAKIS(TRIPHENYLPHOSPHINE)–PALLADIUM AND –PLATINUM possess catalytic activity in the oxygenation of triphenylphosphine, tributylphosphine, and cyclohexyl isocyanide.[1] When either of these complexes was treated with gaseous oxygen in benzene solution, a precipitate was obtained. The i.r. absorption bands at 830 (Pt-complex) and 880 cm.$^{-1}$ (Pd-complex) are similar to those observed in the oxygen adducts prepared by Vaska.[2] The precipitate from the Pt-complex was not identified as $[Pt(O_2)(PPh_3)_2]$,1·5 C_6H_6 until the structure analysis had been carried out. The oxygen adducts, with excess of Ph_3P (under nitrogen) gave Ph_3PO.[1] Thus these oxygen adducts are considered to be an intermediate in the oxygenation using $M(PPh_3)_4$ (M=Pt or Pd) as catalyst.

In order to investigate the bonding of oxygen to the platinum atom, the structure analysis of $[Pt(O_2)(PPh_3)_2]$,1·5 C_6H_6 was undertaken by means of *X*-rays, (Cu-K_α): F.W. = 868·8, monoclinic, $P2_1/c$, a = 18·331(7), b = 22·983(2), c = 9·311(2) Å, β = 92·14(1)°,† V = 3920.0 Å^3, Z = 4, D_c = 1·47 g.cm.$^{-3}$. During the collection of intensity data (by diffractometer) the intensity of the standard reflexion decreased; as it did so uniformly with time, a linear correction factor was applied. The other usual corrections were also applied, including one for absorption (μ = 78·6 cm.$^{-1}$). The structure was solved by the heavy-atom method, and refined by block-diagonal analysis (anisotropic for Pt and P only) to R = 10·3% for 1762 non-zero reflexions.

The molecular structure and the geometry around the platinum atom is shown in the Figure. The atoms Pt, P(1), P(2), O(1), and O(2) lie almost on the same plane. Recently, Ibers and his co-workers reported the structure of some oxygen adducts, and found the O–O distances 1·30, 1·51, and 1·66 Å in $Ir(O_2)Cl(CO)(PPh_3)_2$,[3] $[Ir(O_2)I,(CO)(PPh_3)_2]$, CH_2Cl_2,[4] and $[Ir(O_2)Ph_2PCH_2CH_2PPh_2][PF_6]$,[5] respectively. They also mentioned that if the electronegativity of the substituent on the iridium atom decreases, the strength of the bonding of the O_2 molecule to the iridium atom increases, and the O–O bond length increases. Although in the present complex the central metal atom is different from those in the complexes analysed by Ibers and others, the observed O–O distance of 1·45 Å is close to the value of 1·51 Å in the irreversible complex $[Ir(O_2)I(CO)(PPh_3)_2]$, CH_2Cl_2.



The $[Pt(O_2)(PPh_3)_2]$ *molecule. Five atoms,* Pt, P(1), P(2), *O*(1), *and* O(2) *lie almost on the same plane.* (*Estimated standard deviations in parentheses.*)

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† Professor S. C. Nyburg has kindly informed us that he was engaged on the *X*-ray analysis of $[(PPh_3)_2Pt(O_2)]$ and that his cell dimensions agreed with ours.

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