Two-co-ordinate Phosphine–Palladium(0) Complexes: *X*-Ray Structure of the Tricyclohexyl- and the Di(t-butyl)phenyl-phosphine Derivatives

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Summary The *X*-ray structures of the 14-electron palladium complexes Pd[P(cyclohexyl)$_3$]$_2$ and Pd(PBu$^t_2$Ph)$_2$ complexes show that the P–Pd–P angles are 158° and 175° respectively.

The two-co-ordinate 14-electron Pd(0) complexes[1] Pd[P(cyclohexyl)$_3$]$_2$ (**1**) and Pd(PBu$^t_2$Ph)$_2$ (**2**) do not appear to follow the16- or 18-electron rule.[2] Therefore a single-crystal *X*-ray diffraction study was carried out in order to examine the two-co-ordination of the two complexes.

Lattice parameters and integrated intensities were measured by means of a Philips PW-1100 computer-controlled diffractometer with graphite monochromatized Mo-K_α radiation (λ = 0·71069 Å).

Crystal data: (**1**): $PdP_2C_{36}H_{66}$, M = 667·3, a = 16·858, b = 9·616, c = 22·382 Å, β = 92·11°, Z = 4, D_c = 1·22 g cm^{-3}, $F(000)$ = 1432, space group $C2/c$; (**2**): $PdP_2C_{28}H_{46}$, M = 551·0, a = 45·372, b = 12·593, c = 10·058 Å, Z = 8, D_c = 1·27 g cm^{-3}, $F(000)$ = 2320, space group $Fdd2$.

For complex (**1**), 2516 independent reflections having $2\theta < 46°$ were measured and the 2181 with $I > 3\sigma$ were used in the crystal-structure analysis. For complex (**2**), 1341 independent reflections were measured ($2\theta < 52°$) and 1264 used. The structures were elucidated by Patterson and Fourier methods. Atomic positions and thermal parameters were refined by least squares. For complex (**1**) a R factor 0·066 was obtained considering anisotropic thermal parameters and including the hydrogen atoms contribution. For complex (**2**) the R factor was 0·10 (isotropic thermal parameters, H atoms not included).

A perspective view of the structures of complexes (**1**) and (**2**) is shown in the Figure. The most remarkable occurrence is that the molecules, both having molecular and crystallographic C_2 symmetry, display quite different geometry of the P–Pd–P group. For (**1**) the P–Pd–P group is bent ($\angle$ 158·4 ± 0·3°) whereas for case (**2**) it is almost linear ($\angle$ 175·7 ± 0·3°).

That the bent structure of (**1**) is due to crystal-packing forces can be ruled out since there are no H $\cdots$ H packing distances shorter than 2·32 Å. Moreover, if the linear geometry of (**1**) is the most favourable one for the free molecule, there is no reasonable explanation why a centrosymmetric geometry, which should be expected on steric grounds, is not observed in the crystal. Thus, if the bent geometry of (**1**) is due to electronic factors the *quasi* linear structure of (**2**) remains to be explained. The intramolecular repulsion of the t-butyl groups attached to different phosphorous atoms seems not to play a significant role, all the $CH_3 \cdots CH_3$ distances being greater than 5·0 Å. The two phenyl groups of (**2**) are almost coplanar with the P–Pd–P group (torsional angle about P–C bond 10°). This conformation gives an *ortho* hydrogen atom–metal atom distance of 2·73 Å. Although this conformation is the most sterically favoured, a kind of bonding interaction between the hydrogen atoms and the metal cannot be excluded. Activation of *ortho* hydrogens of aryl phosphines by co-ordination to a metal has been reviewed recently.[3]

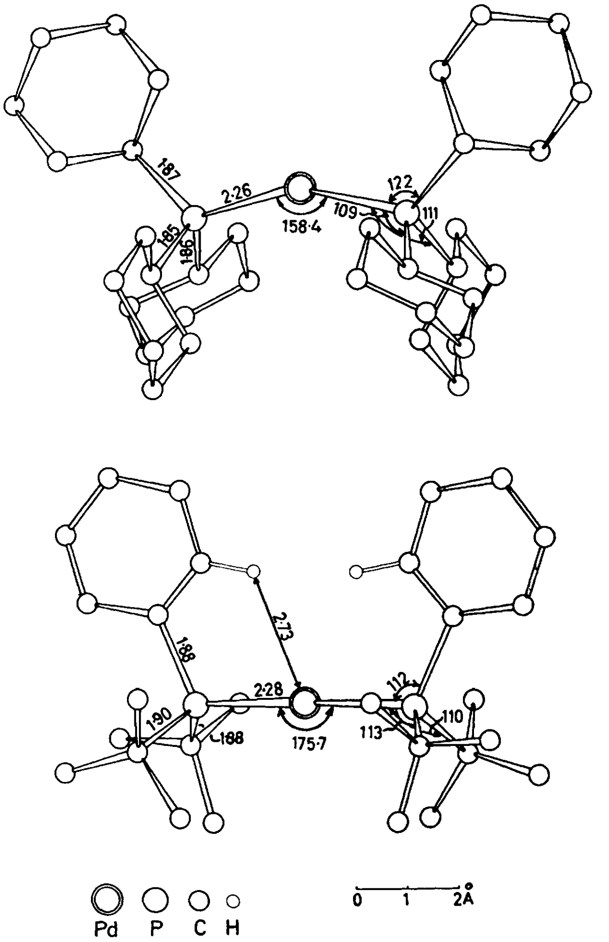

Figure. Molecular models of Pd[P(cyclohexyl)$_3$]$_2$ (above) and Pd(PBu$^t_2$Ph)$_2$ (below) complexes. Hydrogen atoms are omitted except for the *ortho* aromatic H atoms close to the metal. Relevant bond lengths (Å) and valence angles (°) are indicated.

Variable temperature ^{1}H n.m.r. ($C_6D_5CD_3$) experiments have shown that there is restricted rotation around the P–Ph bond, the orientation of the *ortho* hydrogen atoms of the phenyl rings with respect to the metal being maintained in solution. At room temperature the aromatic *ortho* protons give an average signal at τ 1·68 (τ 2·48 in the free phosphine) whereas at −60° two signals are observed at τ 0·93 and 2·48. The low-field resonance is assigned to the *ortho* proton close to the metal.† The t-butyl resonance is

† For low-field shift of *ortho* aromatic protons positioned close to a metal see ref. 4 and references therein.

also temperature dependent. At room temperature a triplet is observed [^3J(P–H) + ^5J(P–H) 13·0 Hz] at τ 8·55 which is the pattern expected for a trans P–Pd–P arrangement.[5] At low temperatures the signal becomes broad which is an indication of restricted rotation around the P–Bu^t bond.

Comparing the structural data of (**1**) and (**2**) the different geometry of the P–Pd–P group cannot at the moment be simply explained. Studies are in progress to ascertain the steric and/or electronic factors which affect the value of the P–Pd–P angle.

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[1] A. Musco, W. Kuran, A. Silvani, and M. W. Anker, *J.C.S. Chem Comm.*, 1973, 938.

[2] C. A. Tolman, *Chem. Soc. Rev.*, 1972, 337.

[3] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[4] D. R. Fahey, *J. Organometallic Chem.*, 1973, **57**, 385.

[5] B. E. Mann ,B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 2976.