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Nucleophilic Attack on $\{(\pi\text{-allyl})Pt[P(C_6H_{11})_3]_2\}PF_6$. Preparation and X-Ray Structure of $Pt[P(C_6H_{11})_3]_2$

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We have previously reported the preparation of *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ (**1**) by reacting $\{(\pi\text{-allyl})Pt[P(C_6H_{11})_3]_2\}PF_6$ (**2**) with sodium methoxide in methanol.[1] The hydride (**1**) may form by interaction of methanol with the two-coordinate species $\{Pt[P(C_6H_{11})_3]_2\}$ (**3**). Indeed we have prepared the two-coordinate complex (**3**) as a white crystalline material in good yields by reacting (**2**) with potassium *t*-butoxide in an aprotic solvent such as tetrahydrofuran. The same compound has been independently obtained with two different routes by reacting bis(cyclo-octa-1,5-diene)platinum(0) with $P(C_6H_{11})_3$ [2] or by reduction of $\{PtCl_2[P(C_6H_{11})_3]_2\}$ with Na/Hg in THF.[3]

The X-ray structures of $\{Pd[P(C_6H_{11})_3]_2\}$ (**4**) and $\{Pd[P(t\text{-}C_4H_9)_2C_6H_5]_2\}$ (**5**) have been reported.[4,5] The P–Pd–P moiety has a bent geometry (158.4 ± 0.3°) in (**4**) whereas it is almost linear (175.7 ± 0.3°) in (**5**). In compound (**5**) a kind of bonding interaction may be recognized between an *ortho* hydrogen atom of the phenyl ring and the metal. The X-ray structure of $\{Pd[P(\text{menthyl})_2 i\text{-}C_3H_7]_2\}$ (**6**) has also been done and the P–Pd–P geometry found to be linear.[6] However the geometry observed in (**6**) may very well be due to the steric bulkyness of the ligand.

We considered it worthwhile to perform a single-crystal X-ray diffraction study on $\{Pt[P(C_6H_{11})_3]_2\}$ in order to ascertain whether the bent geometry observed in (**4**) does reproduce in the Pt complex.

Crystal Data

$PtP_2C_{36}H_{66}$, M = 756.0, λ = 0.7107 Å, a = 16.801, b = 9.659, c = 22.310; β = 92.396, Z = 4; Dc = 1.39 g cm^{-3}, F(000) = 1560, space group C2/c. 4385 independent reflections having $2\theta < 46°$ were measured and 3522 with $I > 3\sigma$ were used in the crystal structure analysis. The close similarity between the unit cell of (**3**) and (**4**) suggests that the compounds are isomorphous. We have assumed for Pt and P atoms the fractional coordinates of Pd and P in compound (**4**) to resolve the structure by the Fourier method. The carbon atom positions were thus obtained from a difference Fourier synthesis. Further refinement by the least squares method (anisotropic parameters, unitary weight factors, 9 X 9 block diagonal matrix) gave an R factor of 0.056. A perspective view of the structure is shown in Fig. 1.

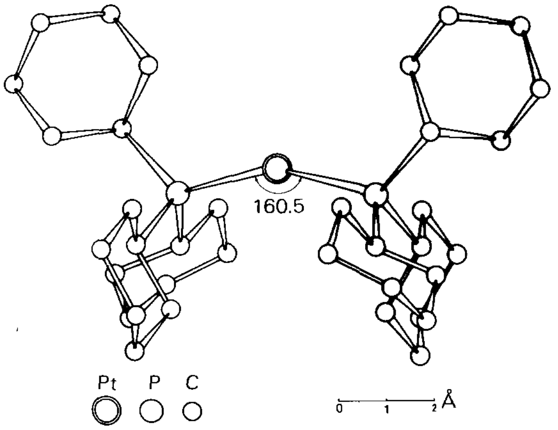

Fig. 1. Molecular structure of $\{Pt[P(C_6H_{11})_3]_2\}$.

The P–Pt–P angle is 160.5 ± 0.2°. The Pt–P bond length 2.231(4) Å compares with that found in *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ (2.26(1) Å). This implies a d_π–d_π interaction between P and Pt comparable in the two complexes. In conclusion the X-ray structure of $\{Pt[P(C_6H_{11})_3]_2\}$ confirms that the P–M–P moiety may be bent in two-coordinate complexes. The steric and/or electronic factors which affect the P–M–P angle remain to be ascertained.

The comparable P–Pt bond length distance of $\{Pt[P(C_6H_{11})_3]_2\}$ and *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ suggests that the reactivity of the two complexes may be related. A study of this theme is underway.

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