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Pt[P(cyclohexyl)$_3$]$_3$. A Surprisingly Uncrowded Molecule

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On the basis of a cone angle of 170° for PCy_3 (Cy = cyclohexyl) [1], the formation of $Pt(CPy_3)_3$ would be surprising and it would be expected that there would be severe steric strains within this molecule. Yet, when $Pt(PCy_3)_2$ is crystallised from heptane at -15 °C in the presence of an excess of PCy_3, yellow crystals of composition $Pt(PCy_3)_3 \cdot 1.5$ heptane are isolated. An X-ray structure determination was performed in order to verify i) whether the third PCy_3 is chemically bound to the metal or merely trapped in the lattice as proposed for $Ni(PPh_3)_4$ [2] ; ii) if it is a three-coordinate complex, how three bulky ligands can be accommodated around the metal.

X-ray diffraction analysis was carried out using 5446 non-zero integrated intensities measured by counter techniques (Philips PW-1100 instrument, MoK_α radiation, 8611 unique reflections with $\theta < 22°$ measured, those with $I < 3\sigma$ rejected). The crystal data are (λ = 0.7107 Å): $PtP_3C_{54}H_{99} + xC_7H_{16}$, M = 1036.4 + x 100.2, rhombohedral R3 (hexagonal axes), $a = b = 35.584(3)$, $c = 28.935$ Å, $D_c = 1.304$ g cm^{-3} for $Z = 21$ and $x = 1.5$.

The platinum atom positions were obtained from the Patterson function and the remaining atoms through iterative Fourier analysis. The structure was only preliminarily refined down to R = 0.067 using anisotropic temperature parameters for Pt atoms only and neglecting the contribution of solvated heptane whose positions are still uncertain. The structure consists of $Pt(PCy_3)_3$ units packed together by three-fold screw axes. There are two independent molecules with approximately C_3 symmetry and one having C_3 crystallographic symmetry (Fig. 1). Actually all three independent molecules have approximately the same molecular conformation.

The average Pt–P distance, 2.303(13) Å, is significantly longer than that observed in $Pt(PCy_3)_2$, 2.231(6) Å, but comparable with that reported for other platinum–phosphine complexes [3]. The platinum atom is only 0.04 Å away from the P_3 plane. All the cyclohexyl rings have the expected chair conformation. The C–P–C bond angles and the torsion angles about P–C bonds (Table) have been compared with those of $Pt(PCy_3)_2$ and *trans*-$PtH_2(PCy_3)_2$ in which any interligand repulsion can be excluded. Furthermore, Tolman's cone angles [4] based on *actual* conformations of phosphines have been evaluated using the formula proposed for unsymmetrical ligands [5]. It is interesting to notice that the coordination of a third ligand i) exerts a moderate but not a dramatic compression of the ligands as shown from the values of the C–P–C bond and cone angles, ii) does not introduce strong interligand stress as the Pt–P–C–H torsion angles of $Pt(PCy_3)_3$ are similar to those of *trans*-$PtH_2(PCy_3)_2$ (triclinic form). Also, the interligand H...H contacts based on calculated H atoms positions have been examined. There are only 3 equivalent H...H contacts less than 2.2 Å (1.85 Å). As the actual hydrogen atom positions may very well change by few tenths of Å upon small variations in C–H bond directions, we may confidently exclude any strong interligand repulsion. Examination of the X-ray structure shows that the PCy_3 ligand adopts a suitable orientation to allow the meshing of the cyclohexyl groups into each other.* The resulting rigid molecule should be destabilized in the dissociation equilibria by the consequentially larger $\Delta S°$.

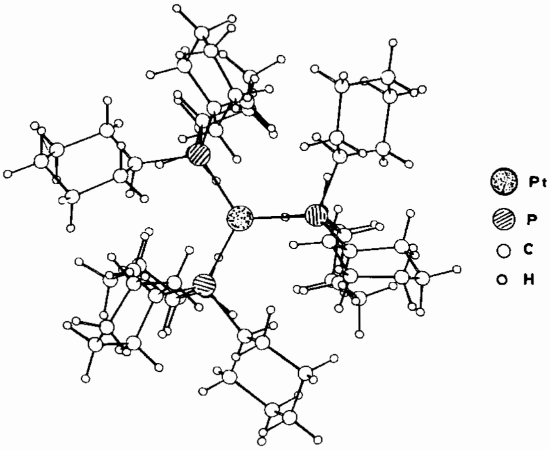

Fig. 1. Molecular structure of $Pt(PCy_3)_3$ showing the unique molecule on the C_3 crystallographic axis. The positions shown for the hydrogen atoms are those calculated assuming tetrahedral carbon atoms and C–H bond lengths of 1.08 Å.

Confirmation of this suggestion comes from ^{31}P n.m.r. spectroscopic investigation. The equilibrium between PCy_3, $Pt(PCy_3)_3$ and $Pt(PCy_3)_2$

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*Previously similar suggestions have been proposed to account for the existence of $[PtH(PCy_3)_2(PEt_3)]^+$ and the dynamic behaviour found in $[\eta^3\text{-}C_3H_5Pt(PCy_3)_2]^+$ (T. G. Attig and H. C. Clark, *J. Organometal. Chem.*, *94*, C49 (1975); *Canad. J Chem.*, *53*, 3466 (1975)).

TABLE I. Cone Angles[a, b], C–P–C Bond and Pt–P–C–H torsion Angles[b] of Some PCy_3 Complexes.

Complex	Cone Angles (°)	C–P–C Bond Angles (°) (avg $\sigma = 0.5°$)	Pt–P–C–H Torsion Angles (avg $\sigma = 1°$)	Ref.
$Pt(PCy_3)_2$	161	103.3, 103.4, 106.5	−178, −52, −98	6
$Pt(PCy_3)_3$	157	95.4, 97.6, 106.1	−169, −61, 36	This work[c,d]
trans-$PtH_2(PCy_3)_2$ (triclinic)	162	102.2, 104.2, 111.4	−173, −61, 44	7
trans-$PtH_2(PCy_3)_2$ (monoclinic)	168	100.5, 103.3, 105.2	−175, −149, −76	7

[a] 170° is Tolman's cone angle (ref. 1). [b] Hydrogen atom positions have been calculated assuming C–H bond lengths 1.08 Å, H–C–H angle 109° and local C_{2v} symmetry on each C atom. The Pt–P–C–H torsion angles are sufficient to define the orientation of the cyclohexyl ring, the other two Pt–P–C–C angles differing appropriately by ± ~ 120°. [c] Angles calculated for the molecule lying on crystallographic 3-fold axis. [d] Previous workers [8] had assumed that the existence of $Ni(PCy_3)_3$ required a cone angle of 120° for PCy_3. However, the calculation given in this table using Tolman's definition of cone angle [1, 4, 5] shows this assumption to be erroneous on account of the inter-meshing of the cyclohexyl rings from separate PCy_3 ligands. It is therefore unjustified to equate cone and valence angles.

was studied as a function of temperature (0 to 40 °C) and concentration to yield $\Delta H° = -13.1 \pm 0.5$ kcal/mol and $\Delta S° = -48.0 \pm 2.0$ e.u. for association in toluene. At higher temperature (0 to 110 °C) only $Pt(PCy_3)_2$ was detected and associative ligand exchange became significant on the n.m.r. time scale. Line shape analysis yielded activation parameters $\Delta H^{\neq} = 2.5 \pm 0.3$ kcal/mol and $\Delta S^{\neq} = -32 \pm 1$ e.u. Hence $\Delta H^{\neq}$ for the dissociation of $Pt(PCy_3)_3$ is *ca.* 15.6 kcal/mol which is very similar to $\Delta H^{\neq}$ for dissociation of the less crowded molecules $Pt(PBz_3)_3$ (15.3 ± 0.9 kcal/mol), $Pt(PMePh_2)_4$ (15.0 ∓ 0.3 kcal/mol) $Pt(PMe_2Ph)_4$ (13.6 ± 0.3 kcal/mol) and $Pt(PMe_3)_4$ (14.1 ± 1.1 kcal/mol). Therefore the interligand repulsive forces only make a small contribution to the enthalpy term in this "crowded" compound. Although the PCy_3 ligand has a cone angle of 157° the interligand repulsions are minimized to a small value by intermeshing of the cyclohexyl groups of the three PCy_3 ligands and there is consequently a destabilization of the molecule from a negative entropy term. We therefore conclude that not only the enthalpy but also the entropy term is important in determining the room temperature solution instability of $Pt(PCy_3)_3$ to dissociation.

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