Unbalanced Packing of Chiral Molecules in the Crystal Structure of the Trigonal Polymorph of Tris(triphenylphosphine)carbonylplatinum, $Pt(PPh_3)_3CO$

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Summary The structure of the trigonal polymorph of $Pt(PPh_3)_3CO$ consists of a packing of both *R* and *S* molecules in the ratio 2 : 1.

WE are presently reporting elsewhere[1] the crystal structure of $Pt(PPh_3)_3CO$ prepared according to Booth;[2] this material is monoclinic with space group $P2_1/c$. When $Pt(PPh_3)_3$ is carbonylated in presence of an excess of phosphine, the carbonyl is obtained as a different polymorph. We have determined the new structure in order to determine whether the metal atom was differently co-ordinated in the two crystal species.

The Laue symmetry of the novel polymorph is $P\bar{3}$. The space group is $P3$; $a = 19{\cdot}09(1)$, $c = 10.780(5)$ Å, $V = 3402$ Å^3, $Z = 3$, $D_c = 1{\cdot}47$ g./cm.^{3}, $D_m = 1{\cdot}45$ g./cm.^{3}).

The structure has been solved by conventional Patterson and Fourier methods on the basis of 1377 independent reflections measured with a PAILRED diffractometer with Mo–K_α monochromatic radiation and corrected for absorption, all having a relative e.s.d. less than 0·25. The refinement was performed by full-matrix least squares; the Pt and P atoms were treated anisotropically and the C and O atoms isotropically. The phenyl rings were constrained to rigid motion.[3]

Because the space group $P3$ lacks planes of symmetry, alternating axes, or inversion centres, two independent refinements have been done on two models related to each other by inversion. Complex scattering factors[4] were used for Pt and P atoms. The final agreement indices were as follows: for the 'better' model $R = \Sigma|F_o - |F_c||/\Sigma F_o = 0{\cdot}0466$ and $R_w = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0{\cdot}0644$ and for the other model $R = 0{\cdot}0468$ and $R_w = 0{\cdot}0649$. The difference among the R_w values is significant although no inversion related couples of reflections were taken into account; according to Hamilton[5] the second model can be rejected at a 99·5% confidence level.

The true structure in the right-handed system fixed by the experimental conditions is shown in Figure 1 which is a projection along the c axis of the cell. There are three independent molecules within the cell, each one possessing the symmetry of the three crystallographically independent threefold axes. In other words each tetrahedral molecule has its Pt–C–O group lying on a ternary axis and possesses three phosphine groups related by symmetry.

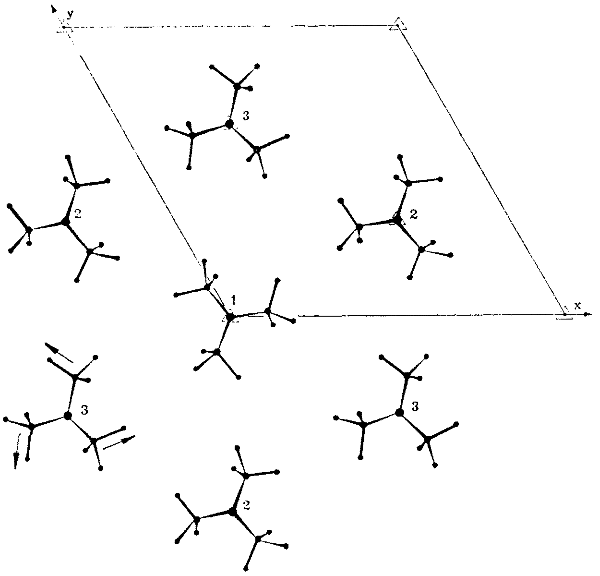

FIGURE 1. *A projection of the structure along the threefold axis. The phenyl rings are omitted for clarity and only the carbon atoms directly bound to the phosphorus atoms are shown.*

If the cell origin—which in this space group has to be fixed arbitrarily along a threefold axis—is placed on the Pt atom of molecule (1), the corresponding atoms in molecules (2) and (3), respectively, are found at levels of 3·17(1) and 5·40(1) Å along the c axis. The three molecules are strictly equivalent in their overall configuration; the different separations between molecular layers 1 and 2 and layers 2 and 3 are due to the fact that both molecules (1) and (2) point their CO groups upward whereas molecule (3) points the same group downward. This fact prevents the lattice from being rhombohedral.

Each molecule can be regarded as a three-bladed propellor. In order to fix its chirality we shall adopt here the 'steering wheel' convention;[6] we regard the CO group as the steering column and further we make the convention that the molecular chirality is determined by the three symmetry-related P–C bonds which lie nearest to the plane of the phosphorus atoms. For molecule (3), which is in the correct orientation in Figure 1 (CO group downward), we go *from P to C* in a counterclockwise direction so that we assign molecule (3) the *S* conformation. The very peculiar situation existing in this structure is illustrated in Figure 2 where the phosphine groups of the three independent molecules are shown in projection along their Pt–P axes, together with the CO groups and the threefold axes. The three projections have been obtained separately, each one by a similarity transformation in such a way as to have the CO group pointing in the same direction. Group 1 is the mirror image of groups 2 and 3; because of the previous assignment of symbol *S* to the molecule (3) the present crystal has to be described as having (*R*,*S*,*S*) packing.

This seems to be the first example of unbalanced packing of chiral molecules. We do not know yet whether a solution of one single crystal will display optical activity; if no rearrangement occurs in solution we will be observing one third of the specific rotatory power of the *S* or *R* enantiomer. We are presently investigating this possibility as well as the possibility that other M(PPh$_3$)$_3$X species give the (*R*,*S*,*S*) and the (*R*,*R*,*S*) packing.

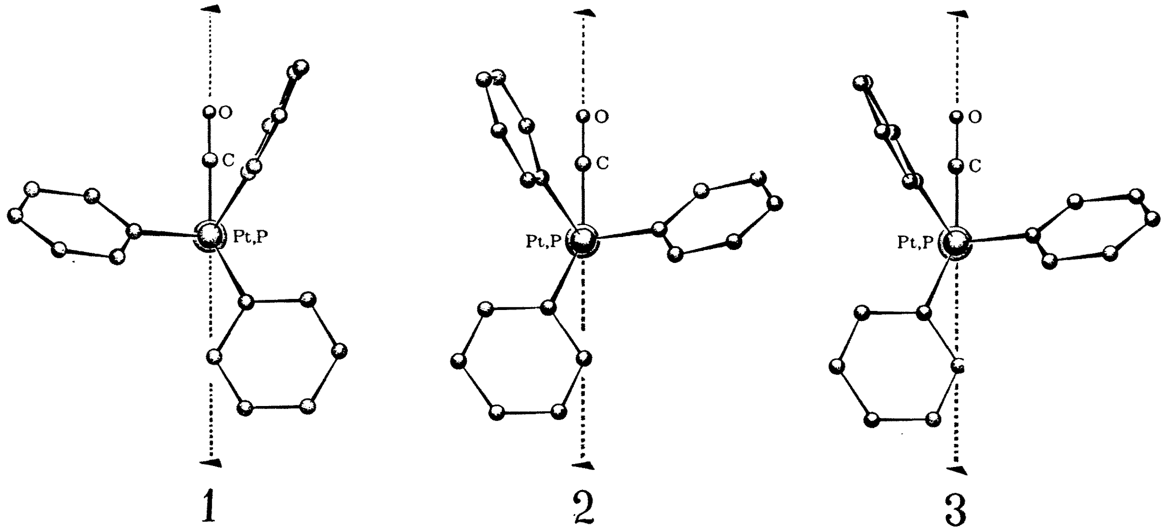

FIGURE 2. *The phosphine groups of the three independent molecules projected along the* Pt–P *bonds.*

The bonding parameters in the present polymorph agree with the corresponding quantities in the monoclinic one. The metal co-ordination is almost perfectly tetrahedral and the Pt–C (carbonylic) distance of 1·84(2) Å compares well with the distance of 1·86(3) Å in the monoclinic crystals. In each nonequivalent molecule of the present structure there are three equal Pt–P distances; for the three molecules these distances are: 2·357(8), 2·369(10), and 2·353(10) Å. In the monoclinic crystals we found, within the same molecule, the following values for the Pt–P distances: 2·333(8), 2·335(8), and 2·352(8) Å.

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