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Structural Studies of Pt Cluster Compounds. II.* The Crystal Structure of the Trinuclear Platinum Cluster $Pt_3[P(C_6H_{11})_3]_3(CO)_3$

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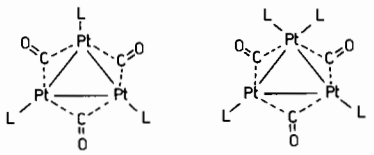
As a part of a systematic study of the reactivity of *trans*-$PtH_2[P(C_6H_{11})_3]_2$ [1, 2] it has been found that this dihydrido reacts in benzene solution giving several different crystalline compounds by reductive elimination. Two of these compounds have been characterized as the trinuclear carbonyl clusters $Pt_3(CO)_3L_3$ (**1**) and $Pt_3(CO)_3L_4$ (**2**) (L = cyclohexylphosphine, $P(C_6H_{11})_3$) and are similar to the clusters described by Chatt and Chini [3, 4]



(1) (2)

prepared by decomposition of the complexes $Pt(CO)_2L_2$ (L = PR_3, R = alkyl or aryl groups); the tetranuclear species $Pt_4(CO)_5L_4$ were also obtained (for a recent review of some aspects of Pt carbonyl compounds see ref. 5), but while a description of the geometry of the latter was given [6], no structural details of the compounds analogous to (**1**) and (**2**) were reported.

We have already described the geometry of $Pt_3(CO)_3L_4$ (L = cyclohexyl phosphine, $P(C_6H_{11})_3$) (**2**), in part I of this paper; we have now carried out an X-ray analysis to obtain a more detailed knowledge of the geometry of compound (**1**), which contains only "unsaturated" platinum atoms (each counting 16 electrons).

Crystal Data

$Pt_3P_3O_3C_{57}H_{99}$, M.W. = 1510.61; Orthorhombic, Space Group Cmca, Z = 16. The least squares refined values of the cell constants are a = 23.756(7); b = 16.569(9); c = 38.661(6); V = 15217.3 Å^3; D_{calc} = 1.23. The crystals (prismatic habit) are of dark red colour and air stable.

A total of 4905 reflexions (3232 with $I \geqslant 3\sigma(I)$ were considered observed) has been collected on a Philips four circles diffractometer up to sin θ/λ = 0.53 Å^{-1} (CuKα, graphite monochromatized radiation, λ = 1.5418 Å).

The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares with anisotropic thermal parameters for Pt and P atoms and isotropic for the others. The scattering factors of Cromer and Mann [7] have been used in the refinement and the correction for the real part of the anomalous dispersion was accounted for [8]. The conventional agreement factor is R = 0.079.

Some relevant bond lengths and angles are given in Table I.

TABLE I. Bond Lengths, Angles and Internal Rotation Angles.[a]

Pt(1)–Pt(2)	2.656(2) Å	P(1)–C(5)	1.86(3) Å
Pt(1)–Pt(1′)	2.653(2)	P(1)–C(6)	1.84(2)
Pt(1)–P(1)	2.267(7)	P(1)–C(7)	1.86(3)
Pt(2)–P(2)	2.282(9)	P(2)–C(3)	1.91(4)
Pt(1)–C(1)	2.06(4)	P(2)–C(4)	1.91(3)
Pt(1)–C(2)	1.92(3)	C(1)–O(1)	1.19(4)
Pt(2)–C(2)	2.21(3)	C(2)–O(2)	1.16(4)
		C–C[b]	1.54(4)

Pt(1)–Pt(2)–Pt(1′)	59.9(1)°
Pt(1′)–Pt(1)–Pt(2)	60.0(1)
Pt(1′)–Pt(1)–P(1)	148.8(3)
Pt(1)–Pt(2)–P(2)	150.0(5)
Pt(2)–Pt(1)–P(1)	151.2(3)
Pt(1)–C(2)–O(2)	155.9(8)
Pt(1)–C(1)–O(1)	140.3(8)
Pt(1)–C(2)–Pt(2)	78.9(2)
Pt(2)–C(2)–O(2)	125.0(3)
Pt(1)–Pt(2)–P(2)–C(3)	92.4(3)
Pt(1)–Pt(2)–P(2)–C(4)	−24.9(7)
Pt(1′)–Pt(1)–Pt(2)–C(2)	−177.2(6)

[a]The e.s.d.'s on the last significant figure are given in parentheses. [b]Average value.

The molecular geometry of $Pt_3(CO)_3[P(C_6H_{11})_3]_3$, which has a crystallographic m-site symmetry, conforms to a D_{3h} symmetry neglecting the distortion of the CO groups (see below) with the three Platinum atoms arranged at the apexes of an equilateral triangle. Figure 1 shows a perspective view of the structure; the mirror plane contains the atoms C(1), O(1), Pt(2) and bisects the Pt–Pt′ bond.

The two independent distances between the Platinum atoms are equal within the e.s.d.'s (average 2.654(2) Å) and are close to the mean value of 2.66(1) Å found in $[Pt_3(CO)_3(\mu\text{-}CO)_3]_n^{2-}$ [9] and the average of 2.675(1) Å found in compound (**2**)

*Part I. A. Albinati, G. Carturan and A. Musco, *Inorg. Chimica Acta, 16*, L3 (1976).

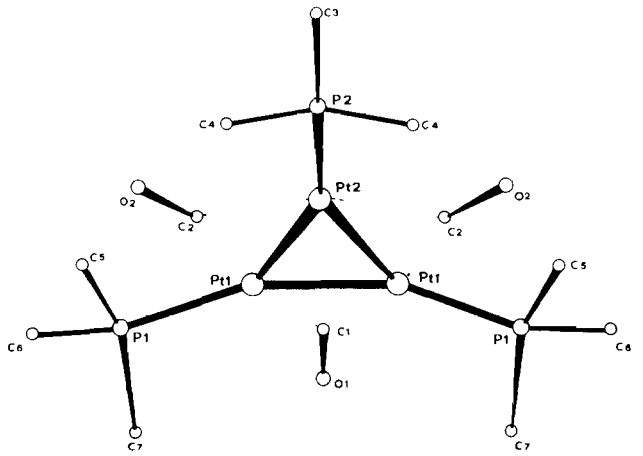


Fig 1 A perspective view of the structure

between the two "16 electrons" Pt atoms, a similar value of 2 65 Å is quoted in ref [9] for $Pt_3(CO)_3(PR_2R')_3$ (R = C_6H_5, R' = $CH_2C_6H_5$) Comparable distances for the Pt–Pt bond can also be found in clusters like $FePt_2(CO)_5[P(OPh)_3]_3$ [10] and $Pt_2S(CO)[P(C_6H_5)_3]_3$ [11], *i e* 2 633(1) and 2 65 Å respectively On the other hand a Pt–Pt bond distance of 2 654(2) Å is shorter, as can be expected from electronic reasons, than the values of 2 736(1) and 2 714(1) Å observed in (2) between the two different types of Platinum atoms, those counting 16 and 18 electrons, or in $Pt_4(CO)_5(PR_2R')_4$ [6] between the two types of CO-bridged Pt–Pt bonds (average values 2 75, 2 79 Å)

The mean Pt–P distance of 2 274(8) Å falls within the expected range, being similar to the one observed for $Pt(P(C_6H_5)(t\text{-}But)_2)_2$ (2 252(1) Å) [12], the average ones of 2 28 Å for compounds of type $Pt(L)[P(C_6H_5)]_2$ (L = aryl, alkyl) [13] and the mean value of 2 294(5) Å for the distance between Phosphorus and Platinum (five coordinated) in compound (2), more examples of similar values are reported 2 287(8) Å in $Pt(Triphos)_3$ [14] and 2 30 Å in $Pt(P(C_6H_{11})_3)_3$ [15, 16] Nonetheless these two Pt–P bonds are significantly shorter than the values of 2 350(4) Å found in (2) for the phosphines coordinated to the same Platinum atom, where a different steric as well as electronic situation occurs

It may be interesting to note the presence of an asymmetrically bonded (μ-CO) group (Pt(1)–C(2) 1 96(3), Pt(2)–C(2) 2 21(3) Å), bridging formally similar Pt atoms

The $Pt(CO)_3$ moiety is essentially planar (mean deviation from the least squares plane 0 088 Å) and all the cyclohexyl rings of the phosphinic ligand are in their normal chain conformation

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