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X-Ray Structure of the Trinuclear Metal Cluster $Pt_3[P(C_6H_{11})_3]_4(CO)_3$

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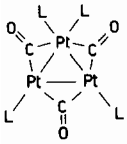
In the course of our studies on the reactivity of *trans*-$PtH_2[P(C_6H_{11})_3]_2$ (1)[1] we have found that the dihydrido complex in benzene solution undergoes a reductive elimination of hydrogen by reaction with carbon monoxide at atmospheric pressure. A red crystalline material (2) was isolated which has an I.R. spectrum [$\nu_{C\equiv O}$ 1825*w*, 1780*s*, 1760*s* (nujol)] comparable to that reported by Chatt and Chini[2] for $Pt_3(CO)_3L_4$ (L = tertiary phosphine). Structure (I) has been found for these complexes,[3,4] which implies that a platinum atom of the triangular cluster is bound to two phosphorus ligands, although the details of this structure have not yet been published.



I

Previously we have isolated $M[P(C_6H_{11})_3]_2$ (M = Pd, Pt) (3) which have been proved to be two-coordinate complexes by X-ray structural determination,[5-7] the P–M–P angle being ~ 160°.
temperature of $Pd[P(C_6H_{11})_3]_2$ in presence of free ligand have shown that at low temperature $Pd[P(C_6H_{11})_3]_3$ (4) is formed, but at room temperature the predominant species is the two-coordinate complex even in the presence of an excess of ligand.[8] If the structure of (2) is of the type (I) we may anticipate a P–Pt–P angle substantially smaller than the angle observed for (3) and possibly similar to the one existing in (4).

With this in mind we decided to carry out an X-ray structural determination of (2).

Crystal Data

$Pt_3P_4O_3C_{75}H_{132}$, M.W. = 1790.14, λ = 0.7107 Å, Triclinic, space group $P\bar{1}$, Z = 2, *a* = 20.342(10), *b* = 15.372(10), *c* = 13.876(10) Å, α = 97.92(4)°, β = 86.89(5)°, γ = 79.36(5)°, D_c = 1.41. The single crystal X-ray data have been collected with an automatic 4 circles diffractometer and the structure solved by Patterson and Fourier methods and refined by least squares procedure. The actual R factor is 0.049 based on 6476 observed reflections with the intensity I ⩾ 3σ(I). Further refinement with the introduction of absorption correction is in progress.

A prospective view of the structure is given in Figure 1 and some relevant data are reported in Table I.

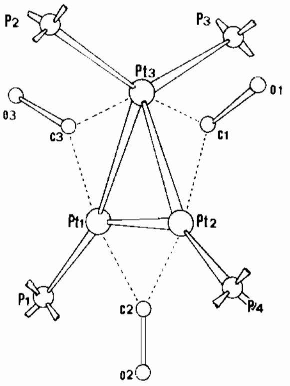


Figure 1.

TABLE I.[a] Bond Lengths and Angles

Pt(1)–Pt(2)	2.675(1) Å
Pt(1)–Pt(3)	2.736(1)
Pt(2)–Pt(3)	2.714(1)
Pt(1)–P(1)	2.303(5)
Pt(2)–P(4)	2.285(5)
Pt(3)–P(2)	2.351(4)
Pt(3)–P(3)	2.349(4)
Pt(1)–C(3)	1.98(2)
Pt(2)–C(1)	2.01(2)
Pt(3)–C(1)	2.11(2)
Pt(3)–C(3)	2.07(2)
Pt–C(2)[b]	2.02(2)
C–O[b]	1.21(2)
P(2)–Pt(3)–P(3)	126.2(1)°
Pt(1)–Pt(2)–Pt(3)	61.02(2)°
Pt(1)–Pt(3)–Pt(2)	58.78(2)°
Pt(2)–Pt(1)–Pt(3)	60.20(2)°

[a] The estimated standard deviation on the last significant figure is given in parenthesis. [b] Average values.

The Pt(1)–P(1) (2.303(5)Å) and Pt(2)–P(4) (2.285(5)Å) bond distances are close to those observed in the cluster $Pt_4[P(C_6H_5)(CH_3)_2]_4(CO)_5$.[3] The Pt(3)–P bonds appear to be substantially longer (2.350(4) Å average value) so as to accommodate the two bulky phosphines on the same center with the

P–Pt–P angle of 126.2(1)°. The lengthening of the Pt(3)–P bonds may also be due to electronic effects.[9] However, steric effects cannot be underestimated when bulky phosphines are coordinated, *e.g.* in $Pd[P(C_6H_{11})_3]_2$ the Pd–P distances are 2.26 Å whereas this distance is 2.32 Å in $Pd[P(menthyl)_2$*i*-$C_3H_7]_2$ where an even bulkier phosphine is coordinated to the metal.[10]

A similar steric factor may be relevant also in $Pd[P(C_6H_{11})_3]_3$ explaining the existence of this complex only at low temperature; *i.e.* coordination of the three bulky phosphine ligands occurs at the expense of the Pd–P bond strength.

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