Journal of Organometallic Chemistry, 267 (1984) C13—C15
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

A DIPLATINUM COMPLEX CONTAINING ONE BRIDGING AND TWO CHELATING dppm LIGANDS. THE X-RAY STRUCTURE ANALYSIS OF $[Pt_2(dppm)_3][PF_6]_2$ (dppm = $Ph_2PCH_2PPh_2$)

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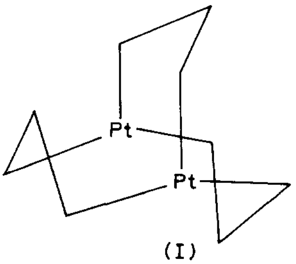
(Received February 9th, 1984)

Summary

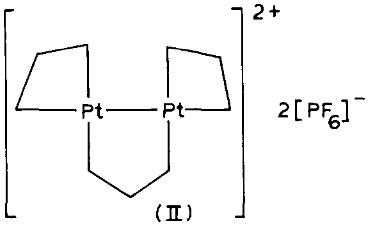
The dinuclear platinum(I) complex $[Pt_2(dppm)_3][PF_6]_2$ unexpectedly contains a Pt—Pt bond, one bridging and two chelating dppm ligands, in marked contrast to the related zerovalent platinum compound $[Pt_2(dppm)_3]$.

There is considerable current interest in the coordination chemistry of bis(diphenylphosphino)methane (dppm), whose usual coordination preference to metal centres involves a bridging rather than a chelating mode [1]. The versatility of this ligand is evidenced by its use in stabilising a variety of metal—metal bonded systems [1—5] 'A' frames [6] and eight membered ring complexes [7—9].

The recent report by Manojlovic-Muir and Muir [10] of the first crystallographic characterisation of a dinuclear complex $[Pt_2(dppm)_3]$ (I), in which the two zerovalent platinum atoms are bridged by three dppm ligands prompts us to report the results of an X-ray diffraction study of the corresponding dicationic complex $[Pt_2(dppm)_3][PF_6]_2$ (II), which has a very different structure.



(I)



(II)

(∧ = $Ph_2PCH_2PPh_2$ = dppm)

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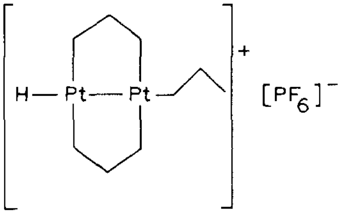
The yellow crystalline complex II was obtained unexpectedly during an attempted synthesis of a phosphaalkyne complex [11] containing a dinuclear platinum system and involved the use of the intermediate diplatinum(I) hydrido complex $[Pt_2H(dppm)(\mu\text{-}dppm)_2][PF_6]$ which previously has been assigned the structure III [12]. The mechanism of formation of II from III is currently under study.



(III)

*Crystal data for II**. $C_{75}H_{66}F_{12}P_8Pt_2$, M = 1833.3, monoclinic, space group $P2_1/n$, a 15.865(4), b 17.499(3), c 31.701(6) Å, β 94.65(2)°, Z = 4, R = 0.085, R' = 0.112 for 4711 reflections with $I > \sigma(I)$ measured on a CAD4 diffractometer.

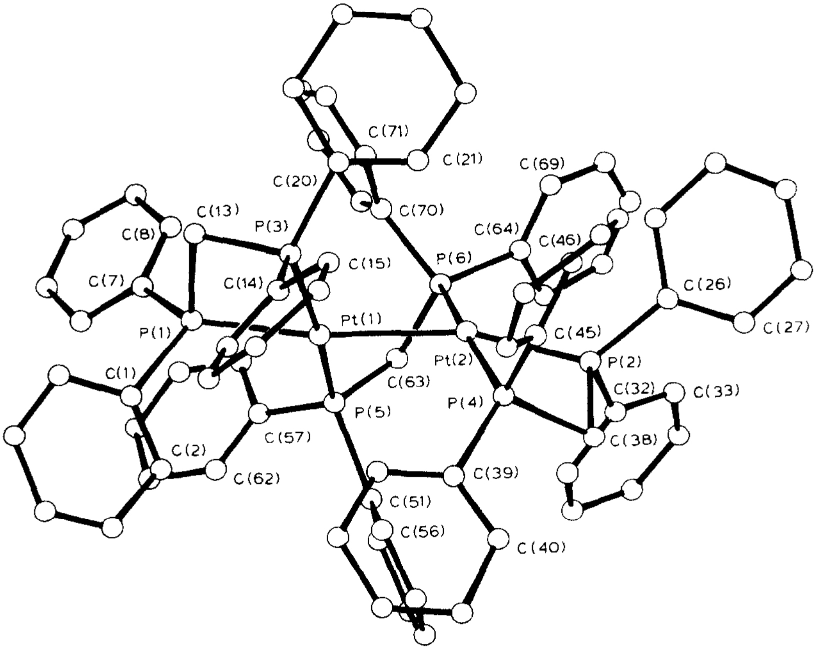


Fig. 1. The structure and atom numbering of the $[Pt_2(dpme)_3]^{2+}$ cation. Relevant bond lengths and angles are: Pt(1)—Pt(2) 2.646(1), Pt(1)—P(1) 2.312(6), Pt(1)—P(3) 2.325(6), Pt(1)—P(5) 2.317(6), Pt(2)—P(2) 2.328(6), Pt(2)—P(4) 2.328(6), Pt(2)—P(6) 2.295(6), Pt(2)—Pt(1)—P(1) 172.4(2), Pt(2)—Pt(1)—P(3) 101.4(2), Pt(2)—Pt(1)—P(5) 83.8(1), Pt(1)—Pt(2)—P(2) 164.8(2), Pt(1)—Pt(2)—P(4) 103.2(2), Pt(1)—Pt(2)—P(6) 81.4(2).

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

The crystal structure consists of discrete $[Pt_2(dppm)_3]^{2+}$ and $[PF_6]^-$ ions in a 1/2 ratio. The cation (Fig. 1) has a Pt—Pt bond length of 2.646(1) Å, with one bridging dppm ligand and two terminal chelating dppm groups. The coordination about each Pt atom is essentially square planar with a maximum deviation of 0.08 Å for Pt(1) from the Pt(1)—P(1)—P(3)—P(5)—Pt(2) plane and 0.18 Å for Pt(2) from the Pt(2)—P(2)—P(4)—P(6)—Pt(1) plane. The angle between the two planes is 59°. (Deviations (Å) of atoms from mean planes (a) Pt(1) −0.08, P(1) 0.04, P(3) 0.00, P(5) 0.01, Pt(2) 0.03. (b) Pt(2) −0.18, P(2) 0.16, P(4) −0.06, P(6) −0.05, Pt(1) 0.13.

So far as we are aware this is the first structural characterisation of a platinum dimer species joined by a Pt—Pt bond and containing only one bridging dppm ligand. As mentioned above the zerovalent dinuclear platinum species $[Pt_2(dppm)_3]$ [10,13] has been shown to have the triply bonded manxane type structure with a relatively long Pt—Pt separation (3.023(1) Å) indicative of no significant Pt ... Pt bonding. Complexes containing both a $Pt^I—Pt^I$ bond and two bridging dppm groups have similar Pt—Pt bond lengths to $[Pt_2(dppm)_3]^{2+}$, but have a smaller angle between the two coordination planes, e.g. $[Pt_2Cl_2(dppm)_2]$ [14,15] Pt—Pt 2.651(1) Å, interplanar angle 39°; $[Pt_2(CO)Cl(dppm)_2]^+$ [16] Pt—Pt 2.620(1) Å and interplanar angle 40°. However the anion $[Pt_2(CO)_2Cl_4]^{2-}$ [17] which has no bridging ligand adopts a conformation with an angle of 60° between the two Pt^I coordination planes, almost the same as in $[Pt_2(dppm)_3]^{2+}$.

Acknowledgment. We thank the Saudi Arabian Government for financial support (for S.I.A.).

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