

The Nature of 'Pt(Ph₂PCH₂CH₂PPh₂). A Platinum(I)–Platinum(I) Dimer containing Bridging Cyclometallated 1,2-Bis(diphenylphosphino)ethane; X-Ray Crystal Structure

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Single-crystal X-ray structural analysis of a complex of empirical formula [Pt(dppe)] (dppe = Ph₂PCH₂CH₂PPh₂) formed by heating [Pt(OH)Me(dppe)] in methanol shows that it should be formulated as [Pt-μ-{o-C₆H₄P(Ph)CH₂CH₂PPh₂}]₂ and that it contains cyclometallated dppe ligands bridging a Pt^I–Pt^I bond.

An air-stable orange crystalline compound of empirical formula [Pt(dppe)] (dppe = Ph₂PCH₂CH₂PPh₂) has been reported¹ to be formed in high yield by heating the hydroxo(methyl)platinum(II) complex [Pt(OH)(Me)(dppe)] in methanol. Molecular weight measurements (by osmometry in CH₂Cl₂ and mass spectrometry) have now shown that the compound is dimeric rather than tetrameric as originally suggested¹ and the i.r. spectrum (Nujol mull) shows bands at 1565(w), 1425(w), and 728(s) cm⁻¹ indicative of *ortho*-metallated phenyl groups.^{2,3} The ³¹P {¹H} n.m.r. spectrum at 24.3 MHz can be analysed as an AA'BB' system with complex satellites arising from isotopomers containing one and two magnetically active ¹⁹⁵Pt nuclei (*I* = ½, 34% abundance), which give rise to AA'BB'X and AA'BB'XX' systems respectively. The magnitude of ¹J(PtPt) (5300 Hz) derived from this analysis suggests the presence of a Pt–Pt bond.^{4†} These data are consistent with a structure (1) containing two platinum(I) (d⁹) atoms symmetrically bridged by a pair of *ortho*-metallated dppe ligands, and this has been confirmed by an X-ray analysis of single crystals grown from chlorobenzene-*n*-heptane.

Crystal data: C₅₂H₄₆P₄Pt₂, *M* = 1185.18, triclinic, space group *P* $\bar{1}$, with *a* = 13.078(4), *b* = 13.910(4), and *c* = 13.382(3) Å, α = 93.92(2), β = 97.50(2), and γ = 93.57(6)°, *Z* = 2, *D*_c = 1.639 g cm⁻³, *D*_m = 1.62(9) g cm⁻³, μ = 60.43 cm⁻¹ (Mo-*K*_α radiation). The 5137 observed reflections [*I* > 3σ(*I*)] having 2θ ≤ 50° were measured with a fully automated Philips PW1100-20 diffractometer. The structure was solved by the heavy-atom method and refined to a current *R* value of 0.057 employing anisotropic thermal parameters for non-hydrogen atoms.[‡]

The molecule (Figure 1) consists of two [Pt(dppe)] fragments bridged by *ortho*-metallation of one phenyl ring of each dppe ligand by the other platinum atom, giving a pair of five-membered rings fused along the Pt–Pt bond. Complex (1) could exist as diastereomers owing to the presence of two chiral phosphorus atoms, but the structure contains only that isomer having four phenyl groups on the same side of the average co-ordination plane of the platinum atoms and there is no evidence from the ³¹P {¹H} n.m.r. spectrum for another isomer in solution. Co-ordination about the platinum atoms is essentially square-planar although the bond angles subtended at them are significantly distorted from 90° [θ_{max} = 104.0(4); θ_{min} = 78.4(1)°]. The ligand atoms are displaced only slightly (<0.08 Å) from the two mean co-ordination

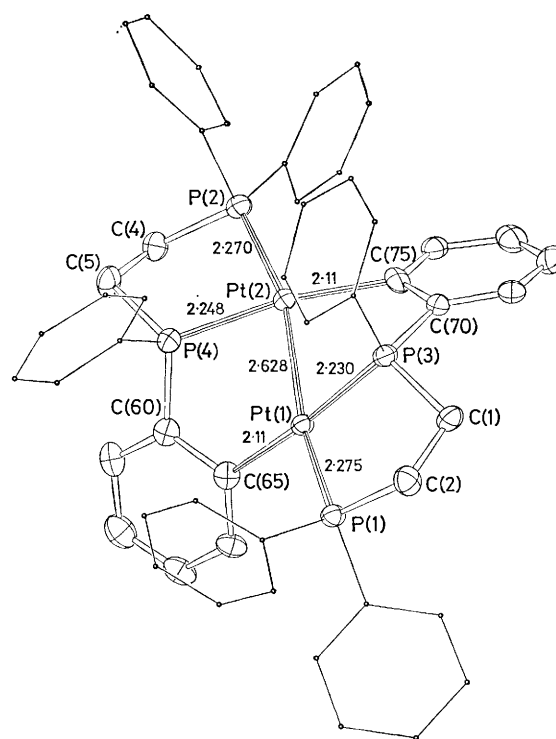
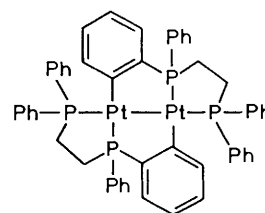


Figure 1. View of the molecule [Pt-μ-{o-C₆H₄P(Ph)CH₂CH₂PPh₂}]₂.



(1)

[Pt(OMe)Me(dppe)]

(2)

† Other parameters are as follows: δ_A 24.6, δ_B 61.4 (p.p.m. to high frequency of external 85% H₃PO₄), *J*(AA') 64.3, *J*(AB) 17.5, *J*(AB') -0.9, *J*(BB') 219.5, *J*(AX) -143.8, *J*(A'X) 1811.0, *J*(BX) 1023.4, *J*(B'X) 1986.3 Hz, where P_A, P_{A'} and P_B, P_{B'} are the phosphorus atoms *trans* to carbon and platinum respectively and the arrangement of Pt_{X,X'} is B(A)X'-X(A')B'.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

planes. The torsion angle about the Pt–Pt bond is 40°, similar to those found in other Pt^I dimers^{5,6} and the Pt–Pt bond length [2.628(1) Å] is normal for a Pt–Pt single bond.^{6,7} The Pt–P bond lengths *trans* to platinum (average: 2.272 Å) are longer than those *trans* to the σ-bonded carbon atoms (average: 2.240 Å) reflecting the high *trans*-influence of the metal–metal bond.

ortho-Metallation of dppe has been demonstrated to occur in the mononuclear fragments $[\text{Fe}(\text{dppe})_2]^8$ and $[\text{ReH}(\text{dppe})_2]^9$ but the present work provides the first example of such a reaction at a dimetal centre. The closest analogy is the cyclometallation of $[\text{Ru}(\text{dmpe})_2]$ to give $[\text{RuH}\{\mu\text{-CH}_2\text{P}(\text{Me})\text{CH}_2\text{CH}_2\text{PMe}_2\}(\text{dmpe})_2]$ ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$).^{10,11}

A probable intermediate in the formation of (1) from $[\text{Pt}(\text{OH})\text{Me}(\text{dppe})]$ and methanol is the methoxo-complex $[\text{Pt}(\text{OMe})\text{Me}(\text{dppe})]$ (2),[§] which can be prepared as a water-sensitive solid by treatment of either $[\text{PtCl}(\text{Me})(\text{dppe})]$ or $[\text{Pt}(\text{Me})(\text{MeOH})(\text{dppe})]^+$ with sodium methoxide in anhydrous methanol at room temperature. Like other methoxo-platinum(II) complexes containing *cis*-tertiary phosphine ligands¹²⁻¹⁴ or chelating ditertiary phosphine ligands,^{14,15} complex (2) is thermally stable as a solid or in benzene solution and does not undergo β -elimination to give a hydrido-complex.[¶] However, complex (1) is formed when (2) is heated in methanol for 24 h, and can also be prepared by heating either $[\text{PtCl}(\text{Me})(\text{dppe})]$ (80% yield after 24 h) or $[\text{PtCl}_2(\text{dppe})]$ (50% yield after 7 days) in methanolic sodium methoxide.

The Pt-C bonds of (1) are readily cleaved by an excess of HCl to give $[\text{PtCl}_2(\text{dppe})]$ but the adducts formed on reaction

with CH_3I , CH_2I_2 , I_2 , $\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me}$, SO_2 , and S_8 retain the cyclometallated dppe diplatinum moiety.

Received, 25th September 1981; Com. 1130

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§ I.r. (Nujol): 1078 cm^{-1} (s) $\nu(\text{C-O})$; ^1H n.m.r., CD_2Cl_2 , 34 °C: δ (MePt) 0.43 dd, $^3J(\text{PH})$ 3.2, 8.0, $^2J(\text{PtH})$ 57 Hz; δ (OMe) 3.78 d, $^4J(\text{PH})$ (*trans*) 5.0, $^3J(\text{PtH})$ 44.6 Hz; $^{31}\text{P}\{^1\text{H}\}$ n.m.r., CH_2Cl_2 , -40 °C: δ (P *trans* to Me) 47.5, $^1J(\text{PtP})$ 1867 Hz; δ (P *trans* to OMe) 36.1, $^1J(\text{PtP})$ 3470, $^2J(\text{PP})$ 5 Hz.

¶ In contrast, platinum(II) complexes containing OMe *trans* to a σ -bonded alkyl or aryl residue readily decompose by β -elimination to give hydrido-complexes (ref. 16).
