

A Novel Diplatinadecaborane with a Pt–Pt Bond: [(PMe₂Ph)₂(Pt₂B₈H₁₄)]

Rohana Ahmad, Janet E. Crook, Norman N. Greenwood,* John D. Kennedy, and Walter S. McDonald

Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

The novel metallaborane [(PMe₂Ph)₂(Pt₂B₈H₁₄)] consists of the four-vertex and eight-vertex subclusters {Pt₂B₂} and {Pt₂B₆} conjoined at a common Pt–Pt edge; it can be regarded as an *iso-arachno*-diplatinadecaborane.

The reaction of 4-Me₂S-7-MeO-*arachno*-B₉H₁₂ with *cis*-[PtCl₂(PMe₂Ph)₂] on a scale of *ca.* 1 mmol in the presence of base yields the expected *arachno*-platinanonaborane [(PMe₂Ph)₂(PtB₈H₁₁OMe)] (yield *ca.* 50%) together with several other products of degradation including the known^{1,2} metallaborane types [(PMe₂Ph)₂(PtB₃H₇)] (*ca.* 8%) and [(PMe₂Ph)₂(Pt₂B₁₂H₁₈)] (*ca.* 35%). In addition there is a smaller yield (2–3%) of a yellow, air-stable, crystalline compound [(PMe₂Ph)₂(Pt₂B₈H₁₄)] which has now been fully characterized by X-ray diffraction analysis in conjunction with n.m.r. spectroscopy. The compound has an unprecedented structure consisting of an *arachno* four-vertex {Pt₂B₂} cluster (which may be regarded as a complex of the hypothetical *arachno*-B₂H₅³⁻ ligand) conjoined by a common Pt–Pt edge to an *arachno* eight-vertex cluster {Pt₂B₆}. The structure is therefore quite different from that of another recently characterized *arachno*-diplatinadecaborane [6,6,9,9-(PMe₂Ph)₄(6,9-Pt₂B₈H₁₀)]³ which geometrically closely resembles the icosahedral fragment B₁₀H₁₄²⁻.

The heavy-atom structure of [(PMe₂Ph)₂(Pt₂B₈H₁₄)] was established by single crystal X-ray diffraction analysis. *Crystal data*: monoclinic, space group P2₁, *a* = 1618.3(9), *b* = 1330.0(7), *c* = 592.3(3) pm, β = 93.62(4)°, *Z* = 2. The structure, based on 1711 independent *F*₀, was refined (including absolute configuration) to *R* = 0.039 (*R*' 0.048).† The

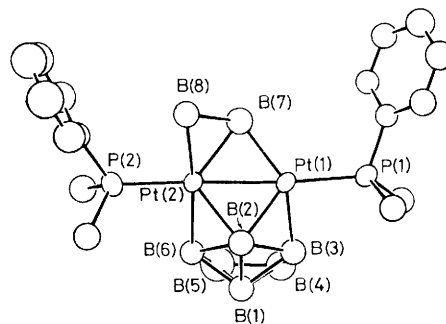
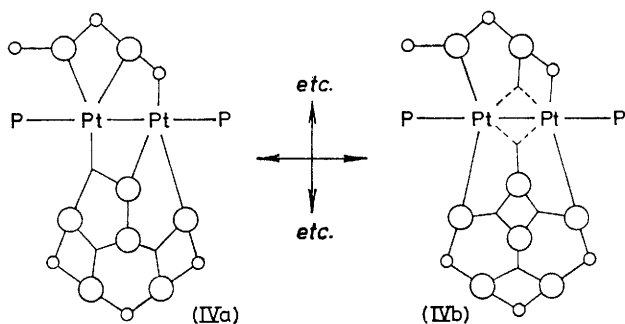
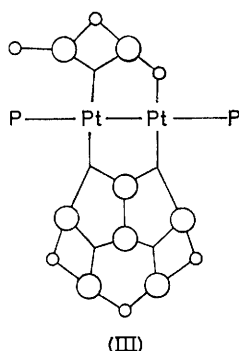
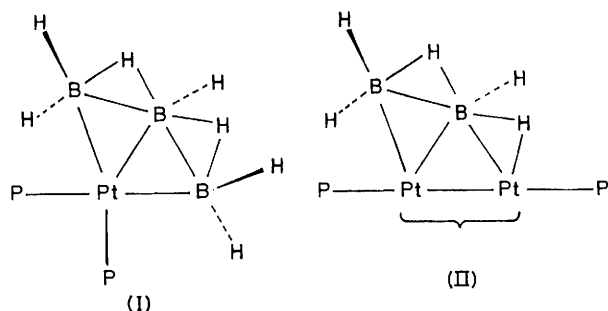


Figure 1. ORTEP drawing of [(PMe₂Ph)₂(Pt₂B₈H₁₄)]. Hydrogen atoms were not located but their presence was confirmed by n.m.r. spectroscopy as discussed in the text. Distances from Pt(1) are as follows: to Pt(2) 262.1(1), to P(1) 228.8(5), to B(2) 218(2), to B(3) 217(3), and to B(7) 222(3) pm. Distances from Pt(2) are as follows: to P(2) 229.2(5), to B(2) 219(2); to B(6) 228(2), to B(7) 216(3), and to B(8) 224(3) pm. Angles Pt(1)–Pt(2)–P(2) and Pt(2)–Pt(1)–P(1) are 178.3(1) and 174.8(1)°, respectively, and the dihedral angle between the Pt(1)Pt(2)B(7) and Pt(2)B(7)B(8) planes is 135.6°. Pt(1)Pt(2)B(2) and Pt(1)Pt(2)B(7) are essentially coplanar (dihedral angle 0.9°).

molecular structure is shown in Figure 1. There is an essentially linear P–Pt–Pt–P system to which a six-boron and a two-boron subcluster are appended. Hydrogen atoms were not located from the X-ray diffraction analysis, but n.m.r. spectroscopy shows that the six-boron subcluster is {B₆H₆}, bonding η³ to Pt–Pt as in the previously described² species [(PMe₂Ph)₂(Pt₂B₁₂H₁₈)]. The two-boron sub-cluster, by contrast, appears to be without precedent; n.m.r. spectroscopy

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



shows that there are five H atoms associated with it, and the correspondence of the detailed n.m.r. behaviour with that of other *arachno* four-vertex cluster species such as $[(PMe_2Ph)_2-$

$(PtB_3H_7)]$ [schematic geometrical structure (I)], $[(PPh_3)_2(CO)-(H)IrB_3H_7]$, and $[(PPh_3)_2(H_2)IrB_3H_8]$, indicates that the disposition of the H atoms is as depicted in structure (II), *i.e.* the $\{Pt_2B_2\}$ unit constitutes the framework of an *arachno* four-vertex cluster and is thus an additional member of the theoretically interesting⁵ *arachno* four-vertex $\{M_nB_{4-n}\}$ cluster series which ranges from *arachno*- B_4H_{10} itself through species $[(PR_3)_2(PtB_3H_7)]$, $[(PR_3)_2(H_2)IrB_3H_8]$ *etc.*, to non-boron-containing 'butterfly' $\{M_4\}$ clusters at the other extreme.

Although a naive valence bond rationale for the entire 10-vertex cluster structure can be written down on the basis of bidentate *nido* $\eta^3-B_2H_5^-$ and bidentate *nido* $\eta^3-B_6H_9^-$ ligation to the linear $Pt^{II}-Pt^{II}$ system $[Pt_2(PMe_2Ph)_2]^{2+}$, as in (III), this interpretation is probably too simple and it is likely that the electronic structure has large contributions from configurations such as (IV) in which the metal atoms are best interpreted as platinum(IV) centres using the definition of metal oxidation state given in ref. 6. The overall structure could then be described as an *arachno* ten-vertex cluster (although any inclusion of the two electrons in the Pt-Pt bond in the cluster electron count would strictly merit the use of the *hypho* descriptor).

We thank the S.E.R.C. for support, the Government of Malaysia for a Scholarship (to R.A.), and Dr. D. Reed, University of Edinburgh, for assistance with high-field n.m.r. spectroscopy.

Received, 28th June 1982; Com. 750

References

- 1 A. R. Kane and E. L. Muetterties, *J. Am. Chem. Soc.*, 1977, **93**, 1041; L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *ibid.*, 1972, **94**, 5665.
- 2 N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1980, 37.
- 3 S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1981, 1415.
- 4 J. Bould and J. D. Kennedy, unpublished observations in these laboratories.
- 5 C. E. Housecroft and T. P. Fehlner, *Inorg. Chem.*, 1982, **21**, 1739, and references cited therein.
- 6 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 346.