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Metallaborane reaction chemistry. A facile and reversible dioxygen capture by a B-frame-supported bimetallic: structure of [(PMe₂Ph)₄(O₂)Pt₂B₁₀H₁₀].

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[(PMe₂Ph)₄Pt₂B₁₀H₁₀] **1** reversibly takes up atmospheric dioxygen to give the fluxional dioxygen-dimetallaborane complex [(PMe₂Ph)₄(O₂)Pt₂B₁₀H₁₀] **2**, which has Pt-Pt 2.7143(3), Pt-O 2.141(4) and 2.151(4), and O-O 1.434(6) Å.

Index words: Dimetallaboranes; Metallaborane reaction chemistry; Cluster bridging ligands; Dioxygen-diplatinum complex, Borane clusters; NMR; X-ray diffraction analysis; Diplatinum complex of molecular dioxygen; Dioxygen, reversible uptake by a dimetal system.

Boron-containing clusters are redox-flexible among the *closo* – *nido* – *arachno* – *etc.* sequence. Metallaboranes that also incorporate redox-flexible transition-element centres thence offer scope for extensive reaction chemistries. The few reported results¹⁻⁶ suggest such potentially wide-ranging chemistries. The positioning of two metal centres, rather than just one, on the electronically flexible 'B-frame' matrix in principle extends the scope.⁴ One focus of interest in this regard derives from the effect of the positioning of the two metal centres in adjacent positions within the electron-deficient 'B-frame' matrix. For example, how will any synergy differ from that encountered in better-examined matrices such as the 'A-frame' and related configurations that can be constructed with electron-rich ligands such as bidentate phosphines? In this general context we now report an unprecedented reversible sequestration of atmospheric dioxygen by a dimetallaborane. This capture occurs at the dimetal site of the twelve-vertex closed species [(PMe₂Ph)₄Pt₂B₁₀H₁₀] **1**.

We previously reported⁴ the isolation of very dark purple [(PMe₂Ph)₄Pt₂B₁₀H₁₀] **1** from the reaction of [(PMe₂Ph)₂PtB₁₀H₁₂] **3**^{7,8} with [PtCl₂(PMe₂Ph)₂] and non-nucleophilic base in CH₂Cl₂ solution. It also forms in the reaction of **3** with PMe₂Ph in refluxing toluene.⁹ The almost black crystals of compound **1** are not very soluble when pure, but we can now report that attempted dissolution under air or under pure dioxygen produces an orange solution from which amber crystals of [(PMe₂Ph)₄(O₂)Pt₂B₁₀H₁₀] **2** can be obtained. Compounds **1** and **2** are characterised by single-crystal X-ray diffraction analyses (Figures 1 and 2)¹⁰ and by NMR spectroscopy.¹¹ Both have metals-adjacent closed twelve-vertex 1,2-diplatinadodecaborane configurations, first noted in [(PMe₂Ph)₃ClPt₂B₁₀H₉(PMe₂Ph)].⁹ They differ in that (a) compound **2** has a dioxygen unit positioned across the diplatinum unit, (b) there is a concomitant reduction in the interplatinum distance, and (c) there is a flexing of the phosphine ligand sphere. The dioxygen addition can be readily reversed upon gentle heating, by removal of solvent and volatiles under reduced pressure, or by purging with an inert gas such as argon or dinitrogen. NMR

spectroscopy shows that these reversible interconversions are quantitative (equation 1). As far as we are aware, this is the first example of a reversible dioxygen capture by a metal-metal system. Two separate metal centres joined by a dioxygen link are well recognised, *e.g.* in the $[(\text{PPh}_3)_2\text{Pt}\{\mu\text{-O}_2\}(\mu\text{-OH})\text{Pt}(\text{PPh}_3)_2]^+$ cation,¹² but there is only one previously reported metal-metal-bonded system for which dioxygen coordination has been reported:¹³ this is for a bis(bidentate-phosphine) diiridium system, in which $[\text{Ir}_2(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ **4** takes up dioxygen, to give $[\text{Ir}_2(\text{CO})_2(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ **5**. This last process is, however, irreversible,¹³ in contrast to the reversibility of the $\{\text{Pt}_2\text{B}_{10}\}$ system reported here. Another contrast is that the $\{\text{Pt}_2\}\text{-}\{\text{O}_2\}$ coordination in **2** is fluxional;¹¹ see captions to Figures 1 and 2. A further contrast is that **2** is much less robust than the $\{\text{Ir}_2(\text{O}_2)\}$ species **5**: at room temperature **2** decomposes in solution overnight, and in the solid state over several days, to give an intractable dark solid. It is, however, stable at < 250 K. The precursor compound **1** appears to be indefinitely stable (years) in the solid state in a normal glass sample tube with a plastic cap.



The interoxygen distance of 1.434(6) Å in **2** is longer than the distance of 1.21 Å in molecular dioxygen; it is more akin to that in peroxide ions or hydrogen peroxide (typically 1.47-1.49 Å), and longer than that in the dioxide anion (*ca.* 1.28 Å).¹⁴ These observations, plus the Pt(1)O(1)O(2)Pt(2) torsion angle of 15.8°, favour a peroxide description. The weak interplatinum bonding interaction of 2.965(1) Å in **1** converts to a stronger linkage at 2.7143(3) Å in **2**. The peroxide formulation for the $\{\text{O}_2\}$ bridge thence implies an oxidative addition to give two platinum(IV) centres. This addition is associated with a significant change in coordination geometry at the platinum atoms, and the $\{(\text{PMe}_2\text{Ph})_4\}$ assembly opens up to accommodate the dioxygen molecule on the $\{\text{Pt}_2\}$ unit (Figure 2). There also appears to be a substantial change in bonding within the cluster. The ¹¹B cluster NMR shielding pattern of non-oxygenated $[(\text{PMe}_2\text{Ph})_4\text{Pt}_2\text{B}_{10}\text{H}_{10}]$ **1** relates to that of its monoplatinum precursor $[(\text{PMe}_2\text{Ph})_2\text{PtB}_{10}\text{H}_{12}]$ **3**,⁸ which in turn relates to that of its non-platinated precursor *nido*- $\text{B}_{10}\text{H}_{14}$. For **1**, this suggests a relatively simple replacement of the two pairs of bridging hydrogen atoms on the $\text{B}_{10}\text{H}_{14}$ residue with bonds to the two platinum centres, without substantially perturbing the essence of the *nido*-decaboranyl bonding system: the metal centres in **1** could thence be regarded essentially as platinum(II) units, with only loose mutual interaction between them, at 2.965(1) Å, in contrast to the more intimately linked platinum(IV) centers in **2**. In accord with this, the ¹¹B shielding pattern of oxygenated $[(\text{PMe}_2\text{Ph})_4(\text{O}_2)\text{Pt}_2\text{B}_{10}\text{H}_{10}]$ **2** does not relate so directly to that of $\text{B}_{10}\text{H}_{14}$, or to that of **3**, and suggests a more fundamental change in intracluster electronics. Here it may be noted that the closer distribution of resonances in the ¹¹B spectrum of **2** is more typical of true *closo* twelve-vertex shielding patterns. The overall behaviour is reminiscent of the changes in intracluster bonding seen in the eleven-vertex monoplatinadecaboranes $[(\text{PR}_3)_2\text{PtC}_2\text{B}_8\text{H}_{10-x}\text{R}'_x]$, for which an intracluster bonding change associated with platinum(II) \rightleftharpoons platinum(IV) interconversion has also been proposed.¹⁵

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Deposited data

Crystallographic data for the structures of **1** and **2** are deposited with the Cambridge Crystallographic Data Centre, deposition Nos. CCDC 115796 and CCDC 235553 respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

References and footnotes

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10. X-ray data for compound **2**: [(PMe₂Ph)₄(O₂)Pt₂B₁₀H₁₀] **2** C₃₂H₅₄B₁₀P₄Pt₂O₂, *M* = 1092.91, monoclinic, space group *P2₁/c*, *a* = 11.16130(10), *b* = 28.0289(4), *c* = 16.3931(2) Å, β = 97.6300(10)°, *U* = 5082.99(11) Å³, *Z* = 4, λ = 0.71073 Å (Mo-Kα), μ = 5.648 mm⁻¹, *T* = 150(2) K; *R*1 = 0.0435 for 7989 reflections with *F*² > 2.0σ(*F*²), and *wR*2 = 0.1166 for all 9930 unique reflections. Two disordered dichloromethane molecules were incorporated in the model using PLATON/SQUEEZE. (P. van der Sluis and A. L. Spek, *Acta Cryst.*, 1990, **A46**, 194; CCDC 235553. Data for [(PMe₂Ph)₄Pt₂B₁₀H₁₀] **1** are previously reported and deposited,⁴ CCDC 115796.
11. Selected NMR data for compounds **1** and **2** (CD₂Cl₂) [δ in ppm, ³¹P rel. H₃PO₄, ¹¹B rel. BF₃(OEt₂) and ¹H rel. SiMe₄]. Compound **1**: δ(³¹P) (188 K): -2.7 [¹J(¹⁹⁵Pt-³¹P) 2705 Hz]; δ(¹¹B) [δ(¹H)] (298 K): BH

(9,12) +22.1 [+4.44, $^1J(^{11}\text{B}-^1\text{H})$ ca. 130 Hz, $^3J(^{195}\text{Pt}-^1\text{H})$ ca. 45 Hz], BH (8,10) -26.8 [+1.20, $^1J(^{11}\text{B}-^1\text{H})$ ca.130 Hz, $^3J(^{195}\text{Pt}-^1\text{H})$ ca. 40 Hz], BH (4,5,7,11) +24.6 [+4.37, $^1J(^{11}\text{B}-^1\text{H})$ ca.125 Hz] and BH (3,6) +18.6 [+4.28]; $\delta(^1\text{H})(\text{PMe}_2\text{Ph})$ (263 K) +1.625 (12H) [$N(^{31}\text{P}-^1\text{H})$ ca. 11 Hz, $^3J(^{195}\text{Pt}-^1\text{H})$ ca. 21 Hz] and +1.695 (12H) [$N(^{31}\text{P}-^1\text{H})$ ca. 10 Hz, $^3J(^{195}\text{Pt}-^1\text{H})$ ca. 25 Hz], and (sharp multiplets) around +7.14 (4H), +7.35 (8H) and +7.40 (8H). Some of the values originally quoted⁴ for **1** are in error because of solubility problems and the (then) unrecognised presence of **2** in solution. Compound **2**: $\delta(^{31}\text{P})$ at 188 K +0.5 [$^1J(^{195}\text{Pt}-^{31}\text{P})$ ca. 2620 Hz] and +0.1 [$^1J(^{195}\text{Pt}-^{31}\text{P})$ ca. 2210 Hz], at 243 K $^2J(^{195}\text{Pt}-^{31}\text{P})(\text{mean})$ ca. 110 Hz, $^2J(^{31}\text{P}-^{31}\text{P})(\text{mean})$ ca. 15 Hz; at 295 K $\delta(^{11}\text{B})$ [$\delta(^1\text{H})$]: BH (9,12) +16.0 [+4.99], BH (8,10) -3.6 [+3.90, $^3J(^{195}\text{Pt}-^1\text{H})$ ca. 60 Hz], BH (4,5,7,11) +1.9 [+3.21] and BH (3,6) +18.2 [+2.84]. At 293 K $\delta(^1\text{H})$ +1.189 [$^3J(^{195}\text{Pt}-^1\text{H})$ 14 Hz, $N(^{31}\text{P}-^1\text{H})$ 10.1 Hz] (12H, PMe) and +1.799 [$^3J(^{195}\text{Pt}-^1\text{H})$ 17 Hz, $N(^{31}\text{P}-^1\text{H})$ 9.7 Hz] (12H, PMe) and around +7.39 (16H) and +7.52 (4H) (PPh). At 173 K $\delta(^1\text{H})$ for PMe gave ca. +1.71 (2 \times 6H, accidentally coincident), +1.64 (6H) and +0.18 (6H). The molecule is fluxional with a reversible twist of the $\{\text{O}_2\}$ unit across the Pt(1)Pt(2) vector: coalescence temperatures give ΔG^\ddagger ca. 37.6 kJ mol⁻¹ at 190-202 K (^{195}Pt satellite structure in 202 MHz ^{31}P spectrum) and ca. 37.5 kJ mol⁻¹ at 208 \pm 4 K (P-methyl resonances in 500 MHz ^1H spectrum).

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Captions for Figures

Figure 1. ORTEP-type representations of the crystallographically determined molecular structures of (top) purple [(PMe₂Ph)₄Pt₂B₁₀H₁₀] **1** (based on data from reference 4) and (bottom) orange-red [(PMe₂Ph)₄(O₂)Pt₂B₁₀H₁₀] **2**.¹¹ Organyl hydrogen atoms are omitted for clarity. For **1** crystallographic symmetry dictates that Pt(1) ≡ Pt(2), B(7) ≡ B(4), B(8) ≡ B(5), B(12) ≡ B(10) and B(11) ≡ B(9); selected interatomic distances for **1** are: from Pt(2) to Pt(1) 2.965(1), to P(1) 2.336(2), to P(2) 2.343(3), to B(6) 2.299(11), to B(7) 2.199(13) and to B(8) 2.238(12) Å; the PPtP angle is 96.94(10)°, and the PtPtP angles are 114.84(6) and 116.80(7)°. For **2**, selected interatomic distances (in Å) are: from Pt(1) to Pt(2) 2.7143(3), to O(1) 2.141(4), to P(11) 2.3525(16), to B(3) 2.312(7), to B(4) 2.192(7), to B(5) 2.201(7), and to B(6) 2.291(7); from Pt(2) to O(2) 2.151(4), to P(21) 2.3898(16), to B(3) 2.287(7), to B(6) 2.317(7), to B(7) 2.212(7), and to B(11) 2.207(8); O(1)-O(2) is 1.434(6) Å. There is a *ca.* 15° twist between the {O₂} and the {Pt₂} units, with torsion angles PtOOPt 19.9°, OPtPtO 10.6°, and OOPtPt 15.8 and 21.6°, with associated differences in the angles to phosphorus: Pt(2)Pt(1)P(11) and O(1)Pt(1)P(11) are 130.55(4)° and 86.38(12)° respectively, whereas Pt(2)Pt(1)P(12) and O(1)Pt(1)P(12) are 117.08(4)° and 76.38(13)° respectively. Pt(2)Pt(1)O(1) is 72.15(11)°, Pt(1)O(1)O(2) is 106.0(3)° and P(11)Pt(1)P(12) is 99.25(6)°; the corresponding angles around Pt(2) are similar to. In solution the {O₂} and the {(PMe₂Ph)₂} units fluxionally exchange to their mirror positions either side of the Pt(1)Pt(2)B(10)B(12) plane (Figure 2), with ΔG[‡] (190-212 K) *ca.* 37.5 kJ mol⁻¹ as measured by ³¹P and ¹H NMR spectroscopy.¹¹

Figure 2. Space-filling representations of the crystallographically determined molecular structures of (extreme left) [(PMe₂Ph)₄Pt₂B₁₀H₁₀] **1** and (centre right and extreme right) [(PMe₂Ph)₄(O₂)Pt₂B₁₀H₁₀] **2**, to illustrate how the {(PMe₂Ph)₄} assembly of **1** (extreme left) opens up with the P-organyl groups twisting out of the way (centre left) to accommodate the dioxygen molecule on the {Pt₂} unit (centre right). The fluxionality of **2** can be envisaged in terms of an interconversion of the centre-right-hand diagram with its mirror image (extreme right).

Suggestion for graphical contents entry.

The {Pt₂} unit of [(PMe₂Ph)₄Pt₂B₁₀H₁₀] **1** reversibly takes up atmospheric dioxygen to give the dioxygen-dimetallaborane complex [(PMe₂Ph)₄(O₂)Pt₂B₁₀H₁₀] **2**; the resulting {Pt₂}-O₂ binding mode is fluxional.

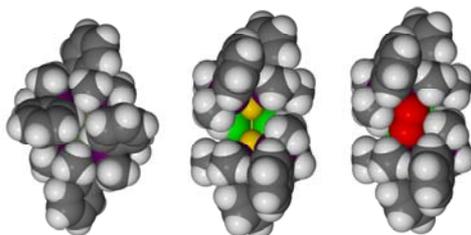


Figure 1

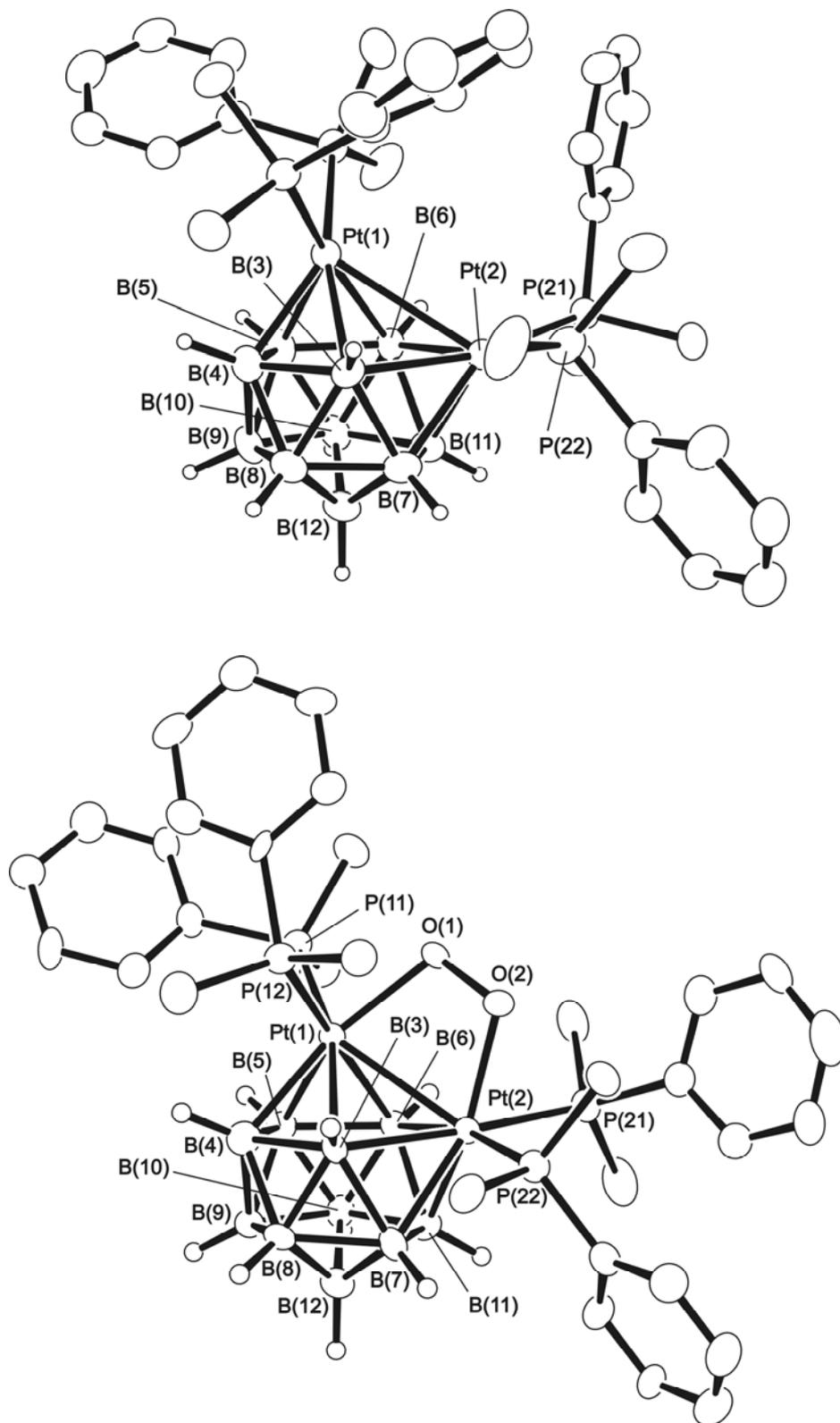


Figure 2

