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Metallaborane reaction chemistry. A facile and reversible dioxygen capture by a B-frame-supported bimetallic: structure of $[(PMe_2Ph)_4(O_2)Pt_2B_{10}H_{10}]$

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$[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ 1 reversibly takes up atmospheric dioxygen to give the fluxional dioxygen–dimetallaborane complex $[(PMe_2Ph)_4(O_2)Pt_2B_{10}H_{10}]$ 2, which has Pt–Pt 2.7143(3), Pt–O 2.141(4) and 2.151(4) and O–O 1.434(6) Å.

Introduction

Boron-containing clusters are redox-flexible within 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 results[1–6] 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 $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ **1**.

We previously reported[4] the isolation of very dark purple $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ **1** from the reaction of $[(PMe_2Ph)_2PtB_{10}H_{12}]$ **3**[7,8] with $[PtCl_2(PMe_2Ph)_2]$ and a non-nucleophilic base in CH_2Cl_2 solution. It also forms in the reaction of **3** with PMe_2Ph 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 $[(PMe_2Ph)_4(O_2)Pt_2B_{10}H_{10}]$ **2** can be obtained. Compounds **1** and **2** are characterised by single-crystal X-ray diffraction analyses (Figs. 1 and 2)[10]† and by NMR spectroscopy.[11] Both have metals-adjacent closed twelve-vertex 1,2-diplatinadodecaborane configurations, first noted in $[(PMe_2Ph)_3ClPt_2B_{10}H_9(PMe_2Ph)]$.[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 [eqn. (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 $[(PPh_3)_2Pt\{(\mu\text{–}O_2)(\mu\text{–}OH)\}Pt(PPh_3)_2]^+$ 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 $[Ir_2I_2(CO)_2(Ph_2PCH_2PPh_2)_2]$ **4** takes up dioxygen to give $[Ir_2I_2(CO)_2(O_2)(Ph_2PCH_2PPh_2)_2]$ **5**. This last process is, however, irreversible,[13] in contrast to the reversibility of the $\{Pt_2B_{10}\}$ system reported here. Another contrast is that the $\{Pt_2\}$–$\{O_2\}$ coordination in **2** is fluxional;[11] see captions to Figs. 1 and 2. A further contrast is that **2** is much less robust than the $\{Ir_2(O_2)\}$ 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

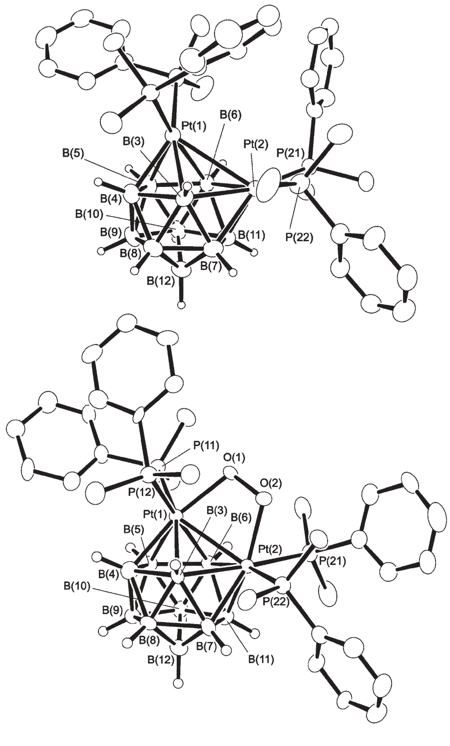

Fig. 1 ORTEP-type representations of the crystallographically determined molecular structures of (top) purple $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ **1** (based on data from reference 4) and (bottom) orange-red $[(PMe_2Ph)_4(O_2)Pt_2B_{10}H_{10}]$ **2**.[11] Organyl hydrogen atoms are omitted for clarity. 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 $\{O_2\}$ and the $\{Pt_2\}$ 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 all these. In solution the $\{O_2\}$ and the $\{(PMe_2Ph)_2\}$ units fluxionally exchange to their mirror positions either side of the Pt(1)Pt(2)B(10)B(12) plane (Fig. 2), with $\Delta G^\ddagger$ (190–212 K) *ca.* 37.5 kJ mol^{-1} as measured by ^{31}P and ^1H NMR spectroscopy.[11]

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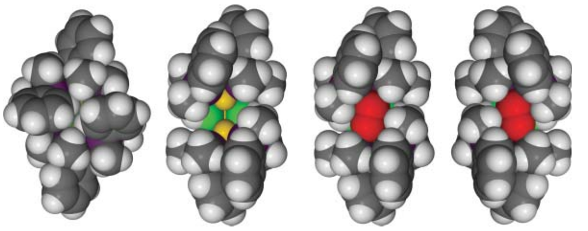

Fig. 2 Space-filling representations of the crystallographically determined molecular structures of (extreme left) $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ **1** and (centre right and extreme right) $[(PMe_2Ph)_4(O_2)Pt_2B_{10}H_{10}]$ **2**, to illustrate how the $\{(PMe_2Ph)_4\}$ assembly of **1** (extreme left) opens up with the P-organyl groups twisting out of the way (centre left) to accommodate the dioxygen molecule on the $\{Pt_2\}$ 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).

precursor compound **1** appears to be indefinitely stable (years) in the solid state in a normal glass sample tube with a plastic cap.

$$[(PMe_2Ph)_4Pt_2B_{10}H_{10}]\ \mathbf{1} + O_2 \equiv [(PMe_2Ph)_4(O_2)Pt_2B_{10}H_{10}]\ \mathbf{2} \qquad (1)$$

The interoxygen distance of 1.434(6) Å in **2** is longer than the distance of 1.21 Å in molecular oxygen; 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 $\{O_2\}$ 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 $\{(PMe_2Ph)_4\}$ assembly opens up to accommodate the dioxygen molecule on the $\{Pt_2\}$ unit (Fig. 2). There also appears to be a substantial change in bonding within the cluster. The ^{11}B cluster NMR shielding pattern of non-oxygenated $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ **1** relates to that of its monoplatinum precursor $[(PMe_2Ph)_2PtB_{10}H_{12}]$ **3**,[8] which in turn relates to that of its non-platinated precursor *nido*-$B_{10}H_{14}$. For **1**, this suggests a relatively simple replacement of the two pairs of bridging hydrogen atoms on the $B_{10}H_{14}$ 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 ^{11}B shielding pattern of oxygenated $[(PMe_2Ph)_4(O_2)Pt_2B_{10}H_{10}]$ **2** does not relate so directly to that of $B_{10}H_{14}$, 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 ^{11}B 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 monoplatinadicarbaboranes $[(PR_3)_2PtC_2B_8H_{10-x}R'_x]$, for which an intracluster bonding change associated with platinum(II)–platinum(IV) interconversion has also been proposed.[15]

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Notes and references

† CCDC 235553. See http://www.rsc.org/suppdata/cc/b4/b406974a/ for crystallographic data for compound **2** in .cif format.

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10 X-Ray data for compound **2**: $[(PMe_2Ph)_4(O_2)Pt_2B_{10}H_{10}]$ $C_{32}H_{54}B_{10}P_4Pt_2O_2$, $M = 1092.91$, monoclinic, space group $P2_1/c$, $a = 11.16130(10)$, $b = 28.0289(4)$, $c = 16.3931(2)$ Å, $\beta = 97.6300(10)°$, $U = 5082.99(11)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å (Mo–Kα), $\mu = 5.648$ mm^{-1}, $T = 150(2)$ K; $R1 = 0.0435$ for 7989 reflections with $F^2 > 2.0\sigma(F^2)$ and $wR2 = 0.1166$ 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 Crystallogr., Sect. A*, 1990, **A46**, 194; CCDC 235553. Data for $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ **1** are previously reported and deposited,[4] CCDC 115796.
11 Selected NMR data for compounds **1** and **2** (CD_2Cl_2) [δ in ppm, ^{31}P rel. H_3PO_4, ^{11}B rel. $BF_3(OEt_2)$ and ^1H rel. $SiMe_4$]. Compound **1**: $\delta(^{31}P)$ (188 K): −2.7 [$^1J(^{195}Pt–^{31}P)$ 2705 Hz]; $\delta(^{11}B)$ [$\delta(^1H)$] (298 K): BH (9,12) +22.1 [+4.44, $^1J(^{11}B–^1H)$ *ca.* 130 Hz, $^3J(^{195}Pt–^1H)$ *ca.* 45 Hz], BH (8,10) −26.8 [+1.20, $^1J(^{11}B–^1H)$ *ca.*130 Hz, $^3J(^{195}Pt–^1H)$ *ca.* 40 Hz], BH (4,5,7,11) +24.6 [+4.37, $^1J(^{11}B–^1H)$ *ca.*125 Hz] and BH (3,6) + 18.6 [+4.28]; $\delta(^1H)(PMe_2Ph)$ (263 K) +1.625 (12 H) [$N(^{31}P–^1H)$ *ca.* 11 Hz, $^3J(^{195}Pt–^1H)$ *ca.* 21 Hz] and +1.695 (12 H) [$N(^{31}P–^1H)$ *ca.* 10 Hz, $^3J(^{195}Pt–^1H)$ *ca.* 25 Hz] and (sharp multiplets) around +7.14 (4 H), +7.35 (8 H) and +7.40 (8 H). Some of the values originally quoted[4] for **1** are in error because of solubility problems and the (then) unrecognised presence of **2** in solution. Compound **2**: $\delta(^{31}P)$ (188 K) +0.5 [$^1J(^{195}Pt–^{31}P)$ *ca.* 2620 Hz] and +0.1 [$^1J(^{195}Pt–^{31}P)$ *ca.* 2210 Hz], at 243 K $^2J(^{195}Pt–^{31}P)$(mean) *ca.* 110 Hz, $^2J(^{31}P–^{31}P)$(mean) *ca.* 15 Hz; at 295 K $\delta(^{11}B)$ [$\delta(^1H)$]: BH (9,12) +16.0 [+4.99], BH (8,10) −3.6 [+3.90, $^3J(^{195}Pt–^1H)$ *ca.* 60 Hz], BH (4,5,7,11) +1.9 [+3.21] and BH (3,6) +18.2 [+2.84]. At 293 K $\delta(^1H)$ +1.189 [$^3J(^{195}Pt–^1H)$ 14 Hz, $N(^{31}P–^1H)$ 10.1 Hz] (12 H, PMe) and +1.799 [$^3J(^{195}Pt–^1H)$ 17 Hz, $N(^{31}P–^1H)$ 9.7 Hz] (12 H, PMe) and around +7.39 (16 H) and +7.52 (4 H) (PPh). At 173 K $\delta(^1H)$ for PMe gave *ca.* +1.71 (2 × 6 H, accidentally coincident), +1.64 (6 H) and +0.18 (6 H). The molecule is fluxional with a reversible twist of the $\{O_2\}$ unit across the Pt(1)Pt(2) vector: coalescence temperatures give $\Delta G^{\ddagger}$ *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 ± 4 K (P–methyl resonances in 500 MHz ^1H spectrum).
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