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Unprecedented Borane, Diborane(3), Diborene, and Borylene Ligands via Pt-Mediated Borane Dehydrogenation

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Supporting Information

ABSTRACT: Reactions of an aryldihydroborane with a Pt^0 complex lead to a range of novel products, including complexes with bridging diborene and diborane(3) ligands and a complex with both borylene and borane ($M \rightarrow B$) ligands. The products imply varying degrees of dehydrogenation of the boron centers with concomitant formation of boron−boron bonds, which in one case is later broken. These reactions show that although the dehydrocoupling of dihydroboranes is not a straightforward process in this case, the reactions are capable of connecting boron atoms in unusual ways, leading to unprecedented bonding motifs.

Dehydrocoupling, the formation of element−element bonds by the loss of dihydrogen (i.e., $EH + E'H \rightarrow EE' + H_2$), is finding increasing utility in the directed synthesis of main-group molecules and polymers. A host of reviews have taken stock of advances in the dehydrocoupling of E-H bonds, including stoichiometric, metal- and non-metal-catalyzed examples.[1] These reviews show a particular emphasis on homodehydrocoupling of Si−H bonds (A, Figure 1), P−H bonds (B), and the recent explosion of interest in heterodehydrocoupling of B−H and N−H bonds of amine-boranes for hydrogen storage applications and the formation of polyaminoboranes (C). The thriving field of catalytic dehydrocoupling is clearly the engine driving what Manners et al. have eloquently termed "catalysis in service of main-group chemistry".[11] While a large majority of the work on dehydrocoupling involving boron has involved heterodehydrocoupling with N−H bonds, homodehydrocoupling of the B−H bonds of polyboranes was discovered in 1984 by the Sneddon group,[2] and a similar process has been studied by Himmel et al.[3] Recently we have extended borane dehydrocoupling to the synthesis of diboranes of relevance to organic chemistry, such as dicatechol- and dipinacoldiborane(4), using both homo- and heterogeneous catalysts (D, Figure 1)[4] as well as its reverse reaction, the hydrogenation of B−B bonds.[5] The homodehydrocoupling of hydroboranes has thus added to a palette of contemporary routes for the selective synthesis of electron-precise B−B bonds; a field that until recently suffered from a distinct lack of diversity.[6]

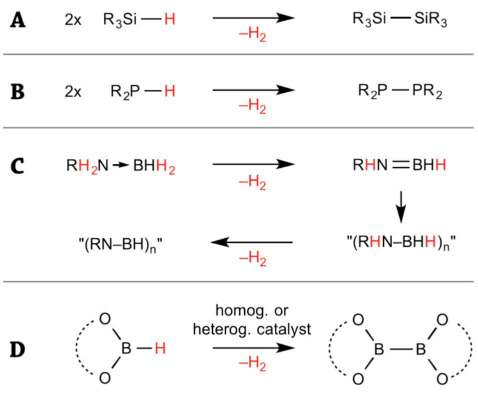

Figure 1. Examples of homo- and heterodehydrocoupling reactions.

Given the facility of dehydrocoupling of monohydroboranes, we set out to determine whether dihydroboranes (H_2BR) could likewise be dehydrocoupled. Conceivably, single dehydrocoupling of two dihydroboranes would yield highly useful, but otherwise difficult to prepare, dihydrodiboranes(4) ($B_2H_2R_2$), from which a series of consecutive intermolecular dehydrocoupling processes could lead to oligo- or polymeric species of the form $H(BR)_nH$. Alternatively, intramolecular dehydrocoupling of $B_2H_2R_2$ would provide a base-free diborene ($RB{=}BR$) that may be detected if unstable or stabilized by the use of large steric bulk or metal π coordination (a coordination mode observed previously via a different synthetic route).[7] The use of dehydrocoupling to form E−E multiple bonds has limited precedence in the literature, notably dehydrocoupling of a dihydroarsine to form a diarsene ($RAs{=}AsR$) by Waterman et al.,[8] and the dehydrogenation of a hydroborane to form a $Ru{=}B$ double bond by Sabo-Etienne et al.[9] However, dehydrogenation has never been used to generate B−B multiple bonds.

Herein we detail our attempts to dehydrocouple a dihydroborane using a zerovalent platinum complex. We observed complicated reactivity patterns, in some cases leading to B−B single- and double-bond formation and cleavage. The reactions led to identification of a number of new coordination motifs of boron-containing ligands, including a borane ligand bridging two platinum centers, perhaps the closest isolated example of a complex containing an unsupported dative metal-to-boron bond (i.e., a borane complex)[10,11] yet observed.

The bulky aryldihydroborane H_2BDur (Dur = 2,3,5,6-tetramethylphenyl) was chosen for dehydrocoupling due to the combination of an electron-poor boron center with imposing steric bulk that could help kinetically stabilize any products. Heating this borane with an equimolar amount of $[Pt(PCy_3)_2]$ at 68 °C led to a color change of the solution to dark red and provided two different compounds as determined by ^{31}P NMR spectroscopy. The major product of the reaction is the colorless dihydroplatinum complex *trans*-$[PtH_2(PCy_3)_2]$ (**1**, Figure 2),

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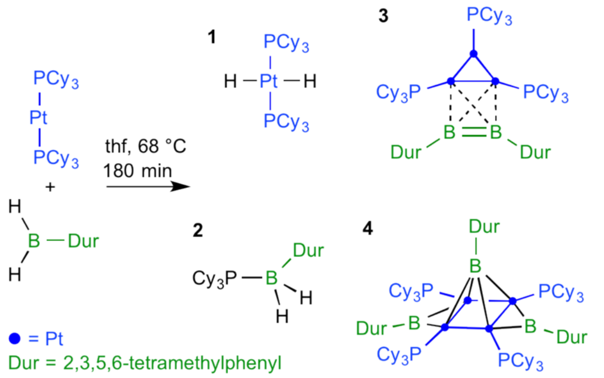

Figure 2. Products **1**−**4** of the reaction of $[Pt(PCy_3)_2]$ with BH_2Dur in equimolar amounts. Dur = 2,3,5,6-tetramethylphenyl.

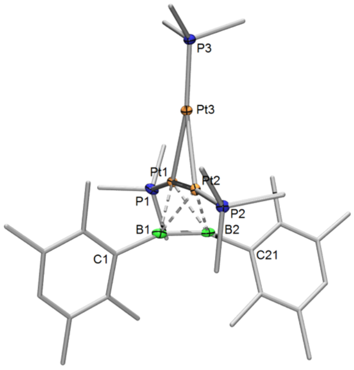

Figure 3. Crystallographically derived structure of **3**. Thermal ellipsoids drawn at the 50% probability level. One molecule of pentane, the cyclohexyl groups and some ellipsoids have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1−Pt2 2.594(1), Pt1−Pt3 2.611(1), Pt2−Pt3 2.680(1), Pt1−P1 2.276(1), Pt2−P2 2.270(1), Pt3−P3 2.188(1), B1−B2 1.614(6), B1−Pt1 2.069(4), B1−Pt2 2.162(4), B2−Pt1 2.140(4), B2−Pt2 2.076(5), B1−C1 1.570(5), B2−C21 1.571(6); P1−Pt1−Pt2 171.73(3), Pt1−Pt2−P2 168.83(3), C1−B1−B2 158.6(3), B1−B2−C21 158.6(3), Pt1−B1−Pt2 75.6(1), Pt1−B2−Pt2 75.9(1), B1−Pt1−B2 45.1(2), B1−Pt2−B2 44.7(2). Torsion angle between B1−B2 and Pt1−Pt2 axes: 85.46°.

which shows a singlet ^{31}P NMR resonance (δ 52.8) with ^{195}Pt satellites ($^{1}J_{PPt}$ = 2872 Hz). From this mixture we were able to isolate the colorless phosphine borane adduct $Cy_3P \rightarrow BH_2Dur$ (**2**, $\delta(^{11}B)$ − 29.9, $\delta(^{31}P)$ 13.6; see Supporting Information (SI)). From here, we turned to fractional crystallization in an attempt to isolate the compound(s) responsible for the intense red color of the mixture. A small amount of red crystals was isolated and determined to be $[(Cy_3P)_3Pt_3(\eta^2{:}\mu_2\text{-}B_2Dur_2)]$ (**3**, Figures 2 and 3) by single-crystal X-ray diffraction. Complex **3** shows three $[Pt(PCy_3)]$ units bound in a near-equilateral triangle, with one Pt−Pt bond bridged by a B_2Dur_2 diborene ligand in a tetrahedral fashion. The B−B distance (1.614(6) Å) is significantly longer than that in the previously reported mononuclear π-diborene complex $[(Et_3P)_2Pt(\eta^2\text{-}B_2Dur_2)]$[7] (1.510(14) Å) and the base-stabilized diborenes IDip → (H)B═B(H) ← IDip (1.561(18) Å, IDip = 1,3-bis(2,6-di-isopropylphenyl)imidazol-2-ylidene),[12] IDip → (Br)B═B(Br) ← IDip (1.546(6) Å)[13] and the related diboracumulene $B_2(CAAC)_2$ (1.489(2) Å; CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene).[14] However, the B═B distance of **3** is identical to that of dicyanodiborene $B_2(CAAC)_2(CN)_2$ (1.614(3) Å)[15] and thus sits at the upper limit of B═B bond lengths. The Pt1−Pt2 distance (2.594(1) Å) is comparable to those in the phosphide-bridged complexes $[Pt(\mu\text{-}PPh_2)(PPh_3)]_2$ (2.6041(1) Å) and $[Pt(\mu\text{-}PtBu_2)(PPh_3)]_2$ (2.6126(2) Å).[16] The two remaining Pt−Pt distances in **3** are slightly longer (2.611(1), 2.680(1) Å). The diborene moiety shows mild bending of the C−B−B−C core (∠C−B−B: 158.6(3), 158.6(3)°) and is slightly more bent than that in $[(Et_3P)_2Pt(\eta^2\text{-}B_2Dur_2)]$ (∠C−B−B: 166.0(8), 164.2(8)°).[7]

A small sample of crystals crystallographically determined to be **4** (see SI) was also isolated from the mixture. This compound showed a signal of higher order (52.1−11.7 ppm) in its $^{31}P\{^{1}H\}$ NMR spectrum, consistent with the crystallographically derived structure, $[\{Pt(PCy_3)\}_4(\mu_2\text{-}BDur)_2(\mu_4\text{-}BDur)]$, comprising a tetraplatinum butterfly unit, two edges of which are bridged by symmetrically bridging borylene ligands, and the Pt_4 square being capped by a tetrabridging borylene. Unfortunately, due to their low yield and instability, we were unable to fully characterize complexes **3** and **4** by solution NMR spectroscopy, although both samples provided elemental analysis data that fit their proposed constitution.

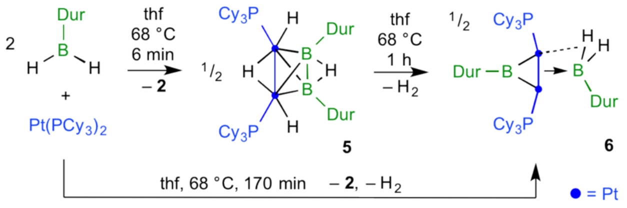

Figure 4. Syntheses of **5** and **6**.

The observation of **2** in the reaction mixture when equimolar amounts of H_2BDur and $[Pt(PCy_3)_2]$ are heated together led us to double the amount of borane in further reactions. Heating these two reactants in THF to 68 °C for 170 min provided a selective reaction. Removal of solvent, extraction with pentane (to remove **2**), and recrystallization from fluorobenzene provided a moderate yield (37%) of complex **6**, which showed two well separated signals in its ^{11}B NMR spectrum (δ 101.3 and 32.8) and a ^{31}P NMR spectrum of higher order. A single-crystal X-ray diffraction study revealed the structure of **6** to be $[\{(Cy_3P)Pt\}_2(\mu\text{-}BDur)(\mu\text{-}BH_2Dur)]$ (Figures 4 and 5): a diplatinum complex containing a bridging durylborylene ligand and a bridging duryldihydroborane ligand. The two boron-containing ligands comprise the "wings" of a Pt_2B_2 butterfly core. The Pt−Pt distance of **6** (2.6242(4) Å) is slightly longer than the diborene-bridged Pt−Pt bond of **3** (2.594(1) Å). The $Pt{-}B^{borane}$ distances of **6** (2.285(4), 2.177(3) Å) are significantly longer than the $Pt{-}B^{borylene}$ distances (1.989(3), 1.974(4) Å), in line with the lower Pt−B multiple bonding in the latter. The two borane hydrogen atoms were crystallographically located, one of which is found to be closely associated with the Pt center (Pt−H 1.94(3) Å), while the other points away from the metals. These hydrogen nuclei appear in the ^{1}H NMR spectrum of **6** as a broad signal (δ 4.98), which upon ^{11}B decoupling sharpens to a multiplet. The structure bears a striking resemblance to a published diplatinaborane complex with a bridging B_2H_5 ligand, $[\{(PhMe_2P)Pt\}_2(\eta^3\text{-}B_2H_5)(\eta^3\text{-}B_6H_9)]$.[17] This complex features an almost identical Pt−Pt distance (2.621(1) Å) to that of **6** (2.6242(4) Å), and the same pattern of short and long Pt−B (2.22(3), 2.16(3) Å) distances, the longer being that from the non-hydrogen-bridged boron atom. The hydrogen atoms were

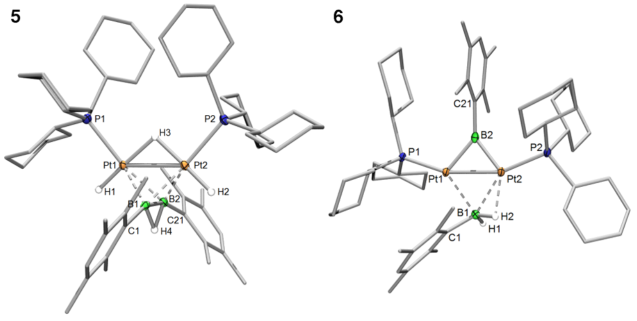

Figure 5. Crystallographically derived structure of **5** (top) and **6** (bottom). Thermal ellipsoids drawn at the 50% probability level. Some ellipsoids have been omitted for clarity. The displayed hydrogen atoms of **5** and **6** were crystallographically located. Selected bond length [Å] and angles [°] for **5:** Pt1−Pt2 2.7689(7), Pt1−P1 2.339(1), Pt2−P2 2.330(1), B1−B2 1.648(7), B1−Pt1 2.182(5), B1−Pt2 2.161(5), B2−Pt1 2.175(5), B2−Pt2 2.175(5), B1−C1 1.571(7), B2−C21 1.570(7); P1−Pt1−Pt2 127.56(4), Pt1−Pt2−P2 131.30(4), C1−B1−B2 156.0(4), B1−B2−C21 156.0(4), Pt1−B1−Pt2 79.1(2), Pt1−B2−Pt2 79.2(2), B1−Pt1−B2 44.4(2), B1−Pt2−B2 44.7(2). Torsion angle between B1−B2 and Pt1−Pt2 axes: 90.58°. For **6**: Pt1−Pt2 2.6242(4), Pt1−P1 2.3007(8), Pt2−P2 2.2857(6), B1−Pt1 2.285(4), B1−Pt2 2.177(3), B2−Pt1 1.989 (3), B2−Pt2 1.974(4), Pt2−H1 1.94(3), B1−C1 1.599(4), B2−C21 1.551(5), B1−H1 1.10(3), B1−H2 1.24(3); P1−Pt1−Pt2 163.10(2), Pt1−Pt2−P2 159.54(2), Pt1−B1−C1 85.9(2), Pt2−B1−C1 136.7(2), Pt1−B2−C21 136.0(2), Pt2−B2−C21 140.8(2), Pt1−B1−Pt2 72.0(1), Pt1−B2−Pt2 82.9(1), B1−Pt1−B2 100.0(1), B1−Pt2−B2 104.2(1).

not located in this reported structure. It should be noted that, apart from a borderline case of an platinum iminoboryl-alane adduct with a Pt═B bond,[18] complex **6** represents the first clear instance of a neutral borylene complex of metals from Group 10 or higher, a synthetic challenge that had eluded us and others for some time.

Metal-to-boron dative bonding, first structurally confirmed in a boratrane complex in 1999 by Hill et al.,[10] has since seen a flurry of research activity[11] and rekindled interest in the use of transition-metal bases in Lewis acid/base adducts.[19,20] However, despite extensive studies on such borane complexes, no complex with an unsupported metal-to-boron bond has been isolated. In 2012 we presented the isolation of a "slipped" borane complex of platinum, where a Pt → B interaction was supported by donation of electron density from the adjacent B−C bond to the metal.[21] A year later we reported the detection of two unsupported borane complexes that were characterized by ^{11}B, ^{19}F, and ^{31}P NMR spectroscopy, though we were unable to structurally confirm the proposed structures.[22] While also containing a non-negligible σ-BH donation to one platinum atom, from the above X-ray data of **6** we can surmise the presence of significant Pt → B character.

The structure of **6** also invites comparison with two structures prepared and analyzed by Paetzold, Boese and Schleyer.[23] These triboron compounds were characterized as aromatic B_2NtBu_3 rings in which the B−B bond donates electron density to the boron atom of a borane BH_2R (**I**: R = H; **II**: R = *t*Bu), based on their solid-state structures and DFT calculations. In the case of **I**, the BH_3 group bridges the remaining B−B bond symmetrically, while in **II**, the BH_2tBu borane adopts an effectively identical geometry to that of **6** (B^{borane}−$H^{bridging}$: 1.24(3) Å; B^{borane}−$H^{terminal}$: 1.10(3) Å), with a bridging hydrogen atom (B^{borane}−$H^{bridging}$: 1.24(4) Å; B^{borane}−$H^{terminal}$: 1.10(5) Å). That the bonding situation of the borane ligand in **6** is predominantly of the Pt_2 → B type is borne out further in DFT calculations which produce the appropriate orbitals for such an interaction (Figure S3) and predict a bond energy for the Pt−Pt → B interaction of −20.5 kcal/mol (Figure S3). This energy is substantially smaller than that calculated for the B−B → B dative bond in **I** (−45.7 kcal/mol), but only slightly weaker than the energy calculated for the B → N bond in ammonia borane (−28.5 kcal/mol).[23a]

When 2 equiv of H_2BDur are heated with $[Pt(PCy_3)_2]$ at 68 °C for only 6 min instead of 170 min, **6** was not detected in the reaction mixture. After reducing the mixture to dryness, the residue was washed with cold (−78 °C) pentane, leaving behind the byproduct **2**, which is poorly soluble at this temperature. Removal of solvent and recrystallization from fluorobenzene provided a yellow solid in moderate yield (**5**, Figure 4; 41%). While multinuclear NMR suggested that this solid was a single compound, we were unable to determine its structure without assistance from single-crystal X-ray diffraction (Figure 5). Complex **5**, $[\{(Cy_3P)HPt\}_2(\mu\text{-}H)\{\mu{:}\eta^2\text{-}B_2Dur_2H\}]$, comprises an unusual *hypercloso* cluster with a tetrahedral Pt_2B_2 core, two terminal Pt−H bonds, and hydride atoms bridging the Pt−Pt and B−B bonds. Interestingly, the B−B distance in **5** (1.648(7) Å) is equivalent to that in the trinuclear diborene complex **3** (1.614(6) Å) within statistical significance, but is significantly longer than that in the mononuclear diborene complex $[(Et_3P)_2Pt(\eta^2\text{-}B_2Dur_2)]$[7] (1.51(1) Å). The C−B−B angles of **5** (156.0(4), 156.0(4)°) are also only slightly more acute than those of **3** (158.6(3), 158.6(3)°), again indicative of a marginal structural difference between the B_2Dur_2 and B_2Dur_2H ligands. The Pt−Pt distance in **5** (2.7689(7) Å) is much larger than the boron-bridged Pt−Pt bonds in **3** (2.594(1) Å) and **6** (2.6242(4) Å). The Pt−B distances in **5** are all equivalent (2.182(5), 2.161(5), 2.175(5), 2.175(5) Å) and are slightly longer than those of **3** (2.069(4), 2.162(4), 2.140(4), 2.076(5) Å), suggesting a more symmetrical coordination of the boron-containing ligand in the former. The angles between B1−B2 and Pt1−Pt2 axes in **5** (90.58°) and **3** (85.46°) confirm this.

Complex **5** shows a single ^{11}B NMR signal (δ 11.7) that sits between those of the $(BH_2Dur)_2$ dimer in benzene (δ 22.4) and adduct (thf)BH_2Dur (δ 4.06), but is massively upfield from that of the diborene complex $[(Et_3P)_2Pt(\eta^2\text{-}B_2Dur_2)]$ (δ 129.9).[7] A broad singlet ^{31}P NMR resonance was observed for **5** (δ 46.7 ppm) with a ^{195}Pt−^{31}P coupling constant of 2661 Hz. A multiplet signal was observed in the ^{1}H NMR spectrum at δ 3.79−3.39 corresponding to the hydrogen nucleus bridging the B−B bond, and two high-field multiplets were found in a 1:2 integral ratio (δ −4.38, −4.68) corresponding to the bridging and terminal hydride ligands, respectively.

The identification of complex **5** in this reaction is a promising sign for the ability of Pt^0 complexes to dehydrocouple dihydroboranes, though the formation of Pt−Pt bonds indicates that H_2BDur oxidatively adds to two separate Pt atoms, facilitating metal−metal bond formation. Complex **5** slowly loses H_2 and rearranges quantitatively in solution after a few days at rt (or 1 h at 68 °C) to form B−B cleavage product **6**. The spontaneity of this reaction ($\Delta G_{298.15K} = -7.0$ kcal/mol; Figure S4) is remarkable when considering that the B−B bond is broken along with multiple Pt−H and B−H bonds. It should also be noted that **5** or **6** can be selectively prepared by addition of 3 equiv of H_2BDur to the complex $[(Cy_3P)Pt(\text{norbornene})_2]$. If the mixture is stirred for 20 min at rt, **5** is formed, while leaving the reaction overnight at 40 °C leads to formation of **6**. These reactions result in concomitant norbornene hydroboration with both borane B−H bonds; these products can be removed by washing with pentane.

The chemistry herein draws parallels with the extensive body of work on the construction of mid/late transition-metal polyboranes using borohydrides and BH_3 from the groups of Fehlner and Ghosh.[24] While both approaches lead to boron−boron coupling, the most salient distinction is that in the current work polyborane clusters are distinctly avoided in favor of mono- or diboron units, presumably due to the bulky duryl group at boron. This point of difference is a promising sign that using bulky dihydroboranes could lead to electron-precise boron networks rather than nonclassical (cluster) structures, provided the right combination of borane and metal−ligand set can be found. The complexes prepared herein also contrast significantly with the σ-borane-type reactivity seen with metals of other groups.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11315.

Synthetic and computational details (PDF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)
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Notes

The authors declare no competing financial interest.

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