VIP B≡O Cyclization

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Cyclodimerization of an Oxoboryl Complex Induced by *trans* Ligand Abstraction**

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As early as in the mid-1930s, it was realized that organoboron oxides do not have the simple monomeric structure RBO. Instead, these anhydrides of boronic acids were assigned cyclotrimeric structures.[1] Such compounds, generally known as boroxines $(RBO)_3$, have become valuable intermediates in organic synthesis.[2] The simplest derivative $(HBO)_3$ (**1**, Figure 1) was identified as the product of different high

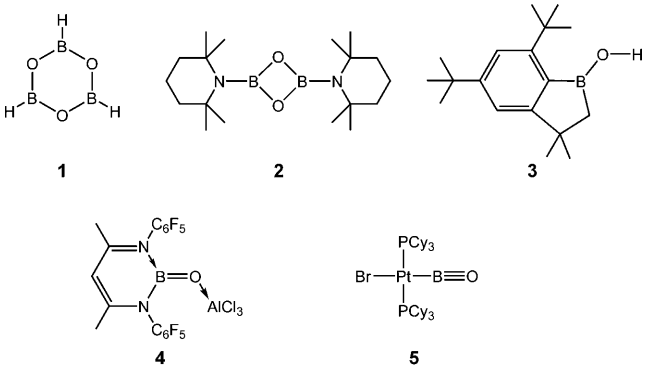

Figure 1. Selected stable derivatives of oxoboranes.

energetic redox processes,[3] and the monomeric counterpart HBO could be observed spectroscopically under similar reaction conditions, either in the gas phase[4] or in low-temperature matrix isolation studies.[5] Cyclization of the methyl substituted analogue MeBO[6] was demonstrated to be a reversible process in flash vacuum-pyrolysis experiments.[7] However, considerable experimental efforts are necessary to obtain a glance at the elusive methyloxoborane or its cyclodimerization product $(MeBO)_2$, as the trimer $(MeBO)_3$ is the predominant species even at very low trapping temperatures of 50 K. In contrast, sterically demanding substituents favor the formation of cyclodimeric structures.[8–10]

Examples of such 1,3,2,4-dioxodiboretanes are however quite limited in number, and to the best of our knowledge, only one derivative has been reliably characterized to date, by means of X-ray crystallography (**2**).[11] Moreover, monomeric oxoboranes with bulky substituents were inferred to be reactive intermediates from various trapping experiments[10,12] and shown to undergo intramolecular stabilization reactions, such as the formation of **3**.[12,13] The first stable monomeric derivative of an oxoborane (**4**) could only be realized by drastic modifications in fundamental electronic parameters, severely reducing the bond order between boron and oxygen.[14]

During the past decade, we and other groups have demonstrated the pronounced propensity of transition metals to stabilize and control the reactivity of otherwise highly reactive borylene species.[15] In this context, we also realized that especially the bis(tricyclohexylphosphine)platinum fragment is particularly well-adapted to generate ligands with two-coordinate boron centers.[16–18] The triple bond between boron and nitrogen of the iminoboryl complexes *trans*-$[(Cy_3P)_2BrPt(B{\equiv}NR)]$ (Cy = cyclohexyl; R = $SiMe_3$, *i*Bu), generated in the coordination sphere of platinum, still displays reactivity patterns[17,18] typical for main-group-element-substituted B≡N triple bond systems.[19] Very recently, we successfully transferred this synthetic strategy and described preparation of and first reactivity studies on the isoelectronic oxoboryl analogue *trans*-$[(Cy_3P)_2BrPt(B{\equiv}O)]$ (**5**).[20] The formation of the B≡O triple bond by liberation of trimethylbromosilane was elucidated to be a reversible process, and **5** reacts with $[Bu_4N]SPh$ by clean metathesis of the bromide, leaving the B≡O moiety intact. Spectroscopic and structural data indicated the presence of a triple bond between boron and oxygen. Further evidence was provided by results of quantum chemical calculations, which revealed a stabilizing contribution of the corresponding dπ orbitals of platinum to the two orthogonal B≡O π bonds, resulting in the extraordinary thermal and light stability of **5**. In continuing studies on the behavior of this new class of compounds, we have turned our attention to the reactivity of **5** towards the bromide abstraction reagent $Ag[Al(pftb)_4]$ (pftb = $OC(CF_3)_3$).[21]

Mixing $[D_2]$dichloromethane solutions of **5** and $Ag[Al(pftb)_4]$ causes the immediate precipitation of a fine brown solid. Analysis of the yellow supernatant solution by ^{31}P NMR spectroscopy reveals complete consumption of the starting complex and almost clean formation of one new phosphorus-containing product **6**. The chemical shift of $\delta = 50.1$ ppm is indicative of cationic platinum(II) centers coordinated in a T-shaped fashion and is shifted downfield with respect to **5** ($\delta =$ 32.5 ppm, $^1J_{Pt\text{-}P} = 2294$ Hz)[20] typically observed for formal *trans* bromide abstraction.[22,23] However, the platinum–phosphorus coupling constant of **6** (2512 Hz) is significantly increased far beyond values that would be expected for this simple reaction, and instead falls in the range observed for

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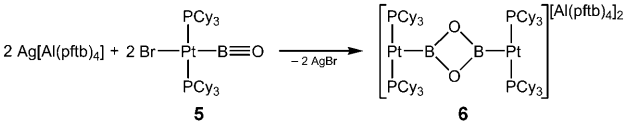
boryl complexes featuring three-coordinate boron atoms.[22–25] Furthermore, IR spectra of isolated **6** did not show the characteristic B≡O resonances reported for **5** (1853 and 1797 cm^{-1}),[20] furthermore indicating a fundamental change in the linkage between boron and oxygen.[26]

Remarkably, ^{11}B NMR spectroscopy only poorly reflects this alteration. Thus, the resonance in the ^{11}B NMR spectrum of the product ($\delta = 15$ ppm) appears only slightly upfield of the signal observed for **5** ($\delta = 17$ ppm). At a first glance, this finding appears counterintuitive, as the ^{31}P NMR data clearly indicate an increase of the coordination number of boron. However, in the past we have observed a pronounced effect of *trans* bromide abstraction on the ^{11}B NMR resonances of boryl complexes. For example, the signals of $[(Cy_3P)_2Pt\{B(Br)R\}]^+$ (R = *o*-Tol: 45; *t*Bu: $\delta = 55$ ppm)[23] are considerably shielded and thus found upfield in comparison to their neutral precursors ($\delta = 73$ and 80 ppm, respectively).[24] Keeping this trend in mind, the ^{11}B NMR chemical shift of **6** strongly resembles the values obtained for 1,3,2,4-dioxodiboretanes ($\delta = 28$–43 ppm)[9,10] and thus suggests formation of the cyclodimerization product $[(Cy_3P)_2Pt(BO_2B)Pt(PCy_3)_2][Al(pftb)_4]_2$ (**6**; Scheme 1).



Scheme 1. Synthesis of **6**.

X-ray crystallographic structure determination performed on yellow single crystals obtained by cooling a solution of **6** in a mixture of dichloromethane and hexane to −35 °C confirmed the proposed constitutional composition (Figure 2).[27] The dioxodiboretanediyl ligand bridges two cationic platinum fragments, which have a distorted T-shaped geometry (P-Pt-P 167.52(6) and 169.94(6)°). The Pt-B separations (194.6(7) and 195.3(7) pm, respectively) are at the lower end but still in the typical region expected for cationic boryl complexes of this type (193.2(4)–204.7(5) pm).[22,23] What is unusual, however, is the orientation of the bridging ligand. Generally, boryl ligands are oriented perpendicular to the platinum bisphosphine axes.[22–25] In contrast, and probably because of steric repulsion of the bulky tricyclohexylphosphine ligands, complex **6** has a helical structure (Figure 2, right). The two platinum fragments are thus twisted by 57.66(13)° with respect to each other, and consequently the B_2O_2 plane is also twisted against the platinum fragments by 20.84(37) and 36.82(25)°.

The most striking structural feature of **6** is no doubt the B_2O_2 quadrangle, which can be described as a rhombus within the 3σ criterion. The structural parameters are statistically indistinguishable from those of the amino-substituted analogue $[TmpBO]_2$ (**2**; Tmp = 2,2,6,6-tetramethylpiperidyl).[11] The presence of strongly antibonding cross-ring interactions of the two electronegative oxygen atoms[28] is reflected in the rather long boron–oxygen bonds (140.4(9)–142.4(9) pm) and acute angles at oxygen (81.2(5) and 82.0(5)°). As a consequence, the distance between the boron atoms is fairly short (184.6(10) pm), which suggests a possible electronic interaction.[29]

In preliminary studies, the neutral complex **5** did not show any signs of decomposition or oligomerization even at elevated temperatures and under photolytic conditions.[20] In contrast, *trans* bromide abstraction induces instant cyclodimerization, yielding the ionic compound **6**. Thus, we have illustrated the dramatic consequences of abstracting the bromide ligand *trans* to B≡O, which therefore can clearly not be considered an innocuous spectator ligand, thus indicating the subtle influence the platinum fragment exerts on the oxoboryl moiety.

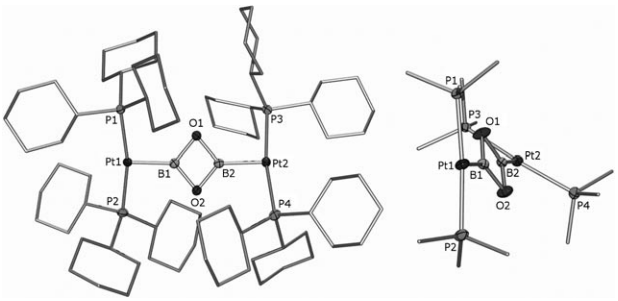


Figure 2. Molecular structure of **6**·2 CH_2Cl_2. Structure of the dicationic complex (left) and an alternative view of its core (right). Thermal ellipsoids are set at 50% probability; solvent molecules, anions and the ellipsoids and disorder of the cyclohexyl groups are omitted for clarity. Selected bond lengths [pm] and angles [°] (estimated standard deviations in parentheses): Pt1–B1 194.6(7), Pt2–B2 195.3(7), B1–O1 142.4(9), B1–O2 141.0(8), B2–O1 141.3(8), B2–O2 140.4(9); B1-O1-B2 81.2(5), B1-O2-B2 82.0(5), O1-B1-O2 98.0(5), O1-B2-O2 98.8(5), B1-Pt1-P1 95.7(2), B1-Pt1-P2 96.8(2), P1-Pt1-P2 167.52(6), B2-Pt2-P3 93.6(2), B2-Pt2-P4 96.2(2), P3-Pt2-P4 169.94(6); ∡(Pt1-B1-P1-P2, B1-O1-O2-B2) 20.84(37), ∡(Pt2-B2-P3-P4, B1-O1-O2-B2) 36.82(25), ∡(Pt1-B1-P1-P2, Pt2-B2-P3-P4) 57.66(13).

Experimental Section

All manipulations were performed under an inert atmosphere of dry argon using either standard Schlenk or glovebox techniques, unless noted otherwise. Hexane and dichloromethane were purified and dried using a M. Braun solvent purification system. $[D_2]$Dichloromethane was dried over molecular sieves and degassed by three freeze–pump–thaw cycles prior to use. All solvents were stored under argon over activated molecular sieves. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer. NMR spectra were referenced to external $SiMe_4$ (^1H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), Cl_3CF (^{19}F), aqueous $AlCl_3$ (^{27}Al), and 85% H_3PO_4 (^{31}P). IR data (not shown) were acquired on a Bruker Vector 22 FT-IR-spectrometer, and the samples were prepared as dichloromethane solutions and KBr pellets. IR spectra of pure materials, handled briefly under atmospheric conditions, were recorded on a Bruker ALPHA FT-IR-apparatus equipped with a Platinum ATR module. Microanalyses were performed by the staff of the Microanalytical Laboratory of the University Bielefeld. The preparations of **5**[20] and $Ag[Al(pftb)_4]$[21] were performed according to literature procedures.

6: A solution of **5** (100.2 mg, 116.2 μmol) in dichloromethane (1 mL) was added to solid $Ag[Al(pftb)_4]$ (128.0 mg, 119.1 μmol) in a J. Young NMR tube. The resulting suspension was treated for 30 min in an ultrasonic bath. The brown solid was removed by filtration and the yellow filtrate layered with hexane (1 mL) and cooled to −35 °C.

After 20 h, the supernatant solution was decanted off the pale yellow crystalline solid (113.0 mg, 56%).

^{1}H NMR (500 MHz, CD_2Cl_2, 296.3 K): $\delta = 2.42$ (br m, 6H, *Cy*), 1.93–1.28 ppm (m, 60H, *Cy*); ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 296.0 K): $\delta = 15$ ppm (vbr s, FWHM = 1714 Hz); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 296.6 K): $\delta = 121.5$ ppm (q, $^1J_{F\text{-}C} = 293$ Hz, CF_3), 35.5 (vt, $N = |{}^1J_{P\text{-}C} + {}^3J_{P\text{-}C}| = 27$ Hz, C_1 *Cy*), 30.8 (s, $C_{3,5}$ *Cy*), 27.5 (vt, $N = |{}^2J_{P\text{-}C} + {}^4J_{P\text{-}C}| = 11$ Hz, $C_{2,6}$ *Cy*), 26.0 (s, C_4 *Cy*); ^{19}F NMR (376 MHz, CD_2Cl_2, 296.0 K): $\delta = -75.7$ ppm (s); ^{27}Al NMR (130 MHz, CD_2Cl_2, 296.1 K): $\delta = 34.6$ ppm (s); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 296.6 K): $\delta = 50.1$ ppm (s, $^1J_{Pt\text{-}P} = 2512$ Hz). C,H analysis (%) calcd for $C_{104}H_{132}Al_2B_2F_{72}O_{10}P_4Pt_2$: C 35.69, H 3.80; found: C 35.74, H 3.97.

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[26] IR spectra of isolated **6** did not show any bands in the region 2800–1500 cm^{-1}. Vibrational frequencies of the B_2O_2 moiety, which would be expected at lower wavenumbers,[7] could not be reliably determined due to strong vibrational bands of the $[Al(pftb)_4]^-$ counterions; these were identified by comparison with the spectra of $Ag[Al(pftb)_4]$.
[27] Crystal data for **6**·2 CH_2Cl_2 were collected on a Bruker x8 APEX diffractometer with a CCD area detector and multilayer-mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the SHELX software package (G. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112—122), and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure-factor calculations. Crystal data for **6**: $C_{106}H_{136}Al_2B_2Cl_4F_{72}O_{10}P_4Pt_2$, $M_r = 3669.59$, yellow plates, $0.20 \times 0.12 \times 0.03$ mm^3, space group $P2_1/c$, $a = 19.6817(14)$, $b = 40.431(3)$, $c = 19.2109(13)$ Å, $\beta = 112.079(2)°$, $V = 14166.1(17)$ $Å^3$, $Z = 4$, $\rho_{calcd} = 1.721$ $g\,cm^{-3}$, $\mu = 2.252$ mm^{-1}, $F(000) = 7280$, $T = 100(2)$ K, $R_1 = 0.0929$, $wR^2 = 0.2404$, 37658 independent reflections [$2\theta \leq 58.1°$] and 1719 parameters. CCDC 773398 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[28] For a detailed consideration of the bonding situation in B_2O_2 rings and other examples of Lewis acid (LA)-stabilized com-

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