Unexpected Bonding Mode of the Diboran(4)yl Ligand: Combining the Boryl Motif with a Dative Pt–B Interaction**

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During the last 15 years, diboranes(4) have become increasingly important as high-value reagents in the catalytic functionalization of unsaturated organic substrates.^[1] In this regard, the commonly observed reactivity of diboranes(4) towards the catalytic active species, which is usually a lowvalent transition-metal complex, consists of the oxidative addition of the B-B bond to generate cis-bis(boryl) species.^[1] For instance, the oxidative addition of tetraalkoxydiboranes(4) to Pd⁰ or Pt⁰ centers has been widely applied in organic chemistry to prepare diverse substrates for Suzuki-Miyaura type coupling reactions.^[1] In addition to B-B bond cleavage, halide substituted diboranes(4) potentially offer the opportunity for oxidative addition of a boron-halide bond eventually resulting in the formation of transition-metal diboran(4)yl species. The latter process was shown to proceed readily for a variety of substituted boron halides XBR₂, and has been used extensively in the preparation of transitionmetal boryl complexes.^[2] By contrast, related studies on the reactivity of halide substituted diboranes(4) still remain scarce, which is somewhat surprising regarding the aforementioned high significance of diboranes(4) as reagents in organic chemistry. Only a single relevant study has appeared in the literature so far. In 1999 the group of Norman studied the reactivity of $B_2(NMe_2)_2Cl_2$ towards $[(\eta^2-C_2H_4)Pt(PPh_3)_2]$. In this case however, no evidence for the oxidative addition of the B-Cl bond could be deduced from the experimental results, and exclusively products arising from B-B bond activation were verified, that is, cis-[(Ph₃P)₂Pt{B- $(NMe_2)(Cl)_2$ and trans- $[(Ph_3P)_2Pt(Cl)\{B(NMe_2)(Cl)\}]$.^[3] An alternative approach towards transition-metal diboran(4)yl complexes has been developed in our group. We demonstrated that the diboran(4)yl moiety can be readily introduced by salt elimination reactions of $B_2(NMe_2)X_2$ (X = Cl,^[4] Br,^[5] I^[6]) with anionic half-sandwich carbonyl species M'- $[CpM(CO)_n]$ (M' = Na, K; M = Mo, W, Fe, Ru).

Owing to our longstanding interest in transition-metal boron chemistry, we recently began to reconsider the reactivity of halide-substituted diboranes(4) towards lowvalent platinum complexes and to evaluate the question, whether a selective oxidative addition of B-X bonds is possible in the presence of a B-B bond. Bearing the experiences of Norman and co-workers in mind, we reasoned that diboranes(4) containing more reactive B-Br bonds might be better suited for this purpose. This assumption proved to be true and we were able to isolate trans-[(Et₃P)₂Pt(Br)- $\{B(Mes)B(Mes)(Br)\}\]$ (1) and $trans-[(iPr_3P)_2Pt(Br)]$ $(NMe_2)B(NMe_2)(Br)$] (2), each prepared by oxidative addition of one B-Br bond to the respective platinum precursors. As discussed later on, the solid-state structure of 1 features a hitherto unknown bonding mode of the diboran(4)yl ligand, that is, an unexpected additional dative Pt-B bond to the second boron center, thus combining two types of electronprecise Pt-B interaction in one molecule. In the early days, dative metal boron bonds played an important role in the development of the concept of transition-metal basicity due to the electron deficiency of the boron center.^[1f,2d,7] Even though these kind of interactions had already been postulated in the 1960s, it was not until 1999 that the first example of a supported dative M-B bond was structurally substantiated for the ruthenium boratrane $[HRu{B(mt)_3}(PPh_3)]$ (mt = 2-sulfanyl-1-methylimidazole),^[8] while structural evidence for unsupported dative M-B bonds still remains elusive. During the last decade a large number of supported species have been structurally characterized containing a variety of different metal centers and donor arm architectures.^[2d,7c-e] For platinum however, the number of known examples is rather limited. To date, only a couple of platinaboratrane species have been published, in which the boron center is part of a rigid tris(methimazolyl)borate (κ^4 -SSSB, **A**),^[9] diphosphanylborane $(\kappa^3 - PPB, \mathbf{B})^{[10]}$ or trisphosphanylborane $(\kappa^4 - PPPB,$



C)^[11] cage structure. The strength of the dative Pt–B interaction, as indicated by the Pt–B bond lengths (2.1–2.5 Å), is found within a large range depending on the ligand framework. However, the rigid ligand design forces the boron center into geometric proximity to the metal center, thus facilitating the dative interaction. This feature is in stark contrast to the dative Pt–B interaction in **1** (see below), in which the flexibility of the pendant diboran(4)yl substituent is at least in principle retained.

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[**] This work was supported by the Deutsche Forschungsgemeinschaft.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201102593.

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The reaction of $[Pt(PEt_3)_3]$ (3) with two equivalents of $B_2Mes_2Br_2$ (4) results in the selective oxidative addition of one B–Br bond to the Pt⁰ center to afford *trans*- $[(Et_3P)_2Pt(Br){B(Mes)B(Mes)(Br)}]$ (1), as judged by multi-nuclear NMR spectroscopy of the reaction mixture (Scheme 1).^[12] However, the reaction is accompanied by the



Scheme 1. Synthesis of 1 by selective oxidative addition.

release of one equivalent of PEt₃ to generate the reactive platinum species $\{Pt(PEt_3)_2\}$. Free PEt₃ subsequently reacts with **4** to form a phosphine–diborane(4) adduct, for which reason this transformation requires the presence of two equivalents of **4** to go to completion. The oxidative addition of the B–Br bond occurs spontaneously and conversion to **1** is quantitative within seconds. After workup, **1** was isolated as a red-orange material in poor yields of 17 %. Higher yields were thwarted by the rather difficult separation of the phosphine– diborane(4) side product by fractional crystallization.

The identity of 1 was unambiguously ascertained by NMR spectroscopy, elemental analysis, and X-ray diffraction.^[12] The ¹H NMR spectrum of **1** in solution (C_6D_6) features wellseparated sets of signals for two chemically nonequivalent PEt₃ groups ($\delta = 0.75$, 1.52 ppm and $\delta = 0.92$, 2.10 ppm). Similarly, the ¹³C NMR spectrum shows two distinct resonances at $\delta = 9.29$ and 9.12 ppm, respectively, for the methyl groups of the PEt₃ ligands, while the assignments were further verified by 2D NMR experiments. In agreement with these findings, the ³¹P NMR spectrum of **1** displays a signal pattern indicative of an ABX spin system. Thus, two doublets are observed at $\delta = 5.32$ and 8.56 ppm with coupling constants of ${}^{1}J_{P-Pt} = 2919 \text{ Hz} ({}^{2}J_{P-P} = 333 \text{ Hz}) \text{ and } 2862 \text{ Hz} ({}^{2}J_{P-P} = 333 \text{ Hz}),$ respectively. As expected, two signals are observed in the ¹¹B NMR spectrum of **1** at $\delta = 56$ and 108 ppm, which appear either high-field or low-field shifted with respect to those of $B_2Mes_2Br_2$ ($\delta = 86 \text{ ppm}$).^[13] The chemical shifts of both resonances are fully consistent with the molecular structure of **1** in the solid state (see below). While the signal at $\delta =$ 108 ppm substantiates the presence of a metal-bound boryl moiety, the pronounced high-field shift of the second resonance ($\delta = 56$ ppm) already indicates a dative Pt-B interaction even in solution.

The most intriguing feature of the molecular structure of **1** in the solid state (Figure 1) is the verification of the dative Pt– B bonding to the second boron center (Pt1 \rightarrow B2), which is nicely illustrated by the short Pt1–B2 distance (2.531(3) Å) and by the small values found for the bond angles Pt1-B1-B2 (86.05(15)°) and B1-Pt1-B2 (40.52(10)°). In comparison to the Pt1–B1 bond (2.038(3) Å), which is found in a typical range for platinum boryl species, the Pt1–B2 bond (2.531(3) Å) is elongated by approximately 25%. However, this bond length is comparable to that observed for the κ^3 -*PPB* platinaboratrane [PtCl₂(dpb)] (dpb = PhB[2-(PiPr₂)C₆H₄]₂, type **B**), in



Figure 1. Molecular structure of 1 (left) and 2 (right) in the solid state. Hydrogen atoms are omitted for clarity.

which a dative Pt-B interaction has been verified.^[11b] The platinum center displays a distorted square-pyramidal geometry with the boron atom B2 involved in the dative bonding in the apical position. While the basal atoms Pt1, Br1, P1, B1, and P2 still form an almost regular square base ($\Sigma_{Pt} = 360.1^{\circ}$), the apical B2 deviates significantly from its ideal position (B1-Pt1-B2 40.52(10)°; B2-Pt1-Br1 138.64(6)°), which has to be ascribed to the rigidity of the diboran(4)yl ligand. The perpendicular orientation of the PtBB triangle with respect to the square base (P1-Pt1-B1-B2 97.02(13)°; P2-Pt1-B1-B2 $-91.12(13)^{\circ}$) is also noteworthy. The structural parameters of the diboran(4)yl unit are only slightly altered upon oxidative addition to the Pt⁰ center (B1-B2 1.649(4) Å, B2-Br2 2.027(3) Å; cf. 4: B-B 1.65 Å, B-Br 1.93 Å).^[13] The transinfluence of the diboran(4)yl ligand in 1 can be estimated by comparison of relevant crystal structure data to those of the related monoboryl species trans-[(Cy₃P)₂Pt(Br){B(Br)(R)}] $[R = NMe_2$ (5), Mes (6), tBu (7)].^[2b] Thus, the Pt1-Br1 (2.6210(4) Å) and Pt1-B1 (2.038(3) Å) bond lengths in 1, which are similar to those in 5-7 (Pt-Br 2.61-2.65 Å; Pt-B 1.98–2.01 Å), suggest that the diboran(4)yl moiety also exerts a strong trans-influence.

Further support for the presence of a dative Pt-B bonding interaction is deduced from DFT calculations.^[12] For this purpose, in addition to single-point calculations on 1 using crystal structure coordinates (1_{cs}) , a geometry optimization without symmetry restraints $(\mathbf{1}_{OPT})$ was conducted at the B3LYP level of theory. To further evaluate the strength of the dative Pt-B bond, we also studied two additional model species, that is, 8 and 9 (Figure 2), in which any dative interactions are suppressed. In 8, the mesityl ligand at B2 is substituted by a NMe₂ functionality, which results in the occupation of the empty p_z orbital at B2 by a B=N π bond without significantly altering the boron environment. In addition, we chose the Lewis acid-base adduct of 1 with HCN (9) to account for both structural and electronic effects on the Pt1-B2 interaction upon changing the hybridization of B2 from sp^2 to sp^3 , which renders any dative interactions impossible. The relative strength of the dative Pt1-B2 bond in 1 was subsequently assessed by comparison of the relevant Wiberg bond indices (WBI, Table 1). While the WBIs of the Pt1-B1 bond are of similar magnitude for all complexes



Figure 2. Natural charges of complexes 1_{CS}, 1_{OPT}, 8, and 9.

Table 1: Calculated relevant WBIs for complexes 1_{cs}, 1_{OPT} 8, and 9.

	Pt1-B1	Pt1- B2	B1- B2
1 _{cs}	0.6163	0.2384	1.1457
1 _{opt}	0.6730	0.1652	1.1082
8	0.7566	0.0404	1.0156
9	0.7830	0.0214	0.9168

studies, the WBIs of the Pt1–B2 bond significantly differ for the species $\mathbf{1}_{CS}/\mathbf{1}_{OPT}$ (0.2384/0.1652) and **8/9** (0.0404/0.0214), respectively. These findings clearly indicate the presence of noticeable dative Pt1–B2 interactions in $\mathbf{1}_{CS}$ and $\mathbf{1}_{OPT}$. As expected, this interaction is much more pronounced in the solid state ($\mathbf{1}_{CS}$) than in the gas phase ($\mathbf{1}_{OPT}$).

Determination of the natural charges (Figure 2) fully confirms these assumptions. Consistent with the stronger dative Pt1–B2 bond in 1_{CS} as compared to 1_{OPT} , the boron atom B2 bears considerably less positive charge in 1_{CS} (+0.19092; cf. 1_{OPT} + 0.26975), indicating enhanced electron donation from the platinum center to the electron-deficient boron atom B2. With regard to the model compounds 8 and 9, the absence of any dative Pt1–B2 interaction is visualized by the strongly diminished positive charge on Pt (8 + 0.10591, 9 + 0.09847; cf. 1_{CS} + 0.13934). Accordingly, the platinum atoms in 8 and 9 are not able to release electron density to the boron center B2, whose formerly empty p_z orbital (1) is already filled with electrons.

To further substantiate the results of the theoretical calculations, we sought to synthesize of a diboran(4)yl species similar to **8**, for which theory predicts the absence of a dative Pt1–B2 bond. The reaction of $[Pt(PiPr_3)_2]$ (**10**) with one equivalent of $B_2(NMe_2)_2Br_2$ (**11**) afforded the envisaged complex *trans*-[(*i*Pr_3P)_2Pt(Br){B(NMe_2)B(NMe_2)(Br)}] (**2**) in 72 % yield (Scheme 2).^[12] The conversion readily proceeded at room temperature and the oxidative addition of one B–Br bond to the Pt⁰ center was found to be highly selective according to NMR spectroscopy of the reaction mixture.

¹H, ¹³C, and ³¹P NMR spectroscopic parameters of **2** in solution are unremarkable and fully consistent with the anticipated structural motif. Conclusive evidence for the absence of a dative Pt1–B2 interaction is provided by ¹¹B NMR spectroscopy. While the two ¹¹B NMR resonances of **1** have been detected either high-field (B2) or low-field (B1) shifted with respect to the diborane(4) precursor, both ¹¹B NMR signals of **2** (B2: $\delta = 41$ ppm; B1 $\delta = 51$ ppm) are shifted to lower field by 3 and 13 ppm in comparison to those of **11** ($\delta = 38$ ppm).^[14] Accordingly, the characteristic high-field shift of the ¹¹B NMR resonance of B2, indicative of the presence of a dative Pt1–B2 bond in **1**, is not observed for **2**, which suggests that such an interaction is indeed absent.

This was confirmed by X-ray diffraction analysis on single crystals of 2.^[12] As depicted in Figure 1, the molecular structure of 2 in the solid state features a square-planar platinum center ($\Sigma_{Pt}\!=\!360.7^{\text{o}})$ without any evidence for a dative bonding interaction between Pt1 and B2. The Pt1-B2 distance of 3.298 Å is considerably elongated with respect to that found in 1 (2.531(3) Å), and dative interactions appear very unlikely. This is also evidenced by the angle B2-B1-Pt1 $(119.4(3)^{\circ})$, which is noticeably widened compared to that observed in 1. However, the Pt-B-B triangle is again oriented almost perpendicular to the plane defined by Pt1, P1, P2, B1, and Br1 (P1-Pt1-B1-B2 92.7(3)°; P2-Pt1-B1-B2 -80.5(3)°). Other parameters involving Pt1 are unremarkable, and bond lengths and angles are found in the typical range for transbisphosphineplatinum(II) species.^[2b] Within the diboran(4)yl moiety, the elongated B-B distance (1.742(8) Å; cf. 1 1.649(4) Å) is noteworthy, which is clearly associated with the presence of NMe₂ π donor functionalities at boron.

In conclusion, we have disclosed a novel bonding mode of the diboran(4)yl ligand consisting of two different electronprecise Pt-B interactions (boryl/dative). For this, the commonly observed reactivity of diborane(4) derivatives towards low-valent platinum species, that is, the activation of the B-B bond, has been successfully suppressed in favor of a selective oxidative addition of the boron-halide bond in 4 and 11. This approach is without precedent in transition-metal boron chemistry and has enabled the isolation and full characterization of the diboran(4)yl complexes 1 and 2. Structural analysis of 1 revealed the presence of an uncommon and unexpected dative Pt-B bonding interaction to the second boron center of the diboran(4)yl ligand, which has already been indicated by NMR spectroscopy in solution. The relative strength of this dative bond has been evaluated by DFT calculations, which also predicted that the introduction of π donor functionalities at boron would eliminate such a dative Pt-B interaction. These findings have been confirmed experimentally with the synthesis of 2, in which no evidence for a dative Pt-B bond was obtained. The extension of this novel reactivity to other Pt⁰ species and other halidesubstituted diborane(4) derivatives is currently being investigated extensively in our laboratories.

Received: April 14, 2011 Published online: June 16, 2011

Keywords: boron · diboran(4)yl ligands · diborane(4) · platinum

Angew. Chem. Int. Ed. 2011, 50, 7179–7182

Scheme 2. Reaction of 10 with B₂(NMe₂)₂Br₂.

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