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Diboran(4)yl Platinum(II) Complexes

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Ⓢ *Supporting Information*

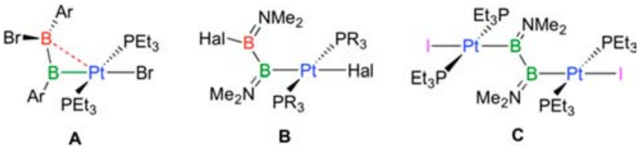
ABSTRACT: The platinum diboran(4)yl complexes **1**−**3** have been prepared by the selective oxidative addition of one B−Hal bond in aryl-substituted diboranes(4) $Hal_2B_2Ar_2$ (Hal = Cl, Ar = mes, dur; Hal = I, Ar = mes). Because of the electron deficiency of the remote B2 atom, all species show a rare dative Pt−B bonding interaction, whose magnitude is strongly dependent on the nature of the halide substituent.

Recently, recognition of the Suzuki−Miyaura cross-coupling reaction as part of the Nobel Prize award in 2010 emphasized the significance of boron reagents in organic synthesis.[1,2] Concomitantly, research in transition-metal boryl complexes considerably increased because they function as important intermediates in the borylation of organic substrates via hydroboration,[3] C−H activation,[4] and diboration reactions.[5] The latter process makes use of diboranes(4) as the boron source, and initially proceeds by B−B bond activation to afford *cis*-bisboryl complexes.[5] However, our latest results have shown that the B−B bond is not the only possible reaction site in diboranes(4), and halide-substituted derivatives preferably react with low-valent platinum phosphines by oxidative addition of the B−Hal bond and formation of diboran(4)yl[6] and diboran(4)-1,2-diyl species.[7] Notable exceptions are (i) $Cl_2B_2(NMe_2)_2$, which shows a rather poor selectivity,[8] and (ii) B_2F_4, which reacts exclusively at the B−B linkage.[9]

Thus, aryl-substituted diboranes(4) $Br_2B_2Ar_2$ (Ar = mes, dur; mes = mesityl, dur = duryl) are converted into platinum diboran(4)yls **A** with high selectivity upon reaction with $[Pt(PEt_3)_3]$, which feature a rare dative Pt−B bonding interaction.[6a,c] Such an interaction is not present in the diboran(4)yl complexes **B**, which were obtained via B−Hal bond activation in $Hal_2B_2(NMe_2)_2$ (Hal = Br, I).[6a,b] Here, π donation from the NMe_2 substituent effectively lowers the electron deficiency of the second boron center, and no further stabilization is required. A third coordination mode (Chart 1) was realized for the iodine derivative $I_2B_2(NMe_2)_2$, which could be converted to the diboran(4)-1,2-diyl species **C** under forcing conditions (165 °C, 10 min).[7]

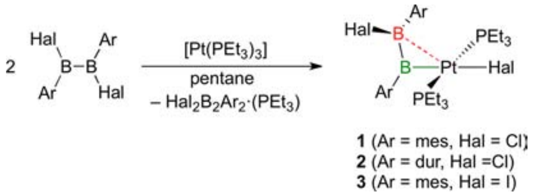
Subsequently, we wondered if and how the nature of the halide influences the dative Pt−B bonding interaction in type **A** complexes. We now present our results regarding the reactivity of $Cl_2B_2Ar_2$ (Ar = mes, dur)[10,11a] and $I_2B_2mes_2$[11b] toward $[Pt(PEt_3)_3]$, which readily afforded the diboran(4)yl complexes *trans*-$[(Et_3P)_2Pt(Cl)\{B(mes)B(mes)(Cl)\}]$ (**1**), *trans*-$[(Et_3P)_2Pt(Cl)\{B(dur)B(dur)(Cl)\}]$ (**2**), and *trans*-$[(Et_3P)_2Pt(I)\{B(mes)B(mes)(I)\}]$ (**3**). We will show that the strength of the dative Pt−B bonding interaction increases with increasing electron deficiency at boron as Cl < Br < I.

Chart 1. Possible Coordination Modes of the Diboran(4)yl Ligand (Ar = mes, dur; R = Et, *i*Pr; Hal = Br, I)



The oxidative addition of one B−Hal bond of $Hal_2B_2Ar_2$ (Hal = Cl, Ar = mes, dur; Hal = I, Ar = mes) proceeds readily at room temperature within minutes upon reaction with $[Pt(PEt_3)_3]$ in a pentane solution (Scheme 1). The transformations show high selectivity, and only the diboran(4)yl complexes **1**−**3** and the diborane−phosphine adducts $Hal_2B_2Ar_2{\cdot}PEt_3$ are evident in the ^{11}B NMR spectra of the reaction mixtures.[12] Because of the release of 1 equiv of PEt_3, which readily forms Lewis acid−base adducts with electrophilic diboranes(4), 2 equiv of $Hal_2B_2Ar_2$ are required to reach quantitative conversion. After recrystallization from concentrated CH_2Cl_2/pentane mixtures, the diboran(4)yls **1**−**3** are isolated as orange/red crystals in 24%, 28%, and 44% yield, respectively. Higher yields were significantly thwarted by the rather difficult removal of the $Hal_2B_2Ar_2{\cdot}PEt_3$ byproducts.

Scheme 1. Synthesis of Diboran(4)yl Complexes 1−**3**



The formation of diboran(4)yl complexes and the presence of a dative Pt−B bonding interaction are clearly obvious in the solution NMR spectra of **1**−**3**. Thus, two doublets are found in the ^{31}P NMR spectra of **1**−**3** (**1**, δ 8.07, 11.4; **2**, δ 7.70, 11.2; **3**, δ 1.40, 2.89) reminiscent of an AB spin system (Table 1). The $^2J_{P-P}$ (**1**, 333 Hz; **2**, 326 Hz; **3**, 226 Hz) and $^1J_{P-Pt}$ coupling constants (2812−2984 Hz) are highly characteristic for platinum(II) complexes with a *trans* configuration of the phosphine ligands. All ^{31}P NMR parameters strongly resemble those found for the related species *trans*-$[(Et_3P)_2Pt(Br)\{B(mes)B(mes)(Br)\}]$ (**4**)[6a] and *trans*-$[(Et_3P)_2Pt(Br)\{B(dur)B(dur)(Br)\}]$ (**5**; Table 1).[6c] The unsymmetrical nature of **1**−**3** is further illustrated by

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Table 1. ^{11}B and ^{31}P NMR Spectroscopic Parameters of Diboran(4)yl Complexes 1–5 in Solution (δ in ppm)

	$\delta(^{11}B)$ [B1]	$\delta(^{11}B)$ [B2]	$\delta(^{31}P)$ [P1]	$\delta(^{31}P)$ [P2]
1[a]	61.5	108	8.07 ($^1J_{P-Pt}$ = 2958 Hz; $^2J_{P-P}$ = 333 Hz)	11.4 ($^1J_{P-Pt}$ = 2912 Hz; $^2J_{P-P}$ = 333 Hz)
2[b]	58.0	109	7.70 ($^1J_{P-Pt}$ = 2984 Hz; $^2J_{P-P}$ = 326 Hz)	11.2 ($^1J_{P-Pt}$ = 2929 Hz; $^2J_{P-P}$ = 326 Hz)
3[a]	51.0	112	1.40 ($^1J_{P-Pt}$ = 2842 Hz; $^2J_{P-P}$ = 226 Hz)	2.89 ($^1J_{P-Pt}$ = 2812 Hz; $^2J_{P-P}$ = 226 Hz)
4[b]	56.6	107	5.54 ($^1J_{P-Pt}$ = 2921 Hz; $^2J_{P-P}$ = 333 Hz)	8.35 ($^1J_{P-Pt}$ = 2869 Hz; $^2J_{P-P}$ = 333 Hz)
5[a]	53.6	109	5.55 ($^1J_{P-Pt}$ = 2931 Hz; $^2J_{P-P}$ = 327 Hz)	8.17 ($^1J_{P-Pt}$ = 2873 Hz; $^2J_{P-P}$ = 327 Hz)

[a] CD_2Cl_2. [b] C_6D_6.

^{11}B NMR spectroscopy (Table 1), which reveals two broad (fwhm 1567–1830 Hz) resonances for B1 (Pt–B; **1**, δ 108; **2**, δ 109; **3**, δ 112) and B2 (B-Hal; **1**, δ 61.5; **2**, δ 58.0; **3**, δ 51.0). Similar to the results of **4** and **5**,[6a,c] the low-field signal (B1) is indicative of a platinum-bound boryl group. By contrast, the B2 signal appears at significantly higher field than the precursor diboranes(4) $Hal_2B_2Ar_2$ (δ 85–89),[11] thus verifying the dative Pt–B2 bonding interaction even in solution.[6a,c] The ^{11}B NMR signals of B2 already imply a considerable influence of the halide nature on the strength of this dative bonding interaction, which evidently becomes stronger in the order Cl (**1**/**2**: δ 61.5/58.0) < Br (**4**: δ 56.6) < I (**3**: δ 51.0).

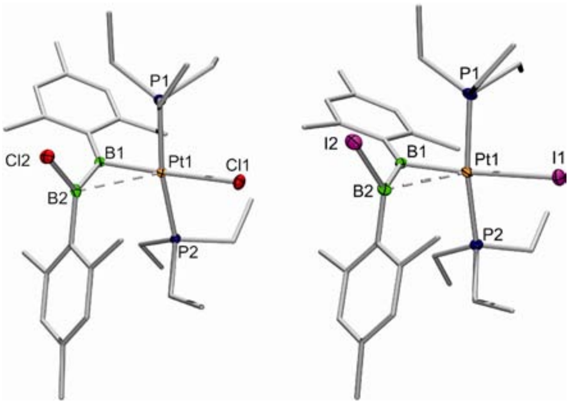

Figure 1. Molecular structure of the mesityl-substituted diboran(4)yl complexes **1** (left) and **3** (right) in the solid state. Thermal ellipsoids are displayed at the 50% probability level. For clarity, hydrogen atoms and thermal ellipsoids of the carbon atoms have been omitted. Selected bond lengths are presented in Table 2 and bond angles in Table 3.

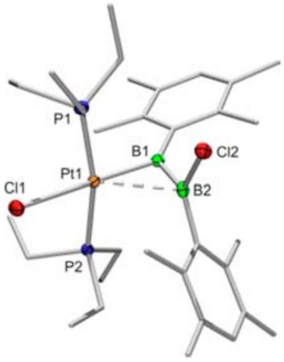

Figure 2. Molecular structure of the duryl-substituted diboran(4)yl complex **2** in the solid state. Thermal ellipsoids are displayed at the 50% probability level. For clarity, hydrogen atoms and thermal ellipsoids of the carbon atoms have been omitted. Selected bond lengths are presented in Table 2 and bond angles in Table 3.

Table 2. Selected Bond Lengths (Å) of Diboran(4)yl Complexes 1–8 in the Solid State

	Pt1–B1	Pt1–B2	B1–B2	Pt1–X1	B2–X2
1	2.035(6)	2.570(6)	1.657(8)	2.501(1)	1.854(6)
2	2.038(7)	2.547(3)	1.648(4)	2.5044(6)	1.853(3)
3	2.057(4)	2.504(4)	1.649(6)	2.7827(3)	2.260(4)
4[6a]	2.038(3)	2.531(3)	1.649(4)	2.621(4)	2.027(3)
5[6c]	2.027(9)	2.506(8)	1.67(1)	2.6276(8)	2.016(9)
6[6a]	2.073(5)		1.742(8)	2.6470(5)	1.963(6)
7[6b]	2.087(4)		1.738(6)	2.8226(3)	2.234(4)
8[7]	2.069(7)		1.725(11)	2.7990(18)	2.242(8)

Table 3. Selected Bond Angles (deg) of Diboran(4)yl Complexes 1–5 in the Solid State

	Σ_{Pt}	P1–Pt1–P2	X1–Pt1–B1	Pt1–B1–B2	B1–Pt1–B2
1	360.15	170.25(1)	176.5(1)	87.4(1)	40.2(1)
2	361.10	166.35(2)	172.9(1)	86.7(1)	40.2(1)
3	360.13	168.70(3)	175.4(1)	84.2(2)	40.9(1)
4	360.12	169.94(2)	176.2(1)	86.0(1)	40.5(1)
5	360.91	167.78(7)	174.3(2)	84.7(5)	41.7(3)

Further evidence for this result comes from X-ray diffraction studies on **1**–**3** (Figures 1 and 2 and Tables 2 and 3). Accordingly, short Pt1–B2 bond distances [**1**, 2.570(6) Å; **2**, 2.547(3) Å; **3**, 2.504(4) Å] clearly imply the presence of a dative Pt1–B2 bonding interaction, which is most pronounced for the iodine derivative **3**. A comparison of the dative Pt1–B2 bonding interaction with the corresponding Pt1–B1 boryl bond [**1**, 2.035(6) Å; **2**, 2.038(7) Å; **3**, 2.057(4) Å] also shows that the strongest effect is present in the iodine species **3**. Thus, the bond elongation between the Pt1–B1 and Pt1–B2 bonds significantly decreases from 26.2% in **1** to 21.7% in **3**, which might also be compared to the values found in the related bromine complexes **4** (24.1%)[6a] and **5** (23.6%).[6c] Obviously, the strength of the dative Pt–B bonding interaction is directly related to the electrophilicity of the boron center B2, which strongly depends on the nature of the halide substituent and increases in the order Cl < Br < I. By contrast, the influence of the aryl substituent is almost negligible, as deduced from the direct comparison of the pairs **1**/**2** (Cl) and **4**/**5** (Br), which feature similar values for the mesityl and duryl derivatives.

In our initial communication on this topic, we evaluated the nature of this dative bonding interaction in detail by a combination of spectroscopy, X-ray diffraction, and density functional theory calculations.[6a] In agreement with the present study, our results clearly suggested an electron-precise bonding situation for the diboran(4)yl ligand with two-center-two-electron Pt1–B1 and B1–B2 bonds and a dative Pt1–B2 bonding interaction. Particularly, short Pt1–B1 and B1–B2 bond lengths in **1**–**5** in comparison to the classical diboran(4)yl species **B** of *trans*-$[(R_3P)_2Pt(X)\{B(NMe_2)B(NMe_2)X\}]$ (**6**, R = *i*Pr, X = Br;[6a] **7**, R = *i*Pr, X = I;[6b] **8**, R = Et, X = I[7]) (Table 2) without any dative bonding interaction support this picture and most likely rule out a three-center-two-electron bonding mode of the Pt1–B1–B2 fragment, which is expected to result in a significant lengthening of these bonds.

The effect of the aryl substituent on the Pt1–Hal1 bond lengths and thus on the *trans* influence of the diboran(4)yl ligand is also insignificant, as shown by the molecular structures of **1**/**2** [Cl; **1**, 2.501(1) Å; **2**, 2.504(4) Å] and **4**/**5** [Br; **4**, 2.611(4) Å; **5**, 2.625(8) Å].[6a,c]

All other structural parameters are unremarkable and strongly resemble those of **4**[6a] and **5**.[6c] The platinum centers in **1**−**3** adopt a distorted square-pyramidal geometry with the B2 atom in the apical position. At the same time, the basis defined by the atoms Pt1, B1, Hal1, P1, and P2 remains almost regular square-planar with Σ_{Pt} of approximately 360° (Table 3), while the Pt1−B1−B2 bond angles are rather acute and successively change from the chlorine derivatives **1** [87.4(1)°] and **2** [86.7(5)°] to 84.2(2)° in the iodine analogue **3**. The Pt1−B1 [**1**, 2.035(6) Å; **2**, 2.038(7) Å; **3**, 2.057(4) Å], Pt1−P1/2 [**1**, 2.3208(5) Å/2.3507(5) Å; **2**, 2.3161(6) Å/2.3478(6) Å; **3**, 2.3258(9) Å/2.3668(9) Å], and B1−B2 [**1**, 1.657(8) Å; **2**, 1.648(4) Å; **3**, 1.649(6) Å] bond lengths are very similar in all species **1**−**5** and do not show any dependency on the nature of the halide or aryl ligands (Table 2).

In this contribution, we have presented further details on the reactivity of aryl-substituted diboranes(4) toward low-valent platinum species. The diboran(4)yl complexes **1**−**3** derived from the electrophilic diboranes(4) $Hal_2B_2Ar_2$ (Hal = Cl, Ar = mes, dur; Hal = I, Ar = mes) also show a rare dative Pt−B bonding interaction between the platinum(II) center and the remote boron atom B2 both in solution and in the solid state. This interaction is considerably influenced by the nature of the halide substituent and strengthens in the order Cl < Br < I.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and crystallographic details, graphical representation of the molecular structure of $Cl_2B_2dur_2$, and crystallographic data of **1**−**3** (CCDC 928667−928669) and $Cl_2B_2dur_2$ (CCDC 928691) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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