EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

SHORT COMMUNICATION

DOI:10.1002/ejic.201402234

Selective Synthesis of Unsymmetrical Diboryl Pt^{II} and Diaminoboryl Cu^{I} Complexes by B–B Activation of Unsymmetrical Diboranes(4) {pinB–B[$(NR)_2C_6H_4$]}

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Keywords: Boron / B–B activation / Boryl complexes / Copper / Platinum

Diaminoboryl ligands are currently intensively investigated because of their unique coordination chemical properties, for example, as part of pincer ligands. Owing to synthetic restrictions, however, access to diaminoboryl complexes is limited. Unsymmetrical diborane(4) derivatives comprising a dialkoxy- and a diaminoboron moiety provide efficient access to diaminoboryl complexes either by oxidative addition or by σ-bond metathesis reactions. Especially, the latter is complementary to existing methods and overcomes the existing limitations. This is illustrated by the modular synthesis of four unsymmetrical diborane(4) derivatives and their application in the selective preparation of unprecedented unsymmetrical diboryl Pt^{II} complexes as well as sterically little encumbered diaminoboryl Cu^{I} complexes.

Introduction

Boryl ligands have been intensively studied for their unique coordination chemical properties and because of their crucial role as active intermediates of transition-metal-catalyzed borylation reactions.[1–6] Whereas dialkoxyboryl and diaryloxyboryl ligands [$(RO)_2B$ (**I**)] are particularly well explored, diaminoboryl ligands [$(RR'N)_2B$ (**II**)] have only recently become a topic of intense research with potential applications, for example, in catalysis.[1–4] Boryl complexes of ligands of types **I** and **II** are generally synthesized by (1) reaction of metal nucleophiles/bases or metals in a low oxidation state with suitable boryl ligand precursors (e.g., containing B–X, B–H, or B–E bonds) following substitution or oxidative addition pathways,[1,3–5] (2) the reaction of a boryl anion with a metal precursor,[1,2] and (3) heterolytic cleavage (e.g., by σ-bond metathesis) of symmetrical diboranes by transition-metal complexes (only for type **I**).[1,6] However, all these methods suffer from inherent restrictions on the type of metal precursor, from limitations of the boryl anion synthesis to sterically bulky diaminoboryl moieties **II**, or are restricted to boryl systems of type **I**.[1,5b] This is especially unsatisfying, because ligands of type **II** are of prime interest as their steric and electronic properties are expected to be tunable by appropriate substitution, analogous to the well-established isoelectronic and isostructural N-heterocyclic carbene (NHC) ligands. Moreover, these ligand types are particularly interesting, as they can be incorporated in pincer-type ligand frameworks.[2,3] To exploit the potential of diaminoboryl ligands **II** in full, versatile, flexible, and modular synthetic access to their metal complexes as well as to the necessary boron precursors is required. We envisaged that unsymmetrical diborane(4) derivatives, consisting of one moiety **I** and one moiety **II**, would be particularly suitable, as they should be converted into diaminoboryl complexes by either oxidative addition or formal σ-bond metathesis reactions (routes 1 and 3). Such unsymmetrical diboranes(4) have only occasionally been reported together with the respective symmetrical compounds. Only recently did a selective synthesis of the unsymmetrical diborane(4) pinB–Bdan (pin = pinacolato, dan = 1,8-diaminonaphthalene) appear in the scientific literature.[7] However, this compound was only used as a reagent in borylation reactions.[7a,7b]

Herein, we report a protocol for the synthesis of unsymmetrical diboranes(4) of the type pinB–B[$(NR)_2C_6H_4$] (R = Me, Bn, TMS). The versatile protocol is modular, as it introduces the R substituent at a late stage by a simple substitution reaction and, hence, may be adapted to other substituents R.

Results and Discussion

On the basis of the procedure described for the preparation of pinB–Bdan, the unsymmetrical diborane(4) pinB–Bdab (**1**, dab = 1,2-diaminobenzene) was obtained selectively from pinacol, 1,2-diaminobenzene, and $B_2(NMe_2)_4$ in 47% yield (Scheme 1), with only little contamination of the symmetrical compounds B_2pin_2 and B_2dab_2 (100:9:3 GC–MS area ratio).[8] By reaction of **1** with *t*BuLi and suitable electrophiles, the bis-*N*,*N*′-substituted derivatives pinB–

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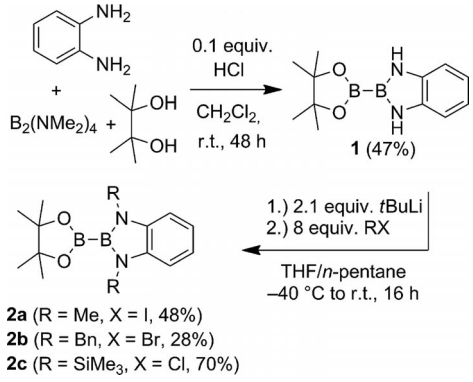
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201402234.

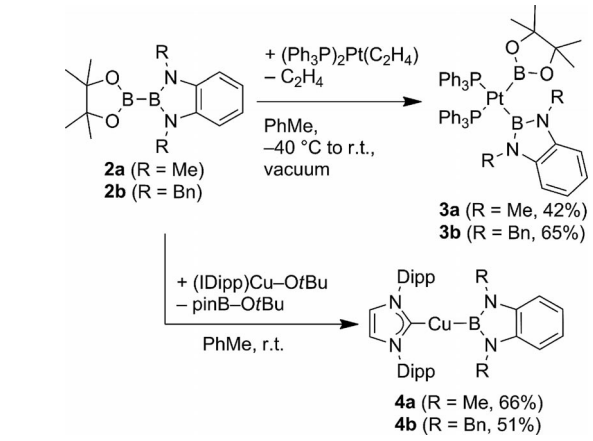
Bdmab [**2a**, dmab = 1,2-di(methylamino)benzene], pinB–Bdbab [**2b**, dbab = 1,2-di(benzylamino)benzene], and pinB–Bdtab [**2c**, dtab = 1,2-di(trimethylsilylamino)benzene] were obtained (Scheme 1).[8–10] In an attempt to prepare **2a** directly from pinacol, 1,2-di(methylamino)benzene, and $B_2(NMe_2)_4$ under the conditions established for **1**, unsymmetrical product **2a** was only obtained in minor amounts along with B_2pin_2 and B_2dab_2 (10:58:6 GC–MS area ratio).[8] This suggested that the presence of the primary amine functionality was crucial for the selective formation of unsymmetrical diborane(4) compounds such as **1**.



Scheme 1. Synthesis of diboranes(4) **1** and **2a**–**c**.

To demonstrate the use of **2a**–**c** as precursors for diaminoboryl metal complexes, the novel unsymmetrical diboranes were treated with $[(PPh_3)_2Pt(C_2H_4)]$ and [(IDipp)CuO*t*Bu], respectively, two metal complexes known to form boryl complexes readily upon reaction with tetraalkoxydiboranes [IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene].[5,6] Unprecedented unsymmetrical diboryl platinum complexes **3a** and **3b** were indeed formed selectively from **2a** and **2b**, whereas **2c** was unreactive under the conditions, possibly because of steric bulk (Scheme 2). Quantitative conversion into **3a** and **3b**, respectively, was only obtained if the formed ethene was removed under reduced pressure. The presence of an equilibrium between diborane **2a** and oxidative addition product **3a** was further corroborated by the increased amount of **2a** observed by NMR spectroscopy upon the addition of 1-hexene or diphenylacetylene to **3a**.[5g,8] Noteworthy, an equilibrium between **2a** and **3a** (and **2b** and **3b**, respectively) was also observed in the absence of an additional ligand in C_6D_6 solution according to the ^1H–^1H NOESY/EXSY spectroscopic data [28:1 (**3a**/**2a**) and 14:1 (**3b**/**2b**) ratio].[11] Thus, the oxidative addition of **2a**/**b** to $[(PPh_3)_2Pt(C_2H_4)]$ as well as the reductive elimination of **2a**/**b** from **3a**/**b** was kinetically and thermodynamically feasible. A similar equilibrium oxidative addition was recently studied in some detail for the reaction of $B_2(OMe)_4$ with $[\{P(Cy)_3\}_2Pt]$ (Cy = cyclohexyl).[5a]

The molecular structures of **3a**/**b** were determined by single-crystal X-ray structure analysis.[8,10] For both Pt^{II} complexes, a distorted square-planar coordination is observed (Figure 1). A comparison of the geometrical data of **3a**/**b** to symmetrical diboryl complexes of the type $[(PPh_3)_2Pt(B(OR)_2)_2]$ {$(OR)_2$ = pin, $[C_2H_3(Ph)O_2]$, $[C_2H_2(CO_2Me)_2O_2]$: B–Pt 2.06–2.08 Å, P–Pt 2.35 Å, B–Pt–B 73.4–75.6°} showed that the pinB–Pt and P2–Pt1 distances were in a comparable range, whereas the B–Pt–B angles were slightly smaller.[5b,5c] A comparison with the diaminoboryl complexes $[(PPh_3)_2Pt(B\{(NiPr)_2C_6H_4\})(Me_3Sn)]$ (**5**) [B–Pt 2.085(6) Å, *trans*-P–Pt 2.376(1) Å] and $[(PPh_3)_2Pt\{B(NMe_2)_2\}(Me_3E)]$ [E = Sn (**6a**): B–Pt 2.136(4) Å, *trans*-P–Pt 2.369(1) Å; Ge (**6b**): B–Pt 2.139(6) Å, *trans*-P–Pt 2.377(1) Å] was also informative.[4a] Whereas similar B–Pt distances were observed for **3a**, **3b**, and **5**, a significantly larger B–Pt distance was found for **6a**/**b**, which suggested a significant influence of the backbone of the diaminoboryl ligand on its coordination properties.



Scheme 2. Synthesis of diaminoboryl complexes **3a**/**b** and **4a**/**b**.

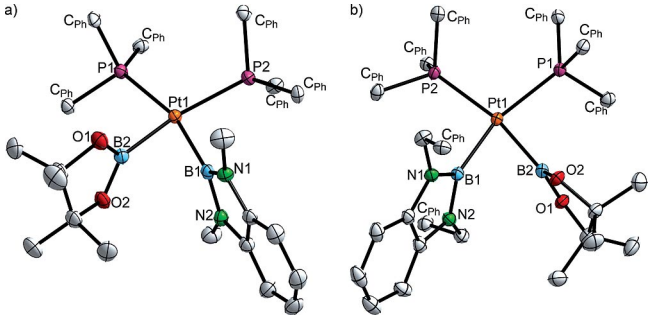


Figure 1. Molecular structure of **3a** (a) and **3b** (b). Selected bond lengths and angles for **3a**: Pt1–B1 2.078(3) Å, Pt1–B2 2.067(3) Å, Pt1–P1 2.340(1) Å, Pt1–P2 2.332(1) Å, B1–B2 2.448(5) Å, B1–Pt1–P1 163.10(8)°, B2–Pt1–P2 160.85(9)°, B1–Pt1–B2 72.4(1)°, P1–Pt1–P2 103.72(3)°; for **3b**: Pt1–B1 2.092(2) Å, Pt1–B2 2.080(2) Å, Pt1–P1 2.3599(7) Å, Pt1–P2 2.3394(6) Å, B1–B2 2.465(3) Å, B1–Pt1–P1 161.65(7)°, B2–Pt1–P2 167.72(7)°, B1–Pt1–B2 72.41(9)°, P1–Pt1–P2 102.23(2)°. For clarity, hydrogen atoms are omitted and only *ipso* carbon atoms of the phenyl groups are shown; thermal ellipsoids are drawn at the 50% probability level.[8,10]

The differences in the coordination properties, specifically the different *trans* influence, between a diaminoboryl and a dialkoxyboryl ligand should be reflected in the *trans*-Pt–P distances.[4b,12] However, the observed differences are small and NMR spectroscopy, namely, the Pt–P coupling constants, is better suited to characterize the ligand properties.

$^{195}Pt,^{31}P$ coupling constants within $[(PPh_3)_2Pt^{II}L_2]$ complexes have been widely used to probe the *trans* influence of the L ligand *trans* to the respective phosphine ligand.[13] With the aid of $^1H–^1H$ NOESY and $^1H–^{31}P$ HMBC NMR spectroscopic data, the coupling constants were assigned to $J_{P,Pt}$(*trans*-Bdmab) = 1715 Hz and $J_{P,Pt}$(*trans*-Bpin) = 1591 Hz for **3a** and $J_{P,Pt}$(*trans*-Bdbab) = 1589 Hz and $J_{P,Pt}$(*trans*-Bpin) = 1530 Hz for **3b**.[8] These data suggest a stronger *trans* influence of the Bpin ligand than the diaminoboryl ligand. This does not correlate well with the order of the *trans* influences of different boryl ligands [(RR′N)$_2$]-B > pinB > catB (cat = catecholato) established both computationally and structurally within the series [$(PR_3)_2$Pt-(X)(BR_2)] of complexes.[12,4b] At the same time, the differences in the *trans*-Bpin P,Pt coupling constants for **3a**, **3b**, and [$(Bpin)_2Pt(PPh_3)_2$] ($J_{P,Pt}$ = 1504 Hz) indicate a significant influence of the *cis*-boryl ligand.[5b] Corroborating the latter, significantly different *trans*-boryl coupling constants of $J_{P,Pt}$ = 1392, 1200, and 1560 Hz were reported for **6a/b** and **5**. This series illustrates also the influence of the backbone of the diaminoboryl ligand on its coordination properties (see above).[4a]

A detailed analysis of the coordination chemical properties of the (unsymmetrical) *cis*-diboryl platinum complexes, especially regarding the *trans* influence and hence the bonding situation (e.g., contribution of σ- and π-bonding, a possible p–p B–B interaction, influence of the ligand backbone) of the boryl ligands has to await more detailed, especially computational, studies.[3g,5]

It should be emphasized that neither during the synthesis of **2a**–**c** nor during the study of **3a/b** was there evidence for scrambling reactions; hence, the formation of symmetrical diborane(4) compounds or Pt^{II} complexes thereof was not observed. Nevertheless, the [$(PPh_3)_2$Pt(OBpin)(OBdbab)] complex was characterized crystallographically as one of the decomposition products of **3b** upon exposure to air.[8]

Reaction of **2a** and **2b** with [(IDipp)CuO*t*Bu] yielded selectively diaminoboryl complexes **4a** and **4b** (Figure 2), respectively, whereas for **2c**, again no reaction was observed by in situ NMR spectroscopy.[8] Moreover, from the reaction of **2a** with CuO*t*Bu in the presence of PPh_3, a few crystals of the [$Cu_5(PPh_3)_2$(O*t*Bu)(Bdmab)$_4$] cluster were obtained, which proved that B–B bond activation was not specific to the (IDipp)Cu fragment.[8,10] The selectivity of the B–B bond cleavage reaction in favor of the formation of diaminoboryl complexes may be explained by the higher Lewis acidity of the Bpin moiety, which favored the formation of pinB–O*t*Bu and diaminoboryl complexes **4a/b**. This was also indicated by the formation of the Lewis acid/base adduct [K(18-crwon-6)(pin(*t*BuO)B–Bdmab)] upon reaction of **2a** with [K(18-crown-6)O*t*Bu].[8,10]

Compound **4a** crystallizes with one molecule in the asymmetric unit in the orthorhombic space group type *Fdd*2. The Bdmab moiety is disordered over two equally occupied positions compromising slightly the geometrical data obtained.[8,10] Complex **4b** crystallizes in the triclinic space group type *P*1 with two independent molecules in the asymmetric unit (molecule A/B).[8,10] The molecular structures of **4a** and **4b** (molecule A and B) are comparable with respect to the approximate linear coordination of the Cu atoms and the similar B–Cu and $C_{carbene}$–Cu distances (Figure 2). However, the angles between the mean planes of the diaminoboryl and the NHC ligand vary significantly and are clearly not only dependent on the steric demand of the boryl ligands but are rather governed by the minimization of repulsive interactions between the peripheral substituents at both ligands. Bond lengths and angles as well as the chemical shifts in the ^{11}B NMR spectra fit well in the series of reported NHC–Cu^I boryl complexes with both dialkoxyboryl and sterically demanding diaminoboryl moieties: [(IDipp)CuBpin] [Cu–B 2.002(3) Å, Cu–C 1.937(2) Å, C–Cu–B 168.1(2)°], [(IMes)Cu(B{C_2H_2(DippN)$_2$})] [Cu–B 1.980(2) Å, Cu–C 1.918(2) Å, C–Cu–B 179.43(9)°], and [(IMes)Cu(B{C_2H_4(DippN)$_2$})] [Cu–B 1.983(3) Å, Cu–C 1.915(3) Å, C–Cu–B 179.4(2)°].[6a,2d]

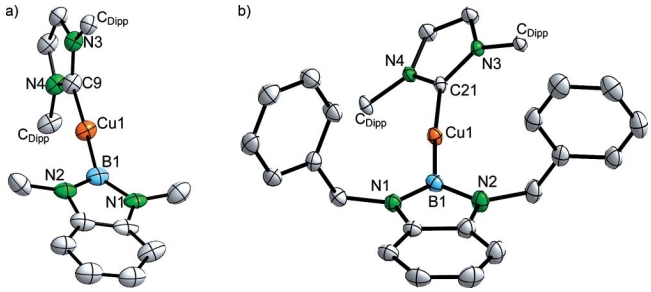


Figure 2. Molecular structure of **4a** (a) and **4b** (b). Selected bond lengths and angles for **4a**: Cu1–B1 1.995(4) Å, Cu1–C9 1.930(4) Å, B1–Cu1–C9 174.8(2)°, angles between the mean planes (Cu1, B1, N1, N2) and (Cu1, C9, N3, N4) 88.3(8)°; for **4b** (molecule A/B; numbering for molecule A only): Cu1–B1 1.994(4)/1.986(4) Å, Cu1–C21 1.932(3)/1.926(3) Å, B1–Cu1–C21 172.1(1)/178.9(1)°, angles between the mean planes (Cu1, B1, N1, N2) and (Cu1, C21, N3, N4) 34.6(1)/55.7(1)°. Hydrogen atoms are omitted for clarity and only *ipso* carbon atoms of the Dipp groups are shown. Thermal ellipsoids are drawn at the 30 and 50% probability level for **4a** and **4b**, respectively.[8,10]

Conclusions

In conclusion, unsymmetrical diborane(4) compounds of the type pinB–B[$(NR)_2C_6H_4$] (**2a**–**c**; R = Me, Bn, $SiMe_3$) were efficiently prepared by functionalization of parent compound **1** (R = H) with electrophiles and provide facile synthetic access to diaminoboryl complexes either by oxidative addition or by selective σ-bond metathesis reactions. The findings presented may facilitate the exploration of this unique class of complexes by providing access to substitution patterns previously inaccessible by the boryllithium route and/or complexes of metals that do not readily undergo oxidative addition of B–X bonds.

Supporting Information (see footnote on the first page of this article): All experimental and spectroscopic details (including in situ NMR experiments) as well as crystallographic and additional structural data.

Acknowledgments

C. K. and C. B. thank the Fonds der Chemischen Industrie for generous support through a Liebig stipend and a PhD stipend. The authors thank BASF SE for a gift of $B_2(NMe_2)_4$ and the Deutsche Forschungsgemeinschaft (DFG) for financial support.

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[10] CCDC-992148 (for **3a**), -992149 (for **1**), -992150 (for **2a**), -992151 (for **S1**), -992152 (for **S3**), -992153 (for **3b**), -992154 (for **4b**), -992155 (for **4a**), -992156 (for **S2**), -992157 (for **2c**), and -992158 (for **2b**) contain 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.

[11] A detailed quantitative analysis of the thermodynamics was prohibited by the rapid decomposition of **3a** and **3b** at elevated temperatures. $[Pt_2(PPh_3)_2(\mu\text{-}PPh_2)_2]$ was identified crystallographically as a decomposition product, see: a) N. J. Taylor, P. C. Chieh, A. J. Carty, *J. Chem. Soc., Chem. Commun.* **1975**, 448–449; b) W. Petz, C. Kutschera, B. Neumüller, *Organometallics* **2005**, *24*, 5038–5043.

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[13] For example, see: L. Rigamonti, A. Forni, M. Manassero, C. Manassero, A. Pasini, *Inorg. Chem.* **2010**, *49*, 123–135.

Received: March 28, 2014
Published Online: April 23, 2014

