Organometallic Chemistry

DOI: 10.1002/anie.200803581

An ansa-Heteroborabenzene Divalent Lanthanide Amide through C–H Bond Cleavage**

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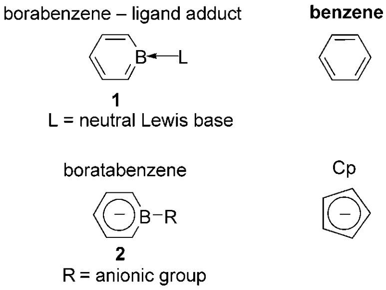
Dedicated to Professor Xiyan Lu on the occasion of his 80th birthday

In 1970, Herberich reported the first borabenzene derivative $[CpCoC_5H_5BPh]^+$.[1] One year later, Ashe described the synthesis of lithium 1-phenylboratabenzene.[2] This pioneering research opened up the fascinating area of borabenzene chemistry. The family of borabenzenes generally consists of neutral borabenzene–ligand adducts (**1**) and anionic boratabenzenes (**2**, Scheme 1); the properties of the former are close to those of benzene while the latter are related to the well-known anionic cyclopentadienide (Cp).[3] Since metal complexes with Cp-type ligands are very useful in polymer and organic synthesis, the study of boratabenzene metal complexes is very attractive. In the last three decades, numerous metal complexes bearing boratabenzenes,[4] in particular the derivatives of Group 4, 6, and 8 metals, have been reported, and some of these show excellent activities. Examples of metal complexes with borabenzene–ligand adducts (**1**) are much less numerous than boratabenzene–metal complexes or benzene–metal complexes, and only very few examples, which are coordinated by $Cr^0(CO)_3$, have been reported.[5] No examples of a metal ligated both by **1** and **2** have been reported to date.



Scheme 1. The family of borabenzenes and their analogues.

Lanthanide complexes bearing Cp-type ligands have rich and diverse coordination properties and reactivities,[6] and promote a variety of useful transformations such as hydrogenation, hydroamination, hydrosilylation, hydrophosphination,[7] olefin and polar monomer polymerizations,[8] reductions, and reductive-coupling reactions.[9] On the other hand, the chemistry of boratabenzene–lanthanide metal complexes remains mostly unexplored.[10] Recently, we prepared several THF-solvated divalent Sm and Yb boratabenzene complexes, $[(C_5H_5BXPh_2)_2Sm(thf)_2]$ (X = N, P)[11] and $[(C_5H_5BNPh_2)_2Yb(thf)_2]$,[12] and studied their reactivities towards methyl methacrylate polymerization or redox transformation with α-diimine ligands. Stimulated by the fact that the THF-free divalent lanthanide metal complexes are usually highly reactive,[9] we set out to synthesize the THF-free divalent lanthanide boratabenzene metal complexes. For this purpose, the THF-free Yb^{II} complex $[Yb\{N(SiMe_3)_2\}_2]$ was used as the starting material instead of the commonly used $[YbI_2(thf)_2]$, and a strategy[10d,13] involving a nucleophilic aromatic substitution reaction of the borabenzene–PMe_3 adduct was employed. We report herein the isolation of an unprecedented ansa-heteroborabenzene divalent lanthanide amide from this reaction, which was formed through C–H bond cleavage within the PMe_3 group. The reactivities of the above complex were also briefly studied.

Reaction of $[Yb\{N(SiMe_3)_2\}_2]$ with two equivalents of borabenzene–PMe_3 in toluene afforded a new complex as a dark-blue crystalline solid. This complex is readily soluble in benzene, and is very sensitive to air and moisture. The NMR spectra of the complex in C_6D_6 are intriguing: the ^{11}B NMR spectrum shows one singlet and one doublet, the singlet ($\delta = 33.7$ ppm) is very close to that of $[(C_5H_5BNPh_2)_2Yb(thf)_2]$ ($\delta = 33.8$ ppm),[12] while the doublet ($\delta = 25.8$ ppm) is further upfield, its J value of 99.0 Hz indicating a B–P linkage. The existence of this B–P linkage was further supported by the ^{31}P NMR spectrum ($\delta = -14.6$ ppm (d, $^1J_{B-P} = 101.4$ Hz)). The ^1H NMR and ^{13}C NMR spectra show many signals in the region containing the borabenzene ring signals (^1H NMR: $\delta =$ 7.43–7.36, 6.90, 6.70, 6.52, and 6.32 ppm; ^{13}C NMR: $\delta = 136.0$, 135.9, 135.0, 134.9, 120.1, and 114.2 ppm), and reveal the presence of an unexpected $-CH_2P(CH_3)_2$ unit (^1H NMR: $\delta =$ 1.46 (d, 2H, $^2J_{P-H} = 17.1$ Hz) and 0.82 ppm (d, 6H, $^2J_{P-H} =$ 11.7 Hz); ^{13}C NMR: $\delta = 15.3$ and 9.8 ppm). The ^{171}Yb NMR spectrum of the complex in $[D_8]$toluene shows a broad signal at 1175 ppm, which is shifted downfield compared to signals reported for other Yb^{II} complexes.[14]

The NMR spectroscopy data did not allow an unambiguous structural assignment of the new complex. Single crystals

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[**] This work was supported by the National Natural Science Foundation of China (Grant No 20672134) and the Chinese Academy of Sciences. We thank Prof. Changtao Qian for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200803581.

of the complex were obtained from a hexane solution and characterized by the X-ray diffraction studies (Figure 1). The complex was shown to be an ansa-heteroborabenzene Yb^{II} amide (**3**, Scheme 2). The bridging mode is impressive, a $-CH_2P(CH_3)_2$ unit links one anionic boratabenzene ring through a $H_2C–B$ covalent bond and one neutral borabenzene ring through a $(R)_3P \rightarrow B$ coordination bond; such a coordination mode has not been reported to date. The $H_2C–B$ bond length of 1.59 Å is almost same as that of the $H_3C–B$ bond in $[(C_5H_5BMe)_2ScCl]_2$ (1.58 Å),[10c] and the $(R)_3P \rightarrow B$ bond length of 1.92 Å is close to that in the borabenzene–PMe_3 adduct $C_5H_5BPMe_3$ (1.90 Å).[15] Inspection of the distance from the Yb^{II} ion to the boratabenzene ring (B1, C1–5) shows that the distances are significantly longer for Yb to B1 (2.95 Å), C1 (2.88 Å), and C5 (2.85 Å) versus Yb to C2- (2.82 Å), C3(2.78 Å), and C4(2.80 Å), which indicates a slippage of the Yb^{II} ion away from the B atom and towards the C3 atom to give an intermediate (η^3–η^6) coordination mode as observed in other boratabenzene transition metal complexes.[3] The average Yb–C(boratabenzene) distance (2.83 Å) is same as that in $[(C_5H_5BNPh_2)_2Yb(thf)_2]$ (2.83 Å).[12]

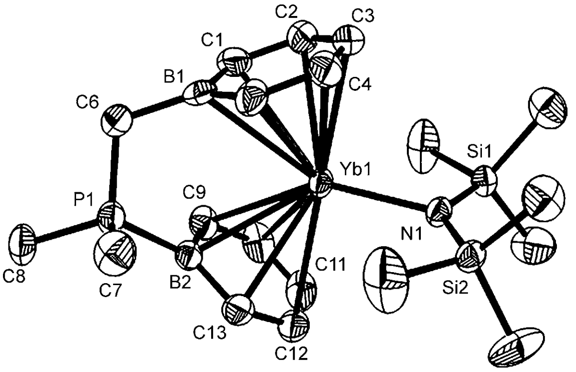
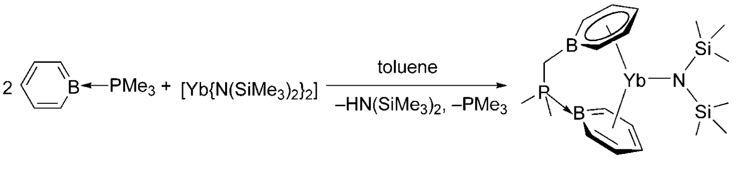


Figure 1. ORTEP drawing of **3**; thermal ellipsoids are set at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1–B1 2.948(6), Yb1–C1 2.879(6), Yb1–C2 2.824(7), Yb1–C3 2.785(6), Yb1–C4 2.802(5), Yb1–C5 2.853(5), Yb1–B2 2.879(6), Yb1–C9 2.879(5), Yb1–C10 2.879(6), Yb1–C11 2.890(7), Yb1–C12 2.881(6), Yb1–C13 2.868(6), Yb1–N1 2.305(4), B1–C6 1.593(9), P1–B2 1.923(6), Si1-N1-Yb1 110.3(2), Si2-N1-Yb1 120.6(2), Si1-N1-Si2 129.0(3).



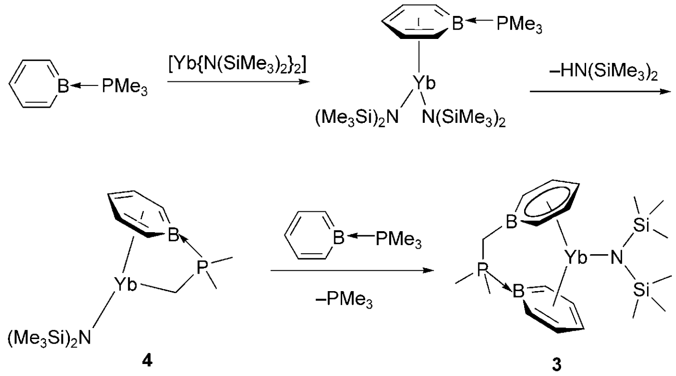
3

Scheme 2. Synthesis of **3**.

The most notable structural feature of **3** is the coordination of the neutral borabenzene to the Yb^{II} ion, which represents the first example of a coordination between neutral borabenzene and a d^0 metal ion, although several Cr^0 complexes[5] have been reported. The average Yb–C distance from the Yb^{II} ion to the borabenzene (2.88 Å) is significantly shorter than those in other ytterbium(II)–arene complexes (from 2.96 to 3.04 Å),[16] and only 0.05 Å longer than the average Yb–C(boratabenzene) distance (2.83 Å) in the same complex, which indicates a rather strong ytterbium(II)–borabenzene interaction. In contrast to the ytterbium(II)–boratabenzene coordination, the distances from the Yb^{II} ion to the atoms of the borabenzene are almost identical (within less than 0.03 Å), to give a nearly ideal η^6 coordination mode. The ^1H NMR spectrum shows that the signals for the borabenzene in **3** ($\delta = 7.43$–7.36 and 6.70 ppm) are further upfield than those of $C_5H_5BPMe_3$ ($\delta = 8.04$, 7.42, and 7.24 ppm), which indicates that the coordination between the borabenzene and the Yb^{II} ion is retained in C_6D_6 solution.

The amide group coordinates to the Yb^{II} ion with a Yb–N bond length of 2.305 Å, which is close to that in the Yb^{III} complex *meso*-$[(CH_2C_9H_6)_2Yb\{N(SiMe_3)_2\}]$ (2.16 Å)[17] when the difference in ionic radii between the Yb^{II} and Yb^{III} ions (0.155 Å) is accounted for. The nitrogen atom displays a trigonal planar geometry (Si1-N1-Yb = 110.3(2), Si2-N1-Yb = 120.6(2), Si1-N1-Si2 = 129.0(3), Σ N1 = 359.9°), which indicates the donation of the lone pair of electrons on the nitrogen atom to the electron-deficient metal center.

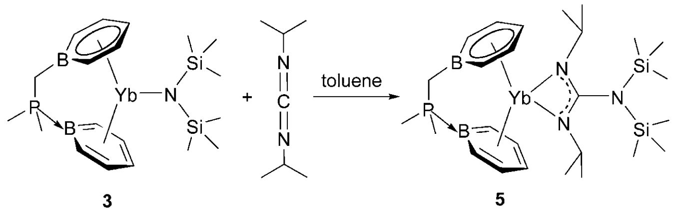
The unexpected formation of **3** from borabenzene–PMe_3 raises the question of how this transformation might take place. To investigate this, the reaction of $[Yb\{N(SiMe_3)_2\}_2]$ with two equivalents of $C_5H_5BPMe_3$ in C_6D_6 was monitored by NMR spectroscopy. The addition of two equivalents of borabenzene–PMe_3 to a rose-colored C_6D_6 solution of $[Yb\{N(SiMe_3)_2\}_2]$ instantaneously resulted in the solution color changing to blue, the ^1H NMR spectrum of this solution shows that the signals for the protons on the borabenzene ring were shifted from $\delta = 8.04$, 7.42, and 7.24 ppm in C_5H_5B–PMe_3 to $\delta = 7.78$ (3H) and 7.12 ppm (2H), whereas the signal for the PMe_3 group moves from $\delta = 0.64$ to 0.81 ppm. Consistent with the change in the ^1H NMR spectrum, the signals in the ^{31}P NMR spectrum changed from a quartet ($\delta = -22.1$ ppm) to a broad singlet ($\delta = -21.7$ ppm). After 8 h, the complex **3** was observed, together with the by-products $HN(SiMe_3)_2$ and PMe_3; the quantities of **3**, $HN(SiMe_3)_2$, and PMe_3 slowly increased with the reaction time. We propose that the reaction proceeds through three steps (Scheme 3): 1) a coordination interaction between the borabenzene ring of $C_5H_5BPMe_3$ and the metal ion of $[Yb\{N(SiMe_3)_2\}_2]$; 2) C–H bond cleavage within PMe_3 to generate intermediate **4** along with $HN(SiMe_3)_2$; 3) a nucleophilic aromatic substitution reaction of borabenzene–PMe_3 and the formation of the final product **3** and the by-product PMe_3. The rapid changes in the NMR spectra and reaction color indicate that the first step is fast; the quantities of $HN(SiMe_3)_2$ increased very slowly, therefore the second step is slow. The ratio of PMe_3 to $HN(SiMe_3)_2$ in the reaction system was nearly 1:1 and the intermediate **4** is not detected, which suggest the third step is much faster than the second step. Preparation of **4** from $[Yb\{N(SiMe_3)_2\}_2]$ with $C_5H_5BPMe_3$ in 1:1 ratio was attempted but only the complex **3** was detected,



Scheme 3. Suggested reaction pathway for the formation of **3**.

which supports the conclusion that the reaction rate of step 3 is higher than that of step 2. It must also be noted that the reaction is very sensitive to the presence of THF, using $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ as the starting material or the addition of several drops of THF to the reaction mixture retarded the formation of **3**. No reaction occurred between borabenzene–PMe_3 and the trivalent lanthanide complex $[Yb\{N(SiMe_3)_2\}_3]$ or $[Lu\{N(SiMe_3)_2\}_3]$, this is possibly because of the greater steric bulk of the trivalent lanthanide complex.

Preliminary reactivity studies showed that, analogous to bisCp trivalent lanthanide amides, the divalent lanthanide amide **3** undergoes an insertion reaction of carbodiimides into the metal–nitrogen bond to form the corresponding lanthanide guanidinate.[18] Therefore, the complex **3** was reacted with *N,N'*-diisopropylcarbodiimide in toluene to give the divalent lanthanide guanidinate **5** in 83 % yield (Scheme 4).



Scheme 4. Insertion reaction of *N,N'*-diisopropylcarbodiimide with **3**.

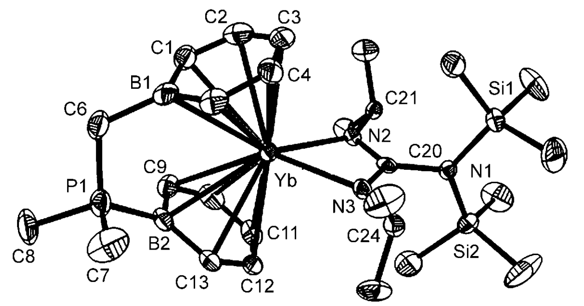


Figure 2. ORTEP drawing of **5**; thermal ellipsoids set at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb–B1 2.919(6), Yb–C1 2.912(8), Yb–C2 2.829(8), Yb–C3 2.825(8), Yb–C4 2.838(8), Yb–C5 2.885(8), Yb–B2 2.919(9), Yb–C9 2.928(5), Yb–C10 2.923(6), Yb–C11 2.881(7), Yb–C12 2.855(7), Yb–C13 2.864(7), B1–C6 1.634(12), P1–B2 1.943(9), Yb–N2 2.365(5), Yb–N3 2.410(6), Yb–C20 2.810(7), N1–C20 1.457(8), N2–C20 1.342(8), N3–C20 1.317(8), N2-Yb-N3 56.32(18), N3-C20-N2 115.9(6), N3-C20-N1 121.2(6), N2-C20-N1 122.8(6).

Single crystals of **5** were grown from a C_6D_6 solution and the solid-state structure was determined by X-ray crystallography (Figure 2).[19] In the complex **5**, the average Yb–C distances for the boratabenzene (2.86 Å) and for the borabenzene (2.89 Å) groups are slightly longer than those in the complex **3** (2.83 and 2.88 Å, respectively), because of an increase in the coordination number of the Yb^{II} ion in **5**. The amidinate group is bound mainly through two nitrogen atoms with Yb–N bond lengths of 2.365(5) and 2.410(6) Å, and the atoms Yb, N2, C20, and N3 are coplanar. The bond lengths N1–C20 (1.457(8) Å) and N2–C20 (1.342(8) Å) are between those of typical single and double bonds, and the atoms C21, N2, C20, N3, C24, and N1 are coplanar, which reveals a delocalized electronic structure. As observed for **3**, the ^1H NMR spectrum of **5** in C_6D_6 showed that the signals for the neutral borabenzene ($\delta = 7.56$ and 6.73 ppm) lie upfield in comparison to those in $C_5H_5BPMe_3$, which is consistent with the occurrence of ytterbium(II)–borabenzene coordination in the solid state. The ^{171}Yb NMR spectrum of the complex in [D$_8$]toluene shows a broad signal at $\delta = 1177$ ppm.

In summary, the reaction of $[Yb\{N(SiMe_3)_2\}_2]$ with borabenzene–PMe_3 provides a novel ansa-heteroborabenzene divalent lanthanide amide (**3**) through C–H bond cleavage of PMe_3. **3** displays several notable structural features: 1) one metal ion is ligated by both neutral borabenzene and anionic boratabenzene groups; 2) two aromatic rings are linked through covalent and coordination bonds; 3) although a divalent lanthanide complex is formed, it has a structure similar to trivalent ansa-Cp lanthanide complexes. **3** undergoes an insertion reaction of *N,N'*-diisopropylcarbodiimide into the metal–nitrogen bond, in a similar manner to bisCp trivalent lanthanide amides. Future studies will probe the reductive properties of **3** as well as the nucleophilic aromatic substitution reaction on the neutral borabenzene fragment in **3** to generate new borabenzene (or boratabenzene) metal complexes.

Received: July 23, 2008
Revised: September 22, 2008
Published online: November 12, 2008

Keywords: amides · boron · bridging ligands · heterocycles · lanthanides

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[19] CCDC-694328 (**3**) and CCDC-694329 (**5**) 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.