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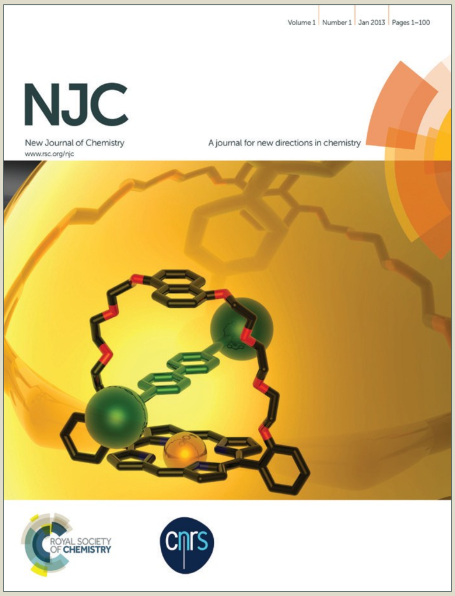

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COMMUNICATION

Reaction of a Bulky Amine Borane with Lanthanide Trialkyls. Formation of Alkyl Lanthanide Imide Complexes†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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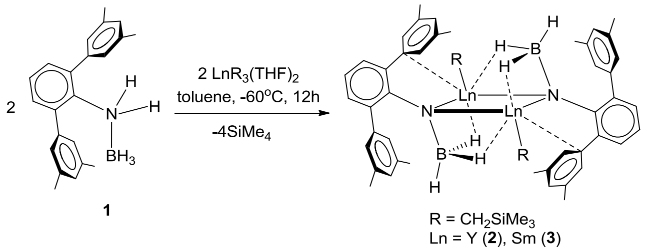
Borane-stabilized lanthanide imides have been synthesized by reactions of lanthanide trialkyls with a bulky amine borane. The X-ray crystal structures indicated the presence of the 3-center-2-electron B–H–Ln bonding and Ln-arene interactions in the solid state.

Amine boranes are potential chemical hydrogen storage materials.[1] The reactions of metal compounds with amine boranes and the isolation of corresponding intermediates have attracted intensive attention since these studies are able to provide preliminary mechanistic insight into the metal-catalyzed amine borane dehydrogenation process. The stoichiometric reactions involved main-group and transition metal complexes have been extensively explored.[2–5] However, there are only a limited number of reports detailing the reactions of lanthanide complexes with amine boranes.[6] It has been shown by Okuda and co-workers that reactions of lanthanum hydride complex $[(1,7\text{-}Me_2TACD)LaH]_4$ (TACD = 1,4,7,10-tetraazacyclododecane) with $Me_2NH{\cdot}BH_3$ afforded lanthanum amidoborane complexes.[7] Trifonov and co-workers have demonstrated that yttrium alkyl complex supported by an amidine–amidopyridinate ligand can react with $NH_3{\cdot}BH_3$ to give yttrium imidoborane complex.[8] Additionally, Hill and co-workers isolated the intermediate $Sc[N(SiHMe_2)_2][NMe_2BH_2NMe_2BH_3]_2$ by the reaction of $Sc[N(SiHMe_2)_2]_3(THF)_2$ with $Me_2NH{\cdot}BH_3$.[9] To understand the reactivity of homoleptic lanthanide alkyls with amino boranes, we employed bulky amino borane for the isolation of possible intermediates. Herein, we report on reactions of lanthanide trialkyls $Ln(CH_2SiMe_3)_3$ (Ln = Y, Sm) with the bulky amine borane $ArNH_2{\cdot}BH_3$ (Ar = 2,6-$(3,5\text{-}Me_2C_6H_3)_2C_6H_3$) and isolation of dimeric lanthanide imides stabilized by BH_3.[10]

The bulky aryl primary amine borane $ArNH_2{\cdot}BH_3$ (**1**) was prepared in 86% yield by reaction of $ArNH_2$ with $BH_3{\cdot}THF$ in THF. Colorless crystals of **1** are air and thermally stable at room temperature. However, **1** is thermally unstable and slowly decomposed when it was heated up to 40 °C as indicated by the liberation of hydrogen gas. Unfortunately, no products can be isolated so far. Therefore, compound **1** was employed immediately once it was prepared. **1** was characterized by elemental analysis, ^1H, ^{13}C, ^{11}B NMR and IR spectroscopy. In the ^{11}B NMR spectrum of **1**, a broad peak was observed at δ −16.1 ppm which is comparable to those observed in the known amine boranes $dippNH_2{\cdot}BH_3$ (dipp = 2,6-$i$$Pr_2C_6H_3$) of δ −15.1 ppm and $Ar'NH_2{\cdot}BH_3$ (Ar' = 2,6-$(Ph_2CH)_2$-4-MeC_6H_2) of δ −16.1 ppm .[3c,11]

Treatment of $Y(CH_2SiMe_3)_3(THF)_2$ with one equivalent of freshly prepared **1** in toluene at −60 °C for 12 hours afforded the dimeric alkyl yttrium imidoborane complex $[Y(CH_2SiMe_3)(\mu_2\text{-}NArBH_3)]_2$ (**2**) as pale yellow crystals in 60% yield (Scheme 1). The samarium imidoborane complex $[Sm(CH_2SiMe_3)(\mu_2\text{-}NArBH_3)]_2$ (**3**) was prepared similarly in 65% yield as dark brown crystals.[12] **2** and **3** are soluble in toluene and THF but poorly soluble in n-hexane. **2** and **3** were characterized by elemental analysis, ^1H, ^{13}C, ^{11}B NMR and IR spectroscopy.



Scheme 1 Reactions of bulky amine borane (**1**) with lanthanide trialkyls.

Analysis of ^1H NMR spectrum of complex **2** indicated the retention of one CH_2SiMe_3 ligand on the yttrium atom. The two doublets at δ −1.25 ppm and −0.44 ppm can be assigned to the protons of methylene group in CH_2SiMe_3 ligand. The coupling constants of $^2J_{HH}$ = 10.5 Hz and $^2J_{YH}$ = 3.2 and 4.0 Hz are consistent with those found in trimethylsilylmethyl yttrium complexes.[13] In the ^{13}C NMR spectrum of **2**, the carbon atom of the methylene group gives rise to a doublet resonance at δ 39.2 ppm of $^1J_{YC}$ = 40.4 Hz.[13] Both ^1H and ^{13}C NMR spectra of **2** showed a singlet (δ 0.29 and 4.7 ppm) for protons and carbons of the methyl groups in the CH_2SiMe_3 group. A broad peak at δ −17.3 ppm was observed in the ^{11}B NMR spectrum of **2**, which is similar to the reported yttrium borane complexes and indicated a four-coordinate boron atom.[14]

The ^{13}C NMR pattern of **3** is very similar to that of **2** although it is slightly affected by the paramagnetism. In the ^{13}C NMR spectrum of **3**, the carbon of methylene group caused a resonance at δ 30.2

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†Electronic Supplementary Information (ESI) available: Experimental details and characterization data for **1**–**3**. See DOI: 10.1039/x0xx00000x

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ppm. The two peaks at δ 0 and 2.3 ppm are caused by the carbons of the methyl on $CH_2Si\mathit{Me}_3$ groups. The resonances of methyl groups on aryl rings appeared as four singlets of δ 19.3, 20.9, 23.7 and 23.9 ppm in the ^{13}C NMR spectrum. The peaks in the ^1H NMR spectrum of **3** is board and shifted because of paramagnetism, but which can be assigned appropriately based on ^1H–^{13}C HMQC experiment. The CH_2SiMe_3 ligands give rise to the resonances at δ 1.36 ppm for methylene protons, δ 0.01 and 1.53 ppm for methyl protons. The four singlets at δ −0.63, 1.25, 3.91 and 4.05 ppm can be assigned to the methyl protons on aryl rings. Resonances of protons of aryl rings are observed in the range from δ 3.98 to 8.80 ppm. The ^{11}B NMR resonance of paramagnetic **3** shows a broad peak at δ −30.7 ppm, which is upfield shifted in comparison with **2**.

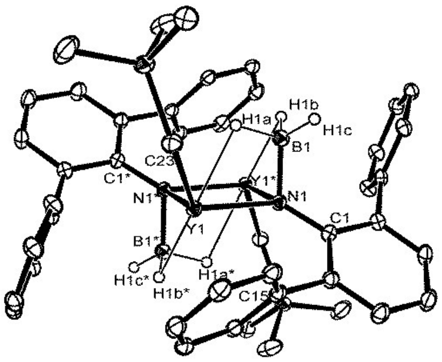

Fig. 1 ORTEP representation of the X-ray structure of **2**. Hydrogen atoms and methyl groups on aryl rings have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

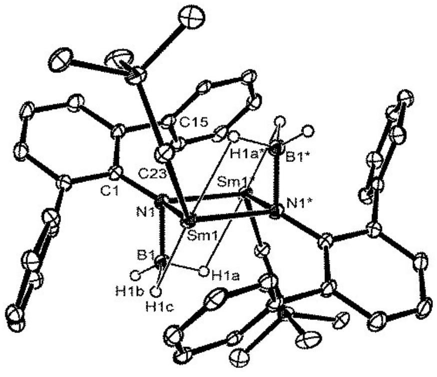

Fig. 2 ORTEP representation of the X-ray structure of **3**. Hydrogen atoms and methyl groups on aryl rings have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

Single crystals suitable for X-ray diffraction of **2** and **3** were obtained from toluene at −40°C.[15] The molecular structures of **2** and **3** are presented in Fig. 1 and Fig. 2, along with selected bond lengths and angles in Table 1. The structure of complex **3** is very similar to that of **2**. Compounds **2** and **3** are dimeric alkyl lanthanide imidoborane complexes with crystallographic central symmetry. Each metal atom is coordinated by one CH_2SiMe_3 ligand and bridged by two imidoborane μ_2-$(NArBH_3)^{2-}$ dianionic ligand. As far as we know, no lanthanide imide complex with a terminal alkyl group has been reported and structural characterized.[16]

The Y−N bond lengths of 2.2969(17) and 2.3352(17) Å in **2** are comparable to those in reported yttrium imide complexes $[Y(N^{Me2}NN^{Me2}C^{Me}N^{Me2})(\mu_2\text{-}NHBH_3)]_2$ ($N^{Me2}NN^{Me2}C^{Me}N^{Me2}$ = amidine−amidopyridinate ligand) (2.243(2) and 2.288(2) Å), $[Y(AlMe_4)(\mu_2\text{-}Nmes)]_2$ (mes = 2,4,6-tBu$_3C_6H_2$) (2.109(9) and 2.291(9) Å) and $[Cp'Y(\mu_3\text{-}NCH_2CH_3)]_4$ (Cp' = η^5-$C_5Me_4SiMe_3$) (2.193(3)−2.342(3) Å).[8,17] The Sm−N bond lengths of 2.361(3) and 2.406(3) Å in **3** are also comparable to those in reported μ_3-phenylimido ligands cap tetranuclear samarium imide complexes $Sm_4(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Ph_2N_2)_4(\mu_3\text{-}NPh)_2(THF)_6$ (2.369(7) Å) and $Sm_4(Me_2Si\{NC(Ph)Ndipp\}_2)_2(\mu_3\text{-}NPh)_4$, (av. 2.382(7) Å), but longer than that in $[(\mu\text{-}NHdipp)Sm(\mu\text{-}Ndipp)(AlMe_3)]_2$ (2.152(8) Å).[18] Each dinuclear complex of **2** or **3** contains a coplanar framework Ln1−N1−Ln1*−N1* (The sum of the angles Ln1−N1−Ln1* and N1−Ln1−N1* is 180°). Two BH_3 units were coordinated by the two N atoms and resided on both sides of the plane Ln1−N1−Ln1*−N1*. The two B−N bonds almost perpendicular to this plane (88.1° in **2**, 88.9° in **3**). In each alkyl lanthanide imidoborane complex, it is worth mentioning that terminal BH_3 interacted to lanthanide metal center through two 3-center-2-electron B−H−Ln bonding.[8,9,14] The Y−B bond distances of 2.802(3) and 2.716(3) Å in **2** are similar to those in $[Y(N^{Me2}NN^{Me2}C^{Me}N^{Me2})(\mu_2\text{-}NHBH_3)]_2$ (2.767(3) and 2.753(3) Å) and slightly longer than those in yttrium borane complex $Y(H_3BNMe_2BH_3)_3$ (2.701(7) and 2.739(7) Å).[14] The Y−B bond distances in **2** are belong to the long end of the range of reported Y−B bond distances in yttrium borohydride complexes (from 2.499 to 2.82 Å).[19] The Sm−B bond distances of 2.858(5) and 2.791(5) Å in **3** are comparable to those in samarium borane complex $Sm(H_3BNMe_2BH_3)_3$ (2.782(3) and 2.849(4) Å), and longer than those in reported samarium borohydride complexes (from 2.579 to 2.702 Å).[14,20] The N−B bond lengths (1.551(3) Å in **2** and 1.5485(5) Å in **3**) are significantly shorter than those in free amine borane complexes (av. 1.630 Å),[11] which indicate the presence of the strong coordination interaction between nitrogen and boron. The close distances between metal atom and the *ipso* carbon of one of the 3,5-$Me_2C_6H_3$ rings (Y···C = 2.860(2) Å in **2**, Sm···C = 2.900(4) Å in **3**) suggest the existence of Ln-arene interactions.

Table 1 Comparison of Important Bond Lengths (Å) and Angles (°) in **2** and **3**

	2 (Ln = Y)	**3** (Ln = Sm)
Ln1−N1	2.2969(17)	2.406(3)
Ln1−N1*	2.3352(17)	2.361(3)
Ln1−B1	2.802(3)	2.793(5)
Ln1−B1*	2.716(3)	2.856(5)
N1−B1	1.551(3)	1.548(5)
Ln1−C15	2.860(2)	2.900(4)
Ln1−C23	2.415(2)	2.468(4)
N1−Ln1−N1*	81.92(6)	80.44(11)
Ln1−N1−Ln1*	98.08(6)	99.56(11)

The vibrational spectra of **2** and **3** exhibited one stretching vibration for the terminal B−H bond (2365 cm^{-1} for **2**, 2391 cm^{-1} for **3**) and two for bridging B−H bond (2270 and 2162 cm^{-1} for **2**, 2269 and 2160 cm^{-1} for **3**),[14,21] consistent with their solid state structures.

We investigated the ability of **2** and **3** in small molecular activation, such as CO and CO_2, but the reactions were complicated and no major product can be isolated. Notably, when **2** or **3** were treated with cyclopentadiene or phenylacetylene, the decomposition product $ArNH_2$ was isolated as the major product. It

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demonstrated the high reactivity of the imido group. **2** showed a very low catalytic activity for styrene polymerization upon activation of $[Ph_3C][B(C_6F_5)_4]$.

We have demonstrated that the reactions of lanthanide trialkyls with the bulky amine borane $ArNH_2{\cdot}BH_3$ yielded the dimeric borane-stabilized lanthanide imides **2** and **3**, which are also the first structural characterized lanthanide imide complexes with a terminal alkyl group. The dehydrogenation of the aminoborane was not observed. Borane might be crucial to stabilize the lanthanide imide complexes and to facilitate the alkyl elimination reaction.

Experimental

Synthesis of $[Y(CH_2SiMe_3)(\mu_2\text{-}NArBH_3)]_2$ (2)

A solution of **1** (0.50 g, 1.6 mmol) in toluene (40 mL) was slowly added to a stirred solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.79 g, 1.6 mmol) in toluene (20 mL) at −78 °C. The mixture was stirred overnight at −60 °C and then warmed to room temperature. The color of the mixture changed to pale yellow gradually. Then the solution was concentrated to 5 mL to give pale yellow crystals of **2** at –40 °C for overnight (0.47 g, 60%). M.p.: 130 °C (dec.). Anal. Calcd for $C_{52}H_{70}B_2N_2Si_2Y_2$ (978.73): C, 63.81; H, 7.21; N, 2.86; Found: C, 63.56; H, 6.98; N, 2.47. ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ 7.54 (s, 2H, Ar-*H*), 7.46 (s, 2H, Ar-*H*), 7.42 (s, 2H, Ar-*H*), 6.96 (s, 2H, Ar-*H*), 6.83 (s, 2H, Ar-*H*), 6.77 (s, 4H, Ar-*H*), 6.56 (s, 2H, Ar-*H*), 6.41 (s, 2H, Ar-*H*), 2.32 (s, 6H, Ar-Me_2), 2.16 (s, 6H, Ar-Me_2), 2.01 (s, 6H, Ar-Me_2), 1.87 (s, 6H, Ar-Me_2), 0.29 (s, 18H, SiMe_3), −0.44 (d, 2H, $^2J_{HH}$ = 10.5 Hz, $^2J_{YH}$ = 4.0 Hz, Y-CH_2), −1.25 (d, 2H, $^2J_{HH}$ = 10.5 Hz, $^2J_{YH}$ = 3.2 Hz, Y-CH_2). ^{13}C NMR (101 MHz, C_6D_6, 23 °C): δ 156.2, 147.3, 145.8, 143.7, 143.6, 138.6, 138.4, 138.3, 136.8, 136.0, 132.8, 132.3, 131.3, 130.5, 129.9, 127.0, 123.9, 119.2 (Ar-*C*), 39.2 (d, $^1J_{YC}$ = 40.4 Hz, Y-CH_2), 22.3, 22.2, 21.9, 21.6 (Ar-Me_2), 4.7 (SiMe_3). ^{11}B NMR (128 MHz, C_6D_6, 23 °C): δ −17.3. IR (KBr, cm^{-1}): $\tilde{\nu}$ (B–H) 2364.8, 2270.3, 2161.6.

Acknowledgements

We are grateful to the National Natural Science Foundation of China and 973 program (2012CB821600, 21202085, 21390401), Natural Science Foundation of Tianjin (12JCYBJC31100), and Programs Foundation of Ministry of Education of China (20120031120001) for financial support.

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