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Group 3 and Lanthanide Boryl Compounds: Syntheses, Structures, and Bonding Analyses of Sc−B, Y−B, and Lu−B σ-Coordinated NHC Analogues

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Supporting Information

ABSTRACT: Reaction of $[Ln(CH_2SiMe_3)_2(THF)_n][BPh_4]$ (Ln = Sc, Y, Lu ; n = 3, 4) with $Li\{B(NArCH)_2\}(THF)_2$ (Ar = 2,6-$C_6H_3{}^iPr_2$) formed the first group 3 and lanthanide boryl compounds, $Sc\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)$ and $Ln\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)_2$ (Ln = Y, Lu), which contain two-center, two-electron Ln−B σ bonds. All of these systems were crystallographically characterized. Density functional theory analysis of the Ln−B bonding found it to be predominantly ionic, with covalent character in the σ-bonding Ln−B HOMO.

Transition-metal boryl compounds $(L)M(BX_2)_x$ containing two-center, two-electron σ bonds have been a topic of outstanding interest for the past 20 years, mainly because of their pivotal roles in a variety of catalytic and stoichiometric transformations, including the hydroboration and diboration of C−C π bonds and the functionalization of alkane and arene C−H bonds.[1] To date, virtually all boryl complexes have been prepared either by B−X (X = H, halogen) or B−B oxidative addition to a low-oxidation-state (L)M species or by nucleophilic attack of an $[(L)M]^-$ anion on XBR_2 or a related source of the boryl moiety. However, the nature of these methodologies has inherently limited the type of $(L)M(BX_2)_x$ compounds that can be prepared, and the overwhelming majority of such species therefore incorporate the late transition metals Fe, Ru, Rh, Ir, and Pt.

Recently, Nozaki and Yamashita introduced the lithium complex $Li\{B(NArCH)_2\}(THF)_2$ (Ar = 2,6-$C_6H_3{}^iPr_2$) as a well-defined nucleophilic source of the boryl fragment.[2] This reagent has allowed access both to boryl complexes of hitherto inaccessible transition-metal groups (e.g., 11 and 12) and to novel main-group complexes.[3] Within the last year, the first examples of group 4 boryls have also been prepared by salt-elimination reactions using metal halide or alkoxide precursors.[4] The chemistry of early metal boryl compounds nonetheless remains almost entirely unexplored. Furthermore, there are to date no reported examples of rare-earth metal boryl compounds,[5] in stark contrast to the very important and well-established fields of rare-earth metal amide[6] and alkyl chemistry.[7] Moreover, as amply demonstrated by the chemistry of metal alkyl compounds, one might expect marked differences in the fundamental reactivity of rare-earth boryl complexes in comparison with their mid- to late-metal analogues. Finally, while rare-earth boryls have yet to be described, compounds of these metals containing two-center, two-electron Ln−Al and Ln−Ga bonds have very recently appeared.[8] Here we report the first group 3 and lanthanide metal boryl compounds.

Initial attempts to prepare rare-earth boryl compounds centered around salt-elimination reactions using $Li\{B(NArCH)_2\}(THF)_2$, drawing on analogies with the above-mentioned gallyl systems $(L)Ln\{Ga(NArCH)_2\}$,[8b,d,e] and rare-earth alkyl and amide chemistry in general. Unfortunately, reactions with a range of metal halide compounds, including $ScI_3(THF)_3$, $YCl_3(THF)_{3.5}$, $CpYCl_2(THF)_3$, and Cp_2YCl, and various amides gave only mixtures. Gratifyingly, however, reaction of the $[BPh_4]^-$ salts of the preformed dialkyl cations $[Ln(CH_2SiMe_3)_2(THF)_n]^+$ (**1_Ln**$^+$; Ln = Sc, Lu, n = 3; Ln = Y, n = 4)[9] in THF at −40 °C led to the formation of the boryl complexes $Sc\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)$ (**2**) and $Ln\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)_2$ [Ln = Y (**3_Y**), Lu (**3_Lu**)] in good isolated yields [Scheme 1; see the Supporting Information (SI) for further details].

The solid-state structures of **2** and **3_Ln** are discussed below. The NMR spectra are consistent with these, showing resonances assigned to coordinated boryl, alkyl, and THF ligands. Notably, the $^{11}B\{^1H\}$ spectra in C_6D_6 show characteristic downfield-shifted resonances at 38, 45, and 62 ppm for **2**, **3_Y**, and **3_Lu**, respectively.[10] These ^{11}B shifts can be compared with values of 45, 38, and 70 ppm for $Li\{B(NArCH)_2\}(THF)_2$,[2b] $Ti\{B(NArCH)_2\}(O^iPr)_3$, and $Cp^*Hf\{B(NArCH)_2\}(CH_2Ph)_2$ (also in C_6D_6).[4a] When followed on the NMR-tube scale in THF-d_8 at −40 °C, the reactions with **1_Sc** and **1_Lu** were complete within 9 h, whereas that for **2_Y** required ~2 h.

The solid-state molecular structures of **2** and **3_Lu** are shown in Figure 1, and that of **3_Y** is given in Figure S1 in the SI. Selected distances and angles are listed in Table 1. The structures confirm that **2** and **3_Ln** are rare-earth mixed boryl−dialkyl compounds. Compound **2** is approximately tetrahedral at Sc(1), and the overall geometry is analogous to that of $Ti\{B(NArCH)_2\}(O^iPr)_3$.[4a] The larger metals yttrium and lutetium coordinate two THF ligands, and their coordination geometries vary between distorted trigonal-bipyramidal (axial THFs) in **3_Y** and square-pyramidal (axial boryl) in

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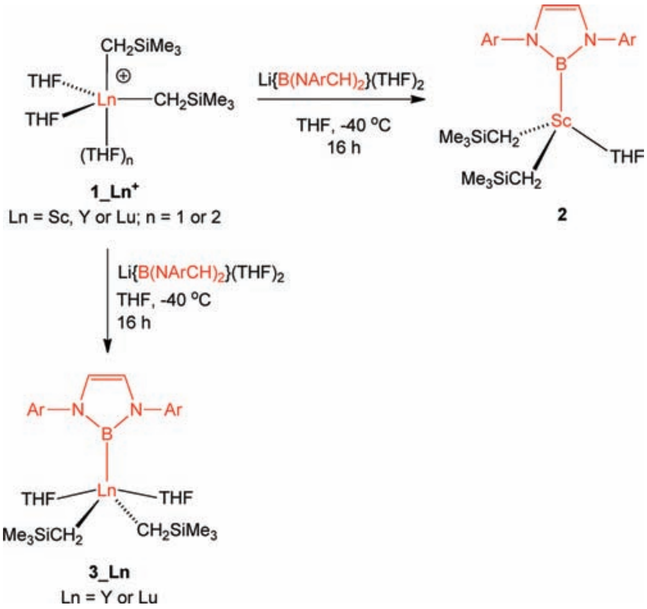
Scheme 1. Synthesis of $Sc\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)$ (2) and $Ln\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)_2$ [Ln = Y (3_Y), Lu (3_Lu)][a]



[a] $[BPh_4]^-$ anion and $Li[BPh_4]$ side products have been omitted for clarity. Ar = 2,6-$C_6H_3{}^iPr_2$.

3_Lu. Both geometries find precedent in the chemistry of five-coordinate d-block boryl systems.[11] The Ln−O and Ln−CH_2 distances are within the expected ranges and are comparable, for example, to those in the corresponding homoleptic tris(alkyl) compounds $Ln(CH_2SiMe_3)_3(THF)_n$ (n = 2, 3),[12] taking into account differing coordination numbers as appropriate. As expected,[13] all of the metal−ligand bond distances follow the periodic trend Sc−X < Y−X > Lu−X.

The main point of interest in regard to **2** and **3_Ln** is the length of the Ln−B bonds. The Sc−B distance of 2.422(2) Å is substantially longer than the Ti−B and Mg−B distances of 2.258(2) and 2.281(6) Å, respectively, in four-coordinate $Ti\{B(NArCH)_2\}(O^iPr)_3$ and $Mg\{B(NArCH)_2\}Br(THF)_2$.[3b,4a] The Y−B distance of 2.696(4) Å is shorter than the Y−Ga separation of 3.1757(4) Å in the yttrium gallyl $Y\{Ga(NArCH)_2\}\{C(PPh_2NSiMe_3)_2\}(THF)_2$, a complex described as containing a "highly polarized" covalent bond;[8d] the difference in bond lengths can almost entirely be accounted for by the variation between the respective covalent radii [0.84(3) and 1.22(3) Å for B and Ga, respectively].[14] The Ln−B distances for all three boryl compounds are comparable with the sums of the respective covalent radii [2.54(10), 2.74(10), and 2.71(11) Å for Sc−B, Y−B, and Lu−B, respectively], consistent with an appreciable covalent contribution to the metal−ligand bond.[14]

Comparisons can also be made with Ln−phenyl and Ln−*N*-heterocyclic carbene (NHC) bonds, for which a range of data are available.[7a,c,12,15] All of the Ln−B distances are longer than the distances for these anionic and neutral C(sp^2) donors. For example, the average Sc−C_{Ph}, Y−C_{Ph}, and Lu−C_{Ph} distances reported in the literature[12] are 2.245, 2.457, and 2.408 Å, respectively; the corresponding Ln−C_{NHC} distances are 0.05−0.10 Å longer than these but still significantly shorter than the Ln−B separations in the present compounds.

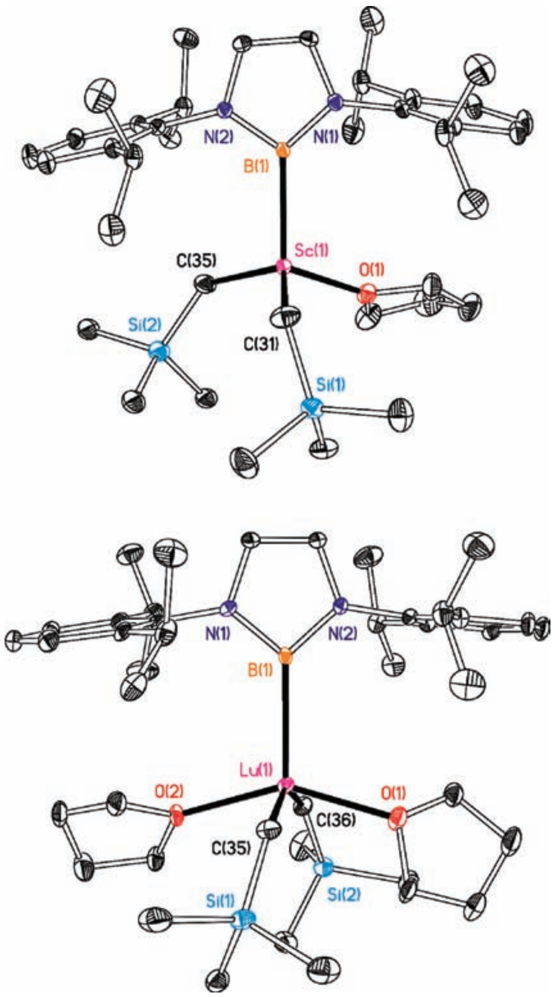


Figure 1. Displacement ellipsoid plots (20% probability) for (top) $Sc\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)$ (**2**) and (bottom) $Lu\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)_2$ (**3_Lu**). H atoms and minor disorder components have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $Sc\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)$ (2) and $Ln\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)_2$ [Ln = Y (3_Y), Lu (3_Lu)]

	Sc	Y	Lu
Ln−B	2.422(2)	2.696(4)	2.555(8)
Ln−C	2.171(3)	2.424(4)	2.354(7)
	2.174(2)	2.394(6)	2.352(8)
Ln−O	2.118(2)	2.350(3)	2.316(6)
	−	2.370(3)	2.314(5)
B−N	1.458(3)	1.456(6)	1.490(9)
	1.454(3)	1.467(5)	1.487(9)
B−Ln−C	105.2(1)	114.3(2)	104.5(3)
	106.3(1)	109.8(2)	106.3(3)
B−Ln−O	111.5(1)	93.9(1)	105.3(2)
	−	106.3(1)	105.9(2)

Scalar relativistic, gradient-corrected density functional theory was employed to study **2**, **3_Y**, and **3_Lu**, and selected results are collected in Table 2. The agreement with experiment for r(Ln−B) is generally good, although r(Lu−B) is overestimated by 0.078 Å. The calculations suggest, however, that caution should be employed when analyzing the r(Ln−B) distances, as

Table 2. **Selected Computational Results for 2, 3_Y, and 3_Lu (Energies in kJ mol^{-1}, AIM Data Obtained at the Ln−B Bond Critical Point)**

	2	3_Y	3_Lu
r(Ln−B) (Å)	2.458	2.692	2.633
Ln−B interaction energy	−346.6	−359.4	−375.1
pre-relaxation ("steric") energy	316.4	352.2	386.0
orbital energy	−663.0	−711.6	−761.2
ρ (electron density)	0.052	0.046	0.050
$\nabla^2\rho$ (electron density Laplacian)	−0.020	0.040	0.050
H (energy density)	−0.012	−0.009	−0.011
Δq (Hirshfeld charge difference, Ln−boryl group)	0.69	0.82	0.82
normalized Ln/B Mulliken contributions to HOMO (%)	38/62	30/70	34/66

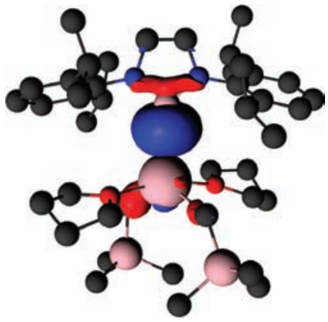


Figure 2. Three-dimensional representation of the highest occupied molecular orbital of **3_Y**. H atoms have been omitted for clarity.

for all three compounds, alteration of r(Ln−B) by ±0.05 Å from equilibrium changes the Ln−B interaction energy by no more than 1 kJ mol^{-1}. The Ln−B interaction energies increase steadily from Sc to Lu, and the Ziegler−Rauk breakdown indicates that this occurs because the increase in the favorable orbital term outweighs that in the unfavorable pre-relaxation ("steric") term. However, the orbital term can involve electron-pair, charge-transfer, and/or donor−acceptor interactions.[16] Therefore, the ionic/covalent nature of the Ln−B bond could not readily be inferred from the orbital term, so we turned to other analysis tools to probe the bonding further.

Atoms-in-molecules (AIM) data for the Ln−B bond critical points are given in Table 2. The electron density ρ, its Laplacian $\nabla^2\rho$, and the energy density H all indicate that the Ln−B bond is predominantly ionic,[17] a conclusion supported by the significant Hirshfeld charge difference between the Ln atom and the boryl fragment. Both the AIM data and the Hirshfeld Δq values suggest that **2** contains the least ionic Ln−B bond and **3_Y** the most ionic one (p is largest at the Sc−B bond critical point, while $\nabla^2\rho$ and H are the most negative). Analysis of the Kohn−Sham orbital structure indicates that the HOMO of each system is a Ln−B σ-bonding orbital and that it is the only orbital to display any significant mixing of metal and boron, the latter being much the larger contributor (Table 2). The HOMO of **3_Y** is shown in Figure 2. In agreement with the AIM/Hirshfeld data, metal/boron mixing in the HOMO after normalization (i.e., after neglect of contributions from all atoms except Ln and boron) is largest for **2**. These calculations therefore show that the Ln−B bonding in **2** and **3_Ln** is largely ionic, albeit with a (highly polarized) covalent contribution to the interaction. It is notable that the sum of the first three ionization energies for Sc, Y, and Lu are 4255, 3755, and 3886 kJ mol^{-1}, respectively, indicating that the most ionic Ln−B bond is formed by the metal whose three valence electrons are easiest to remove.[18]

In conclusion, we have prepared the first group 3 and lanthanide complexes of a σ-bound boryl ligand. The Ln−B bonding in these complexes is mainly ionic, with a covalent component concentrated in the HOMO. The "charge-neutralization" synthetic approach to these complexes should be widely applicable, especially given the large number of cationic organometallic rare-earth complexes now known.[7b] We are currently developing the range of boryl complexes of these metals and the reaction chemistry of the hitherto unexplored Ln−B bond.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthesis details and characterization data for **2**, **3_Y**, and **3_Lu**; displacement ellipsoid plot for **3_Y**; crystallographic data (CIF); and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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