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ARTICLE TYPE

# Half-Sandwich Scandium Boryl Complexes Bearing a Silylene-Linked Cyclopentadienyl–Amido Ligand

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A boryl scandium complex supported by the silylene-linked cyclopentadienyl–amido ligand was synthesized for the first time, which on reaction with nitric oxide (NO) afforded a novel scandium boryldiazoniumdiolate [ON(boryl)NO] complex.

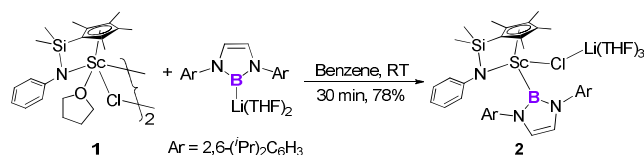
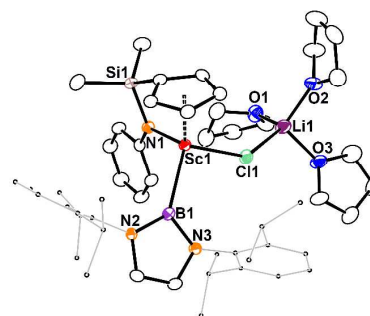
Boryl complexes of main group and d-block transition metals have been extensively studied over the past two decades.<sup>1–3</sup> In contrast, analogous rare-earth (group 3 and lanthanide) boryl compounds have remained scarce,<sup>4</sup> because the synthetic routes reported for other metal complexes are in most cases not suitable for the synthesis of rare-earth boryl compounds. The first rare-earth boryl compounds were reported in 2011, which were prepared by the use of rare-earth dialkyl ion-pair complexes as starting materials to react with a lithium boryl compound.<sup>4</sup> This reaction is the only successful route reported so far for the synthesis of rare-earth boryl compounds, and the resulting mixed dialkyl/boryl ligand combination remained to date the only structure pattern known for the rare-earth boryl complexes.<sup>4,5</sup>

Cyclopentadienyl (Cp) groups are the most widely used supporting ligands for rare-earth complexes, including highly reactive alkyls and hydrides.<sup>6</sup> The synthesis of rare-earth boryl complexes with Cp ligands is therefore of remarkable interest and importance. However, previous attempts to synthesize the boryl rare-earth complex bearing a Cp ligand were not successful.<sup>4</sup> Here we report a half-sandwich scandium boryl complex bearing a silylene-linked Cp–amido ligand, which represents the first example of a Cp-ligated rare-earth boryl complex.

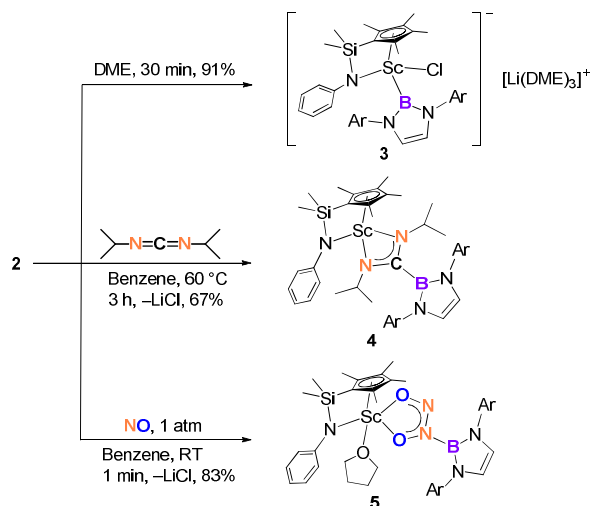
In the course of our studies on half-sandwich rare-earth alkyl and hydride complexes,<sup>7,8</sup> we became interested in the analogous boryl compounds. Our initial attempts to synthesize a half-sandwich Sc boryl compound by the metathetical reaction of [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>t</sup>Bu)ScCl(THF)]<sup>9</sup> with [Li{B(N(Ar)CH)<sub>2</sub>}(THF)<sub>2</sub>] (Ar = 2,6-(<sup>i</sup>Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sup>2a,2e</sup> did not give an isolable product, similar to previous attempts using other rare-earth metal halide precursors.<sup>4a</sup> To our delight, when [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(NPh)Sc(μ-Cl)(THF)<sub>2</sub>] (**1**)<sup>10</sup> was employed to react with the lithium boryl compound [Li{B(N(Ar)CH)<sub>2</sub>}(THF)<sub>2</sub>], the corresponding half-sandwich boryl scandium complex **2** was obtained as a crystalline product in 78% yield (Scheme 1). Single crystals suitable for X-ray diffraction studies were obtained by recrystallization from hexane. It was revealed that **2** is a LiCl(THF)<sub>3</sub> adduct of the half-sandwich scandium boryl species

[Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(NPh)Sc{B(N(Ar)CH)<sub>2</sub>}], in which the Sc atom is bonded to one Cp–amido ligand, one boryl group and one chloride (Figure 1). The bond length of the Sc–B bond in **2** (2.529(4) Å) is about 0.1 Å longer than that found in Sc{B[N(Ar)CH]<sub>2</sub>}(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) (2.422(2) Å,<sup>4a</sup> 2.433(12) Å<sup>4b</sup>), probably because of the steric hindrance of the Cp–amido ligand and the higher coordination number around the Sc atom in **2**.

Complex **2** showed well resolved <sup>1</sup>H and <sup>13</sup>C NMR spectra in C<sub>6</sub>D<sub>6</sub>. The two Me groups in the SiMe<sub>2</sub> unit showed two singlets (δ 0.67 and 0.80), and the four Me groups in the C<sub>5</sub>Me<sub>4</sub> moiety exhibited four singlet peaks (δ 1.71, 2.03, 2.14, 2.53) in the <sup>1</sup>H NMR spectrum, in agreement with the solid structure (C<sub>1</sub> symmetry) of **2**. The <sup>11</sup>B NMR spectrum of **2** showed a broad signal at δ 38.8, which is comparable with that found in Sc{B[N(Ar)CH]<sub>2</sub>}(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) (δ 38,<sup>4a</sup> 35.5<sup>4b</sup>).

Scheme 1 Synthesis of a half-sandwich scandium boryl complex **2**

**Figure 1.** ORTEP drawing of **2** with thermal ellipsoids at the 30% level except for the 2,6-(<sup>i</sup>Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> groups in the boryl unit. Hydrogen atoms and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å): Sc1–B1 2.529(4), Sc1–N1 2.125(3), B1–N2 1.473(5), B1–N3 1.477(4), Sc1–Cl1 2.463(1), Sc1–centroid of Cp 2.186, Li1–Cl1 2.384(6).

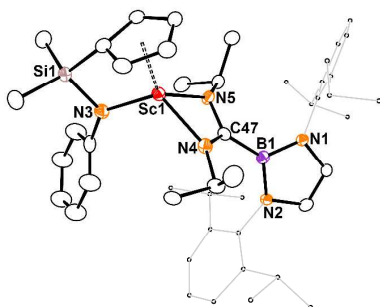


**Scheme 2.** Reactions of the scandium boryl complex **2**

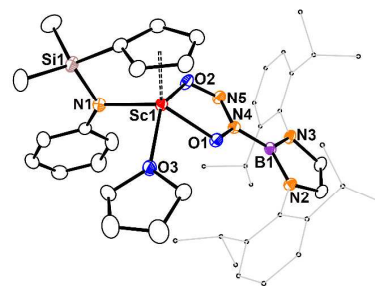
Treatment of **2** with 1,2-dimethoxyethane (DME) yielded a separated ion-pair complex,  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NPh})\text{Sc}\{\text{B}(\text{N}(\text{Ar})\text{CH}_2)_2\}\text{Cl}][\text{Li}(\text{DME})_3]$ , in which the Li ion is bonded to three DME molecules, while the Sc moiety adopts a similar structure to that of **2** (Scheme 2; see ESI). The bond lengths of the Sc–B (2.499(5) Å) and Sc–Cl (2.403(1) Å) bonds in **3** are slightly shorter than those in **2** (2.529(4) Å and 2.463(1) Å, respectively), probably because of the separation of Cl and Li in **3**. The  $^{11}\text{B}$  NMR chemical shift of **3** ( $\delta$  38.7) is almost the same as that of **2**.

The reaction of **2** with *N,N'*-diisopropylcarbodiimide gave the LiCl-free amidinate complex **4** through nucleophilic addition of the boryl group to the central carbon atom of the carbodiimide (Scheme 2 and Figure 2), similar to what was observed previously.<sup>4b</sup>

When **2** was exposed to nitric oxide (NO) (1 atm) at room temperature in benzene, a boryldiazoniumdiolate complex **5** was obtained as orange crystals in 83% yield (Scheme 2). This reaction might proceed by insertion of NO into the Sc–B bond in **2** followed by coupling of the resulting [ON(boryl)] radical anion species with a second molecule of NO.<sup>11</sup> Although a large number of metal boryl compounds have been reported, this is the first example of insertion of an NO molecule into the M–B bond of any metal, as far as we are aware.<sup>12</sup>



**Figure 2.** ORTEP drawing of **4** with thermal ellipsoids at the 30% probability except for the 2,6-(Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> groups in the boryl unit. Hydrogen atoms and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å): B1–C47 1.617(6), Sc1–N3 2.078(4), Sc1–N4 2.154(3), Sc1–N5 2.141(3), B1–N1 1.435(5), B1–N2 1.439(6).



**Figure 3.** ORTEP drawing of **5** with thermal ellipsoids at the 30% probability except for the 2,6-(Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> groups in the boryl unit. Hydrogen atoms and the Me groups on the Cp ring have been omitted. Selected bond lengths (Å): Sc1–N1 2.113(2), Sc1–O1 2.124(2), Sc1–O2 2.154(2), Sc1–O3 2.198(2), N4–O1 1.337(2), N5–O2 1.294(2), N4–N5 1.287(2), B1–N4 1.485(3), B1–N2 1.409(3), B1–N3 1.418(3).

An X-ray diffraction study revealed that the boryldiazoniumdiolate unit in **5** is bonded to the Sc atom in a chelate fashion (Figure 3), similar to the allyldiazoniumdiolate yttrium complex  $(\text{C}_5\text{Me}_5)_2\text{Y}[\text{ONN}(\text{CH}_2\text{CH}=\text{CH}_2)\text{O}-\kappa^2\text{O},\text{O}']$ .<sup>11a</sup> The Sc1–O1 (2.124(2) Å) bond is significantly shorter than the Sc1–O2 bond (2.154(2) Å) in **5**, while the N4–O1 bond (1.337(2) Å) is longer than the N5–O2 bond (1.294(2) Å). The difference in bond length between the two N–O bonds in **5** (0.043 Å) is larger than that in  $(\text{C}_5\text{Me}_5)_2\text{Y}[\text{ONN}(\text{CH}_2\text{CH}=\text{CH}_2)\text{O}-\kappa^2\text{O},\text{O}']$  (0.019 Å),<sup>11a</sup> while the N–N bond length in **5** (1.287(2) Å) is comparable with that in  $(\text{C}_5\text{Me}_5)_2\text{Y}[\text{ONN}(\text{CH}_2\text{CH}=\text{CH}_2)\text{O}-\kappa^2\text{O},\text{O}']$  (1.281(2) Å).<sup>11a</sup> These data suggest that the negative charge of the boryldiazoniumdiolate unit in **5** is to some extent localized to the O1 atom; i.e., the N4–O1 bond is more like an N–O single bond, while the N5–O2 bond is closer to an N–O double bond. The bond distance of the B1–N4 bond (1.485(3) Å) in **5**, which is formed by the reaction of the Sc–boryl unit in **2** with NO, is somewhat longer than those of the B1–N2 (1.409(3) Å) and B1–N3 (1.418(3) Å) bonds, and could be viewed as a B–N single bond. Complex **5** represents the first example of a well-defined boryldiazoniumdiolate complex of any metal, as far as we are aware.

In summary, we have successfully synthesised a half-sandwich scandium boryl complex bearing a silylene-linked Cp–amido ligand by the metathetical reaction between the scandium chloride precursor and a lithium boryl compound, thus constituting the first example of a structurally characterized Cp-ligated rare-earth boryl complex. The reaction of the scandium boryl complex **2** with NO afforded a boryldiazoniumdiolate complex **5**, which represents the first example of a boryldiazoniumdiolate compound. Studies on the synthesis and reactivity of other Cp-supported rare-earth boryl complexes are in progress.

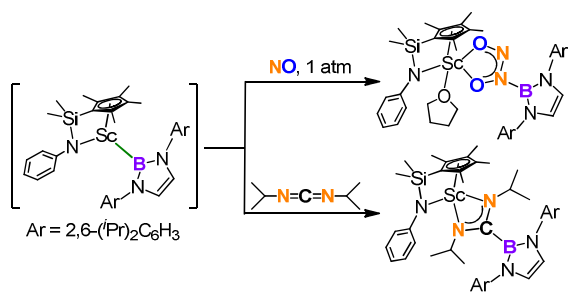
We are grateful to Mrs Akiko Karube for micro elemental analyses. Financial support by Grant-in-Aid for Scientific Research (B) (No. 24350030) and (S) (No. 21225004) from JSPS is gratefully acknowledged.

## Notes and references

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- † Electronic Supplementary Information (ESI) available: Synthesis and characterization of compounds **1**, **3**, and **4**, ORTEP drawing. CCDC 981558 (**1**), 981559 (**2**), 988055 (**3**), 981560 (**4**) and 981564 (**5**) contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/
- †† Syntheses and characterization data. Synthesis of **2**. A hexane (5 mL) solution of boryl lithium (0.526 g, 0.98 mmol) was added dropwise to a benzene solution of dimeric **1** (0.412 g, 0.49 mmol) at room temperature and the mixture was stirred for 30 min. After solvent removal under reduced pressure, the residue was extracted with hexane and the resulting suspension was filtered to remove the inorganic salts. The filtrate was further concentrated and crystallized at  $-30^{\circ}\text{C}$  to give **2** as colorless crystals (0.732 g, 78%).  $\delta_{\text{H}}$  (400 MHz;  $\text{C}_6\text{D}_6$ ;  $\text{Me}_4\text{Si}$ ) 0.67, 0.80 (6H, s,  $\text{Si}(\text{Me})_2$ ), 1.16–1.28 (12H, m,  $\text{CH}(\text{Me})_2$ ), 1.25–1.28 (12H, m, THF), 1.39 (6H, d, 6.4 Hz,  $\text{CH}(\text{Me})_2$ ), 1.59 (6H, d, 6.8 Hz,  $\text{CH}(\text{Me})_2$ ), 1.71, 2.03, 2.14, 2.53 (12H, s,  $\text{Cp}(\text{Me})_4$ ), 3.17–3.21 (12H, m, THF), 3.57 (2H, sep, 6.8 Hz,  $\text{CH}(\text{Me})_2$ ), 3.87 (2H, sep, 6.6 Hz,  $\text{CH}(\text{Me})_2$ ), 6.30 (2H, s,  $\text{N}-\text{CH}=\text{CH}-\text{N}$ ), 6.68 (1H, t, 7.1 Hz, Aryl), 7.10–7.29 (10H, m, Aryl).  $\delta_{\text{C}}$  (100 MHz;  $\text{C}_6\text{D}_6$ ;  $\delta\text{C}_6\text{D}_6 = 128.06$ ) 4.0, 4.9 (2C, s,  $\text{Si}(\text{Me})_2$ ), 12.3, 13.3, 13.8, 15.5 (4C, s,  $\text{Cp}(\text{Me})_4$ ), 22.5, 24.5, 25.0 (6C, s,  $\text{CH}(\text{Me})_2$ ), 25.4 (6C, s, THF), 27.7 (2C, s,  $\text{CH}(\text{Me})_2$ ), 28.1, 29.7 (4C, s,  $\text{CH}(\text{Me})_2$ ), 68.2 (6C, s, THF), 120.6 (2C, s,  $\text{N}-\text{CH}=\text{CH}-\text{N}$ ), 106.8, 116.6, 119.7, 122.7, 123.6, 125.7, 125.8, 126.5, 129.5, 130.7, 146.2, 146.4, 146.8, 155.1 (aromatic and Cp ring carbons).  $\delta_{\text{B}}$  (160 MHz;  $\text{C}_6\text{D}_6$ ) 37.0 (br s). Found: C 69.07; H 8.46; N 4.60. Calc. for  $\text{C}_{55}\text{H}_{83}\text{BCIN}_3\text{O}_3\text{ScSi}$ : C 68.77; H 8.71; N 4.37. Synthesis of **5**. A benzene solution (5 mL) of **2** (0.351 g, 0.365 mmol) in a 20-mL Schlenk tube was frozen in liquid nitrogen, evacuated under vacuum and then backfilled with nitric oxide (1 atm). The reaction solution was warmed to room temperature and stirred for 1 min. Then NO and solvent was removed under reduced pressure, and the residue was extracted with hexane. Orange crystals of **5** (0.253 g, 83%) were grown from a concentrated hexane solution at  $-30^{\circ}\text{C}$ .  $\delta_{\text{H}}$  (400 MHz;  $\text{C}_6\text{D}_6$ ;  $\text{Me}_4\text{Si}$ ):  $\delta$  0.83, 0.89 (6H, s,  $\text{Si}(\text{Me})_2$ ), 0.97 (4H, br s, THF), 1.16–1.32 (24H, m,  $\text{CH}(\text{Me})_2$ ), 1.74 (3H, s,  $\text{Cp}(\text{Me})_4$ ), 1.89 (6H, s,  $\text{Cp}(\text{Me})_4$ ), 2.08 (3H, s,  $\text{Cp}(\text{Me})_4$ ), 3.08, 3.18 (4H, sep, 6.8 Hz,  $\text{CH}(\text{Me})_2$ ), 3.18–3.37 (4H, m, THF), 5.98 (2H, s,  $\text{N}-\text{CH}=\text{CH}-\text{N}$ ), 6.55–6.57 (2H, m, Aryl), 6.75 (1H, t, 7.1 Hz, Aryl), 7.05–7.19 (8H, m, Aryl).  $\delta_{\text{C}}$  (100 MHz;  $\text{C}_6\text{D}_6$ ;  $\delta\text{C}_6\text{D}_6 = 128.06$ ) 3.5, 5.3 (2C, s,  $\text{Si}(\text{Me})_2$ ), 11.1, 11.5 (2C, s,  $\text{Cp}(\text{Me})_4$ ), 14.1, (2C, s,  $\text{Cp}(\text{Me})_4$ ), 23.5, 24.1, 24.6, 24.7 (8C, s,  $\text{CH}(\text{Me})_2$ ), 25.2 (2C, s, THF), 28.9, 29.1 (2C, s,  $\text{CH}(\text{Me})_2$ ), 71.7 (2C, s, THF), 120.1 (2C, s,  $\text{N}-\text{CH}=\text{CH}-\text{N}$ ), 107.6, 115.7, 120.0, 123.4, 124.1, 126.1, 127.4, 129.1, 137.9, 145.2, 146.4, 155.7 (aromatic and Cp ring carbons).  $\delta_{\text{B}}$  (160 MHz;  $\text{C}_6\text{D}_6$ ) 18.8 (br s). Found: C 67.43; H 7.90; N 8.10. Calcd. for  $\text{C}_{47}\text{H}_{67}\text{BN}_3\text{O}_3\text{ScSi}$ : C 67.69; H 8.10; N 8.40.
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A boryl scandium complex supported by the silylene-linked cyclopentadienyl-amido ligand was synthesized for the first time.