VIP Boryl Complexes

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Rare Earth Metal Boryl Complexes: Synthesis, Structure, and Insertion of a Carbodiimide and Carbon Monoxide**

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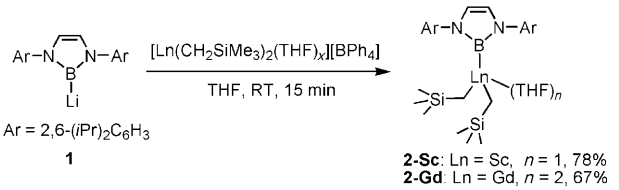
The chemistry of transition metal complexes bearing boryl ligands (R_2B^-) has fascinated scientists in organometallic and synthetic chemistry over the past two decades, because of their important roles in functionalization of organic substrates by borylation processes and their interesting chemistry in their own right.[1–5] Since transition metal boryl complexes were first postulated in 1963[2a] and structurally characterized in 1990,[2b,c] numerous metal boryl complexes have been reported. However, most research in this area has focused on complexes of late and middle transition metals.[1,2] In contrast, early transition metal complexes bearing boryl ligands have been much less extensively studied, because of difficulties in synthesis.[3,4] In particular, a Group 3 or f-block metal boryl complex has not been reported previously, as far as we are aware.[6]

For many years, we have been pursuing the fundamental chemistry and synthetic applications of rare earth metal complexes ligated by various electron-rich donor ligands containing C, N, O, P, and so on.[7,8] We were intrigued by the electron-deficient nature of boryl moieties,[1,5] which motivated us to explore the chemistry of rare earth metal complexes bearing boryl ligands. Herein, we report the synthesis, structure, and some reactions of the first rare earth metal boryl complexes.

Our initial attempt to obtain a rare earth boryl complex through deprotonation[7,8] of a hydroborane compound with rare earth trialkyl complexes $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Sc, Gd) was not successful because of the weak acidity of the B–H group. We then treated boryl lithium compound **1**, which was reported previously by Nozaki, Yamashita, and coworkers,[5] with rare earth metal alkyl ion-pair complexes $[Ln(CH_2SiMe_3)_2(THF)_x][BPh_4]$, reported by Okuda et al.[8k,9] Reaction of $[Sc(CH_2SiMe_3)_2(THF)_3][BPh_4]$ with 1 equiv of **1** in THF proceeded smoothly at room temperature to afford corresponding boryl-ligated scandium dialkyl complex **2-Sc** in 78% yield as deep purple crystals after recrystallization from hexane (Scheme 1). In a similar manner, gadolinium boryl complex **2-Gd** was obtained in 67% yield as pale yellow crystals.



Scheme 1. Synthesis of rare earth metal boryl dialkyl complexes.

Diamagnetic Sc complex **2-Sc** showed well-resolved ^1H and ^{13}C NMR spectra in [D$_8$]toluene, while paramagnetic Gd complex **2-Gd** did not give informative ^1H or ^{13}C NMR signals. The resonances of the methylene and methyl groups of the CH_2SiMe_3 units in **2-Sc** overlapped around $\delta =$ 0.12 ppm in the ^1H NMR spectrum, but showed distinct singlets at $\delta = 59.4$ and 3.6 ppm, respectively, in the ^{13}C NMR spectrum. The methyl protons of the isopropyl groups of the boryl ligand appeared as two doublets ($^3J_{H,H} = 6.9$ Hz) at $\delta =$ 1.24 and 1.40 ppm, and the methine protons gave one septet at $\delta = 3.52$ ppm ($^3J_{H,H} = 6.9$ Hz) in the ^1H NMR spectrum, suggesting that rotations around the N–Ar and *i*Pr–Ar bonds in the boryl ligand are restricted. The vinyl protons in the diazaborole ring showed a singlet at $\delta = 6.25$ ppm. The ^{11}B NMR spectra of **2-Sc** and **2-Gd** showed broad signals at $\delta = 35.5$ ppm and 29.2 ppm, respectively, which are shifted to high field compared to lithium boryl compound **1** ($\delta =$ 45.4 ppm),[5a,d] and are in sharp contrast with those found in scandium borohydride complexes such as $[(C_5Me_4\text{-}C_6H_4\text{-}o\text{-}NMe_2)Sc(BH_4)_2]$ ($\delta = -19.7$ ppm)[10a] and $[(C_5H_5)_2Sc(BH_4)]$ ($\delta = -17.7$ ppm).[10b] The ^{11}B NMR signal of scandium boryl complex **2-Sc** is close to that of the titanium boryl complex $[(L)Ti(OiPr)_3]$ ($L = C_{26}H_{36}N_2B$; $\delta = 38.2$ ppm).[4a]

An X-ray diffraction study revealed that the Sc atom in **2-Sc** is coordinated by one boryl, two alkyl, and one THF ligands in a distorted tetrahedral fashion (Figure 1, left). In contrast, the Gd atom in **2-Gd** is bonded to one boryl, two alkyl, and two THF ligands in a slightly distorted square-based pyramidal geometry, in which the boron atom B1 occupies the apex position and the oxygen atoms (O1, O2) of the two THF ligands and the methylene carbon atoms (C1, C2) of the two CH_2SiMe_3 groups form the square-based plane (Figure 1, right). That the gadolinium complex **2-Gd** bears an additional THF ligand compared to **2-Sc** is apparently due to its larger ionic radius. No rare earth metal–boron σ-bond lengths are available for comparison in the literature, but the Sc–B bond length in **2-Sc** (2.433(12) Å) is comparable to the Gd–B bond length in **2-Gd** (2.699(4) Å), when the difference

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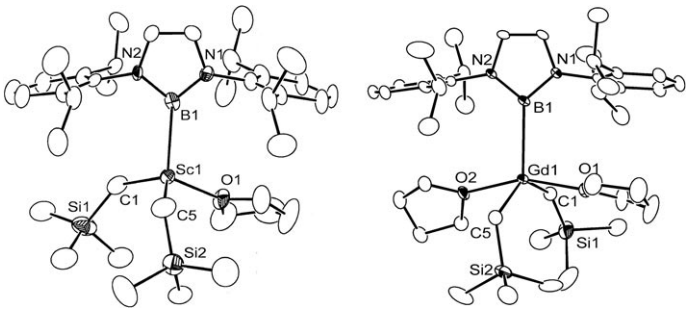
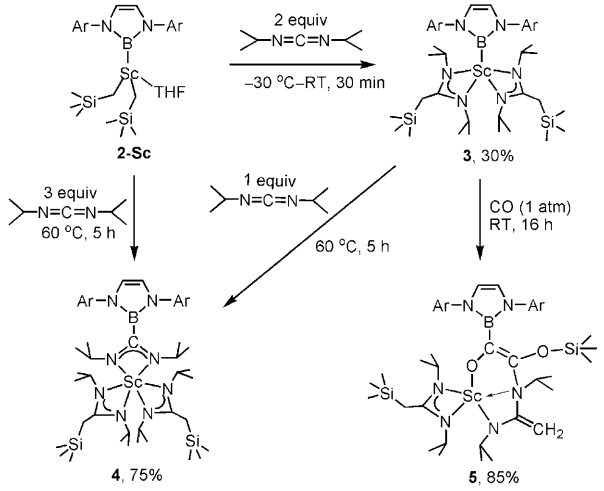


Figure 1. ORTEP diagrams of **2-Sc** (left) and **2-Gd** (right) with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: **2-Sc**: Sc1–B1 2.433(12), Sc1–O1 2.116(6), Sc1–C1 2.151(10), Sc1–C5 2.170(11). **2-Gd**: Gd1–B1 2.699(4), Gd1–O1 2.386(3), Gd1–O2 2.399(3), Gd1–C1 2.423(5), Gd1–C5 2.446(5).

in ionic radii between Sc and Gd and the difference in coordination numbers between **2-Sc** and **2-Gd** are taken into account.[11] These Ln–B bond lengths in **2-Sc** and **2-Gd** are respectively much shorter than the sum of the covalent radii (Sc–B: 2.54 Å, Gd–B: 2.80 Å)[12] and much longer than the Ln···B interatomic distances in the borohydride complexes (Sc···B: 2.341 Å,[10a] Gd···B: 2.587 Å[10c]). The Ln–C bond lengths in **2-Sc** (av 2.161 Å) and **2-Gd** (av 2.435 Å) are comparable with the corresponding Ln–CH_2SiMe_3 bond lengths in related complexes.[8,13]

The reaction of **2-Sc** with 2 equiv of *N*,*N*′-diisopropylcarbodiimide in [D_8]toluene at room temperature took place rapidly, and the starting materials disappeared within 30 min, as monitored by ^{1}H NMR. Bis(amidinate)-ligated boryl complex **3**, formed through carbodiimide insertion into the two Sc–CH_2SiMe_3 bonds in **2-Sc**,[7d,e,8c,g–i] was isolated as a pale yellow microcrystalline solid in 30% yield from a concentrated solution of the reaction mixture in THF/hexane. A certain amount of tris(amidinate) complex **4**, formed by carbodiimide insertion into both Sc–C bonds and the Sc–B bond, was also observed in the mother liquor. When 3 equiv of *N*,*N*′-diisopropylcarbodiimide reacted with **2-Sc**, complex **4** was obtained in 75% yield as pale yellow crystals. Alternatively, addition of 1 equiv of the carbodiimide compound to a solution of **3** in C_6D_6 gave **4** quantitatively in 5 h, as monitored by ^{1}H NMR spectroscopy (Scheme 2).



Scheme 2. Reactions of scandium boryl complexes with carbodiimide and carbon monoxide.

An X-ray crystallographic study revealed that **3** adopts a distorted pyramidal geometry around the scandium center, with the B1 atom occupying the apex and the four nitrogen atoms N3–N6 residing in the basal plane (Figure 2). The Sc–B bond length in **3** (2.508(3) Å) is about 0.075 Å longer than that in **2-Sc**, and reflects increasing steric encumbrance around the metal center in **3**. The ^{1}H NMR spectrum of **3** in C_6D_6 showed a sharp singlet at $\delta = 1.94$ ppm assignable to the methylene protons of the CH_2SiMe_3 groups in the amidinate units. The ^{11}B NMR spectrum of **3** in C_6D_6 showed a broad peak at $\delta = 36.3$ ppm, which is close to that of **2-Sc**.

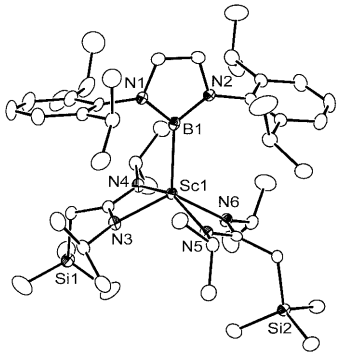


Figure 2. ORTEP diagram of **3** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Sc1–B1 2.508(3), Sc1–N3 2.147(2), Sc1–N4 2.206(2), Sc1–N5 2.196(2), Sc1–N6 2.154(2).

The X-ray structure of **4** is shown in Figure 3. The Sc atom is bonded to six N atoms in a distorted octahedral fashion. The Sc–N bond lengths in **4** (av 2.221 Å) are slightly longer than those in **3** (av 2.176 Å). The ^{11}B NMR signal of **4** in C_6D_6 appeared at $\delta = 22.2$ ppm, which is shifted to higher field compared with those of **2-Sc** and **3** owing to transfer of the boryl ligand from the metal center to the carbodiimide moiety.[5a,d]

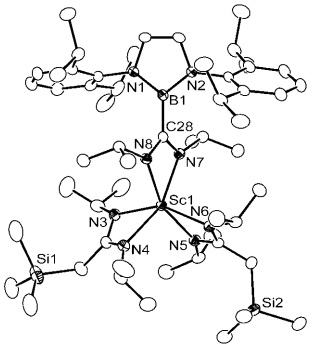


Figure 3. ORTEP diagram of **4** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: B1–C28 1.619(4), Sc1–N3 2.213(2), Sc1–N4 2.224(2), Sc1–N5 2.221(2), Sc1–N6 2.220(2), Sc1–N7 2.237(2), Sc1–N8 2.210(2).

When a solution of **3** in benzene was stirred under an atmosphere of CO at room temperature for 16 h, complex **5** was obtained as a pale yellow crystalline solid in 85% yield (Scheme 2).[14] An X-ray diffraction study established that **5** contains a *trans*-O–C(B)=C(N)–O moiety with one oxygen atom bonded to the scandium atom and the other to an $SiMe_3$ group (Figure 4). One of the two carbon atoms is bonded to a

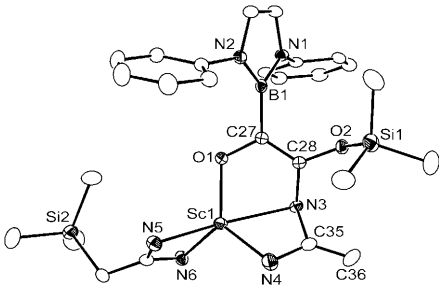


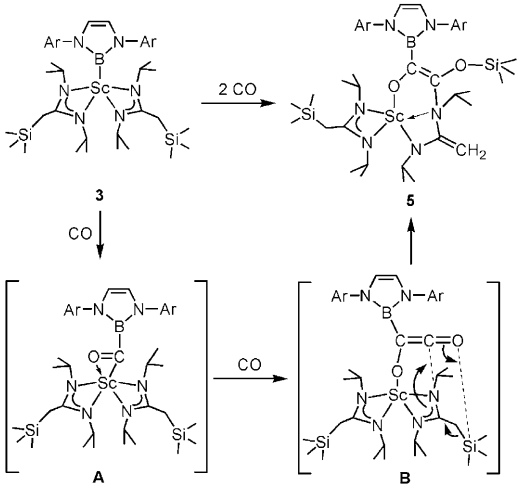
Figure 4. ORTEP diagram of **5** with thermal ellipsoids at 30% probability. The isopropyl groups of the boryl and amidinate ligands and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Sc1–O1 1.961(1), Sc1–N3 2.383(2), Sc1–N4 2.081(2), Sc1–N5 2.143(2), Sc1–N6 2.153(2), B1–C27 1.570(3), O1–C27 1.377(2), C27–C28 1.347(3), O2–C28 1.381(2), Si1–O2 1.670(1), N3–C28 1.454(2), N3–C35 1.478(3), N4–C35 1.351(3), C35–C36 1.331(3), N5–C40 1.337(3), N6–C40 1.340(3).

boryl unit and the other to a nitrogen atom of a former amidinate unit, which has now lost its $SiMe_3$ group and become a 1-aminovinylamido unit chelating the Sc atom. The other amidinate group remains chelating the Sc center. The OCCO unit is planar with a maximum deviation of 0.012 Å. The scandium and boron atoms lie slightly above (0.524 Å) and below (0.160 Å) this plane, respectively. In agreement, the C27–C28 bond length is 1.347(3) Å and can be assigned to a C=C double bond. The Sc1–O1 distance in **5** (1.961 (1) Å) is significantly shorter than the Sc–O(THF) distance in **2-Sc** (2.116(6) Å), and could be regarded as a Sc–O covalent bond. Reflecting the presence of a terminal Sc–amido covalent bond, the Sc1–N4 bond length (2.081(2) Å) is much shorter than the Sc1–N3 amino coordination bond (2.383(2) Å) and also significantly shorter than the Sc–N amidinate bonds (Sc1–N5 2.143(2), Sc1–N6 2.153(2) Å). The B–C distance of **5** (1.570(3) Å) is shorter than that of **4** (1.619(4) Å).

Complex **5** was further characterized by NMR spectroscopy, including DEPT and C–H COSY experiments. The methyl protons of the CH_2SiMe_3 and $OSiMe_3$ groups showed two singlets at $\delta = 0.069$ and 0.436 ppm, respectively, in the ^{1}H NMR spectrum in C_6D_6 at room temperature. The terminal vinyl methylene protons gave two sharp singlets at $\delta = 3.47$ and 3.62 ppm. In the ^{13}C NMR spectrum, the terminal vinyl methylene carbon atom showed a singlet at $\delta = 69.66$ ppm. The ^{11}B NMR spectrum of **5** showed a singlet at $\delta = 25.49$ ppm, which is comparable with that of **4**.

Formation of the OCCO unit in **5** was also confirmed by reaction of ^{13}CO with **3**. The ^{13}C NMR spectrum of the resulting complex showed two prominent doublets with $J_{C,C} = 96.9$ Hz at $\delta = 140.05$ and 142.49 ppm, suggesting the presence of a ^{13}C=^{13}C unit.[15c,f] The ^{13}C NMR signal at $\delta = 142.49$ ppm could be assigned to the carbon atom bonded to the boryl group, because it was broadened, presumably due to ^{13}C–^{11}B coupling. These results strongly support that both carbon atoms in the OCCO unit originate from external CO molecules.

A possible pathway for formation of **5** is given in Scheme 3. Insertion of one molecule of CO into the Sc–B bond in **3** would give an η^2-CO(boryl) species such as **A**, which on reaction with another molecule of CO could afford a ketene-like intermediate such as **B**.[15] Nucleophilic attack of an amidinate unit on the ketene unit, accompanied by migration of the $SiMe_3$ group from the amidinate unit to the oxygen atom of the ketene species, would yield **5**.



Scheme 3. Possible mechanism of formation of complex **5**.

In summary, we have demonstrated for the first time that rare earth metal boryl dialkyl complexes such as **2-Sc** and **2-Gd** can be easily obtained by reaction of a lithium boryl salt with dialkyl rare earth tetraphenylborate ion-pair compounds. Preliminary reactivity studies have shown that the Ln–B bonds in **2-Sc** or **3** can undergo insertion reactions with carbodiimide and carbon monoxide to give new boron-containing rare earth metal complexes such as **4** and **5**. Further studies on the synthesis of other rare earth metal boryl complexes and on the reactivity of this new class of complexes are in progress.[16,17]

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[16] The analogous yttrium, erbium, and lutetium boryl complexes were also obtained in a similar way, see Supporting Information for details.

[17] **Note added in proof** May 24, 2011: After submission of this work, the groups of Aldridge, Mountford, Jones, and Kaltsoyannis reported the synthesis and structural characterization of the Sc, Y, and Lu boryl complexes. See: L. M. A. Saleh, K. H. Birjkumar, A. V. Protchenko, A. D. Schwarz, S. Aldridge, C. Jones, N. Kaltsoyannis, P. Mountford, *J. Am. Chem. Soc.* **2011**, *133*, 3836 – 3839.

