Bis(imidazolin-2-ylidene-1-yl)borate Complexes of the Heavier Alkaline Earths: Synthesis and Studies of Catalytic Hydroamination

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Heteroleptic complexes of the heavier alkaline earth elements, calcium and strontium, containing bis(imidazolin-2-ylidene-1-yl)borate ligands may be synthesized by deprotonation of boronium salt ligand precursors with [KN(SiMe$_3$)$_2$] in the presence of CaI$_2$ or SrI$_2$. The silylamide complexes [{H$_2$B(Im^{t}Bu)$_2$}M{N(SiMe$_3$)$_2$}(THF)$_n$] (M = Ca, n = 1; M = Sr, n = 2), containing N-*tert*-butyl-substituted imidazolin-2-ylidene fragments, are stable to intermolecular solution redistribution despite some evidence of solution fluxionality in the case of M = Ca. Attempts to synthesize heteroleptic iodide-containing species led to the isolation of the homoleptic compounds [{H$_2$B(Im^{t}Bu)$_2$}$_2$MTHF)$_n$] (M = Ca, n = 1; M = Sr, n = 2) most likely because of the reduced steric demands of the halide coligand. Although extension of the "one pot" synthetic method to precursors containing N-mesityl-substituted imidazoles resulted in extensive ligand degradation, use of [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] as both base and group 2 element source provided the target heteroleptic silylamide complex. X-ray diffraction analyses demonstrated that the borate ligands adopt a *facial* η^3-binding mode in which coordination is provided through the two N-heterocyclic carbene (NHC) donors and an additional agostic-type interacton from one hydrogen of the BH$_2$ residue. Analysis of this ligand binding by DFT methods indicates that, although the bonds from the carbon centers are similar in character to those provided by neutral NHC ligands, the bonding is supplemented by an electrostatic component which is manifested as a coordination of a hydridic BH bond. The ionic nature of the overall interaction is sufficient to maintain the metal−ligand binding in the presence of amine donors and has allowed the evaluation of the Ca and Sr complexes [{H$_2$B(Im^{t}Bu)$_2$}M{N(SiMe$_3$)$_2$}(THF)$_n$] as precatalysts for the intramolecular hydroamination of aminoalkenes. While the calcium catalyst provides activities commensurate with our previously reported β-diketiminato complex, [CH{C(Me)N(2,6-^{i}Pr$_2$C$_6$H$_3$)}Ca{N(SiMe$_3$)$_2$}(THF)], the strontium derivative is superior in all cases.

Introduction

The successful application of coordination complexes in homogeneous catalysis has relied to a large extent upon the use of suitable coligands. Selection of appropriate donor identity, denticity, charge and ligand topology has, particularly in transition metal catalysis, resulted in a sophisticated appreciation of steric and electronic factors in the management of catalytic turnover. Our own,[1] and others',[2] efforts in the development of a defined catalytic reaction chemistry for the heavier group 2 elements (Ca, Sr and Ba) have relied upon compounds such as Chisholm's β-diketiminato complex (**I**) as a convenient prototype reagent and have yielded a plethora of new compounds.[3] Although a wide range of derivatives and new reaction types have been facilitated through the use of compound **I**, an underlying concern has always been the propensity of this compound to undergo solution (Schlenk-type) redistribution equilibria.[4] This feature, coupled with a tendency toward protonation by substrates of lower pK_a than the free β-imidoimine ligand precursor, has been a source of particular frustration in our efforts to understand and study several catalytic reactions. Chisholm has made similar observations and has reported, for example, that the reaction of **I** with *iso*-propanol results in the isolation of the homoleptic species [CH{C(Me)N(2,6-^{i}Pr$_2$C$_6$H$_3$)}$_2$Ca] rather than the desired heteroleptic alkoxide.[3b] The observation that the β-diketiminate anion provided insufficient kinetic protection when combined with coligands of reduced steric demands led this group to use the ubiquitous tris(pyrazolyl)borate ligands in the synthesis of calcium complexes such as **II** for the catalytic polymerization of *rac*-lactide.[3b]

We have recently described the synthesis of several N-heterocyclic carbene (NHC) adducts of the homoleptic alkaline earth silylamides, [(NHC)M{N(SiMe$_3$)$_2$}$_2$] (M = Ca, Sr, Ba).[5] Although these complexes are somewhat more tolerant of ambient moisture than the uncomplexed silylamides, the NHC ligand is easily displaced by harder neutral bases such as amines and phosphine oxides. Similar observations in 4f element chemistry have led to the successful development of NHC-

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[1] For example: (a) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042. (b) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. *Organometallics* **2007**, *26*, 2953. (c) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. *Organometallics* **2008**, *27*, 497.

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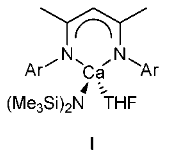
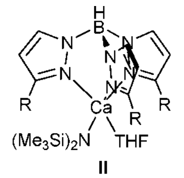
10.1021/om8010933 CCC: $40.75



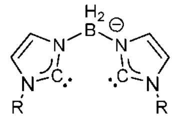
I

Ar = 2,6-di-*iso*-propylphenyl

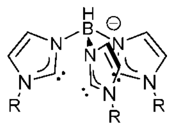


II

R - *tert*-butyl



III



IV

containing ligands in which the ligand is tethered to the hard electropositive center by an anionic alkoxo or amido functionality.[6] With these observations in mind, our attention was drawn to the bis- and tris(imidazolin-2-ylidenyl)borate ligands, **III** and **IV**, as possibly useful scaffolds for the stabilization of catalytically active heavier group 2 centers. Ligands of the general structure **IV** bear a clear topological relationship to the ligand utilized in the synthesis of **II**. We also hoped that the anionic nature of the NHC-based borate ligands would provide a stable and electrostatically bound coordination pocket for the group 2 center while the carbon-centered donors would display a reduced tendency toward the μ-metal bridging interactions which are probable intermediates in the redistributive processes outlined above.

Although bi- and tridentate ligands exemplified by the general structures **III** and **IV** were first reported by Fehlhammer in the late 1990s,[7] the use of these ligands, in either transition element or main group chemistry, is relatively limited. Smith has more recently provided several reports in which the anionic ligand is generated by reaction of a lithium or magnesium base with a boronium salt ligand precursor.[8,9] While initial studies were centered upon deprotonation of the potentially tridentate species $[HB(^tBuIm)_3]Br_2$ (^tBuIm = 1-*tert*-butylimidazole), more recent explorations have advanced to include the bidentate anion $[H_2B(^tBuIm)_2]$, which has been isolated as the lithium and nickel derivatives $[H_2B(^tBuIm)_2Li]_2$ and $[\{H_2B(^tBuIm)_2\}_2Ni]$.[8d] In this contribution we describe our initial syntheses of a series of bis(imidazol-2-ylidene)borate complexes of calcium and strontium along with some preliminary observations of silylamide derivatives in intramolecular hydroamination catalysis.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either dinitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in an MBraun Labmaster Glovebox. NMR spectra were collected on either a Bruker AV-400 spectrometer ($^{13}C\{^1H\}$ NMR 100 MHz, $^{11}B\{^1H\}$ NMR 96.3 MHz), or a Bruker AV-300 spectrometer ($^{13}C\{^1H\}$ NMR 75 MHz). BH proton resonances in the ^1H NMR spectra were observed through selective decoupling from the ^{11}B Nuclei. Solvents (toluene, benzene, THF, hexane) were dried by passage through the columns of a commercial solvent purification system. C_6D_6 and d_8-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distillation under nitrogen and storage over molecular sieves. The heavier group 2 amides $[M\{N(SiMe_3)_2\}_2(THF)_2]$ (M = Ca, Sr),[10] *tert*-butylimidazole,[11] mesitylimidazole,[12] $Me_3N.BH_2I$,[13] $Me_3N.BH_2Br$[14] and all aminoalkenes were prepared by literature procedures.[15] Attempts to acquire satisfactory elemental analyses on compounds **7**, **8** and **9** were unsuccessful; ^1H spectra of the isolated compounds are provided in the Supporting Information as corroborative evidence of purity.

Synthesis of Dihydro-bis(imidazole)boronium Bromides and Iodides (Compounds 1−4). General Procedure. Two molar equivalents of the relevant imidazole and one molar equivalent of Me_3NBH_2X (X = Br, I) were stirred at reflux (133 °C) under argon in dry chlorobenzene for 3−5 h (X = I) or 10−15 h (X = Br). Upon cooling to room temperature, a white precipitate formed. The solvent was removed *in vacuo,* the crude white solid was dissolved in CH_2Cl_2, precipitated with Et_2O and dried consecutively in air and on a vacuum line for a day to remove traces of residual chlorobenzene. Crystallization solvents are noted for the individual reactions.

$[H_2B(Im^tBu)_2]I$, 1. 1-*tert*-Butyl-imidazole (6.00 g, 48.3 mmol) and Me_3NBH_2I (4.80 g, 24.2 mmol). Crystallized from water: colorless solid (7.72 g, 82%), mp 135 °C. ^1H NMR ppm ($CDCl_3$, 298 K): 9.21 (s, 1H, ring-NCHN), 7.16 (d, 1H, ring-CH═CHN^{t}Bu, ^3J = 1.8 Hz), 7.12 (d, 1H, ring-CH═CHN^{t}Bu, ^3J = 1.8 Hz), 3.43 (br. s, 2H, BH_2), 1.70 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR ppm ($CDCl_3$, 298 K): 138.3 (ring-NCHN), 130.0 (ring-CH═CHN^{t}Bu), 126.0 (ring-CH═CHN^{t}Bu), 59.2 (CCH_3), 30.9 (CH_3). $^{>11}B\{^1H\}$ NMR ppm ($CDCl_3$, 298 K): −7.60. IR (Nujol): υ_{B-H} 2434 cm^{-1}, br. Anal. Calcd for $C_{14}H_{26}BIN_4$: C, 43.33; H, 6.75; N, 14.44%. Found: C, 43.0; H, 6.70; N, 14.0%.

$[H_2B(Im^tBu)_2]Br$, 2. 1-*tert*-Butyl-imidazole (2.00 g, 16.4 mmol) and $Me_3N.BH_2Br$ (1.25 g, 8.2 mmol). Crystallized from CH_2Cl_2: colorless solid (2.92 g, 100%), mp 110 °C. ^1H NMR ppm ($CDCl_3$, 298 K): 9.49 (t, 1H, ring-NC*H*N, ^4J = 1.5 Hz), 7.15 (t, 1H, ring-C*H*═CHN^{t}Bu, $^{3/4}J$ = 1.5 Hz), 7.08 (t, 1H, ring-CH═C*H*N^{t}Bu, $^{3/4}J$ = 1.5 Hz), 3.43 (br. s, 2H, BH_2), 1.70 (s, 9H, C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR ppm ($CDCl_3$, 298 K): 130.1 (ring-N*C*HN), 129.0 (ring-*C*H═CHN^{t}Bu), 126.0 (ring-CH═*C*HN^{t}Bu), 59.0 (*C*CH_3), 30.8 (*C*H_3). $^{11}B\{^1H\}$ NMR ppm ($CDCl_3$, 298K): −9.09. IR (Nujol): υ_{B-H} 2434 cm^{-1}, br. Anal. Calcd for $C_{14}H_{26}BBrN_4$: C, 49.2; H, 7.53; N 16.67%. Found: C, 49.30; H, 7.68; N, 16.43%.

$[H_2B(ImMes)_2]I$, 3. 1-Mesityl-imidazole (2.00 g, 10.7 mmol) and $Me_3N.BH_2I$ (1.07 g, 5.4 mmol). Crystallized from $CHCl_3$: colorless solid (2.35 g, 85%), mp 172 °C. ^1H NMR ppm ($CDCl_3$ 298 K): 9.20 (s, 1H, ring-NC*H*N), 7.60 (s, 1H, ring-C*H*═CHNMes),

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7.05 (s, 1H, ring-CH═C*H*NMes), 6.98 (s, 2H, Ar-*m*-H), 3.67 (br. s, 2H, BH_2), 2.33 (s, 3H, *p*-CH_3), 2.04 (s, 6H, *o*-CH_3). ^{13}C{^{1}H} NMR ppm (CDCl$_3$, 298 K): 141.1 (ring-N*C*HN), 140.2 (Ar-*i*-C), 134.8 (ring-*C*H═CHNMes), 130.1 (Ar-*m*-C), 126.8 (Ar-*p*-C), 123.2 (Ar-*o*-C), 115.1 (ring-CH═*C*HNMes), 21.5 (*p*-CH$_3$), 18.2 (*o*-CH$_3$). ^{11}B{^{1}H} NMR ppm (CDCl$_3$, 298 K): −6.10. IR (Nujol): $\upsilon_{\mathrm{B-H}}$ 2444 cm^{-1}, br. Anal. Calcd for $C_{24}H_{30}BIN_4$: C, 56.27; H, 5.90; N, 10.94%. Found: C, 56.7; H, 5.89; N, 10.7%.

[H$_2$B(ImMes)$_2$]Br, 4. 1-mesityl-imidazole (2.00 g, 10.74 mmol) and Me$_3$N.BH$_2$Br (0.82 g, 5.37 mmol). Crystallized from CHCl$_3$: white solid (1.30 g, 52%), mp 190−192 °C. ^{1}H NMR ppm (CDCl$_3$, 298 K): 9.55 (s, 1H, ring-NC*H*N), 7.60 (s, 1H, ring-C*H*═CHNMes), 7.00 (s, 1H, ring-CH═C*H*NMes), 6.97 (s, 2H, Ar-*m*-H), 2.32 (s, 3H, *p*-CH_3), 2.04 (s, 6H, *o*-CH_3). ^{13}C{^{1}H} NMR ppm (CDCl$_3$, 298 K): 140.4 (ring-N*C*HN), 140.3 (Ar-*i*-C), 134.3 (Ar-*m*-C), 129.4 (ring-*C*H═CHNMes), 126.1 (Ar-*p*-C), 122.1 (Ar-*o*-C), 114.4 (ring-CH═*C*HNMes), 20.9 (*p*-CH$_3$), 17.4 (*o*-CH$_3$). ^{11}B{^{1}H} NMR ppm (CDCl$_3$, 298 K): −7.90. IR (Nujol): $\upsilon_{\mathrm{B-H}}$ 2441 cm^{-1}, br. Anal. Calcd for $C_{24}H_{30}BBrN_4$: C, 61.91; H, 6.50; N, 12.04%. Found: C, 61.7; H, 6.48; N, 11.9%.

Synthesis of Bis(imidazolyl-2-ylidenyl)borate Alkaline Earth Compounds 5−8. General Procedure. In a glovebox, the appropriate ligand precursor (**1**−**4**), calcium iodide and potassium bis(trimethylsilyl)amide were weighed at a 1:1:3 or 4 ratio into a dry Schlenk flask. Dry THF was added at −78 °C and the mixture was left to stir at room temperature overnight until the calcium iodide beads had been consumed. The solvent was removed *in vacuo* and hexane/toluene added. The resultant milky solution was stirred for another hour then allowed to settle prior to filtration and concentration of the solution to incipient crystallization. After 3−7 days at −20 °C, the mother liquor was filtered into a second Schlenk and the transparent crystals completely dried on vacuum line. Samples suitable for X-ray diffraction analyses were selected under a cryogenic flow of dinitrogen to prevent melting at ambient temperatures.

[{H$_2$B(Im^{t}Bu)$_2$}Ca{N(SiMe$_3$)$_2$}(THF)], 5. (a)Compound **2** (2.08 g, 6.1 mmol), calcium iodide (1.79 g, 6.1 mmol) and KN(SiMe$_3$)$_2$ (3.66 g, 18.3 mmol): pale yellow transparent solid, very air- and temperature- sensitive, oily solid at 21 °C; crystalline at −16 °C (0.55 g, 18%). (b) Compound **1** (2.00 g, 5.2 mmol), calcium iodide (1.51 g, 5.2 mmol) and KN(SiMe$_3$)$_2$ (3.08 g, 15.5 mmol): off-white powder (1.55 g, 56%). ^{1}H NMR ppm (C$_6$D$_6$, 298 K): 7.23 (d, 2H, ring-C*H*═CHN^{t}Bu, ^3J = 1.5 Hz), 7.13 (s, 2H, ring-CH═C*H*N^{t}Bu), 6.59 (d, 2H, ring-CH═C*H*N^{t}Bu, ^3J = 1.5 Hz), 6.52 (s, 2H, ring-CH═C*H*N^{t}Bu), 4.31 (br. s, 2H, BH_2), 3.63 (m, 4H, THF), 1.36 (m, 4H, THF), 1.31 (s, 18H, CH_3), 0.45 (broad s, 18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR ppm (C$_6$D$_6$, 298 K): 195.0, (carbene-C), 125.0, (ring-*C*H═CHN^{t}Bu), 114.4 (ring-CH═*C*HN^{t}Bu), 68.6 (THF), 54.8 (THF), 31.1 (*C*CH$_3$), 25.0 (C*C*H$_3$), 2.3 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR ppm (C$_6$D$_6$, 298 K): −5.8. In d$_8$-toluene, the imidazol-2-ylidene ^{1}H NMR signals split at low temperatures. IR (Nujol): $\upsilon_{\mathrm{B-H}}$ 2385 (non agostic B−H), 2252 (agostic B−H) cm^{-1}. Anal. Calcd for $C_{24}H_{52}BCaN_5OSi_2$ (533.8): C, 54.00; H, 9.82; N, 13.12%. Found: C, 54.09; H, 9.41; 13.23.

[{H$_2$B(Im^{t}Bu)$_2$}Sr{N(SiMe$_3$)$_2$}(THF)$_2$], 6. Compound **1** (1.00 g, 2.6 mmol), strontium iodide (0.88 g, 2.6 mmol) and KN(SiMe$_3$)$_2$ (1.54 g, 7.7 mmol): colorless crystals after 1 day at −20 °C from hexane (1.85 g, 76%), mp 137−140 °C. ^{1}H NMR ppm (C$_6$D$_6$, 298 K): 7.23 (broad s, 2H, ring-C*H*═CHN^{t}Bu), 6.62 (s, 2H, ring-CH═C*H*N^{t}Bu), 4.32 (br. s, 2H, BH_2), 3.59 (m, 8H, THF), 1.35 (s, 18H, CH_3), 1.30 (m, 8H, THF), 0.37 (s, 18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR ppm (C$_6$D$_6$ 298 K): 201.5 (carbene-C), 126.0 (ring-*C*H═CHN^{t}Bu), 115.2 (ring-*C*H═CHN^{t}Bu), 69.0 (THF), 55.5 (THF), 32.3 (*C*CH$_3$), 25.8 (*C*H$_3$), 5.9 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR ppm (C$_6$D$_6$ 298 K): −5.7. NMR also showed presence of hexane in the lattice; confirmed by X-ray study. IR (Nujol): $\upsilon_{\mathrm{B-H}}$ 2363 (nonagostic B−H), 2252 (agostic B−H) cm^{-1}. Anal. Calcd for $C_{29.5}H_{61.5}BN_5O_2Si_2Sr$ (937.82): C, 52.63; H, 9.21; N, 10.41%. Found: C, 52.75; H, 9.43; 10.33.

[{H$_2$B(Im^{t}Bu)$_2$}$_2$Ca(THF)], 7. Redistribution product from the attempted synthesis of [{H$_2$B(Im^{t}Bu)$_2$}CaI(THF)]: Compound **1** (0.50 g, 1.29 mmol), calcium iodide (0.38 g, 1.29 mmol) and KN(SiMe$_3$)$_2$ (0.51 g, 2.58 mmol): colorless crystals after 3 days at −20 °C (0.20 g, 49% based on CaI$_2$). ^{1}H NMR/ ppm (C$_6$D$_6$): 7.26 (d, 4H, ^3J = 1.5 Hz, ring-C*H*═CHN^{t}Bu), 6.60 (d, 4H, ^3J = 1.5 Hz, ring-CH═C*H*N^{t}Bu), 4.44 (br. s, 2H, BH_2), 3.59 (m, 4H, THF), 1.38 (m, 4H, THF), 1.36 (s, 36H, CH_3). ^{13}C{^{1}H} NMR ppm (C$_6$D$_6$, 298 K): 195.0 (carbene-*C*), 124.0 (ring-*C*H═CHN^{t}Bu), 113.3 (ring-CH═*C*HN^{t}Bu), 66.7 (THF), 53.8 (*C*CH$_3$), 30.0 (THF), 24.3 (CH$_3$). ^{11}B{^{1}H} NMR ppm (C$_6$D$_6$, 298 K): −5.42. IR (Nujol): $\upsilon_{\mathrm{B-H}}$ 2363 (nonagostic B−H), 2255 (agostic B−H) cm^{-1}.

[{H$_2$B(Im^{t}Bu)$_2$}$_2$Sr(THF)$_2$], 8. Redistribution product from the attempted synthesis of [{H$_2$B(Im^{t}Bu)$_2$}SrI(THF)]$_2$: Compound **1** (0.50 g, 1.29 mmol), strontium iodide (0.44 g, 1.29 mmol) and KN(SiMe$_3$)$_2$ (0.51 g, 2.58 mmol): colorless crystals after 3 days at −20 °C (0.21 g, 43%). Loses one molecule of THF on isolation. ^{1}H NMR ppm (C$_6$D$_6$, 298 K): 7.29 (d, 4H, ^3J = 1.5 Hz, ring-C*H*═CHN^{t}Bu), 6.63 (d, 4H, ^3J = 1.5 Hz, ring-CH═C*H*N^{t}Bu), 4.44 (br. s, 2H, BH_2), 3.67 (m, 4H, THF), 1.30 (s, 36H, CH_3), 1.30 (m, 4H, THF). ^{13}C{^{1}H} NMR ppm (C$_6$D$_6$ 298 K): 198.9 (carbene-*C*), 124.3 (ring-*C*H═CHN^{t}Bu), 113.1 (ring-CH dbd═*C*HN^{t}Bu), 67.2 (THF), 53.7 (*C*CH$_3$), 30.0 (THF), 24.2 (*C*H$_3$). ^{11}B{^{1}H} NMR ppm (C$_6$D$_6$ 298 K): −5.64.

[{H$_2$B(ImMes)$_2$}Ca{N(SiMe$_3$)$_2$}(THF)], 9. Compound **3** (0.74 g, 1.46 mmol), [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (0.50 g, 0.98 mmol): light-pink powder (0.14 g, 50%). ^{1}H NMR ppm (C$_6$D$_6$ 298 K): 7.21 (d, 2H, ^3J = 1.5 Hz, ring-CH═C*H*NMes), 6.77 (s, 4H, Ar-*H*), 6.27 (d, 2H, ^3J = 1.5 Hz, ring-CH═C*H*NMes), 4.41 (br. s, 2H, BH_2), 3.52 (m, 4H, THF), 2.12 (s, 6H, Ar-*p*-CH_3), 1.93 (s, 2H, Ar-*o*-CH_3), 1.14 (m, 4H, THF), 0.12 (s, 18H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR ppm (C$_6$D$_6$ 298 K): 196.0 (carbene-*C*), 137.1 (Ar-*i*-*C*), 136.2 (Ar-*m*-*C*), 135.0 (Ar-*p*-*C*), 128.2 (Ar-*o*-*C*), 123.6 (ring-*C*H═CHNMes), 117.7 (ring-CH═*C*HNMes), 67.6 (THF), 23.7 (THF), 19.6 (Ar-*p*-CH$_3$), 16.4 (Ar-*o*-CH$_3$), 3.9 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR ppm (C$_6$D$_6$ 298 K): −5.87.

Crystallographic Data. Data for **1**, **3**, **6**, **7** and **10** were collected at 150 K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystem, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data were processed using the Nonius Software.[16]

For **1**, **3**, **6** and **10** a symmetry-related (multiscan) absorption correction had been applied. Crystal parameters and details on data collection, solution and refinement for the complexes are provided in Table 1. Structure solution, followed by full-matrix least-squares refinement was performed using the WINGX-1.70 suite of programs throughout.[18]

For compounds **1** and **3** the -BH$_2$ hydrogen atoms were identified in the difference Fourier map and refined freely. In the structure of **6**, the main compound contained one disordered (80:20)THF ligand and the voids contained some solvent which could be modeled as hexane since the NMR data indicated that hexane was present. Each main molecule cocrystalized with 1/4 of hexane which was disordered about a center of inversion. For **7**, the sample consisted of low melting crystals which were selected using a modified device, similar to that of Veith and Bärnighausen.[17] The crystals turned out to be very weakly diffracting which resulted in a high R(int)

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(16) DENZO-SCALEPACK: Otwinowski Z. and Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode*; Methods in Enzymology Volume *276*: Macromolecular Crystallography, part A; Carter, C. W., Jr., Sweet R. M., Eds., Academic Press: New York, 1997; pp 307−326.

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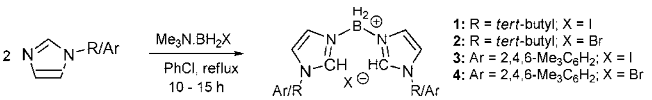
Table 1. Crystallographic Data for Compounds 1, 3, 6, 7 and 10

	1	**3**	**6**	**7**	**10**
Molecular formula	$C_{14}H_{26}BIN_4$	$C_{24}H_{30}BIN_4$	$C_{29.5}H_{61.5}BN_5O_2Si_2Sr$	$C_{32}H_{56}B_2CaN_8O$	$C_{63}H_{80}B_2Ca_2I_2N_8O_2$
Formula weight (g mol^{-1})	388.10	512.23	672.95	630.55	1336.93
Crystal system	monoclinic	monoclinic	tetragonal	orthorhombic	triclinic
Space group	$P2_1/c$	$P2_1/m$	$P4_2/n$	*Pbca*	$P\bar{1}$
a (Å)	11.9656(2)	8.2566(1)	20.5450(1)	16.0309(3)	12.7284(4)
b (Å)	10.0655(1)	19.2495(3)	20.5450(1)	19.9759(4)	15.4087(6)
c (Å)	15.1879(2)	8.8410(1)	18.9151(2)	23.0604(5)	18.6707(8)
α (deg)	90	90	90	90	88.910(1)
β (deg)	96.405(1)	115.216(1)	90	90	84.771(1)
γ (deg)	90	90	90	90	65.664(2)
V (Å^3)	1817.81(4)	1271.25(3)	7984.01(10)	7384.7(3)	3321.9(2)
Z	4	2	8	8	2
μ (mm^{-1})	1.759	1.276	1.440	0.205	1.147
ρ (g cm^{-3})	1.418	1.338	1.120	1.134	1.337
121 > range (deg)	3.03−30.00	3.53−30.01	3.67−27.49	3.81−24.21	3.67−24.94
R_1,[a] wR_2 [$I > 2\sigma(I)$][b]	0.0682, 0.1256	0.0269, 0.0597	0.0566, 0.1267	0.0609, 0.1191	0.1107, 0.2617
R_1,[a] wR_2 (all data)[b]	0.0921, 0.1397	0.0351, 0.0630	0.0928, 0.1493	0.1067, 0.1410	0.1665, 0.2925
Measured/independent reflections/R_{int}	34042/5294/0.0409	25876/3804/0.0413	132210/9125/0.0736	9209/5875/0.2578	30202/11375/0.1265

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Scheme 1



1: R = *tert*-butyl; X = I
2: R = *tert*-butyl; X = Br
3: Ar = 2,4,6-$Me_3C_6H_2$; X = I
4: Ar = 2,4,6-$Me_3C_6H_2$; X = Br

and a lower resolution data set ($\Theta_{max} = 24.2°$). The compound contains one THF ligand which shows a 1:1 disorder in C32. In **10** **t**he asymmetrical unit consists of two molecules of CaI-dimer and one solvent molecule of toluene. Both THF groups binding to Ca show potential disorder. However, due to a very weak data set this could not be resolved. The -BH_2 hydrogens could be located in the difference Fourier map but had to be constrained.

Computational Details

The model heteroleptic complexes [{HB{(NMeCH)$_2$C}M-{N(SiH$_3$)$_2$}(OMe$_2$)$_2$] **11** (M = Ca) and **12** (M =Sr) were examined using the B3LYP density functional theory and LAN2DZ pseudopotentials (and basis set) implemented in Gaussian03.[29] The geometry optimizations were performed by selecting an initial geometry based upon that deduced for the structure of the heteroleptic strontium complex **6** and, in both cases, were confirmed as true minima by independent frequency calculations. Details of atomic coordinates for both optimized structures and energies are available as Supporting Information.

Results and Discussion

Synthetic and Structural Studies of Group 2 Bis(imidazolin-2-ylidene-1-yl)borates. The ligand precursor salt [H$_2$B(^{t}BuIm)$_2$]I, **1**, was synthesized in a manner similar to that recently described by Smith but employing the reaction of two equivalents *tert*-butylimidazole with Me$_3$N.BH$_2$I in refluxing chlorobenzene rather than the lower boiling solvent toluene (Scheme 1).[8d] The analogous bromide salt, compound **2**, and the respective 1-mesityl iodide and bromide analogues, compounds **3** and **4**, were synthesized by the same method and isolated as colorless crystalline solids after recrystallization from water (**1**), dichloromethane (**2**), or chloroform (**3** and **4**). Compound **1** provided ^{1}H and ^{13}C{^{1}H} NMR chemical shift data in concordance with those quoted recently by Smith and co-workers and all four salts displayed characteristic low field resonances at *ca*. 9.5 ppm attributed to the imidazole H-2 proton in the ^{1}H NMR spectra. The structures of compounds **1** and **3** are illustrated in Figure 1a and b, while details of the X-ray analyses and selected bond length and angle data are provided in Tables 1 and 2, respectively. Although showing some internal variation, the B−N distances within the cationic units of **1** [1.545(8), 1.568(8) Å] and **3** [1.567(2) Å] are within the range of distances observed in the previously reported boronium cations, [(*tert*-butylamine)(1-methylimidazole)BH$_2$]$^+$ [1.557(4) Å] and [(Me$_3$N)(1-methylimidazole)BH$_2$]$^+$ [1.555(3), 1.604(3) Å].[19,20] In common with these previous studies the imidazolium rings within **1** and **3** do not display any significant distortions due to incorporation into the boronium cation.

The majority of our previous work has employed a "one pot" procedure to provide large quantities of the β-diketiminate complex **I**.[3] With a similar motivation in mind, addition of THF at low temperature to a solid mixture of three equivalents of [KN(SiMe$_3$)$_2$] and single molar equivalents of the ligand precursor (**1** or **2**) and either CaI$_2$ or SrI$_2$ provided after workup the desired heteroleptic complexes **5** and **6** (Scheme 2). To date, analogous reactions employing BaI$_2$ as the alkaline earth starting material have not yielded any tractable products. It is also notable that NMR analysis of the crude reaction mixtures indicated the formation of a complex mixture of products formed, most likely, by the fragmentation of the ligand precursors during the reactions (*vide infra*). Despite these observations, the materials separated from the KI byproduct were extremely soluble in hydrocarbon solvents and storage of concentrated solutions at −20 °C for extended periods allowed the isolation of both compounds as colorless crystalline solids in moderate to good (50−70%) yields. The ^{1}H and ^{13}C{^{1}H} NMR data were consistent with the expected structures. Particularly diagnostic were the signals ascribed to the coordinated C-2 position of the carbenoid carbon centers of the borate ligands which appeared at 195.0 ppm (**5**) and 201.5 ppm (**6**) in the respective ^{13}C{^{1}H} NMR spectra. We have recently described a series of calcium and strontium adducts with neutral NHC ligands, [(NHC)M{N(SiMe$_3$)$_2$}$_2$], and noted that the magnitude of the upfield shifts ($\Delta\delta$) induced in the resonance of the C-2 center from that of the free carbene were dependent

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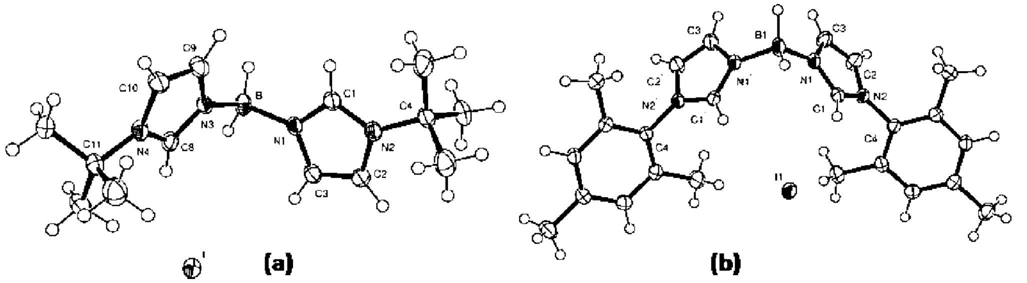


Figure 1. (a) ORTEP plot of compound **1**; (b) ORTEP plot of compound **3**. Thermal ellipsoids at 30% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1 and 3

	1	**3**[a]		**1**	**3**[a]
B−N(1)	1.545(8)	1.567(2)	N(1)−B−N(3)	109.0(5)	107.38(18)[d]
B−N(3)	1.568(8)	−	C(1)−N(1)−C(3)	106.3(5)	107.58(13)
C(1)−N(1)	1.343(7)	1.3267(19)	C(1)−N(1)−B	126.5(5)	125.51(16)
C(3)−N(1)	1.383(7)	1.379(2)	C(3)−N(1)−B	127.2(5)	126.91(16)
C(1)−N(2)	1.336(7)	1.3376(19)	C(1)−N(2)−C(2)	107.7(5)	107.67(13)
C(2)−N(2)	1.382(7)	1.378(2)	C(1)−N(2)−C(4)	127.5(5)	126.42(13)
C(8)−N(3)	1.332(7)	−	C(2)−N(2)−C(4)	124.8(5)	125.78(13)
C(9)−N(3)	1.382(7)	−	C(8)−N(3)−C(9)	107.3(5)	−
C(8)−N(4)	1.344(7)	−	C(8)−N(3)−B	125.5(5)	−
C(10)−N(4)	1.382(7)	−	C(9)−N(3)−B	127.1(5)	−
B−H(1A)	1.10(6)	1.14(3)[b]	−	−	−
B−H(1B)	1.07(7)	1.11(3)[c]	−	−	−

[a] Symmetry transformations used to generate equivalent atoms: *x*, −*y* + 1/2, *z*. [b] B(1)−H(1). [c] B(1)−H(2). [d] N(1)−B(1)−N(1)′.

Scheme 2

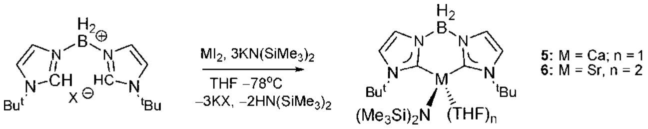
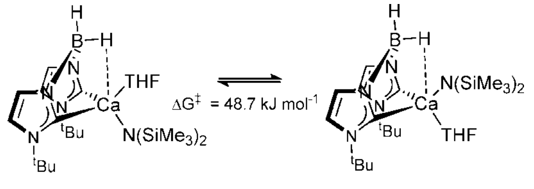


Table 3. Comparative M−C$_{carbene}$ and δ_{13C} NMR data for Ca and Sr NHC Complexes

compound[a]	M−C$_{NHC}$ (Å)	δ_{13C} C$_{NHC}$ (ppm)	ref
5	−	195.0	This work
7	2.583(3)−2.646(4)	195.0	This work
9	−	196.0	This work
$[Ca(L^1)\{N(SiMe_3)_2\}_2]$	2.598(2)	193.3	5
$[Ca(L^2)\{N(SiMe_3)_2\}_2]$	2.6259(2)	195.4	5
$[(Cp^*)_2Ca\{L^3\}]$	2.562(2)	196.2	21
6	2.739(3)−2.757(4)	201.5	This work
8	−	198.9	This work
$[Sr(L^1)\{N(SiMe_3)_2\}_2]$	2.731(3)	199.0	5
$[(Cp^*)_2Sr\{L^3\}]$	−	198.2	21
$[(Cp^*)_2Sr\{L^3\}_2]$	2.868(5), 2.854(5)	203.7	21

[a] L^1 = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; L^2 = 1,3-bis-(2,6-di-iso-propylphenyl)imidazol-2-ylidene; L^3 = 1,3-bis(methyl)imidazol-2-ylidene.

Scheme 3



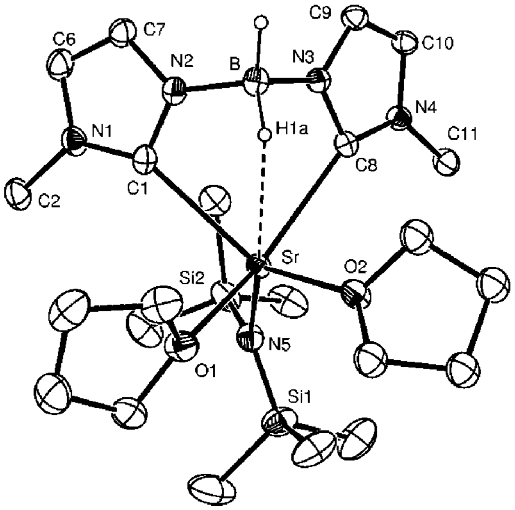


Figure 2. ORTEP Plot of compound **6.** Thermal ellipsoids at 30% probability. Hydrogen and *tert*-butyl carbon methyl atoms removed for clarity.

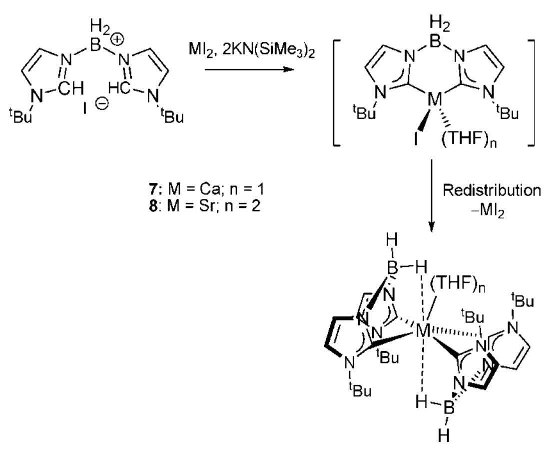
Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds 6 and 7

	6[a]	**7**[b]		**6**[a]	**7**[b]
M−C(1)	2.757(4)	2.583(3)	C(1)−M−C(8)	83.29(11)	83.74(11)[i]
M−C(8)	2.739(3)	2.646(4)[d]	C(1)−M−N(5)	112.20(11)	85.77(11)[j]
M−N(5)	2.510(3)	2.640(4)[e]	C(1)−M−O(1)	86.55(10)	81.75(10)[k]
M−O(1)	2.592(3)	2.607(3)[f]	C(1)−M−O(2)	121.65(14)	79.14(10)[l]
M−O(2)	2.606(4)[c]	2.467(3)[g]	C(8)−M−N(5)	108.27(11)	105.37(11)[m]
M−H(1A)	2.87(3)	−	C(8)−M−O(1)	145.81(10)	106.67(11)[n]
B−N(3)	1.544(5)	1.552(6)[h]	C(8)−M−O(2)	85.49(12)	160.72(11)[o]
C(1)−N(1)	1.367(4)	1.365(4)	N(5)−M−O(1)	105.80(10)	108.21(11)[p]
C(1)−N(2)	1.367(5)	1.378(4)	N(5)−M−O(2)	125.67(14)	−
B−H(1A)	1.12(3)	−	O(1)−M−O(2)	72.36(12)	−
B−H(1B)	1.14(4)	−			

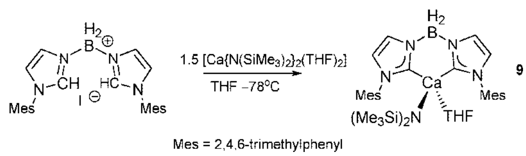
[a] M = Sr. [b] M = Ca. [c] Sr−O(2A), 2.621(19). [d] Ca−C(4). [e] Ca−C(7). [f] Ca−C(10). [g] Ca−O. [h] B(1)−N(3). [i] C(1)−Ca−C(4). [j] C(7)−Ca−C(10). [k] C(1)−Ca−O. [l] C(10)−Ca−O. [m] C(10)−Ca−C(4). [n] C(7)−Ca−C(4). [o] C(1)−Ca−C(10). [p] C(1)−Ca−C(7).

upon the Lewis acidity of the metal (Ca > Sr > Ba).[5] A similar effect is apparent from consideration of the chemical shift data of **5** and **6**, which are closely comparable to those encountered in the neutral adducts. Examination of these and other relevant literature data listed in Table 3 reveal that the nature of the Lewis basic carbene donors are apparently not perturbed by incorporation into the bidentate anionic borate ligand. Variable temperature ^1H and $^{13}C\{^1H\}$ NMR studies performed on compound **5** revealed some evidence for fluxional behavior in solution. Cooling of a sample in d_8-toluene revealed a decoalescence of the bis(imidazolin-2-ylidene-1-yl)borate ligand resonances into a series of singlets of equal intensity as the temperature was lowered. Although a splitting of the broad B−H resonance was also observed down to the low temperature limit (208 K) of the $^1H\{^{11}B\}$ NMR spectrum, consistent with the formation of a labile agostic interaction, this process was ill defined due to the likely diastereotopic nature of the BH_2 protons and the presence of the 20% quadrupolar ^{10}B nucleus. The fluxional process was best characterized, therefore, by examination of the aromatic protons of the imidazolin-2-ylidene residues which provided a value of $\Delta G^‡$ 48.7 kJ mol^{-1} for a coalescence temperature of 238 K. It is noticeable that the C-2 imidazolin-

Scheme 4



Scheme 5



2-ylidene resonance in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum also splits into two (198.7 and 198.8 ppm) at the low temperature limit (208K) of the experiment. Smith has recently reported that the structure of the homoleptic nickel complex $[\mathrm{Ni}\{(^t\mathrm{BuIm})_2\mathrm{BH}_2\}_2]$ is best described as square planar despite the boat conformation that is adopted by the borate ligands, a geometry that is retained in solution at room temperature.[8] This bonding situation contrasted with that of an octahedral bis(pyrazolyl)borate complex, $[\mathrm{Ni}\{(^t\mathrm{BuPz})_2\mathrm{BH}_2\}_2]$, in which two agostic Ni−H−B bonds completed the metal's coordination sphere and was reasoned to be a consequence of the more strongly donating carbene-based ligand.[22] Similar M−H-B interactions are observed in the solid state analyses of the group 2 complexes reported herein (*vide infra*) and are reminiscent of the coordinating behavior of "scorpionate" bis(pyrazolato)borate coordination complexes.[23] Further evidence for the maintenance of an agostic-type M−H−B interaction in the solid state was provided by inspection of the IR spectra of compounds **5** and **6**, where two distinct $\upsilon_{\mathrm{B-H}}$ stretches were observed for both compounds (**5**: 2385, 2252 cm^{-1}; **6**: 2363, 2252 cm^{-1}). The lower frequency vibrations are assigned to be a result of the M−H-B agostic interactions, a deduction supported by the frequency calculations performed upon the model complexes, **11** and **12** (*vide infra*). Although alternative processes cannot be discounted unequivocally, we propose, therefore, that the fluxional solution behavior observed for compound **5** is a consequence of the lability of the metal to ligand interactions typically observed in heavier group 2 complexes and indicative of equilibration of the geometric isomers illustrated in Scheme 3. Variable temperature studies performed upon the strontium analogue of **5**, compound **6**, revealed similar, but less defined, fluxional behavior most likely as a consequence of the reduced charge density of the larger Sr^{2+} cation.

Crystals of compound **6** suitable for X-ray diffraction analysis were isolated from hexane solution at −20 °C. The results of this experiment are illustrated in Figure 2 and details of the X-ray analysis and selected bond length and angle data are provided in Tables 1 and 4 respectively. Compound **6** adopts a distorted pseudo-octahedral coordination geometry in the solid state with a *facial* $\mathrm{O_2N}$ donor set provided by two molecules of THF and the silylamide coligand. The other face is occupied by the bis(imidazolin-2-ylidene-1-yl)borate ligand which adopts a boat conformation and an effective η^3-coordination mode. In this latter case, donation to the strontium cation is provided by the two imidazolin-2-ylidene carbene centers and an apparent agostic-type interaction from a boron B−H bond. The Sr−C distances [Sr−C(1), 2.757(4) Å; Sr−C(8), 2.739(3) Å] are comparable to that observed within our recently reported three-coordinate complex $[\mathrm{Sr(NHC)}\{\mathrm{N(SiMe_3)_2}\}_2]$ (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) [Sr−C = 2.731(3) Å] despite the increased coordination number at strontium (Table 3).[5] The interaction between Sr and a hydridic hydrogen of the $\mathrm{BH_2}$ unit [2.87(3) Å], although long, is within the range established [2.59(3)−2.89(3) Å] within several borohydride and phosphinoborane-substituted carbanion strontium derivatives.[24,25]

In an attempt to synthesize heteroleptic alkaline earth iodide derivatives, similar reactions employing the ligand precursor, compound **1**, were attempted using two molar equivalents of $[\mathrm{KN(SiMe_3)_2}]$ rather than three (Scheme 4). Reactions employing calcium and strontium iodides provided similar results and homoleptic species, compounds **7** $[\mathrm{Ca}\{(^t\mathrm{BuIm})_2\mathrm{BH}_2\}_2(\mathrm{THF})]$ and **8** $[\mathrm{Sr}\{(^t\mathrm{BuIm})_2\mathrm{BH}_2\}_2(\mathrm{THF})_2]$, which are evidently formed due to the reduced steric demands of the intended iodide in

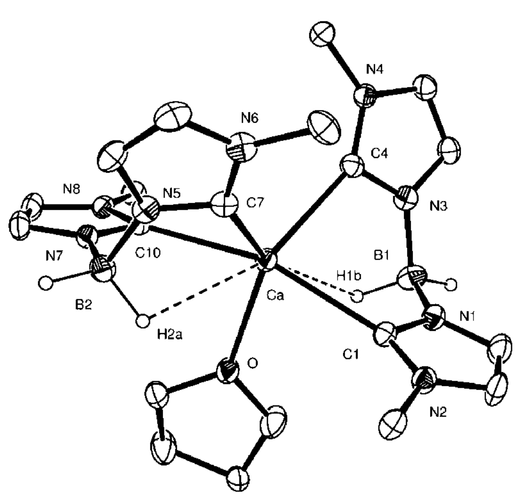


Figure 3. ORTEP Plot of compound **7**. Thermal ellipsoids at 30% probability. Hydrogen and *tert*-butyl carbon methyl atoms removed for clarity.

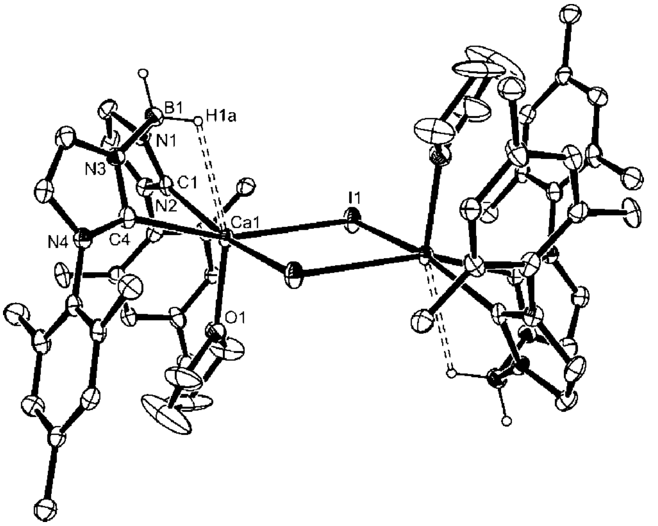


Figure 4. ORTEP Plot of compound **10** with thermal ellipsoids at 20% probability.

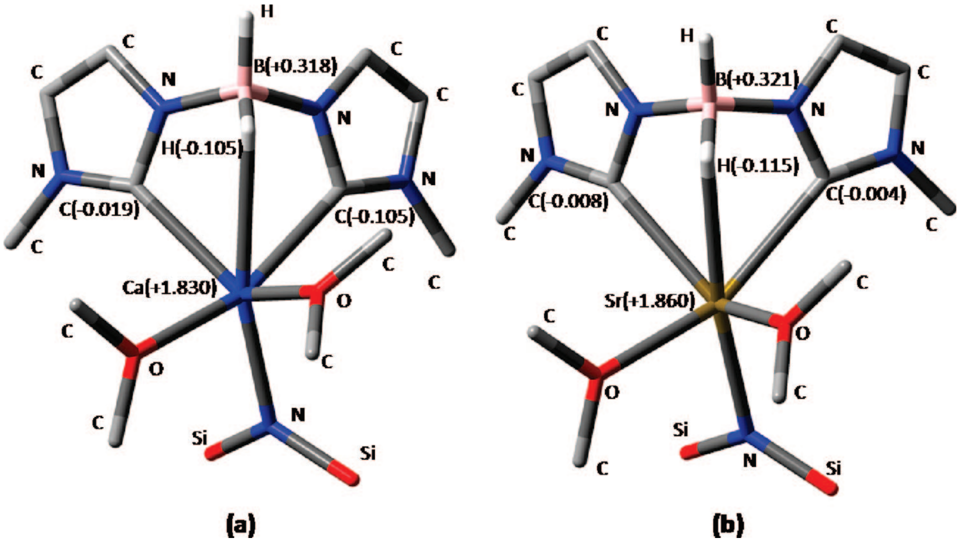
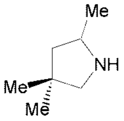
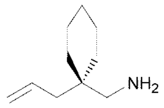
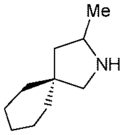
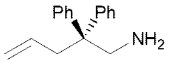
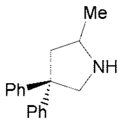
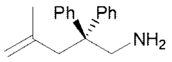
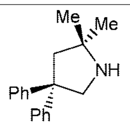
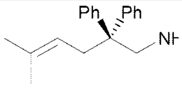
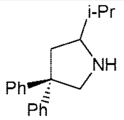
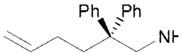
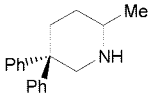
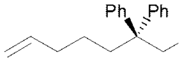
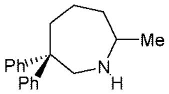


Figure 5. Representations of the optimized (DFT, B3LYP/LAN2DZ) structures of compounds (a) **11** and (b) **12**. Calculated NBO charges for selected atoms shown in parenthesis. Selected bond lengths (Å); **11**: Ca−C(avg.) 2.63; Ca−N 2.47; Ca−HB 2.93; Ca−O(avg.) 2.48. **12**: Sr−C(avg.) 2.79; Sr−N 2.55; Sr−HB 2.87; Sr−O(avg.) 2.62.

Table 5. Intramolecular Hydroamination of Terminal Aminoalkenes Catalyzed by Compounds 5 and 6

Entry	Substrate	Product	Catalyst (mol %)	Time / h	Temp / °C	NMR yield / %
1			**5** (10 mol %)	2	25	>95
2			**6** (5 mol %)	1	25	>95
3			**5** (5 mol %)	0.5	25	30
4			**5** (5 mol %)	0.15	70	>95
5			**6** (5 mol %)	0.15	25	95
6			**5** (5 mol %)	0.3	25	95
7			**6** (5 mol %)	0.15	25	>99
8			**5** (5 mol %)	1 d	25	50
9			**5** (5 mol %)	1	70	>99
10			**5** (5 mol %)	2 d	70	0
11			**5** (20 mol %)	3 d	70	<5
12			**5** (5 mol %)	1 d	25	60
13			**5** (10 mol %)	6	25	86
14			**6** (5 mol %)	4	25	88
15			**5** (10 mol %)	3 d	75	75
16			**6** (10 mol %)	2 d	75	80

comparison to the hexamethyldisilazide coligands employed in the syntheses of compounds **5** and **6**. Although both compounds proved to be extremely air-, moisture- and temperature-sensitive, preventing the acquisition of accurate microanalytical data, promptly prepared samples analyzed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy displayed similar spectral features suggestive of a single borate ligand environment. The chemical shifts attributed to the donor-carbon carbene resonances [**7**, 195.0; **8**, 198.9 ppm] also bore close comparison to those observed for the heteroleptic species **5** and **6**, indicative of comparable binding modes and charge donation (Table 3). This deduction was confirmed by a further X-ray structural analysis obtained for the calcium compound **7**. Although crystals of **7** required handling under a cryogenic N_2 stream to prevent decomposition and were weakly diffracting, the structure was unambiguous and revealed a similar η^3-binding of the borate ligands to that observed for **6**. The structure of compound **7** is illustrated in Figure 3 and details of the X-ray analysis and selected bond length and angle data are provided in Tables 1 and 4 respectively. The range of calcium−carbon distances [2.583(3)−2.646(4) Å] are similar to those observed within the neutral NHC adducts $[(NHC)Ca\{N(SiMe_3)_2\}_2]$ [NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, 2.598(2) Å; NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) 2.6285(16) Å][5] and $[(C_5Me_5)_2Ca\{C(NMeCMe)_2\}]$ [2.5629(2) Å] (Table 3),[21] as well as the range of distances reported by Harder for several calcium bis(iminophosphoranyl)methandiyl derivatives [2.528(2)−2.805(1) Å].[26] Although substantially longer than those observed within our previously reported dialkyldihydridoborate $[HC\{C(Me)CN(2,6\text{-}^{i}Pr_2C_6H_3)\}_2\}CaH_2BR_2]$ (R = the anion formed from 9-borabicyclo[3.3.1]nonane) [2.17(4) − 2.31(4) Å][27] and the calcium tetrahydoborate $[(DME)_2Ca(BH_4)_2]$ (range: 2.35(3) − 2.58(3) Å),[24] the Ca−H(1b/2a) distances within **7** [2.97, 2.83 Å] again describe a structurally significant interaction such that the calcium center may be depicted as effectively seven-coordinate. It is also notable that the chelating framework of the borate ligand evidently possesses little flexibility as the N−B−N bond angles display little variation across the precursor **1** [109.0(5)°] and the calcium and strontium complexes **7** [111.0(3), 111.2(3)°] and **6** [112.0(3)°] respectively.

Attempts to elaborate a rational synthesis of these homoleptic species have so far been unsuccessful. Although an analogous "one pot" procedure employing four equivalents of the silylamide base produced materials with ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra reminiscent of those of **7**, these materials contained no coordinated THF. Rather, additional singlet resonances at δ_H 0.84 (9H), 6.36 (1H) and 7.13 (1H) ppm were attributed to coordinated 1-*tert*-butylimidazole which was evidently produced by rupture of the B−N bonds of the ligand precursor during borate anion formation. Although we have observed no evidence of ligand degradation subsequent to anion formation, it appears that such B−N cleavage is a common feature of this ligand class at some stage in the deprotonation of, and the necessary charge distribution within, the ligand precursors.[28]

Similar difficulties have also blighted our attempts to synthesize analogues of compounds **5**−**8** utilizing the N-mesityl substituted precursors, **3** and **4** *via* the "one pot" procedure illustrated in Scheme 2. In these cases the reactions turned deep crimson in color, which were shown by NMR analysis to contain a complex and intractable mixture of products. This problem was partially circumvented through the adoption of an alternative synthetic route, which utilized the homoleptic calcium amide $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ as both base and source of the group 2 metal. Reaction of 1.5 equivalents of $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ with the boronium iodide salt precursor compound **3** (Scheme 5) provided the colorless complex **9**, which provided NMR spectra indicative of the intended heteroleptic formulation. Although the δ_c carbene resonance of **9** (196.0 ppm) was again similar to that observed in compounds **5** and **7**, variable temperature NMR studies revealed none of the fluxional behavior attributed to the heteroleptic species described above. While compound **9** provided well-formed single crystals at low temperature, multiple attempts to acquire X-ray diffraction data were frustrated by the extremely rapid decomposition of the material once removed from the chilled mother liquor. A data set collected on a more durable crystal from one of these reactions yielded the structure of an unanticipated heteroleptic iodide species, compound **10** (Figure 4). Although the data set for **10** was very weak and yielded residuals for the structure which were unacceptably high ($R1 = 0.1107$, $wR2 = 0.2617$) precluding any detailed discussion, the connectivity was unambiguous. The borate ligands again adopt a tridentate coordination mode, while the presence of the iodide ligands highlights the propensity toward redistributative processes of heavier group 2 centers.

The nature of the metal to ligand coordination in complexes **5**−**10** was assessed by DFT calculations on the model heteroleptic complexes $[\{HB\{(NMeCH)_2C\}M\{N(SiH_3)_2\}(OMe_2)_2]$ **11** (M = Ca) and **12** (M =Sr) using the B3LYP density functional theory and LAN2DZ pseudopotentials (and basis set) implemented in Gaussian03.[29] The geometry optimizations were performed by selecting an initial geometry based upon that deduced for the structure of the heteroleptic strontium complex **6** and, in both cases, were confirmed as true minima by independent frequency calculations. To reduce computational expense the *tert*-butyl groups of the borate ligands were replaced by methyl groups, the methyl groups of the silyl amide ligands were replaced by hydrogen and the coordinated THF molecules were simplified to two molecules of dimethyl ether. The second molecule of coordinated solvent was retained within the coordination sphere of the calcium center of **11** despite the lower coordination number determined for the "real case" of compound **5**. It was felt that this was necessary to take into account the reduced steric demands of the truncated ligands and to allow for internal consistency when comparing the two calculated structures. Figure 5 illustrates the results of this study. In both

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[28] We have also often observed B-N cleavage in our attempts to synthesize heavier group 2 derivatives of tris(imidazolin-2-ylidene-1-yl)borate derivatives; Arrowsmith, M.; Hill, M. S. unpublished results.

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cases the calcium and strontium contacts to the carbon donors of the η^3-coordinated ligands replicate the distances observed within the structures of compounds **7** and **6** respectively to within ca. 0.02 Å (see Figure 5 caption). Especially notable was the agreement between the calculated M···HB distances [**11**, 2.93 Å; **12**, 2.87 Å] and the values determined in the X-ray studies. The calculated υ_{B-H} stretching vibrations for both model compounds (**11**: 2503 (nonagostic), 2412 (agostic) cm^{-1}; **12**: 2499 (nonagostic), 2401 (agostic) cm^{-1}) are somewhat higher than those observed for the heteroleptic species **5** and **6**. However this may be ascribed to the decreased reduced mass of the oscillators within the simplified models and it is notable that $\Delta\upsilon$, the difference between the stretching vibrations in both the real and model compounds, is of a similar magnitude, ca. 100 cm^{-1}, across all four sets of data. For both **11** and **12** natural bond orbital (NBO) calculations were undertaken and the calculated charges on the Ca^{2+} (**11**, +1.83 Å) and Sr^{2+} (**12**, +1.86 Å) centers were suggestive of essentially ionic bonding. In both cases the donor carbon centers bear only a modest negative charge (<−0.03) indicating that they retain the essentially pure σ-donor character implicated in the formation of neutral adducts such as [(NHC)Ca{N(SiMe$_3$)$_2$}$_2$] (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene).[5] Although the majority of the anionic charge of the ligands is borne by the boron-bound imidazolinylidenyl nitrogen centers (*ca.* −0.63), the electrostatic nature of the M···HB interactions is indicated by the hydridic nature (*ca.* −0.11 for the coordinated hydrogen) of the borohydride subunits.

Catalytic Reactivity. We have reported previously that neutral NHC ligands readily dissociate in solution in the presence of harder (e.g., N- and O-centered) donors. This observation is especially relevant to the potential application of group 2 complexes in hydroamination catalysis where the reaction conditions are innately disposed toward carbene displacement.[5] Encouraged by the results described above, therefore, compounds **5** and **6** were assessed for the intramolecular hydroamination of a range of substituted aminoalkenes on an NMR scale in C_6D_6. In all cases, careful inspection of the NMR spectra revealed no observable protonation or dissociation of the borate ligand throughout reaction times up to a period of one week. The imidazole ^{1}H signals and the ^{13}C{^{1}H} carbene resonances remained effectively unaltered and no conclusive evidence for Schlenk-type ligand redistribution was observed.

Examination of the results listed in Table 5 indicated that the amidocalcium complex **5** displayed similar activity to that reported for the β-diketiminato calcium precatalyst, **I**.[1a] In common with these previous studies, bulky geminal substituents in the β-position of the amine favored cyclization due to a Thorpe-Ingold effect (entries 3−7), while terminal monosubstitution considerably hindered the reaction and terminal disubstitution prevented it entirely (entries 8−11). Catalytic activity also rapidly diminished with increasing ring-size (5 > 6 > 7; entries 12−16). Generally, cyclization occurred faster, with better conversion, and at lower temperature and catalyst loading with the strontium complex **6** than with its calcium counterpart. This is consistent with our observations of similar reactions catalyzed by heteroleptic calcium and strontium triazenide complexes but conflicts with the recent reports of Roesky and Blechert.[2,30] In this latter case, aminotropiniminate complexes [{(^{i}Pr)ATI}M{N(SiMe$_3$)$_2$}(THF)$_2$] (M = Ca or Sr) were applied to the cyclization of a series of substrates similar to that listed in Table 5. It was found that the strontium complex was significantly less active than its calcium counterpart for all reactions studied and led to the conclusion that the origin of this effect was the change in radius (for CN 6 (Å); Ca^{2+} 1.00; Sr^{2+} 1.18)[31] on descending the group.[2b] We would suggest at this time that this is something of an oversimplification and that any relative reduction in rate is more likely a function of the kinetic protection and propensity to solution redistribution of the supporting ligand rather than an intrinsic feature of the group 2 metal selected. We have carried out extensive experimental and theoretical experiments in support of this statement and will describe these data in subsequent publications.

Acknowledgment. We thank the Engineering and Physical Sciences Research Council (EPSRC) for provision of a project studentship (MA).

Supporting Information Available: NMR spectra for compounds **7**, **8** and **9,** atomic coordinates for the calculated structures of compounds **11** and **12** and further details of the X-ray analysis of compound **10**. Crystallographic information files (CIF) for **1, 3, 6**, **7** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8010933

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