4550 *Organometallics* **2009,** *28,* 4550–4559
DOI: 10.1021/om9003994

ORGANOMETALLICS
Article

Tris(imidazolin-2-ylidene-1-yl)borate Complexes of the Heavier Alkaline Earths: Synthesis and Structural Studies

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Received May 15, 2009

Heteroleptic tris(imidazolin-2-ylidene-1-yl)borate complexes of the heavier alkaline earth elements calcium, strontium, and barium have been synthesized by deprotonation of boronium salt ligand precursors with $[KN(SiMe_3)_2]$ in the presence of CaI_2, SrI_2, or BaI_2. Complex formation invariably involved partial B−N bond cleavage of the ligand precursors, leading to the formation of the silylamide complexes $[\{HB(Im^tBu)_3\}M\{N(SiMe_3)_2\}(N\text{-}Im^tBu)_n]$ (M = Ca, n = 0; Sr, n = 1; Ba, n = 1.5). All three silylamide complexes are stable toward Schlenk-type ligand redistribution in solution and show catalytic activity in the intramolecular hydroamination of aminoalkenes. In the case of M = Ca attempts to synthesize heteroleptic halide-containing species led to a 1:9 mixture of monomeric $[\{HB(Im^tBu)_3\}CaI(THF)]$ and $[\{HB(Im^tBu)_3\}CaI(N\text{-}Im^tBu)]$ following deprotonation of the boronium salt ligand precursor with $[KN(SiMe_3)_2]$ in the presence of CaI_2 or to dimeric $[\{HB(Im^tBu)_3\}CaBr]_2$ when using $[Ca\{N(SiMe_3)_2\}(THF)_2]$ as both base and calcium source. However, similar reactions with M = Sr resulted in the formation of only homoleptic $[\{HB(Im^tBu)_3\}_2Sr]$ probably due to the larger ionic radius of the strontium center combined with a less sterically demanding halide co-ligand. X-ray diffraction analyses of all compounds demonstrated in each case that the monoanionic borate ligand coordinates to the alkaline earth metal center in a C_3-symmetric *facial* κ^3-binding mode via the three N-heterocyclic carbene (NHC) σ-donors.

Introduction

In recent years, analogies between lanthanide ions in the 3+ oxidation state and the divalent cations of the heavier alkaline earth metals have resulted in increasing interest in the applications of heavier group 2 metal complexes in homogeneous catalysis.[1,2] In lanthanide chemistry, the use of kinetically stabilizing ligands with tailored steric and electronic properties has resulted in improved control over the catalytic process.[3] The development of a similar catalytic reaction chemistry for the heavier alkaline earths (Ca, Sr, Ba) by our group and others has mainly focused on the use of Chisholm's β-diketiminato complex **I**, which has demonstrated its efficiency in a variety of catalytic reactions and led to the synthesis of numerous derivatives.[4−6] The applicability of compound **I**, however, is limited by its tendency to undergo Schlenk-like redistribution to form catalytically inactive homoleptic species when combined with less sterically demanding co-ligands.[7] Additionally, heteroleptic species of the strontium and barium analogues could not be isolated, as these larger, less Lewis acidic metal centers provide a lower activation barrier for ligand redistribution toward the homoleptic species.[7] These considerations have led to the introduction of the widely employed C_3-symmetric tris(pyrazolyl)borate ligands, whose increased denticity and steric demands afford enhanced kinetic protection of the

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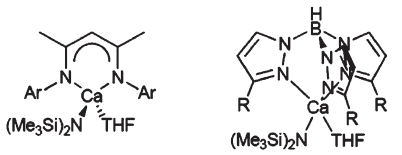
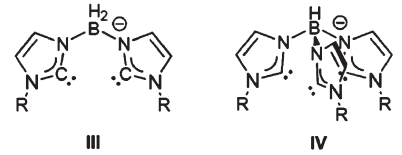
 Published on Web 07/09/2009

metal center and also partially perturb ligand redistribution equilibria for compound **II**.[6b]



I **II**

Ar = 2,6-di-*iso*-propylphenyl R - *tert*-butyl



III **IV**

Our group has recently reported a series of neutral N-heterocyclic carbene (NHC) adducts of the homoleptic heavier group 2 silylamides, $[(NHC)M\{N(SiMe_3)_2\}_2]$ (M = Mg, Ca, Sr, Ba; NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).[8] Although these compounds are stable in solution at elevated temperatures, the NHC proved labile under catalytically relevant conditions in the presence of protic substrates or other Lewis basic donors. Comparable behavior in lanthanide chemistry has been effectively overcome by designing bi- or tridentate NHC-containing ligands in which an anionic amido or alkoxo functionality provides significantly enhanced kinetic stability.[9] These considerations led us to investigate the monoanionic bis- and tris-(imidazolin-2-ylidenyl)borate ligands **III** and **IV** [HB(ImR)], whose topological similarities to the tris(pyrazolyl)borates used in compound **II** promised similar kinetic, electronic, and solubility properties, as well as scope for steric and electronic tuning by variation of the imidazole substituents.

Although the relatively rigid and anionic tris(imidazolin-2-ylidene)borate ligands were first reported by Fehlhammer in 1996,[10] to date, their application in organometallic chemistry remains limited to a small number of main group and transition metals.[7,9,10] Recently Smith reported a new synthetic route toward bulkier ligands of this type in which deprotonation of a boronium salt precursor, $[HB(ImR)_3Br_2]$ (R = 2,4,6-trimethylphenyl, ^{t}Bu), by a lithium or magnesium base yielded the anionic ligand.[11,12] Recently, this procedure has been extended by the same group to the synthesis of the bidentate $H_2B(Im^tBu)_2Br$ ligand precursor and its lithium and nickel derivatives.[11d]

Our group has recently described a series of calcium and strontium bis(imidazolin-2-ylidene)borate derivatives obtained from a simple low-temperature "one-pot" synthesis of the boronium salt precursor $H_2B(Im^tBu)_2I$ with 3 equiv of $[KN(SiMe_3)_2]$ and 1 equiv of CaI_2 or SrI_2.[13] The resulting heteroleptic silylamide complexes $[\{H_2B(Im^tBu)_2\}M\{N(SiMe_3)_2\}(THF)_n]$ (M = Ca, n = 1; Sr, n = 2) were successfully tested in a range of intramolecular hydroamination reactions, showing no Schlenk-type ligand redistribution and with the strontium catalysts proving superior in all ways to the previously used β-diketiminato calcium silylamide **I**. Attempts to substitute the bis(trimethylsilyl)amide co-ligand with smaller amines, however, often led to the formation of the homoleptic species, while the reaction with other Brønsted acids such as terminal acetylenes resulted in protonation and displacement of the bidentate ligand. In this contribution we describe the synthesis of a series of tris(imidazolin-2-ylidene)borate complexes of calcium, strontium, and barium with enhanced steric protection of the metal center as well as synthetic limitations of these ligands under the described reaction conditions.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk and glovebox techniques under an inert atmosphere of 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 128.3 MHz) or a Bruker AV-300 spectrometer ($^{13}C\{^1H\}$ NMR 75 MHz, $^{11}B\{^1H\}$ NMR 96.3 MHz). BH proton resonances in the ^{1}H NMR spectra were observed through selective decoupling from the ^{11}B nuclei. Solvents (toluene, THF, hexane) were dried by passage through the columns of a commercial solvent purification system. D_8-toluene was 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),[14] *tert*-butylimidazole,[11b] and the ligand precursor $[HB(Im^tBu)_3]Br_2$[11a] were prepared according to literature procedures. $Me_3N\cdot BHBr_2$ was prepared by a variation of the procedure reported for the synthesis of $Me_3N\cdot BBr_3$.[15a] Ph_2BBr was synthesized by the method of Haubold.[15b] Product yields are based upon the initial amount of alkaline earth iodide employed. Melting points were not determined, as the majority of compounds tended to melt at room temperature. Elemental analyses were provided by Mr. Stephen Boyer of London Metropolitan Enterprises. Attempts to acquire satisfactory elemental analyses on compound **4** were unsuccessful due to rapid decomposition at room temperature; a ^{1}H NMR spectrum of the isolated compound is provided in the Supporting Information as corroborative evidence of purity.

$[Me_3N\cdot BHBr_2]$. A solution of Br_2 (3.86 mL, 75.3 mmol) in toluene (50 mL) was added dropwise to a solution of $Me_3N\cdot BH_3$ (3.65 g, 50 mmol) in toluene (80 mL) while under a purge of N_2, and the evolved HBr was absorbed by passage of the exhaust gases through a trap filled with aqueous NaOH. Over the course

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of 2 h, the solution turned bright yellow. Removal of volatiles, addition of hexane, and cooling to −30 °C for 2 h provided colorless crystals, which were isolated by filtration (8.87 g, 77%). ^{1}H NMR ppm ($CDCl_3$): 2.90 (s, 9H, C*H*$_3$), 4.24 (q, 1H, B*H*, $^1J_{11BH}$ = 156 Hz). ^{13}C NMR ppm ($CDCl_3$): 50.6 (*C*H$_3$). ^{11}B-{^{1}H} NMR ppm ($CDCl_3$): −0.73.

[HB(Im^{t}Bu)$_3$]Br$_2$, 1. 1-*tert*-Butylimidazole (8.00 g, 64.4 mmol) and $Me_3N\cdot BHBr_2$ (4.95 g, 21.5 mmol) were refluxed in dry chlorobenzene (25 mL) under nitrogen for 18 h. Upon cooling to room temperature, a white precipitate formed, which was isolated by filtration. The crude white solid was dissolved in CH_2Cl_2, precipitated with Et_2O, and dried consecutively in air and *in vacuo* for a day to remove residual traces of chlorobenzene. Crystallization from $CHCl_3$ afforded a colorless solid (8.26 g, 71%, lit.[11a] 68%), mp 270 °C (lit. 273−275 °C).[11a] ^{1}H NMR ppm ($CDCl_3$): 9.85 (s, 1H, ring-NC*H*N), 8.45 (s, 1H, ring-C*H*=CHN^{t}Bu), 7.26 (s, 1H, ring-CH=C*H*N^{t}Bu), 1.73 (s, 9H, C*H*$_3$). ^{13}C NMR ppm ($CDCl_3$): 138.1 (ring-N*C*HN), 126.0 ring-*C*H=CHN^{t}Bu), 120.1 (ring-CH=*C*HN^{t}Bu), 60.1 (*C*CH$_3$), 30.7 (*C*H$_3$). ^{11}B NMR ppm ($CDCl_3$): −2.16 (BH).

Synthesis of Tris(imidazolin-2-ylidenyl)borate Alkaline Earth Compounds 2−5. General Procedure. In a glovebox, compound **1**, MI_2 (M = Ca, Sr, Ba), 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 stirred at room temperature overnight or until the metal iodide beads had been consumed. The solvent was removed *in vacuo* and toluene added. The resultant milky solution was stirred for another hour and then allowed to settle prior to cannula and Celite filtration and concentration of the solution to incipient crystallization. After between 3 and 7 days at −20 °C, the mother liquor was filtered into a second Schlenk flask and the transparent crystals completely dried on a vacuum line.

[{HB(Im^{t}Bu)$_3$}Ca{N(SiMe$_3$)$_2$}], 2. Compound **1** (0.5 g, 0.92 mmol), calcium iodide (0.27 g, 0.92 mmol), [KN(SiMe$_3$)$_2$] (0.73 g, 3.67 mmol): colorless crystals after 2 days at −20 °C (0.62 g, 88%). ^{1}H{^{11}B} NMR ppm (d_8-tol, 298 K): 7.33 (s, 3H, ring-C*H*=CHN^{t}Bu), 6.65 (s, 3H, ring-CH=C*H*N^{t}Bu), 4.97 (s, 1H, B*H*), 1.37 (s, 27H, C*H*$_3$), 0.27 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR ppm (d_8-tol, 298 K): 198.5 (carbene-*C*), 127.3 (ring-*C*H=CHN^{t}Bu), 113.9 (ring-CH=*C*HN^{t}Bu), 55.8 (*C*CH$_3$), 31.2 (C*C*H$_3$), 2.6 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR ppm (d_8-tol, 298 K): 2.53 (*B*H). Anal. Calcd for $C_{27}H_{52}BCaN_7Si_2$ (581.8): C, 55.74; H, 9.01; N, 16.85. Found: C, 55.69; H, 8.96; N, 16.91.

[Ca{N(SiMe$_3$)$_2$}(N-Im^{t}Bu)$_2$], 8. 10% byproduct of the above reaction, isolated in the first crystallization fraction. ^{1}H{^{11}B} NMR ppm (d_8-tol, 298 K): 8.02 (br s, 1H, ring-NC*H*N), 6.98 (br s, 1H, ring-C*H*=CHN^{t}Bu), 6.42 (br s, 1H, ring-CH=C*H*N^{t}Bu), 1.03 (s, 9H, C*H*$_3$), 0.44 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR ppm (d_8-tol, 298 K): 135.7 (ring-N*C*HN), 124.9 (ring-*C*H=CHN^{t}Bu), 114.8 (ring-CH=*C*HN^{t}Bu), 53.5 (*C*CH$_3$), 28.7 (C*C*H$_3$), 4.8 (Si(*C*H$_3$)$_3$).

[{HB(Im^{t}Bu)$_3$}Sr{N(SiMe$_3$)$_2$}(N-Im^{t}Bu)], 3. Compound **1** (1.00 g, 1.84 mmol), strontium iodide (0.62 g, 1.84 mmol), [KN(SiMe$_3$)$_2$] (1.46 g, 7.34 mmol): colorless crystals after 1 day at −20 °C (0.55 g, 64%). ^{1}H{^{11}B} NMR ppm (d_8-tol, 298 K): 7.47 (br s, 1H, coordinated Im^{t}Bu NC*H*N), 7.33 (d, 3H, ligand ring-C*H*=CHN^{t}Bu, ^3J = 1.5 Hz), 7.19 (br s, 1H, coordinated Im^{t}Bu C*H*=CHN^{t}Bu), 6.65 (d, 3H, ligand ring-CH=C*H*N^{t}Bu, ^3J = 1.5 Hz), 6.55 (br s, 1H, coordinated Im^{t}Bu CH=C*H*N^{t}Bu), 5.00 (s, 1H, B*H*), 1.39 (s, 27H, ligand C*H*$_3$), 0.99 (s, 9H, coordinated Im^{t}Bu C*H*$_3$), 0.27 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C-{^{1}H} NMR ppm (d_8-tol, 298 K): 201.5 (carbene-*C*), 137.1 (coordinated Im^{t}Bu N*C*HN), 129.3 (coordinated Im^{t}Bu *C*H=CHN^{t}Bu), 127.6 (ligand ring-*C*H=CHN^{t}Bu), 113.6 (ligand + coordinated ring-CH=*C*HN^{t}Bu), 55.7 (ligand + coordinated Im^{t}Bu *C*CH$_3$), 31.2 (ligand C*C*H$_3$), 30.0 (coordinated Im^{t}Bu C*C*H$_3$), 2.59 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR ppm (d_8-tol, 298 K): 3.35 (*B*H). Anal. Calcd for $C_{34}H_{64}BN_9Si_2Sr$ (753.5): C, 54.19; H, 8.56; N, 16.73. Found: C, 54.29; H, 8.56; N, 16.79.

[{HB(Im^{t}Bu)$_3$}Sr{N(SiMe$_3$)$_2$}(THF)], 3′. Compound **1** (1.33 g, 2.45 mmol), strontium iodide (0.31 g, 0.92 mmol), [KN(SiMe$_3$)$_2$] (0.73 g, 3.67 mmol), filtration through filter cannula only, all glassware prewashed with a basic 2-propanol solution of potassium hydroxide before drying 1 day at 150 °C: colorless crystals after 1 day at −20 °C (0.26 g, 40%). A second crystallization fraction yielded 0.15 g of compound **3**. ^{1}H{^{11}B} NMR ppm (d_8-tol, 298 K): 7.20 (d, 3H, ring-C*H*=CHN^{t}Bu, ^3J = 1.2 Hz), 6.48 (d, 3H, ring-CH=C*H*N^{t}Bu, ^3J = 1.2 Hz), 4.86 (s, 1H, B*H*), 3.55 (m, 4H, THF), 1.39 (m, 4H, THF), 1.37 (s, 27H, C*H*$_3$), 0.40 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR ppm (d_8-tol, 298 K): 198.7 (carbene-*C*), 126.8 (ring-*C*H=CHN^{t}Bu), 113.8 (ring-CH=*C*HN^{t}Bu), 68.3 (THF), 55.3 (*C*CH$_3$), 31.3 (C*C*H$_3$), 25.5 (THF), 6.7 (Si(*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR ppm (d_8-tol, 298 K): 2.40 (*B*H). Anal. Calcd for $C_{31}H_{60}BN_7OSi_2Sr$ (701.5): C, 53.08; H, 8.62; N, 13.98. Found: C, 52.99; H, 8.55; N, 13.88.

[{HB(Im^{t}Bu)$_3$}Ba{N(SiMe$_3$)$_2$}(N-Im^{t}Bu)$_{1.5}$], 4. Compound **1** (1.00 g, 1.84 mmol), barium iodide (0.72 g, 1.84 mmol), [KN(SiMe$_3$)$_2$] (1.46 g, 7.34 mmol): colorless crystals after 7 days at −20 °C (0.77 g, 48%). In solution each barium center is solvated by two *tert*-butylimidazole fragments. ^{1}H{^{11}B} NMR ppm (d_8-tol, 298 K): 7.34 (br s, 2H, coordinated Im^{t}Bu NC*H*N), 7.30 (s, 3H, ligand ring-C*H*=CHN^{t}Bu), 6.98 (s, 2H, coordinated Im^{t}Bu C*H*=CHN^{t}Bu), 6.54 (s, 3H, ligand ring-CH=C*H*N^{t}Bu), 6.42 (s, 2H, coordinated Im^{t}Bu CH=C*H*N^{t}Bu), 4.98 (s, 1H, B*H*), 1.30 (s, 27H, ligand C*H*$_3$), 0.97 (s, 27H, coordinated Im^{t}Bu C*H*$_3$), 0.51 (s, 18H, SiC*H*$_3$). ^{13}C{^{1}H} NMR ppm (d_8-tol, 298 K): 205.9 (carbene-*C*), 135.5 (coordinated Im^{t}Bu N*C*HN), 129.2 (coordinated Im^{t}Bu *C*H=CHN^{t}Bu), 126.5 (ligand ring-*C*H=CHN^{t}Bu), 115.5 (coordinated Im^{t}Bu CH=*C*HN^{t}Bu), 113.1 (ligand ring-CH=*C*HN^{t}Bu), 55.0 (ligand *C*CH$_3$), 53.9 (coordinated Im^{t}Bu *C*CH$_3$), 31.2 (ligand C*C*H$_3$), 29.7 (coordinated Im^{t}Bu C*C*H$_3$), 6.5 (Si*C*H$_3$). ^{11}B{^{1}H} NMR ppm (d_8-tol, 298 K): 1.32 (*B*H).

[{HB(Im^{t}Bu)$_3$}CaI(N-Im^{t}Bu)], 5. Compound **1** (0.5 g, 0.92 mmol), calcium iodide (0.27 g, 0.92 mmol), [KN(SiMe$_3$)$_2$] (0.55 g, 2.76 mmol): off-white powder after 2 days at −20 °C (0.42 g, 68%). ^{1}H{^{11}B} NMR ppm (d_8-tol, 298 K): 7.91 (br s, 1H, coordinated Im^{t}Bu NC*H*N), 7.19 (d, 3H, ligand ring-C*H*=CHN^{t}Bu, ^3J = 1.5 Hz), 6.55 (br s, 1H, coordinated Im^{t}Bu C*H*=CHN^{t}Bu), 6.44 (d, 3H, ligand ring-CH=C*H*N^{t}Bu, ^3J = 1.5 Hz), 6.10 (br s, 1H, coordinated Im^{t}Bu CH=C*H*N^{t}Bu), 4.88 (s, 1H, B*H*), 1.31 (s, 27H, ligand C*H*$_3$), 0.84 (s, 9H, coordinated Im^{t}Bu C*H*$_3$). ^{13}C{^{1}H} NMR ppm (d_8-tol, 298 K): 195.5 (carbene-*C*), 129.0 (coordinated Im^{t}Bu N*C*HN), 125.4 (coordinated Im^{t}Bu *C*H=CHN^{t}Bu), 125.0 (ligand ring-*C*H=CHN^{t}Bu), 115.3 (coordinated Im^{t}Bu CH=*C*HN^{t}Bu), 113.4 (ligand ring-CH=*C*HN^{t}Bu), 54.3 (ligand + coordinated Im^{t}Bu *C*CH$_3$), 29.9 (ligand C*C*H$_3$), 28.8 (coordinated Im^{t}Bu C*C*H$_3$). ^{11}B{^{1}H} NMR ppm (d_8-tol, 298 K): 1.7 (*B*H). Anal. Calcd for $C_{28}H_{46}BCaNI_8$ (672.5): C, 50.01; H, 6.89; N, 16.66. Found: C, 49.93; H, 6.87; N, 16.58.

[{HB(Im^{t}Bu)$_3$}CaI(THF)], 5′. 5−10% byproduct of the above reaction. Although colorless single crystals were isolated for X-ray crystallography, sufficient pure material was not available for NMR or even elemental analysis.

Synthesis of Tris(imidazolin-2-ylidenyl)borate Alkaline Earth Compounds 6 and 7. General Procedure. In a glovebox, compound **1** and [M{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (M = Ca, Sr) were weighed at a 1:1.5 ratio into a dry Schlenk flask. Dry THF was added at −78 °C, and the mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and toluene added. The resultant milky solution was stirred for another hour and then allowed to settle prior to cannula filtration and concentration of the solution to incipient crystallization. After 3−5 days at −20 °C, the mother liquor was filtered into a second Schlenk flask, and the transparent crystals were completely dried on vacuum line.

[{HB(Im^{t}Bu)$_3$}CaBr]$_2$, 6. Compound **1** (0.5 g, 0.92 mmol) and [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (0.70 g, 1.38 mmol): colorless crystals

after 2 days at −20 °C (0.32 g, 69%). $^1H\{^{11}B\}$ NMR ppm (d_8-tol, 298 K): 7.24 (d, 3H, ring-C*H*=CHN^{t}Bu, ^3J = 1.2 Hz), 6.53 (d, 3H, ring-CH=C*H*N^{t}Bu, ^3J = 1.2 Hz), 4.94 (s, 1H, B*H*), 1.54 (s, 27H, CH_3). $^{13}C\{^1H\}$ NMR ppm (d_8-tol, 298 K): 199.4 (carbene-*C*), 125.9 (ring-*C*H=CHN^{t}Bu), 114.0 (ring-CH=*C*HN^{t}Bu), 55.9 (*C*CH$_3$), 32.2 (C*C*H$_3$). $^{11}B\{^1H\}$ NMR ppm (d_8-tol, 298 K): 1.91 (*B*H). Anal. Calcd for $C_{21}H_{34}BBrCaN_6$ (501.3): C, 50.31; H, 6.84; N, 16.76. Found: C, 50.28; H, 6.76; N, 16.67.

[{HB(Im^{t}Bu)$_3$}$_2$Sr], 7. Redistribution product from the attempted synthesis of [{HB(Im^{t}Bu)$_3$}SrBr]$_2$: Compound **1** (0.5 g, 0.92 mmol) and [Sr{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (0.76 g, 1.38 mmol): colorless crystals after 4 days at −20 °C (0.21 g, 54% based on ligand). $^1H\{^{11}B\}$ NMR ppm (d_8-tol, 298 K): 7.25 (d, 3H, ring-C*H*=CHN^{t}Bu, ^3J = 1.5 Hz), 6.57 (d, 3H, ring-CH=C*H*N^{t}Bu, ^3J = 1.5 Hz), 4.92 (s, 1H, B*H*), 1.31 (s, 27H, CH_3). $^{13}C\{^1H\}$ NMR ppm (d_8-tol, 298 K): 201.6 (carbene-*C*), 128.1 (ring-*C*H=CHN^{t}Bu), 113.8 (ring-CH=*C*HN^{t}Bu), 55.7 (*C*CH$_3$), 31.3 (C*C*H$_3$). $^{11}B\{^1H\}$ NMR ppm (d_8-tol, 298 K): 3.84 (*B*H). Anal. Calcd for $C_{42}H_{68}B_2N_{12}Sr$ (850.3): C, 59.33; H, 8.06; N, 19.77. Found: C, 59.27; H, 8.14; N, 19.69.

[Ph$_2$B(Im^{t}Bu)$_2$Br]. *N*-*tert*-Butylimidazole (2.00 g, 16.4 mmol) in chlorobenzene (25 mL) was added at room temperature to Ph$_2$BBr (2.00 g, 8.20 mmol), resulting in the immediate precipitation of a colorless powder. This was isolated by filtration and crystallized from a mixture of CH_2Cl_2 and E_2O (2.14 g, 71%). $^1H\{^{11}B\}$ NMR ppm ($CDCl_3$, 298 K): 8.20 (t, 2H, NC*H*N), 7.34 (t, 2H, ring-C*H*=CHN^{t}Bu), 7.17−7.23 (m, 6H, *o*-, *p*-Ph), 7.03−7.06 (m, 6H, *m*-Ph and ring-CH=C*H*N^{t}Bu), 1.59 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR ppm ($CDCl_3$, 298 K): 138.2 (*i*-Ph), 134.7 (N*C*HN), 132.2 (*o*-Ph), 126.6 (*m*-Ph), 126.0 (ring-CH=*C*HN^{t}Bu), 124.5 (*m*-Ph), 118.0 (ring-*C*H=CHN^{t}Bu), 57.7 (*C*(CH$_3$)$_3$), 28.9 (*C*H$_3$). $B\{^1H\}$ NMR ppm ($CDCl_3$), 298 K): 1.97.

[Ph$_2$B(Im^{t}Bu)]$_2$, 9. Only isolable product of the reaction of [Ph$_2$B(Im^{t}Bu)$_2$Br] and [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] in 1:1.5 ratio at −78 °C in THF. Reaction mixture turned brown at room temperature and yielded compound **9** as colorless crystals from toluene after 10 days at −20 °C (17%). $^1H\{^{11}B\}$ NMR ppm (C_6D_6, 298 K): 7.59 (dd, 4H, *o*-Ph, ^3J = 8.1 Hz, ^4J = 1.5 Hz), 7.19−7.29 (m, 6H, *m*/*p*-Ph), 6.91 (d, 1H, ring-C*H*=CHN^{t}Bu, ^3J = 1.8 Hz), 6.45 (d, 1H, ring-CH=C*H*N^{t}Bu, ^3J = 1.8 Hz), 0.74 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR ppm (d_8-tol, 298 K): 182.9 (carbene-*C*), 136.6 (Ph-*i*-*C*), 129.7 (Ph-*o*-*C*), 128.9 (Ph-*p*-*C*), 127.8 (Ph-*m*-*C*), 126.0 (ring-*C*H=CHN^{t}Bu), 124.3 (ring-CH=*C*HN^{t}Bu), 59.2 (*C*CH$_3$), 31.7 (C*C*H$_3$). $^{11}B\{^1H\}$ NMR ppm (d_8-tol, 298 K): −2.53 (*B*H). Anal. Calcd for $C_{38}H_{42}B_2N_4$ (576.4): C, 79.18; H, 7.34; N, 9.72. Found: C, 79.13; H, 7.29; N, 9.72.

Crystallographic Data. Data for compounds **3**, **4**, **6**, **7**, **8**, and **9** were collected at 150 K on a Nonius KappaCCD diffractometer (**5′** at 173 K on a Enraf Nonius FR590 diffractometer) equipped with an Oxford Cryosystem, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were processed using Nonius software.[16] 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.[17]

For compounds **4**, **6**, and **7** −BH hydrogen atoms were identified in the difference Fourier map and refined freely. For compound **3** there is a potential disorder in the second solvent molecule of toluene (C42−C48). However, resolving the disorder did not lead to a better result. For **4**, the sample consisted of low melting crystals, which were selected using a modified device, similar to that of Veith and Bärnighausen.[18] The asymmetric unit is composed of two nonidentical barium complexes and two solvent molecules of toluene. The disordered *tert*-butyl group of one of the imidazole adducts is responsible for the high *R*(int). In the structure of **5′**, the disordered carbon atoms in the THF ligand were left isotropic. Each main molecule cocrystallized with two disordered toluene solvate molecules, which were included with rigid C6 rings and isotropic carbon atoms. For compound **7** the crystals lost solvent quickly. During data collection the crystal must have moved, hence the bad *R*(int). It was not possible to use all collected data for integration, which led to a lower completeness of data (97%). Each asymmetric unit consists of half a molecule of the homoleptic complex and two molecules of toluene in three positions. One toluene molecule is sitting on a 2-fold axis. Another is located around a center of inversion with 50% occupation factor. The third is heavily disordered in four positions in the ratio 50:15:15:20. Carbon atoms for the heavily disordered toluene have been fitted to a regular hexagon and are all refined isotropically.

Results and Discussion

Synthetic and Structural Studies of Group 2 Tris(imidazolin-2-ylidene-1-yl)borate Complexes. The ligand precursor salt HB[Im^{t}Bu]$_3$Br$_2$ was synthesized following the procedure described by Smith (Scheme 1)[11a] and crystallized from dichloromethane. ^1H and $^{13}C\{^1H\}$ chemical shift data were in accordance with those reported by Smith et al., with a characteristic low-field H-2 imidazole proton resonance at 9.85 ppm in the ^1H NMR spectrum.

We have recently reported the synthesis of a variety of heavier group 2 bis(imidazolin-2-ylidene-1-yl)borates[13] employing a similar procedure to that used for the very successful "one-pot" synthesis of the β-diketiminate complex **I**.[6] Using a similar procedure, addition of THF at −78 °C to a mixture of 4 equiv of [KN(SiMe$_3$)$_2$], 1 equiv of the ligand precursor **1**, and either CaI_2, SrI_2, or BaI_2 provided, after extraction into toluene, the desired heteroleptic group 2 amides **2**, **3**, and **4** (Scheme 2). Contrary to the previously described group 2 bis(imidazolin-2-ylidene-1-yl)borate amides, whose coordination sphere is completed by THF, NMR and X-ray data of compounds **3** and **4** showed the presence of 1-*tert*-butylimidazole adducts arising from fragmentation of the ligand precursor during the reaction. Such decomposition had already been observed in the NMR spectra of the crude reaction mixtures of the bis(imidazolin-2-ylidene-1-yl)borate compounds.[13] After separation from KI and KBr byproduct and storage of concentrated toluene solutions at −20 °C, complexes **2**−**4** could, however, be isolated as colorless crystalline, very low melting solids in moderate to good (48−88%) yields. Repeating the synthesis of **3** without the use of the potentially acidic Celite during filtration and washing of the Schlenk flasks with a basic 2-propanol solution of potassium hydroxide before drying them for 1 day at 150 °C yielded a 60:40 mixture of the expected THF adduct **3′** and compound **3**. Although suitable crystals of compound **3′** could not be prepared for X-ray crystallography, ^1H and $^{13}C\{^1H\}$ NMR spectra and elemental analyses of **3′** were in accordance with the expected structure. Analogous reaction and filtration conditions for the synthesis of the barium silylamide complex did not yield the THF adduct and instead resulted in decomposition of the ligand. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2**, **3**, and **4** were consistent with the expected structures.

(16) DENZO-SCALEPACK: Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology*, Vol. *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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(18) Veith, M.; Bärnighausen, H. *Acta Crystallogr. B* **1974**, *30*, 1806.

Table 1. Crystallographic Data for Compounds 3, 4, 5′, 6, and 7

	3	4	5′	6	7
molecular formula	$C_{48}H_{80}BN_9Si_2Sr$	$C_{89}H_{156}B_2Ba_2N_{20}Si_4$	$C_{25}H_{42}BCaIN_6O\cdot 1{,}5\ (C_7H_8)$	$C_{70}H_{100}B_2Br_2Ca_2N_{12}$	$C_{70}H_{100}B_2N_{12}Sr$
fw (g mol^{-1})	937.82	1915.00	758.64	1371.22	1218.86
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	*Pcab*	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$
a (Å)	19.1624(1)	22.0042(1)	18.4848(16)	10.8142(1)	25.2604(6)
b (Å)	20.4613(1)	13.9524(1)	10.5873(9)	12.5304(1)	11.2390(2)
c (Å)	27.5283(2)	34.0515(2)	20.6304(15)	14.9414(2)	25.2461(6)
α (deg)	90	90	90	69.799(1)	90
β (deg)	90	91.565(1)	93.155(5)	88.483(1)	105.289(1)
γ (deg)	90	90	90	77.947(1)	90
V (Å^3)	10793.50(11)	10450.30(11)	4031.3(6)	1855.92(3)	6913.7(3)
Z	8	4	4	1	4
μ (mm^{-1})	1.082	0.845	0.95	1.277	0.828
ρ (g cm^{-3})	1.154	1.217	1.25	1.227	1.171
θ range (deg)	3.12 to 27.49	3.52 to 27.47	3.47 to 26.02	3.01 to 30.01	3.34 to 27.45
R_1,[a] wR_2 [$I > 2\sigma(I)$][b]	0.0467, 0.0909	0.0399, 0.0797	0.059, 0.123	0.0452, 0.1062	0.0600, 0.1435
R_1, wR_2 (all data)[b]	0.0848, 0.1051	0.0724, 0.0900	0.090, 0.138	0.0710, 0.1189	0.0992, 0.1699
measd/indep refls/R_{int}	176 037/12 336/0.1222	13 5871/23 755/0.0801	24 028/7870/0.060	51 329/10 759/0.0578	26 486/7654/0.1566

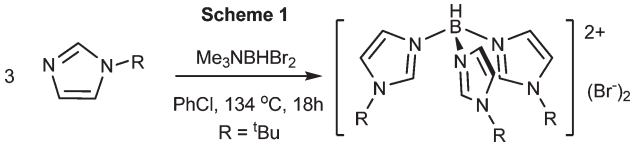
[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Comparative M−$C_{carbene}$ and δ_{13C} NMR Data for Ca, Sr, and Ba NHC Complexes[a]

compound	M−C_{NHC} (Å)	$\Delta^{13}C$ C_{NHC} (ppm)	ref
2		198.5	this work
5		195.5	this work
5′	2.582(5)−2.510(5)−2.526(4)		this work
6	2.544(2)−2.564(2)−2.559(2)	199.5	this work
[(L^1)Ca{N(SiMe$_3$)$_2$}(THF)]		195.0	10
[(L^1)$_2$Ca(THF)]	2.583(3)−2.646(4)	195.0	10
[(L^2)Ca{N(SiMe$_3$)$_2$}(THF)]		196.0	10
[Ca(L^3){N(SiMe$_3$)$_2$}$_2$]	2.598(2)	193.3	5
[Ca(L^4){N(SiMe$_3$)$_2$}$_2$]	2.6259(2)	195.4	5
[(Cp*)$_2$Ca{L^5}]	2.562(2)	196.2	16
3	2.749(3)−2.776(3)−2.811(3)	201.5	this work
3′		198.7	this work
7	2.810(3)−2.802(3)−2.805(3)	201.6	this work
[(L^1)Sr{N(SiMe$_3$)$_2$}(THF)$_2$]	2.739(3)−2.757(4)	201.5	10
[(L^1)$_2$Sr(THF)$_2$]		198.9	10
[Sr(L^3){N(SiMe$_3$)$_2$}$_2$]	2.731(3)	199.0	5
[(Cp*)$_2$Sr{L^5}]		198.2	16
[(Cp*)$_2$Sr{L^5}$_2$]	2.868(5)−2.854(5)	203.7	16
4	2.977(3)−2.947(3)−2.978(3)	205.9	this work
[(Cp*)$_2$Ba{L^5}]	2.951(3)	203.5	16

[a] L^1 = bis(1-*tert*-butylimidazolin-2-ylidene)borate; L^2 = bis(1-2,4,6-trimetyhylphenylimidazolin-2-ylidene)borate; L^3 = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; L^4 = 1,3-bis(2,6-di-isopropylphenyl)imidazol-2-ylidene; L^5 = 1,3-bis(methyl)imidazol-2-ylidene.

Scheme 1



Particularly characteristic were the low-field $^{13}C\{^1H\}$ signals attributed to the metal-coordinated C-2 carbene centers of the borate ligand appearing at 196.2 ppm (**2**), 201.5 ppm (**3**), 198.7 (**3′**), and 205.9 ppm (**4**), respectively. We have previously reported a similar trend in calcium and strontium bis(imidazolin-2-ylidene-1-yl)borate species[13] as well as in the neutral NHC adducts [(NHC)M{N(SiMe$_3$)$_2$}$_2$],[8] showing that the magnitude of the upfield shifts of the C-2 center from that of the free carbene decreases with the Lewis acidity of the group 2 metal (Table 2).[8] As for its bidentate counterpart, it appears that the incorporation of the NHC into the tridentate anionic borate ligand does not affect the behavior of the C-2 carbene centers as pure -donors.

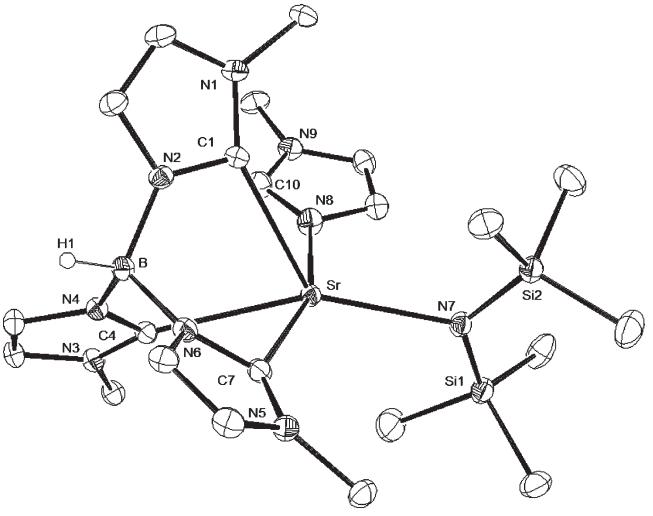


Figure 1. ORTEP representation of compound **3**. Thermal ellipsoids at 30% probability. Hydrogen and *tert*-butyl carbon methyl atoms are removed for clarity.

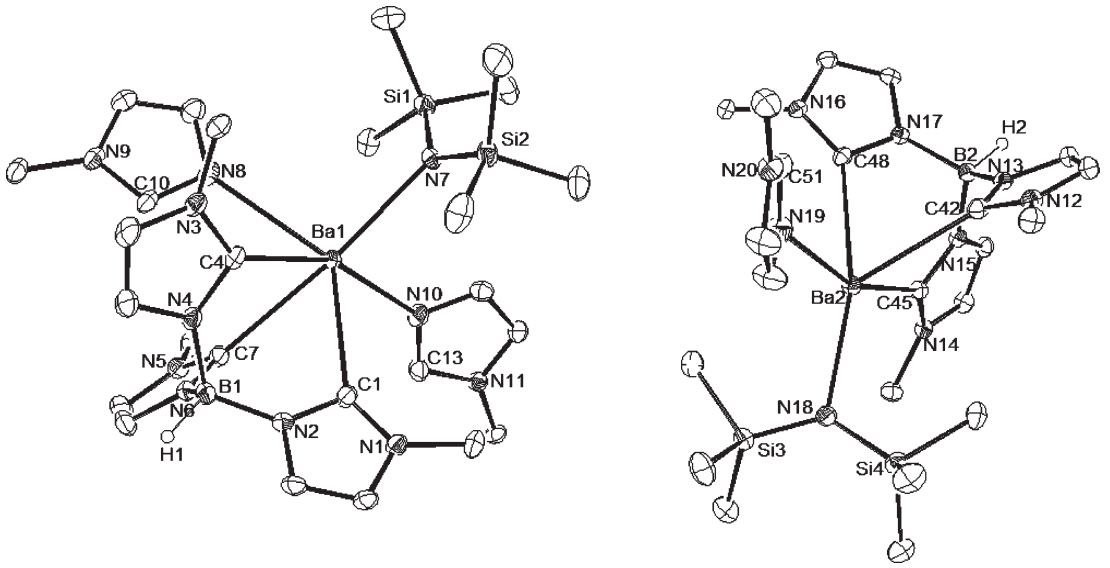


Figure 2. ORTEP representation of compound **4**. Thermal ellipsoids are at 30% probability. Hydrogen and *tert*-butyl carbon methyl atoms are removed for clarity.

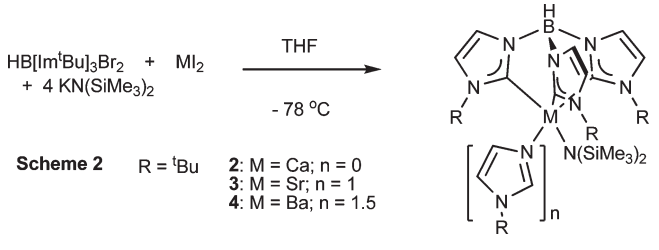
Table 3. Selected Bond Lengths (Å) for Compounds 3, 4, 5′, 6, and 7

	3	4	5′	6	7
B(1)−N(2)	1.555(3)	1.546(4)	1.547(6)	1.552(3)	1.555(4)
B(1)−N(4)	1.554(4)	1.549(4)	1.559(6)	1.554(3)	1.552(4)
B(1)−N(6)	1.557(4)	1.554(4)	1.546(6)	1.554(3)	1.553(4)
B(2)−N(13)		1.555(4)			
B(2)−N(15)		1.551(4)			
B(2)−N(17)		1.563(4)			
C(1)−N(1)	1.373(3)	1.373(4)	1.364(6)	1.367(3)	1.372(4)
C(1)−N(2)	1.372(3)	1.372(4)	1.369(6)	1.367(3)	1.378(4)
C(4)−N(3)	1.374(3)	1.372(4)	1.366(6)	1.368(3)	1.371(4)
C(4)−N(4)	1.370(3)	1.364(4)	1.364(6)	1.364(3)	1.379(4)
C(7)−N(5)	1.369(3)	1.370(4)	1.363(6)	1.367(3)	1.368(4)
C(7)−N(6)	1.375(3)	1.365(4)	1.368(6)	1.366(3)	1.367(4)
C(42)−N(12)		1.371(4)			
C(42)−N(13)		1.369(4)			
C(45)−N(14)		1.364(3)			
C(45)−N(15)		1.374(3)			
C(48)−N(16)		1.369(3)			
C(48)−N(17)		1.366(3)			
B−H(1)	1.0000	1.14(3)	1.0000	1.13(2)	1.15(3)
B(2)−H(2)		1.14(2)			
Ca−I			3.0490(9)		
Ca−Br				2.8930(4)	
Ca−Br’				2.9040(4)	

Table 4. Selected Bond Angles (°) for Compounds 3, 4, 5′, 6, and 7

	3	4	5′	6	7
N(2)−B(1)−N(4)	110.9(2)	112.6(3)	109.5(4)	112.42(17)	111.6(2)
N(2)−B(1)−N(6)	113.2(2)	112.9(3)	110.6(4)	111.33(17)	112.4(2)
N(6)−B(1)−N(4)	112.1(2)	111.3(2)	112.3(4)	109.57(17)	112.9(2)
N(13)−B(2)−N(15)		113.1(2)			
N(13)−B(2)−N(17)		112.3(2)			
N(17)−B(2)−N(15)		110.5(2)			
C(1)−N(2)−B(1)	128.7(2)	129.4(2)	127.2(4)	127.07(17)	128.8(2)
C(4)−N(4)−B(1)	128.5(2)	128.3(2)	125.4(4)	127.26(17)	128.7(2)
C(7)−N(6)−B(1)	128.4(2)	128.6(2)	126.0(4)	126.67(17)	127.9(2)
C(42)−N(13)−B(2)		128.6(2)			
C(45)−N(15)−B(2)		127.9(2)			
C(48)−N(17)−B(2)		127.3(2)			
N(1)−C(1)−N(2)	103.5(2)	103.6(2)	104.4(4)	104.24(17)	103.8(2)
N(3)−C(4)−N(4)	103.9(2)	103.9(2)	104.0(4)	104.50(17)	103.5(2)
N(5)−C(7)−N(6)	103.7(2)	103.8(2)	104.4(4)	104.11(17)	103.9(2)
N(12)−C(42)−N(13)		103.9(2)			
N(14)−C(45)−N(15)		103.8(2)			
N(16)−C(48)−N(17)		103.9(2)			

Scheme 2



Crystals of compound **3** and **4** suitable for X-ray diffraction analysis were obtained from toluene solutions at −20 °C. The results of these experiments are illustrated in Figures 1 and 2, and details of the X-ray analyses and selected bond length and angle data are provided in Tables 3 and 4, respectively. Compound **3** adopts a highly distorted square-pyramidal coordination geometry in the solid state ($\tau = 0.16$)[19] in which the axial position is occupied by one of the arms of the ligand. The strontium center is bound to all three carbene carbons of the C_{3v} symmetric anionic ligand. The Sr−C distances [Sr−C(1), 2.776(3); Sr−C(4), 2.811(3); Sr−C(7), 2.749(3) Å] are very similar to those of our recently reported strontium bis(imidazolin-2-ylidene-1-yl)borate silylamide analogue, [{H_2B(Im^{t}Bu)$_2$}Sr{N(SiMe$_3$)$_2$}(THF)] [Sr−C, 2.757(4) and 2.739(3) Å],[13] and the neutral carbene adduct [Sr(NHC){N(SiMe$_3$)$_2$}$_2$] (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) [Sr−C = 2.731(3) Å][8] despite the increased coordination number at strontium (Table 2).

Although crystals of compound **4** were extremely temperature sensitive and had to be selected under a cryogenic flow of N_2 to avoid melting, the structure was unambiguous. The asymmetric unit of compound **4** is composed of two distinct barium tris(imidazolin-2-ylidene-1-yl)borate silylamide units solvated by one and two imidazole heterocycles, respectively. ^{1}H NMR study of the compound showed that

(19) Addison, A. W.; Rao, T. N.; Reedijk, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

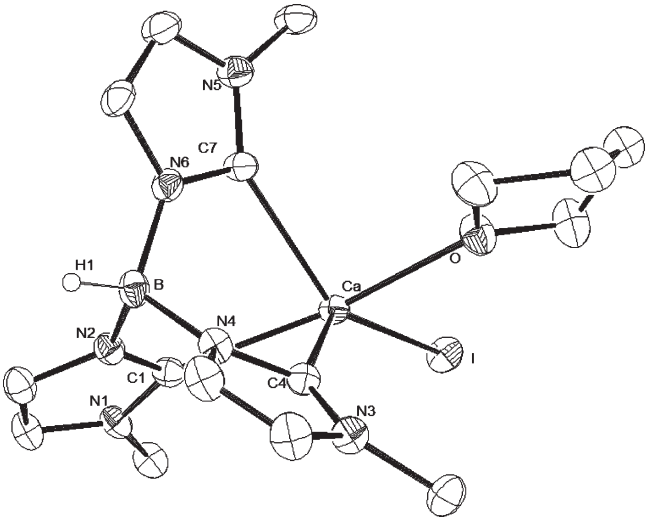
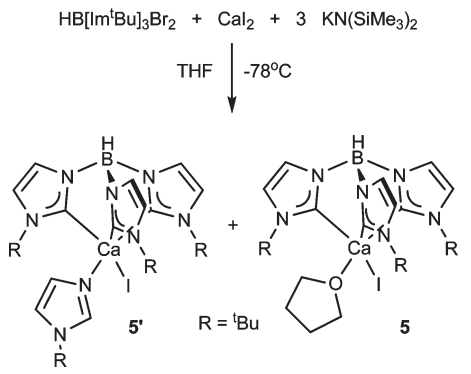


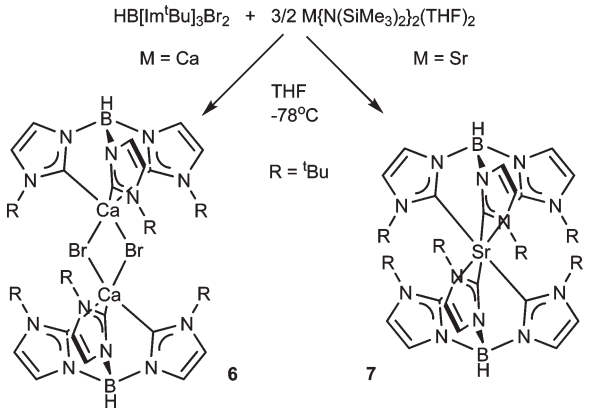
Figure 3. ORTEP representation of compound **5′**. Thermal ellipsoids are at 30% probability. Hydrogen and *tert*-butyl carbon methyl atoms are removed for clarity.

Scheme 3



in solution, however, each barium complex is solvated by two imidazole fragments. The five-coordinate barium complex adopts a distorted square-pyramidal coordination geometry (τ = 0.33).[19] Two arms of the tris(imidazolin-2-ylidene-1-yl)borate ligand occupy equatorial positions together with the silylamide co-ligand and the imidazole adduct, while the third arm of the tridentate ligand occupies the axial position. The other six-coordinate barium monomer adopts a very distorted pseudo-octahedral geometry instead with a *facial* C_3 donor set provided by the tridentate carbene ligand, while the other face is occupied by the silylamide co-ligand and the two coordination imidazole ligands. As observed for the strontium analogue **3**, the C_3-symmetric anionic ligand adopts a κ^3-coordination mode through all three carbene carbons. The Ba−C distances [Ba(1)−C(1), 2.977(3); Ba(1)−C(4), 2.947(3); Ba(1)−C(7), 2.978(3); Ba(2)−C(42), 2.904(3); Ba(2)−C(49), 2.934(3); Ba(2)−C(56), 2.953(3) Å] are comparable to those within the neutral carbene adducts reported by Arduengo [Ba−C, 2.951(3) Å][20] and by our group [(NHC)Ba{N(SiMe$_3$)$_2$}$_2$] (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) [Ba−C, 2.915(4) Å].[8] In both compounds **3** and **4** the carbene−metal vectors do not lie in the plane of the

Scheme 4



imidazole rings so that the NHC fragments are slightly distorted from the ideal C_3 symmetry, most likely due to crystal-packing forces. Similar observations have already been made by Arduengo for his neutral adducts.[20]

The synthesis of the heteroleptic calcium iodide derivative followed a similar reaction scheme (Scheme 3) employing 3 rather than 4 equiv of [KN(SiMe$_3$)$_2$] and yielded monomeric compound **5** [{HB(Im^{t}Bu)$_3$}CaI(N-Im^{t}Bu)] and compound **5′** [{HB(Im^{t}Bu)$_3$}CaI(THF)] in a 9:1 mixture. Fractional crystallization from toluene allowed isolation of crystals of the THF adduct **5′** after 2 days at −20 °C and of the imidazole adduct **5** after another 2 days at −20 °C. Although suitable for an X-ray crystallographic analysis, quantities of **5′** did not allow the collection of NMR spectra or elemental analysis. Repeated attempts to isolate larger amounts of the complex for these purposes failed. Although complex **5** was repeatedly obtained in good yield (68%), no crystals suitable for X-ray diffraction could be isolated. Elemental analysis as well as ^{1}H and ^{13}C{^{1}H} NMR spectra were, however, in accordance with the expected structure containing a single borate ligand environment. The ^{13}C{^{1}H} chemical shift of the carbene carbon at 195.5 ppm was slightly further upfield than that observed for the silylamide analogue **2** (198.5 ppm) and compares well with the carbene shifts in previously described calcium bis(imidazolin-2-ylidene-1-yl)borate compounds (Table 2).[13] X-ray structural studies of compound **5′** confirmed a similar κ^3-binding mode of the borate ligand to that observed in compounds **3** and **4**. The results of this experiment are illustrated in Figure 3, and details of the X-ray analysis and selected bond length and angle data are provided in Tables 3 and 4, respectively. The complex presents a highly distorted square-pyramidal geometry (τ = 0.39)[19] in which the third arm of the ligand occupies the axial position. The Ca−I distance [3.0490(9) Å] is slightly shorter than the range of bond lengths reported by Westerhausen in a series of arylcalcium iodides [3.178(3)−3.306(1) Å][21] or by Roesky for his [{(^{t}Pr)ATI}CaI(THF)$_3$] complex [3.1365(8) Å].[22] The Ca−C distances [Ca−C(1), 2.582(5); Ca−C(4), 2.510(5); Ca−C(8), 2.526(4) Å] are similar to those of the neutral calcium carbene adducts [(NHC)Ca{N(SiMe$_3$)$_2$}$_2$] (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-

(20) Arduengo, A. J.III; Davidson, F.; Krafczyk, R.; Marshall, W. J.; Tamm, M. *Organometallics* **1998**, *17*, 3355.

(21) (a) Fischer, R.; Gärtner, M.; Görls, H.; Yu, L.; Reiher, M.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1618. (b) Fischer, R.; Gärtner, M.; Görls, H.; Westerhausen, M. *Organometallics* **2006**, *25*, 3496. (c) Fischer, R.; Gärtner, M.; Görls, H.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2006**, *118*, 624.

(22) Datta, S.; Gamer, M. T.; Roesky, P. W. *Dalton Trans.* **2008**, 2839.

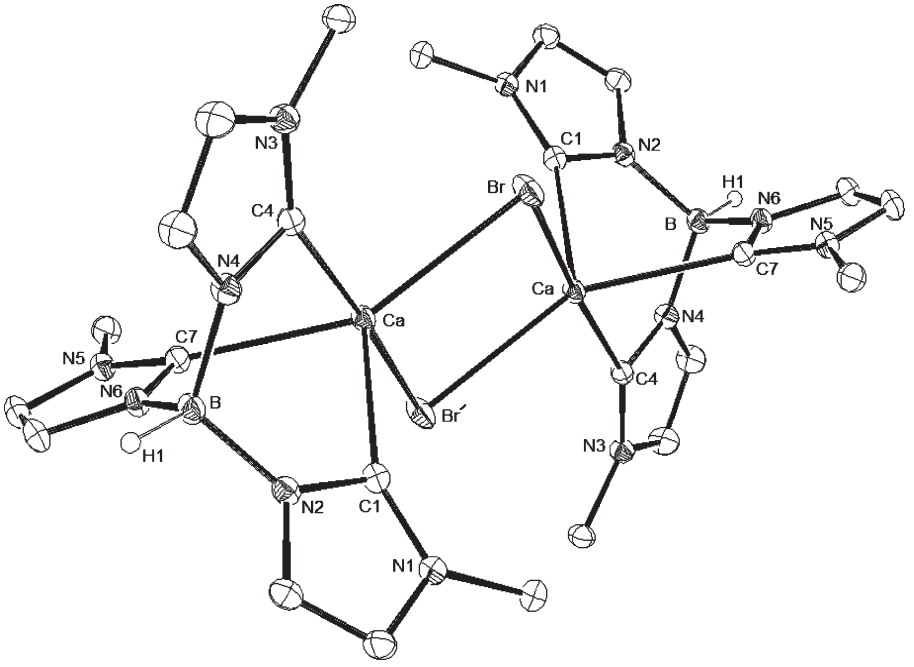


Figure 4. ORTEP representation of compound **6**. Thermal ellipsoids are at 30% probability. Hydrogen and *tert*-butyl carbon methyl atoms are removed for clarity.

ylidene, 2.598(2) Å; NHC = 1,3-bis(2,6-di-isopropylphenyl)-imidazol-2-ylidene), 2.6285(16) Å)[8] and the homoleptic species [{$H_2B(Im^tBu)_2$}$_2$Ca(THF)] [2.583(3)−2.646(4) Å] previously reported by our group,[13] as well as the range of calcium−carbene carbon distances described by Harder for his bis(iminophosphoranyl)-methandiyl calcium complexes [2.528(2)−2.805(1) Å] (Table 2).[23]

To obtain the calcium tris(imidazolin-2-ylidene-1-yl)borate bromide, 1.5 equiv of the homoleptic silylamide species [Ca{$N(SiMe_3)_2$}$_2$(THF)$_2$] and 1 equiv of the boronium ligand precursor **1** were combined in THF at low temperature. Extraction with toluene followed by concentration of the solution and 2 days at −20 °C afforded compound **6** in good purity and yield (69%) as a colorless solid. ^{1}H and ^{13}C{^{1}H} NMR data were in agreement with the expected calcium bromide species. The characteristic ^{13}C{^{1}H} NMR chemical shift for the carbene carbon at 199.4 ppm is the furthest downfield of all calcium NHC derivatives described so far. X-ray structural analysis of the crystals showed that the compound crystallizes as a dimer with bridging bromides. The result of this experiment is shown in Figure 4, and selected bond lengths and angles are provided in Tables 3 and 4, respectively. As in compounds **3**, **4**, and **5′**, the calcium center adopts a highly distorted square-pyramidal geometry ($\tau = 0.39$).[19] Ca−Br distances [Ca−Br, 2.8930(4) Å; Ca−Br′ 2.9040(4) Å] are similar to those reported by Westerhausen in his phenylcalcium bromide complex [Ca−Br, 2.8899(8) Å] and the simple [$CaBr_2(THF)_4$] compound [Ca−Br, 2.8425(3) Å].[17,24] The calcium−carbene carbon bond lengths [Ca−C(1), 2.544; Ca−C(4), 2.564(2); Ca−C(8), 2.559(2) Å] are similar to those of the mononuclear calcium iodide complex **5′** described above.

An analogous synthesis using the homoleptic strontium silylamide [Sr{$N(SiMe_3)_2$}$_2$(THF)$_2$] provided the homoleptic species [{$HB(Im^tBu)_3$}$_2$Sr] in 54% yield based on the initial amount of the ligand precursor. Among byproducts, free imidazole and compound **3** could be identified in the crude NMR. ^{1}H and ^{13}C{^{1}H} NMR data displayed similar features to those of complexes mentioned above, suggesting a single borate ligand environment. The downfield ^{13}C{^{1}H} chemical shift of the donor-carbon carbene resonances at 201.6 ppm was very similar to that of the heteroleptic strontium silylamide species **3**. Fine needle-like crystals suitable for X-ray diffraction confirmed the homoleptic nature of this complex, which is evidently a result of the lesser steric demands of the bromide ligand compared to the bulky bis(trimethylsilyl)-amide substituent of compound **3**, combined with the larger

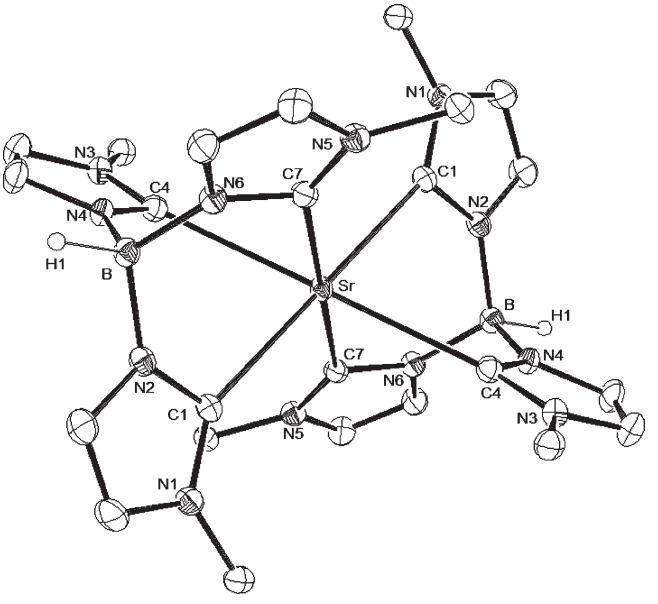


Figure 5. ORTEP representation of compound **7**. Thermal ellipsoids are at 30% probability. Hydrogen and *tert*-butyl carbon methyl atoms are removed for clarity.

(23) Orzechowsky, L.; Jansen, G.; Harder, S. *J. Am. Chem. Soc.* **2006**, *128*, 14676.
(24) Gärtner, M.; Görls, H.; Westerhausen, M. *J. Organomet. Chem.* **2008**, *693*, 221.

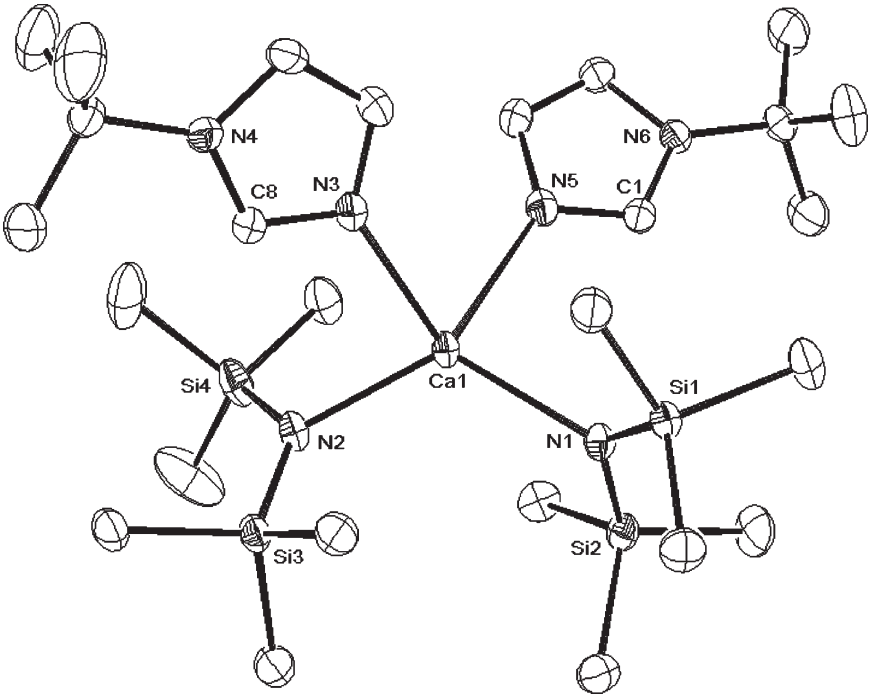


Figure 6. ORTEP representation of compound **8**. Thermal ellipsoids are at 30% probability. Hydrogen atoms are removed for clarity.

ionic radius of strontium compared to the calcium center of compound **6**. Repeated attempts to synthesize the strontium iodide analogue of compounds **5** and **5′** also failed and gave complex mixtures of free 1-*tert*-butylimidazole, compound **3**, and the homoleptic species **7**. After consideration of these results, no attempts were made to synthesize an analogous barium halide species. The structure of **7** is displayed in Figure 5, and selected bond lengths and angles are provided in Tables 3 and 4, respectively. The complex adopts an octahedral geometry with equatorial angles of 103.87(9)° and 76.13(9)° and crystallographically imposed C_3 symmetry around the (BSrB) axis. In this case, contrary to all previously described structures, the imidazole rings are perfectly coplanar with the Sr−C bonds. The Sr−C distances [Sr−C(1), 2.810(3); Sr−C(4), 2.802(3); Sr−C(8), 2.805(3) Å] can be considered identical and are similar to those in compound **3**. Over the whole series of compounds described in this study, the geometry of the ligand varies only slightly, with N−B−N angles ranging from 109.5(4)° to 113.2(2)°, showing the relative rigidity of the tris(imidazolyl)borate ligand even in the presence of large metals such as strontium and barium. A similar observation had already been made for our recently described calcium and strontium bis(imidazolin-2-ylidene-1-yl)borate compounds.[13]

Attempted intramolecular hydroamination with **2** and **3** was much less efficient than with their bidentate counterparts $[\{H_2B(Im^tBu)_2\}M\{N(SiMe_3)_2\}(THF)_n]$ (M = Ca, $n = 1$; M = Sr, $n = 2$).[13] For aminoalkenes requiring high temperatures yields did not exceed 20% due to complete decomposition of the tris(carbene)borate ligands at temperatures above 50 °C into free *tert*-butylimidazole fragments, easily detected by the appearance of a *tert*-butyl ^{1}H NMR singlet at 0.98 ppm in d_8-toluene and disappearance of the equivalent ligand signal around 1.3−1.4 ppm, leading to solutions turning first yellow then brown. A slight amount of ligand decomposition (5−20%) was also observed at lower temperatures but did not prevent catalysis. Heating of d_8-toluene solutions of **2**, **3**, and **4** at 80 °C over a period of 6 days, however, did not result in any visible decomposition nor in ligand redistribution toward the homoleptic species. The presence of a protic substrate seems, therefore, to be required to degrade the ligand by protonation of the carbene fragments, a process that inevitably competes with the amide-amine exchange of the catalytic insertion step. Similar decomposition and the formation of intractable products were also observed in the presence of 1 equiv of other protic substrates such as diphenylamine or phenylacetylene.

The low conversion rates, especially for calcium catalyst **2**, could be due to the high kinetic activation barrier of the insertion step of the catalytic cycle, as the metal center is tightly encapsulated by the ligand and access is blocked by the very bulky bis(trimethylsilyl)amide co-ligand. Although the larger ionic radius of strontium in **3** allows better access to the catalytic metal center, the steric demands of the tridentate carbene ligand still noticeably hinder the insertion step compared to our previously reported bidentate carbene analogue.[13] Despite these limitations, the strontium complex **3** was significantly more active (at 5 mol %, room temperature, 1-amino-2,2-diphenylpent-5-ene **10**: 1.8 h, 97% yield; 1-amino-2,2-cyclohexylpent-5-ene **11**: 1 day, 86% yield) than its calcium counterpart **2** (at 5 mol %, 45 °C, **10**: 4 days, 85% yield; **11**: 3 days, 11% yield). This observation is consistent with our previous findings with the bis(carbene)borate[13] but contrasts with the recent reports of Ca and Sr triazenide complexes, which were much more prone to detrimental redistribution.[25] Barium complex **4** showed little activity even with **10** and heating at 50 °C for 7 days. At 5 mol % catalyst loading the amount of cyclized product indicated a single turnover most likely achieved before the catalyst was entirely dismantled by B−N bond cleavage.

(25) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B.; Kociok-Köhn, G.; Procopiou, P. A. *Inorg. Chem.* **2008**, *47*, 7366.

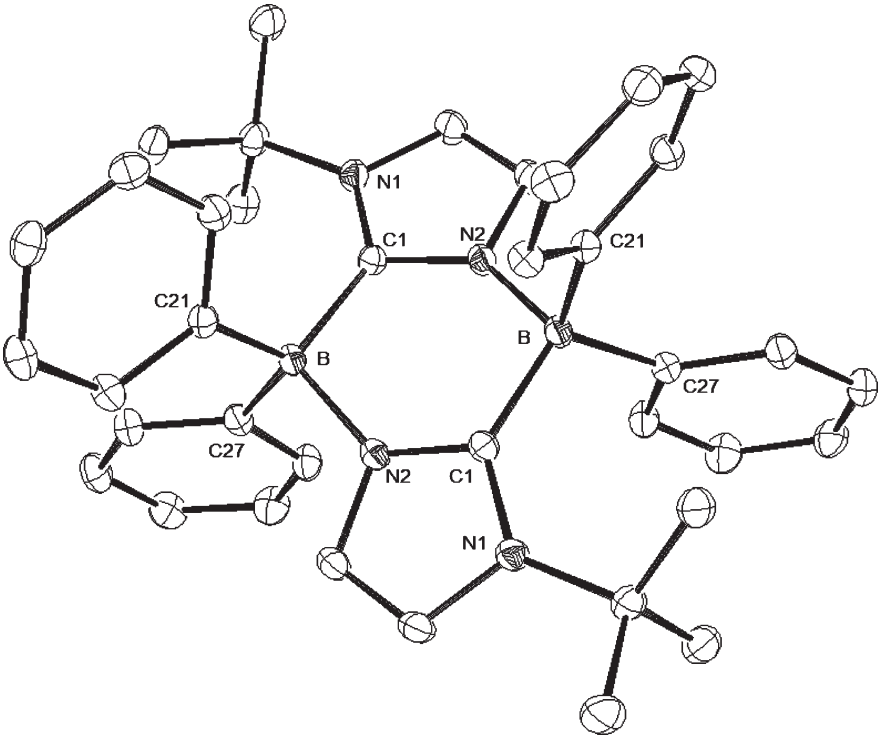


Figure 7. ORTEP representation of compound **9**. Thermal ellipsoids are at 30% probability. Hydrogen atoms are removed for clarity.

Limitations of These Compounds. The synthesis of these compounds seems to invariably involve a certain amount of ligand decomposition by B−N bond cleavage. As shown in the synthesis of compounds **3′** and **5′**, even precautions such as washing all glassware with a base solution and avoiding filtration through potentially acidic Celite leads to various proportions of (THF) and imidazole adduct mixtures. Crystallization and selection of crystals was made particularly difficult due to the presence of oily noncoordinated 1-*tert*-butylimidazole in the toluene solution. Coordination-induced B−N bond cleavage of tris(pyrazolyl)borate ligands has previously been observed.[26] For example Hamon has described the formation of *trans*-$FeCl_2(^tBu\text{-}pzH)_4$ as the only isolable product from the attempted synthesis of an iron tris(pyrazolyl)borate complex.[27] Similar partial decomposition has also been observed in the synthesis of lanthanum and neodymium tris(pyrazolyl)borate complexes.[28] The synthesis of compound **2** yielded crystals of byproduct **8**, which was structurally characterized as the homoleptic compound **8** [$Ca\{N(SiMe_3)_2\}_2(N\text{-}Im^tBu)_2$] (Figure 6). ^1H and $^{13}C\{^1H\}$ NMR shifts of this compound allowed identification of compound **8** in the crude mixtures of **5** and **6**, as well as the analogous strontium and barium species in the crude mixtures of **3**, **4**, and **7**. A possible indication as to the fate of the boron backbone in such ligand cleavage reactions was provided by the unexpected structure of the single isolable compound of the attempted synthesis of the diphenyl-substituted $[\{Ph_2B(Im^tBu)_2\}Ca\{N(SiMe_3)_2\}(THF)]$ analogue of our recently published $[\{H_2B(Im^tBu)_2\}Ca\{N(SiMe_3)_2\}(THF)]$. X-ray diffraction analysis of compound **9** revealed the dimeric boron NHC complex displayed in Figure 7 containing a single imidazolinylidene-1-yl arm coordinated to a second boron center. As suggested by the reaction conditions in the synthesis of compound **3′**, which did not completely avoid B−N bond cleavage, residual acid traces on the glassware are only partly implied in the decomposition mechanism of the ligand. It is likely, therefore, that other factors, such as the necessary redistribution of charge within the ligand framework during deprotonation, are implicated in the degradative pathways. We are continuing to examine these possibilities and will report our findings in subsequent publications.

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

Supporting Information Available: Description of representation aminaoalkene synthesis and NMR-scale hydroamination catalysis. NMR spectra for compounds **4** and **8**. Crystallographic information files (CIF) for **3**, **4**, **5′**, **6**, **7**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

(26) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolborate Ligands*; Imperial College Press, 1999.
(27) Graziani, O; Toupet, L.; Hamon, J.-R.; Tilset, M. *Inorg. Chim. Acta* **2002**, *341*, 127.
(28) Bell, Z. R.; Motson, G. R.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Polyhedron* **2001**, *20*, 2045.