Reactions of β-Diketiminate-Stabilized Calcium Amides with 9-Borabicyclo[3.3.1]nonane (9-BBN)

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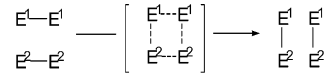
Summary: The reaction of a β-diketiminate-stabilized calcium diphenylamide with the dialkylborane 9-BBN allows the synthesis of a β-diketiminate-stabilized calcium borohydride along with an amidoborane reaction coproduct via a likely σ-bond metathesis mechanism.

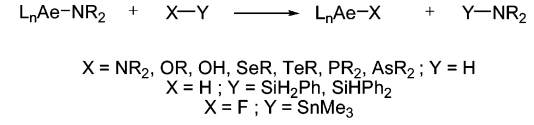
σ-bond metathesis is a reaction of fundamental importance to synthetic chemistry. As shown in Scheme 1, this reaction permits the simultaneous construction and destruction of two σ-bonds in a single step. Usually catalyzed by d^0 transition metal, lanthanide ($4f^n5d^0$), or actinide ($5f^n6d^0$) based catalysts, the σ-bond metathesis mechanism has found application in a host of dehydrocoupling reactions for the catalytic construction of new heteroatom−heteroatom and carbon−heteroatom bonds, important examples of which include the dehydropolymerization of silanes[1] and C−H activation of simple hydrocarbons.[2−4] More recently, σ-bond metathesis processes have received attention for potential application in hydrogen generation and storage.

Our interest in such reactivity stems from the study of well-defined complexes of the heavier alkaline earths (Ca, Sr, and Ba) and the supposition that direct parallels may be drawn between reactions described as occurring via σ-bond metathesis and classical acid−base chemistry. While stoichiometric acid−base reactions have long been applied to the construction of new alkaline earth−heteroatom bonds in both homoleptic and heteroleptic organometallic complexes (Scheme 2),[5] it has only recently been shown that such reactivity may be included into catalytic cycles reminiscent of trivalent organolanthanide chemistry, allowing the heterofunctionalization of unsaturated carbon−carbon bonds.[5g,6]

Scheme 1. σ-Bond Metathesis



Scheme 2. Acid−Base Reactions of Heavier Alkaline Earth Amides



As work toward extending the scope of catalytic group 2 reactivity, we now report that the heteroleptic calcium amide **1** and the related β-diketiminate-stabilized calcium diphenylamide **2** participate in selective σ-bond metathesis (or acid−base) reactions with the dialkylborane 9-borabicyclo[3.3.1]nonane (9-BBN). These metathesis reactions allow for the synthesis of the novel β-diketiminate-stabilized calcium borohydride **3** and, perhaps more importantly, in the case of **2** an amidoborane byproduct through the construction of a new nitrogen−boron σ-bond.

The reaction of **1** with 1 equivalent of dimeric 9-BBN was conducted on an NMR scale using C_6D_6 as a solvent and monitored by ^1H and ^{11}B NMR spectroscopy. A slow reaction occurred at room temperature over a period of 12 h, apparent from the appearance of a series of new resonances in the ^1H NMR that were consistent with a coordination complex containing both the β-diketiminate ligand and a cyclic borane moiety. ^{11}B NMR revealed a new product peak at −12.1 ppm (t, $J_{^1H-^{11}B}$ = 68 Hz) similar to that of −13.3 ppm (d, $J_{^1H-^{11}B}$ = 50 Hz) reported for the calcium borohydride [{1,2,4-$C_5(SiMe_3)_3H_2$}-

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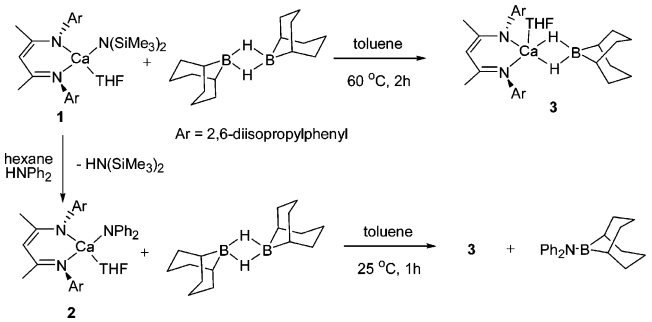
Scheme 3. Reaction of Calcium Amides 1 and 2 with the Dialkylborane 9-BBN



$Ca(HBEt_3)(THF)_2$].[7] The reaction time could be shortened to 2 h by performing the experiment at 60 °C. Accordingly, repetition of the reaction on a preparative scale using toluene as a solvent, extraction into hexane, and concentration by evaporation in vacuo gave the molecular borohydride **3** as a colorless crystalline solid (Scheme 3).[8] Examination of the reaction byproducts by ^{1}H NMR spectroscopy revealed a number of new species incorporating the trimethylsilyl group. Similarly ^{11}B NMR revealed multiple products, including a resonance at 56.2 ppm tentatively assigned as the amidoborane $(Me_3Si)_2N-BR_2$ (vide infra).

Due to the apparent fragility of the nitrogen−silicon bond under these reaction conditions,[9] we sought to synthesize a more robust heteroleptic calcium amide species and study its reaction with 9-BBN. We have previously reported that **1** reacts with relatively acidic amines to yield the corresponding heteroleptic calcium amides with liberation of $HN(SiMe_3)_2$.[5e,f] Indeed, the stoichiometric reaction of **1** with diphenylamine allowed the isolation of the β-diketiminate-stabilized calcium diphenylamide **2** (Scheme 3).[10]

The heteroleptic calcium diphenylamide **2** also reacted with 9-BBN to yield the calcium complex **3**. In this case the reaction was considerably faster than with **1** and was complete within 1 h at room temperature, most likely due to the decreased steric demands of the diphenylamide coligand as well as the increased Lewis basicity of the coordinated diphenylamide during the course of reaction (vide infra). Analysis of the reaction by ^{11}B NMR revealed, in addition to **3**, a coproduct observed as a broad singlet resonance at 53.0 ppm in C_6D_6 solution, a value comparable to that of 49.6 ppm (in CCl_4) reported for Me_2B-NPh_2.[11] The amidoborane **4**, which was isolated by sublimation directly from the crude reaction mixture, was characterized in both solution and the solid state. Mass spectrometry showed a diagnostic set of peaks at *m*/*z* 289/290 for $[M]^+$, and both ^{1}H and ^{13}C NMR are consistent with the proposed structure, which has been confirmed unambiguously by an independent synthesis (see the Supporting Information).[12] Given that the diphenylamide **2** is synthesized from diphenylamine and **1**, this two-step sequence represents a calcium-mediated dehydrocoupling of an amine with a dialkylborane.

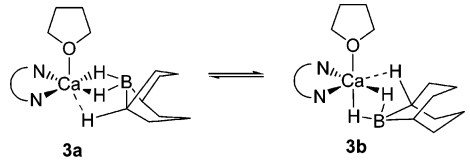


Figure 1. Isomers **3a** and **3b** of the isolated calcium borohydride.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 3a and 3b

bond length			bond angle		
	3a	**3b**		**3a**	**3b**
Ca−H1a	2.27(4)	2.15(4)	N2−Ca−N1	81.36(14)	82.18(13)
Ca−H1b	2.17(4)	2.31(4)	O−Ca−H34	152.8(12)	87.4(10)
B−H1a	1.17(4)	1.25(4)	H1a−Ca−H1b	50.8(16)	50.0(15)
B−H1b	1.28(5)	1.19(5)	O−Ca−H1a	96.2(11)	140.1(11)
Ca···H34	2.33(5)	2.30(4)	O−Ca−H1b	81.1(12)	90.6(12)
Ca···B	2.549(6)	2.543(6)	H1a−Ca−H34	71.9(17)	73.1(15)
C34−H34	1.05(5)	1.06(4)	H1b−Ca−H34	69.4(16)	68.2(15)
			H1a−B−H1b	102(3)	102(3)

The calcium borohydride **3** was characterized by multinuclear NMR and infrared spectroscopy and by single-crystal X-ray diffraction. X-ray analysis of a single crystal of **3** revealed the presence of two unique conformers, **3a** and **3b**, within the asymmetric unit (Figure 1). The H atoms involved in interactions with the calcium centers were refined, while other H atoms were included in riding mode. Selected bond angles and distances are presented in Table 1, and complete data are provided in the Supporting Information. Each conformer demonstrates pseudo-octahedral geometry at calcium, with the coordination sphere being provided by the β-diketiminate ligand, two hydride units

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(8) Reaction of **1** with 9-BBN: a stirred solution of **1** (500 mg, 0.74 mmol) and 9-BBN dimer (244 mg, 0.74 mmol) in toluene (10 mL) was heated to 60 °C for 2 h. The reaction mixture was cooled to room temperature and the solvent removed in vacuo. The crude product was then extracted into hexane and the extract filtered. Slow removal of the solvent induced crystallization, and the product **3** was isolated as a white crystalline solid (116 mg, 0.178 mmol, 24%). Mp (hexane): 135 °C dec. ^{1}H NMR (d_8-tol, 400 MHz, 298 K, δ): 0.67 (broad singlet, 2H), 1.14 (d, 12H, J = 6.8 Hz), 1.25 (d, 12H, J = 6.8 Hz), 1.28 (m, 4H), 1.48−1.60 (m, 4 H), 1.57 (s, 6H), 1.70−1.78 (m, 4 H), 1.86−1.96 (m, 4 H), 3.06 (hept, 4H, J = 6.8 Hz), 3.64 (m, 4H), 4.67 (s, 1H), 6.97−7.07 (m, 6H). ^{13}C NMR (d_8-tol, 100 MHz, 298 K, δ): 24.3, 24.5 (broad signal), 25.0, 25.3, 26.0, 28.6, 34.6, 69.8, 93.4, 123.2, 137.4, 141.5, 145.4, 166.2. ^{11}B NMR (d_8-tol, 128 Hz, 298 K): −12.5 (t, J = 68 Hz). Infrared (KBr disk, cm^{-1}): 3057, 2960, 2923, 2867, 2827, 2754, 2054, 2023, 1931, 1618, 1543, 1459, 1398, 1314, 1262, 1169. Anal. Found for $C_{41}H_{65}BCaN_2O$: C, 75.52; H, 9.88; N, 4.40. Calcd: C, 75.43; H, 10.00; N, 4.30. Yield based upon NMR analysis using tetrakis(trimethylsilyl)silane as an internal standard: 81%.

(9) Wrackmeyer, B.; Schwarze, B.; Milius, W. *J. Organomet. Chem.* **1995**, *489*, 201.

(10) Synthesis of [[ArNC(Me)CHC(Me)NAr]Ca(NPh_2)(THF)] (**2**): to an unstirred solution of **1** (500 mg, 0.74 mmol) in hexane (20 mL) was added diphenylamine (125 mg, 0.74 mmol) as a solution in the same solvent (5 mL). The addition was undertaken as to layer the two solutions, and the reaction mixture was left to stand indisturbed. After 14 h the reaction yielded large colorless crystals of the β-diketiminate-stabilized calcium amide (206 mg, 0.30 mmol, 41%). ^{1}H NMR (400 MHz, C_6D_6, δ): 0.97 (m, 4H), 1.12 (d, 12H, J = 6.8), 1.19 (d, 12H, J = 6.8), 1.69 (s, 6H), 3.11 (m, 4H), 3.20 (hept, 4H, J = 6.8), 4.85 (s, 1H), 6.53−6.56 (m, 6H), 6.91 (dd, 4H, J = 7.6, 8.0), 7.12−7.15 (m, 6H). ^{13}C NMR (100.7 MHz, C_6D_6, δ): 24.5, 24.8, 25.1, 28.6, 69.0, 94.3, 115.8, 118.5, 124.4, 125.1, 130.4, 141.9, 146.0, 155.7, 166.4. Anal. Found for $C_{45}H_{59}CaN_3O$: C, 77.55; H, 8.60; N, 5.97. Calcd: C, 77.42; H, 8.51; N, 6.01.

(11) Casanova, J.; Geisel, M. *Inorg. Chem.* **1974**, *13*, 2783.

(12) Reaction of **2** with 9-BBN: a solution of **2** (700 mg, 1.0 mmol) and 9-BBN dimer (1.0 mmol) in toluene was stirred for 1 h at room temperature. The crude product was then extracted into hexane and the extract filtered. Slow removal of the solvent induced crystallization, and the product **3** was isolated as a colorless crystalline solid (132 mg, 0.20 mmol, 20%). The solvent was removed from the filtrate, and the remaining crude product sublimed at 130 °C and 4 × 10^{-1} mbar to yield the amidoborane **4** as a colorless crystalline solid (35 mg, 0.12 mmol, 12%). This latter product is moisture sensitive and could not be purified by fractional crystallization, due to contamination by **3**. Although **4** has been reported in the literature,[21] no characterization data have been described. ^{1}H NMR (C_6D_6, 400 MHz, 298 K, δ): 1.44 (m, 2H), 1.48−1.55 (m, 2H), 1.82−1.87 (m, 8H), 1.92−2.02 (m, 2H), 6.91−6.95 (m, 2H), 7.05−7.07 (m, 8H). ^{11}B NMR (C_6D_6, 128 Hz, 298 K, δ): 53.0. ^{13}C NMR (C_6D_6, 100 MHz, 298 K, δ): 23.8, 24.7 (broad signal), 33.8, 125.2, 127.5, 129.0, 148.8. Infrared (KBr disk, cm^{-1}): 2917, 2885, 2837, 1591, 1560, 1491, 1451, 1409, 1338, 1296, 1259. MS (CI, ammonia, positive ion, *m*/*z*): 289/290 ($[M]^+$, 30%), 170 ($[M - C_8H_{13}B]^+$, 100%). The structure was confirmed by an independent synthesis from the reaction of *B*-MeO-9-BBN with $LiNPh_2$ (see Figure S1, Supporting Information).

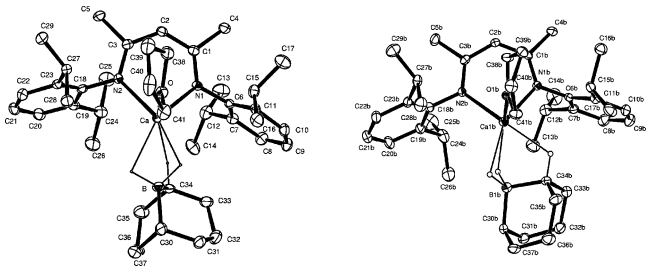

Figure 2. ORTEP representations of **3a** (left) and **3b** (right) (thermal ellipsoids at 20% probability). H atoms (with the exception of the hydridic and agostic H atoms) are omitted for clarity.

of the H_2BR_2 moiety, a molecule of THF, and an apparent agostic interaction with the methine unit adjacent to boron upon the borohydride ligand (Figure 2). The conformers differ by their coordination geometry at calcium. Conformer **3a** displays a pseudo-trans relationship between the agostic hydrogen and the coordinated THF, while **3b** demonstrates a pseudo-cis relation between the same two substituents. In both isomers the borate anion binds to calcium via two three-center/two-electron Ca−H−B bridging interactions. The Ca−H bond distances take values between 2.17 and 2.31(4) Å and compare well to the calcium−hydride bond lengths of 2.21(4) and 2.10(3) Å quoted for the calcium borohydride [{1,2,4-$C_5(SiMe_3)_3H_2$}Ca($HBEt_3$)-$(THF)_2$] and the recently described calcium hydride [{(Ar)NC-(Me)CHC(Me)N(Ar)}CaH$(THF)]_2$, respectively.[5j,7] The geometries at the calcium metal centers deviate significantly from ideal octahedra, due to the tight bite angle provided by not only the β-diketiminate (N1−Ca−N2 bond angles 81.36(14) and 82.18(13)°) but also the H_2BR_2 ligands (H−Ca−H bond angles of 50.8(16) and 50.0(15)°). The geometry at boron is unambiguously tetrahedral, and the boron−hydride bond lengths range between 1.17(4) and 1.28(5) Å. In both conformers there is a close contact between the calcium and boron metal centers with Ca···B distances of 2.549(6) Å in **3a** and 2.543(6) Å in **3b**. The agostic interactions of the calcium centers with the methines of the borohydride ligands are significant, with Ca···H bond lengths of 2.33(5) and 2.30(4) Å in **3a** and **3b**, respectively. These interactions are only marginally longer than the calcium−hydride distances quoted above and are considerably shorter than the Ca···H agostic interaction of 2.582 Å observed in the related heteroleptic calcium anilide [{(Ar)NC(Me)CHC(Me)N-(Ar)}Ca(NHAr)(THF)],[5f] suggestive of a significant degree of bonding such that the borohydride moiety may be realistically described as a tridentate ligand. Similar agostic interactions have been observed in homoleptic lanthanide and alkali-metal borohydride complexes[13,14] and in the related compound [{1,2,4-$C_5(SiMe_3)_3H_2$}Ca($HBEt_3$)$(THF)_2$].[7]

Infrared analysis (KBr disk) confirmed the presence of the borohydride moiety and showed both symmetric and asymmetric ν(BH) stretching modes at 2054 and 2023 cm^{-1}, respectively. These values lie well within the range established for lanthanide-(II) dihydridoborates of 2118−2012 cm^{-1}.[13] Notably, the infrared spectrum also displayed a low-intensity and low-frequency ν(CH) vibration at 2754 cm^{-1}, which may be attributed to the CH stretch of the methine unit weakened by the agostic interaction with the calcium center.

The β-diketiminate-stabilized calcium borohydride proved stable in solution. Heating samples of **3** in C_6D_6 to 60 °C for 14 h resulted in only a small amount of irreversible (Schlenk-like) redistribution to the known homoleptic compound [{(Ar)-NC(Me)CHC(Me)N(Ar)$\}_2$Ca].[15] In the ^{1}H NMR spectrum of compound **3** the protons of the methine unit of the borohydride ligand exhibited a considerable upfield shift (ca. 0.7 ppm) compared to those in both 9-BBN and the amidoborane **4** and were apparent as an unresolved broad singlet at 0.67 ppm. This assignment was confirmed by additional COSY experiments. The observation of this increased shielding of the methine unit implies that the agostic interaction of the H_2BR_2 moiety with the calcium center is retained in solution on the NMR time scale. Cooling of a d_8-toluene solution of **3** resulted in a noticeable broadening of the resonances attributed to the diisopropyl moiety of the β-diketiminate ligand in the ^{1}H NMR spectrum. At temperatures below 223 K the isopropyl methine resonance, apparent as a heptet at 3.06 ppm (4H, $^3J_{H-H} = 6.8$ Hz) in the room-temperature spectrum, appeared as two broad but distinct (2H by integration) resonances at 2.85 and 3.34 ppm. Over the same temperature range the isopropyl methyl peaks changed in a similar manner, and both sets of data yielded a Gibbs free energy of activation, $\Delta G^{\ddagger}$, of 43.8 kJ mol^{-1} for this process. This fluxionality may be attributed to a hindered rotation about the N−aryl bonds due to steric congestion provided by the auxiliary ligands around calcium. We have previously observed a similar behavior in the related heteroleptic compounds [{(Ar)NC(Me)CHC(Me)N(Ar)}Ca(C≡C-t-Bu)$]_2$ and [{(Ar)NC-(Me)CHC(Me)N(Ar)}Ca(Cp^{4Me})(THF)].[5h] Despite the observation of temperature-dependent fluxional behavior in the β-diketiminate spectator ligand, no decoalescence of the ^{11}B NMR resonance of **3** was observed down to temperatures of 193 K, suggesting facile interconversion of the extremes represented by the conformers **3a** and **3b** in solution.

The ease of this interconversion was assessed by DFT calculations on the model complexes **5** and **6** [{$(PhNC(H))_2CH$}-Ca$(OMe_2)(\mu$-$H_2BMe_2)$], using the B3LYP density functional theory and LANL2DZ pseudopotentials (and basis set) implemented in Gaussian 03.[16] The geometry optimizations were performed by selecting initial geometries in which the sixth coordination site about the calcium center was provided by a short "agostic-type" interaction to the boron-bonded methyl group. This was oriented with either a trans or cis configuration to the coordinated dimethyl ether based upon simplified coordinates provided by the solid-state configurations of **3a** (for **5**) and **3b** (for **6**), respectively. As expected, there was negligible difference (ca. 3 kJ mol^{-1}) between the overall energies of the two calculated conformations, while the bond lengths and angles of the fully optimized structures were, in general, within 2% of the experimentally determined parameters. It is notable, however, that the Ca···HC agostic distances were overestimated by approximately 0.3 Å in both model structures. The calculated ν(CH) vibrations associated with the "coordinated" methyls (**5**, 2897 cm^{-1}; **6**, 2918 cm^{-1}), although significantly lowered by interaction with the calcium centers, are also somewhat higher than those observed in the solid state. It seems likely that both of these discrepancies may be ascribed to the simplifications (i.e., modified steric demands and decreased reduced mass), which were introduced with the structures of **5** and **6** to reduce computational cost.

We propose that the reaction leading to the formation of compounds **3** and **4** proceeds via (i) initial formation of a borate complex by coordination of the borane to the nitrogen of the

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(14) Knizek, J.; Nöth, H. *J. Organomet. Chem.* **2000**, *614*−*615*, 168.

(15) Harder, S. *Organometallics* **2002**, *21*, 3782.

(16) Frisch, M. J., et al. *Gaussian 03*, Revision C.02; Gaussian, Inc., Wallingford, CT, 2004.

diphenylamide ligand of **2**, (ii) decomposition of the latter species to a coordinatively unsaturated heteroleptic calcium hydride and **4**, and (iii) subsequent trapping of this calcium hydride with a further 1 equiv of the dialkylborane to form the calcium borohydride **3**. This hypothesis is supported by several literature precedents. While the reaction of group 1 amides and alkoxides with hydridodialkylboranes to yield the corresponding metal borohydride complexes is well established,[17] the intermediacy of a heteroleptic calcium hydride is also supported by the documented synthesis of $Ca(BH_4)_2$ by the reaction of CaH_2 with B_2H_6.[18,19] Further evidence for this hydride intermediate was provided by an NMR-scale reaction of [{(Ar)NC(Me)CHC(Me)N(Ar)}CaH(THF)]$_2$, generated in situ, with 9-BBN, which also gave the borohydride **3**.

In conclusion, the stoichiometric σ-bond metathesis reaction of a readily accessible heteroleptic calcium amide with a dialkylborane yielded the novel calcium borohydride **3** along with an amidoborane side product. The latter compound represents the construction of a new nitrogen−boron bond by a dehydrocoupling reaction, and the potential remains to render this reaction catalytic with respect to the group 2 organometallic reagent by interception of the calcium hydride intermediate. We are continuing to study the scope of this reaction and to investigate the possible application of group 2 mediated σ-bond metathesis reactions for the catalytic construction of new heteroatom−heteroatom and carbon−heteroatom bonds.

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Supporting Information Available: Text and figures giving full experimental details and characterization data and CIF files giving crystal data for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The reaction of **1** with some alternative common group 13 hydrides proved unsuccessful. Thus, the reaction of **1** with $BH_3{\cdot}OEt_2$ resulted in the isolation of a product in which the β-diketiminate ligand had undergone reduction by the borane complex (see Figure S2, Supporting Information). These results demonstrate the fragility of the complex **1** as a model for developing a reaction chemistry of calcium and suggest the properties of the substrate are important for a selective σ-bond metathesis reaction to occur. In this respect, it is likely that the bulky bicycloborane moiety acts to temper further reactivity by sterically encapsulating the reactive calcium center.