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Olefin Hydroborations with Diamidocarbene–BH_3 Adducts at Room Temperature

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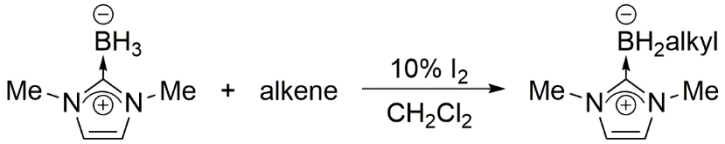
Abstract: An isolable *N*,*N*′-diamidocarbene (DAC) was previously shown to promote the B–H bond activation of various BH_3 complexes. The resultant DAC–BH_3 adducts facilitated olefin hydroborations under mild conditions and in the absence of exogenous initiators. The substrate scope for such transformations was further explored and is described herein. While organoboranes were obtained in quantitative yields from various terminal and internal olefins, use of the latter substrates resulted in intramolecular ring-expansion of the newly formed DAC–borane adducts.

Keywords: hydroboration; carbenes; organocatalysis; Lewis adducts; diamidocarbene

1. Introduction

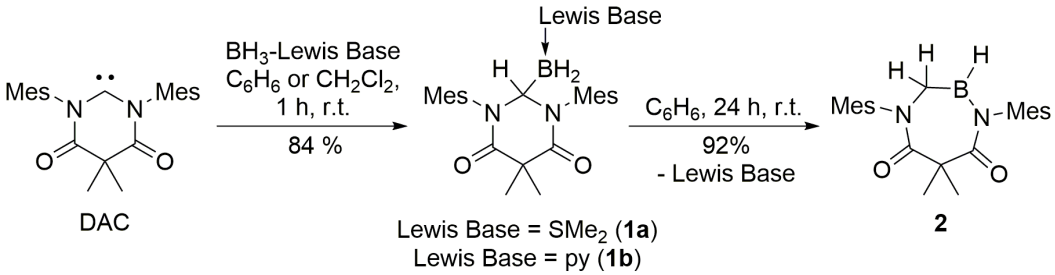
The hydroboration of unsaturated compounds followed by oxidation is a common and versatile method for the preparation of a broad range of alcohols [1,2]. Moreover, hydroboration chemistry has been extended to afford halogenated and other oxidized hydrocarbons as well as their reduced congeners [3–5]. Numerous transition metal-based hydroboration catalysts have been developed over the past several decades to improve chemo-, regio- and/or stereo-selectivities [5–9]. Efforts toward the development of organocatalyzed analogues have also been pursued, with particular attention focused on stable carbenes, including the cyclic (alkyl)(amino) carbenes (CAACs) and the *N*-heterocyclic carbenes (NHCs) [10–14]. These carbenes form Lewis acid–base adducts upon exposure to various BH_3 complexes containing dative ligands, such as dimethylsulfide (SMe_2) [15–19]. In the absence of any external initiators, the NHC–BH_3 adducts typically do not react with olefins. However, as shown in Scheme 1, the NHC–BH_3 adducts do facilitate the hydroboration of a wide range of organic molecules at elevated temperatures and/or upon the addition of a radical initiator [19–27].



Scheme 1. Iodine initiated alkene hydroborations using *N*-heterocyclic carbene (NHC)–BH_3 adducts (Me = methyl) [24,25].

As shown in Scheme 2, we previously demonstrated that the *N*,*N*′-diamidocarbenes (DACs), a unique class of stable carbenes [28], afford **1** upon exposure to either BH_3–pyridine or BH_3–SMe_2 [29].

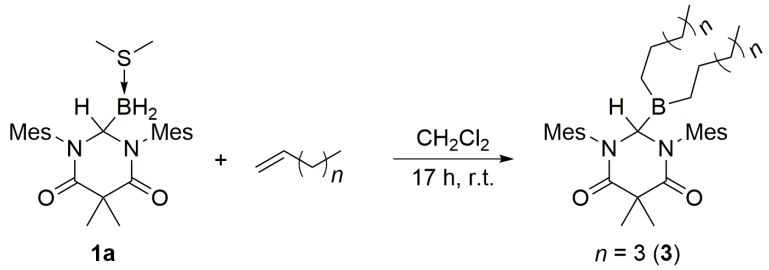
Unlike NHCs and CAACs, the DACs did not displace the datively bonded Lewis base, but instead facilitated B–H activation. The relative basicity of the coordinated ligand was found to directly correlate with the stability of the corresponding DAC–BH_3 adduct. For example, adduct **1a**, which contains SMe_2, was prone to intramolecular ring-expansion to **2** and de-coordination (Scheme 2). The use of a stronger Lewis base, such as pyridine, afforded an adduct (**1b**) that exhibited increased stability toward water and air; ring-expansion was not observed, even at elevated temperatures. To explore the hydroboration chemistry displayed by DAC–BH_3 adducts, **1a** and **1b** were independently treated with a series of unactivated olefins. While **1a** was successfully used as a hydroboration reagent and operated in the absence of exogenous radical initiators at room temperature, adduct **1b** was found to require relatively high reaction temperatures; as such, subsequent efforts focused on the former.



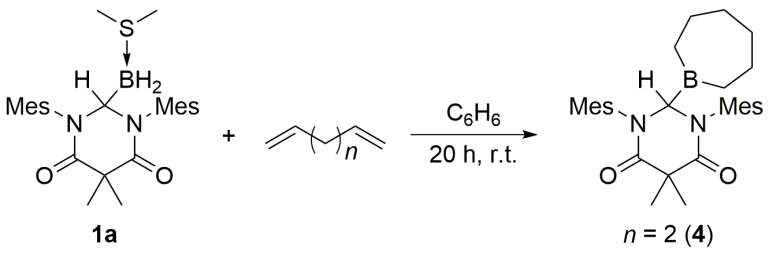
Scheme 2. *N,N′*-diamidocarbene (DAC)-mediated B–H bond activation and subsequent intramolecular ring-expansion (Mes = mesityl) [29].

2. Results and Discussion

As summarized in Scheme 3, the addition of an excess of a terminal olefin, such as 1-hexene, to a solution of **1a** in CH_2Cl_2 resulted in the formation of **3**, as determined by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy as well as high resolution mass spectrometry. Inspection of the ^{1}H NMR data revealed a diagnostic singlet at δ 6.09 ppm (C_6D_6), which was assigned to the methine group of **3**. When an excess of 1,5-hexadiene was added to **1a**, both double bonds underwent hydroboration, and **4** was obtained as the exclusive product (Scheme 4).

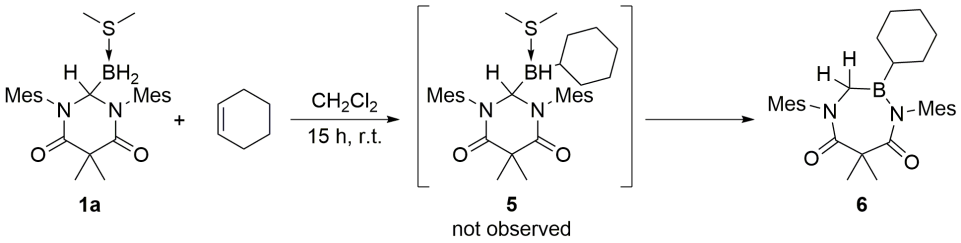


Scheme 3. Hydroboration of 1-hexene with **1a**.

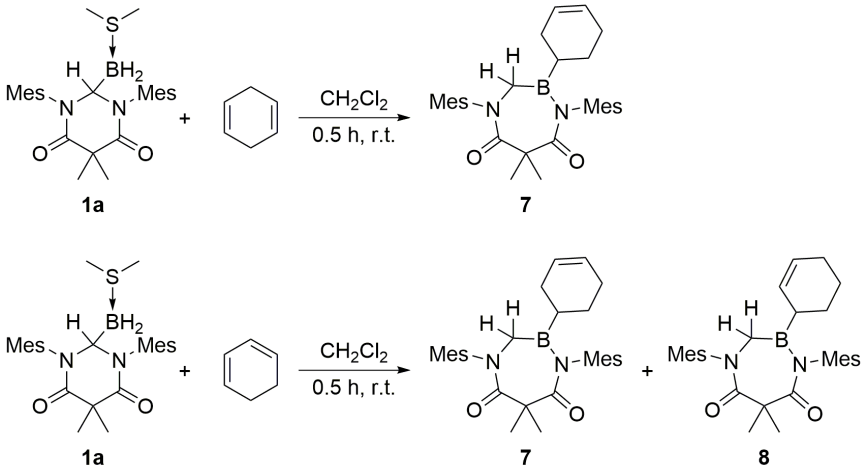


Scheme 4. Hydroboration of 1,5-hexadiene with **1a**.

The ability of **1a** to facilitate the hydroboration of internal olefins was also explored. When **1a** was treated with an excess of cyclohexene, a product (**6**) containing only one cyclohexyl moiety was obtained (Scheme 5). The ^{1}H NMR recorded for **6** showed a diagnostic singlet at δ 3.61 ppm (C_6D_6), which corresponded to the two hydrogen atoms at the former carbenoid center. As no reaction was observed between **2** and cyclohexene, we hypothesized that the initial formation of **5** (not observed) was rapidly followed by intramolecular ring-expansion. The hydroboration chemistry of **1a** with internal olefins was further explored by independently treating **1a** with 1,3- or 1,4-cyclohexadiene. Similar to the results obtained when cyclohexene was used as a substrate, the formation of ring-expanded products was observed (Scheme 6). While the hydroboration of 1,4-cyclohexadiene readily produced **8** as a single product, as evidenced by the appearance of a doublet of triplets at δ 3.56 ppm (C_6D_6), the hydroboration of 1,3-cyclohexadiene yielded an equimolar mixture of **7** and **8**. The mixture of isomers was supported by two distinct ^{1}H NMR doublet of triplets at δ 3.56 ppm and δ 3.73 ppm (C_6D_6), which were assigned to the two hydrogen atoms attached to the former carbenoid centers in the respective compounds.

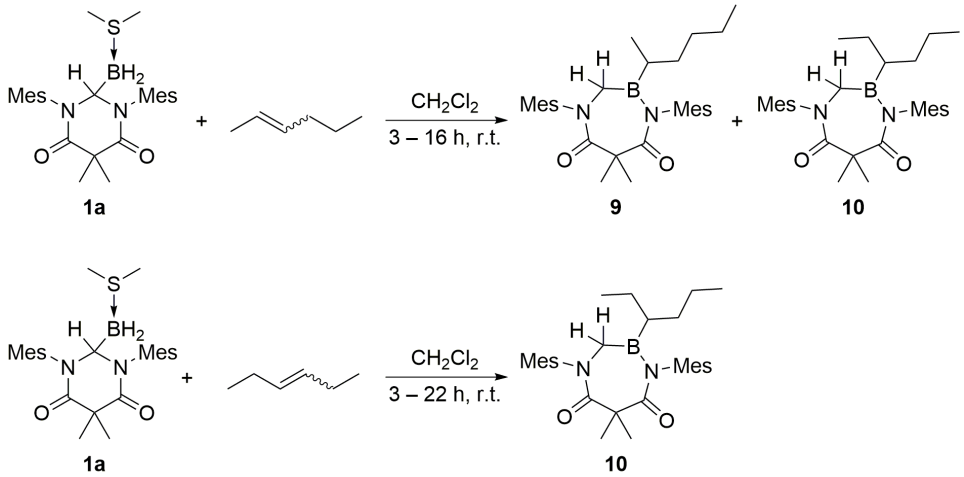


Scheme 5. Hydroboration of cyclohexene with **1a** followed by intramolecular ring-expansion.



Scheme 6. Hydroboration of cyclic olefins with **1a**.

Acyclic internal olefins were also studied as hydroboration substrates. Upon the addition of *cis*- or *trans*-2-hexene to a CH_2Cl_2 solution of **1a**, the appearance of overlapping multiplets at δ 3.67 ppm was observed in a 1:2 ratio in the corresponding ^{1}H NMR spectrum (C_6D_6) recorded for the respective products **9** and **10** (Scheme 7). Over time or upon heating the reaction mixture to 55 °C, the two multiplets converted to a single multiplet resonance at δ 3.67 ppm (see Supplementary Materials, Figure S17). Similar results were reported by Curran and co-workers, who attributed the phenomena to "chain walking" of a carbene–BH_3 adduct [19–26]. Additionally, when *cis*- or *trans*-3-hexene was introduced to **1a**, compound **10** was obtained as the sole product, as indicated by the presence of a single multiplet at δ 3.67 ppm (C_6D_6). The structure of **10** was also unambiguously confirmed using single crystal X-ray crystallography (Figure 1).



Scheme 7. Hydroboration of internal acyclic olefins with **1a**.

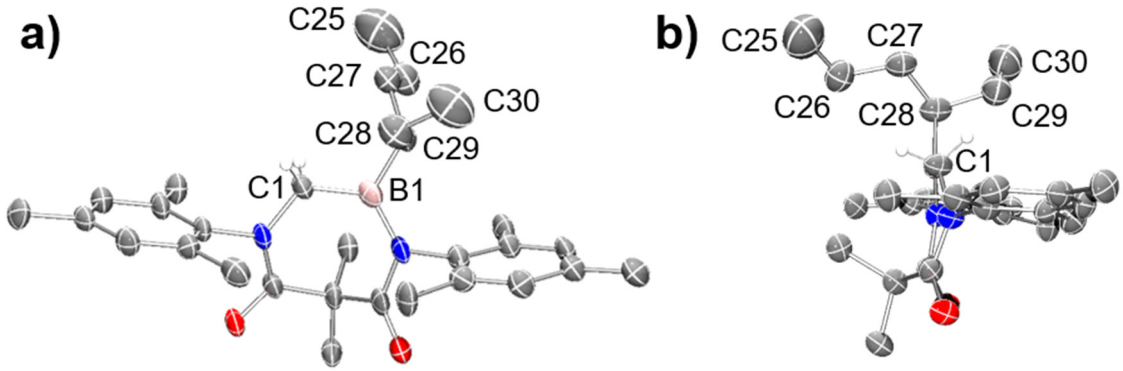
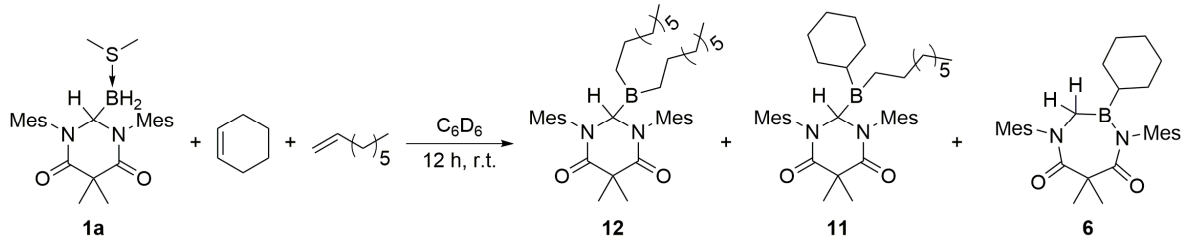


Figure 1. (**a**) Front and (**b**) side views of the Persistence of Vision Raytracer (POV-ray) representations of **10** showing ellipsoids at 50% probability. Most of the hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (°): C1–B1, 1.580 (9); B1–C28, 1.580 (9); C25–C26, 1.484 (14); C26–C27, 1.527 (10); C27–C28, 1.524 (10); C28–C29, 1.580 (10); C29–C30, 1.484 (12); C1–B1–C28, 116.0 (5). Gray = Carbon, Blue = Nitrogen, Red = Oxygen, Pink = Boron, White = Hydrogen.

Finally, efforts were directed toward the determination of conditions which facilitate a stepwise hydroboration of an internal olefin and a terminal olefin to obtain the corresponding mixed product. Upon the initial addition of excess cyclohexene to a benzene solution of **1a**, the ring-expanded compound **6** was observed as the exclusive product via ^{1}H NMR spectroscopy analysis of the crude reaction mixture. No reaction was observed upon the subsequent addition of 1-octene. In a separate experiment, a stoichiometric mixture of cyclohexene and 1-octene was added in excess to a benzene solution of **1a**. The product of this reaction was determined by ^{1}H NMR spectroscopy and mass spectrometry to contain a nearly equimolar mixture of the mixed product **11**, the ring-expanded product **6**, and **12** [29] (Scheme 8). We surmise that after the initial hydroboration of cyclohexene, the respective product did not enable the hydroboration of 1-octene, but instead underwent intramolecular ring-expansion to yield **6**. These results indicated that **1a** facilitated the hydroboration of two olefins, but only when the first reaction was with a terminal olefin. Furthermore, a ^{1}H NMR spectrum recorded after the addition of 0.5 equiv of 1-hexene to a CD_2Cl_2 solution of **1a** exhibited singlets at δ 6.08 ppm and δ 5.69 ppm in a 1:3 ratio, which were assigned to the methine groups of **3** and residual **1a**, respectively. Based on these results, we concluded that hydroboration preceded intramolecular ring-expansion.



Scheme 8. Competitive hydroboration reactions between terminal and internal olefins. A mixture of the three products shown was observed in a 1:1:1 ratio.

3. Materials and Methods

3.1. General Information

All procedures were performed in a nitrogen-filled glove box unless otherwise noted. Solvents were dried and degassed by a Vacuum Atmospheres Company solvent purification system (Vacuum Atmosphere Co., Hawthorne, CA, USA) and stored over 4 Å molecular sieves in a nitrogen-filled glove box. Unless otherwise specified, reagents were purchased from commercial sources and used without further purification. *N,N′*-dimesityl-4,6-diketo-5,5-dimethylpyrimidin-2-ylidene, as well as adducts **1a** and **1b**, were synthesized according to previously-reported procedures [29,30]. The hydroboration reactions described herein are unoptimized. Melting points were obtained using a MPA100 OptiMelt automated melting point apparatus (Stanford Research Systems Inc., Sunnyvale, CA, USA) and are uncorrected. NMR spectra were recorded on a MR 400, Inova 500, or DirectDrive 600 MHz spectrometer (Varian, Inc., Palo Alto, CA, USA), MR 400 MHz spectrometer (Agilent Technologies, Santa Clara, CA, USA) or an Ascend™ 400 MHz spectrometer (Bruker Co., Fällanden, Switzerland via Bruker Korea Co., Ltd., Seongnam-si, Korea). Chemical shifts (δ) are given in ppm and are referenced to the residual solvent (^{1}H: C_6D_6, 7.16 ppm; ^{13}C: C_6D_6, 128.06 ppm). Linear predictions were applied to all ^{11}B NMR spectra to remove the signals that corresponded to the boron found in the glass of the NMR tubes used in the corresponding experiments; the ^{11}B NMR spectrum of C_6D_6 as a "blank" was also collected as a reference. Infrared (IR) spectra were recorded on a Nicolet iS5 system (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an iD3 attenuated total reflectance (ATR) attachment (diamond crystal) or in a KBr pellet. High resolution mass spectra (HRMS) were obtained with a Autospec-Ultima mass spectrometer (Waters Co., Milford, MA, USA) using chemical ionization (CI) or a 6530 QTOF mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) using electrospray ionization (ESI). Low resolution mass spectra (LRMS) were obtained with a 6130 single quadrupole mass spectrometer equipped with an 1200 LC system (Agilent Technologies, Santa Clara, CA, USA). Elemental analyses were performed with a 2000 Organic Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA).

3.2. DAC–BH_3 SMe_2 + 1-Hexene to Obtain **3**

An excess of 1-hexene (0.1 mL, 0.8056 mmol, 4.6 equiv.) was added dropwise to a stirred solution of **1a** (79.6 mg, 0.1759 mmol) in dichloromethane (2.0 mL). The resulting mixture was stirred for 17 h at ambient temperature, whereupon the volatiles were removed under reduced pressure to afford **3** as a white solid (0.0961 g, 0.1720 mmol, 98% yield). mp = 120–123 °C. ^{1}H NMR (C_6D_6, 499.86 MHz): δ 0.98 (br m, 26H), 1.59 (s, 3H), 2.01 (overlapping s, 9H), 2.08 (s, 6H), 2.41 (s, 6H), 6.09 (s, 1H), 6.58 (overlapping s, 2H), 6.66 (overlapping s, 2H). ^{13}C NMR (C_6D_6, 125.70 MHz): δ 14.28, 19.45, 19.47, 20.78, 21.26, 22.84, 22.97, 24.34, 31.94, 48.40, 67.49, 129.76, 129.91, 135.24, 136.02, 138.01, 138.66, 172.26. ^{11}B NMR (C_6D_6, 128.39 MHz): δ 78.42 (s). IR (KBr): ν = 3447.0, 2956.3, 2920.9, 2856.1, 1692.8, 1658.4, 1606.3, 1481.4, 1464.9, 1456.9, 1410.5, 1357.2, 1321.5, 1211.5, 1165.5 cm^{-1}. HRMS (ESI): $[M + H]^+$ calcd for $C_{36}H_{56}N_2O_2B$: 559.4435; found: 559.4442. Anal. Calcd for $C_{36}H_{55}N_2O_2B$: C, 77.40; H, 9.92; N, 5.01; found: C, 77.05; H, 10.11; N, 5.12.

3.3. DAC–BH_3 SMe_2 + 1,5-Hexadiene to Obtain **4**

An excess of 1,5-hexadiene (ca. 0.03 mL) was added dropwise to a stirred solution of **1a** (10.8 mg, 0.0237 mmol) in benzene (1.0 mL). The mixture was stirred for 20 h at ambient temperature, whereupon the volatiles were removed under reduced pressure to afford **4** as a white solid (0.0106 g, 0.0224 mmol, 95% yield). mp = 173–176 °C. ^{1}H NMR (C_6D_6, 499.86 MHz): δ 0.41–1.07 (br m, 12H), 1.57 (t, J = 5.0 Hz, 3H), 2.00 (overlapping s, 9H), 2.07 (s, 6H), 2.38 (t, J = 4.5 Hz, 6H), 5.98 (s, 1H), 6.57 (s, 2H), 6.66 (s, 2H). ^{13}C NMR (C_6D_6, 125.70 MHz): δ 19.16, 19.30, 19.40, 19.47, 20.77, 21.30, 22.88, 22.95, 32.69, 33.31, 48.36, 66.41, 129.49, 129.88, 135.15, 136.04, 138.06, 138.76, 172.24. ^{11}B NMR (C_6D_6, 160.37 MHz): δ 78.98 (s). IR (KBr): ν = 3427.4, 2976.9, 2918.2, 2859.3, 1684.9, 1656.9, 1606.3, 1482.0, 1459.5, 1441.0, 1410.2, 1372.3, 1358.4, 1311.52, 1187.8, 1099.1, 1012.4, 849.6, 725.4, 569.5, 511.7 cm^{-1}. HRMS (ESI): $[M + H]^+$ calcd for $C_{30}H_{42}N_2O_2B$: 473.3339; found: 473.3345. Anal. Calcd for $C_{30}H_{41}N_2O_2B$: C, 76.26; H, 8.75; N, 5.93; found: C, 76.08; H, 8.39; N, 5.93.

3.4. DAC–BH_3 SMe_2 + Cyclohexene to Obtain **6**

An excess of cyclohexene (ca. 0.05 mL) was added dropwise to a stirred solution of **1a** (80.6 mg, 0.1781 mmol) in dichloromethane (1.0 mL). The mixture was stirred for 15 h at ambient temperature, whereupon the volatiles were removed under reduced pressure to afford **6** as a white solid (0.0780 g, 0.1651 mmol, 93% yield). mp = 81–84 °C. ^{1}H NMR (C_6D_6, 499.86 MHz): δ 0.74 (br m, 4H), 1.32 (br m, 2H), 1.40 (br m, 4H), 1.77 (s, 6H), 2.05 (s, 6H), 2.09 (s, 3H), 2.13 (s, 3H), 2.16 (s, 6H), 3.61 (s, 2H), 6.76 (s, 2H), 6.81 (s, 2H). ^{13}C NMR (C_6D_6, 125.70 MHz): δ 17.82, 19.06, 20.87, 20.92, 26.02, 26.41, 27.40, 29.39, 31.78, 47.39, 129.70, 129.87, 134.26, 134.41, 136.70, 136.84, 138.92, 142.24, 168.38, 176.76. ^{11}B NMR (C_6D_6, 160.37 MHz): δ 53.35 (s). IR (KBr): ν = 3445.4, 2919.8, 2847.9, 2372.4, 2280.5, 1694.6, 1645.2, 1620.3, 1607.6, 1485.7, 1458.2, 1398.7, 1382.1, 1367.63, 1343.7, 1243.7, 1197.6, 1168.4, 1091.0, 755.9, 688.0 cm^{-1}. HRMS (ESI): $[M + H]^+$ calcd for $C_{30}H_{41}N_2O_2B$: 473.33390; found: 473.33470.

3.5. DAC–BH_3 SMe_2 + 1,4-Cyclohexadiene to Obtain **7**

An excess of 1,4-cyclohexadiene (ca. 0.04 mL) was added to a stirred solution of **1a** (20 mg, 0.0442 mmol) in dichloromethane (0.5 mL). The mixture was stirred for 30 min at ambient temperature, whereupon the volatiles were removed under reduced pressure to afford **7** as a white solid (0.0187g, 0.03975 mmol, 90% yield). mp = 153–159 °C. ^{1}H NMR (C_6D_6, 499.86 MHz): δ 0.96 (s, 2H), 1.57 (s, 4H), 1.77 (s, 3H), 1.80 (s, 3H), 2.03 (s, 6H), 2.05 (s, 3H), 2.14 (s, 6H), 2.15 (s, 3H), 3.56 (dt, J_d = 35.00 Hz, J_t = 21.00 Hz, 2H), 5.43 (t, J = 1.5 Hz, 1H), 5.60 (m, 1H), 6.70 (m, 1H), 6.72 (m, 1H), 6.81 (s, 2H). ^{13}C NMR (C_6D_6, 125.70 MHz): δ 17.80, 17.84, 19.02, 19.06, 20.84, 20.92, 25.34, 25.77, 26.00, 26.03, 26.07, 26.76, 27.43, 47.07, 124.61, 126.86, 129.68, 129.79, 129.85, 129.86, 134.20, 134.26, 134.28, 134.47, 136.80, 136.85, 138.77, 142.21, 168.31, 176.69. ^{11}B NMR (C_6D_6, 160.37 MHz): δ 52.87 (s). IR (KBr): ν = 3016.7, 2916.6, 1700.13, 1683.9, 1668.4, 1652.5, 1506.1, 1484.0, 1457.2, 1398.0, 1367.9, 1344.8, 1305.3, 1256.5, 1235.3, 1207.5, 1164.1, 1095.3, 850.4 cm^{-1}. HRMS (ESI): $[M + H]^+$ calcd for $C_{30}H_{39}N_2O_2B$: 472.32130; found: 472.32120. Anal. Calcd for $C_{30}H_{39}N_2O_2B$: C, 76.59; H, 8.36; N, 5.95; found: C, 76.64; H, 8.32; N, 6.02.

3.6. DAC–BH_3 SMe_2 + 1,3-Cyclohexadiene to Obtain a Mixture of **7** + **8**

An excess of 1,3-cyclohexadiene (ca. 0.04 mL) was added to a stirred solution of **1a** (20 mg, 0.0442 mmol) in dichloromethane (0.5 mL). The mixture was stirred for 30 min at ambient temperature, whereupon the volatiles were removed under reduced pressure to afford a mixture of **7** + **8** as a white solid in quantitative yield. mp = 72–96 °C. ^{1}H NMR (C_6D_6, 499.86 MHz): δ 0.91–1.70 (br m, 14H), 1.76 (s, 3H), 1.77 (s, 3H), 1.80 (overlapping s, 6H), 2.03 (s, 6H), 2.05 (s, 6H), 2.08 (overlapping s, 6H), 2.10 (s, 3H), 2.13 (s, 3H), 2.14 (s, 6H), 2.15 (s, 6H), 3.56 (dt, J_d = 34.49 Hz, J_t = 20.99 Hz, 2H), 3.73 (dt, J_d = 35.99 Hz, J_t = 14.50 Hz, 2H), 5.35 (m, 1H), 5.49 (m, 1H), 5.67 (m, 1H), 5.85 (m, 1H), 6.73 (m, 6H), 6.81 (s, 2H). ^{13}C NMR (C_6D_6, 125.70 MHz): δ 17.78, 17.80, 17.84, 19.02, 19.03, 19.05, 19.13, 20.85, 20.87, 20.90, 20.92, 22.33, 22.59, 22.79, 22.93, 24.69, 25.22, 25.34, 25.40, 25.45, 25.77, 26.00, 26.03, 26.05, 26.71, 27.43,

29.40, 30.01, 47.07, 47.64, 53.34, 53.44, 124.73, 129.82, 129.91, 134.13, 134.20, 134.26, 134.28, 134.47, 134.50, 136.76, 136.80, 136.85, 136.86, 138.77, 138.91, 142.16, 142.20, 168.24, 168.31, 176.69, 176.78. ^{11}B NMR (C_6D_6, 160.37 MHz): δ 52.81 (br s). IR (KBr): ν = 3014.0, 2920.1, 2856.7, 1700.2, 1652.5, 1484.0, 1464.9, 1397.7, 1367.2, 1305.6, 1239.8, 1164.0, 1095.3, 850.5 cm^{-1}. HRMS (ESI): $[M + H]^+$ calcd for $C_{30}H_{39}N_2O_2B$: 471.31830; found: 471.31870. Anal. Calcd for $C_{30}H_{39}N_2O_2B$: C, 76.59; H, 8.36; N, 5.95; found: C, 76.70; H, 8.39; N, 5.57.

3.7. DAC–BH_3 SMe_2 + cis-2-Hexene to Obtain a Mixture of **9** + **10**

An excess of *cis*-2-hexene (ca. 0.05 mL) was added to a stirred solution of **1a** (84.4 mg, 0.1865 mmol) in dichloromethane (2.0 mL). The mixture was stirred for 16 h at ambient temperature, whereupon the volatiles were removed under reduced pressure to afford products **9** and **10** as a white solid in 1:2 ratio (0.0765 g, 0.1612 mmol, 86% yield). mp = 60–63 °C. ^{1}H NMR (C_6D_6, 499.86 MHz): δ 0.79 (m, 7H), 1.16 (m, 6H), 1.64 (s, 3H), 1.70 (s, 3H), 2.01 (m, 12H), 2.10 (s, 12H), 2.12 (s, 3H), 2.14 (s, 3H), 2.25 (m, 9H), 2.31 (m, 6H), 3.70 (m, 2H), 6.86–6.91 (s, 2H), 6.95 (s, 4H). ^{13}C NMR (C_6D_6, 125.70 MHz): δ 14.03, 16.47, 17.80, 17.86, 19.01, 20.85, 20.90, 22.71, 22.96, 24.61, 24.73, 25.93, 26.01, 26.04, 26.11, 31.34, 33.45, 46.27, 53.35, 129.53, 129.60, 129.70, 129.88, 134.19, 134.22, 134.67, 136.74, 136.83, 138.76, 142.32, 168.37, 176.57. ^{11}B NMR (C_6D_6, 160.37 MHz): δ 53.72 (br s). IR (KBr): ν = 3480.4, 2922.6, 2869.5, 2857.6, 1699.5, 1695.0, 1652.2, 1608.7, 1483.7, 1464.0, 1397.7, 1381.4, 1366.5, 1262.7, 1241.6, 1229.0, 1199.1, 1164.0 cm^{-1}. HRMS (CI): $[M + H]^+$ calcd for $C_{30}H_{44}N_2O_2B$: 475.3496; found: 475.3492. Anal. Calcd for $C_{30}H_{43}N_2O_2B$: C, 75.94; H, 9.13; N, 5.90; found: C, 75.83; H, 9.26; N, 5.76.

3.8. DAC–BH_3 SMe_2 + trans-2-Hexene to Obtain a Mixture of **9** + **10**

An excess of *trans*-2-hexene (ca. 0.05 mL) was added to a stirred solution of **1a** (89.4 mg, 0.1976 mmol) in dichloromethane (2.0 mL). The mixture was stirred for 3 h at ambient temperature, whereupon the volatiles were removed under reduced pressure to afford a mixture of **9** + **10** as a white solid (0.0860 g, 0.1812 mmol, 92% yield). mp = 64–67 °C. ^{1}H NMR (C_6D_6, 499.86 MHz): δ 0.63 (m, 3H), 0.72 (t, J = 7.25 Hz, 3H), 0.79–1.18 (m, 7H), 1.79 (s, 6H), 2.07–2.12 (m, 12H), 2.16 (m, 3H), 3.66 (m, 2H), 6.76 (s, 2H), 6.79 (s, 2H). ^{13}C NMR (C_6D_6, 125.70 MHz): δ 14.03, 16.47, 17.80, 17.86, 19.02, 20.85, 20.91, 22.71, 22.98, 24.61, 24.73, 25.94, 26.02, 26.04, 26.11, 31.34, 33.45, 46.27, 53.35, 129.53, 129.60, 129.70, 129.88, 134.20, 134.23, 134.67, 136.73, 136.82, 138.79, 142.34, 168.33, 176.58. ^{11}B NMR (C_6D_6, 160.37 MHz): δ 53.72 (bs). IR (KBr): ν = 3480.4, 2954.6, 2922.6, 2869.5, 2857.6, 1699.5, 1695.0, 1652.2, 1608.7, 1483.7, 1464.0, 1397.7, 1381.4, 1366.5, 1262.7, 1241.6, 1229.0, 1199.1, 1164.0 cm^{-1}. HRMS (CI): $[M + H]^+$ calcd for $C_{30}H_{44}N_2O_2B$: 475.3496; found: 475.3503. Anal. Calcd for $C_{30}H_{43}N_2O_2B$: C, 75.94; H, 9.13; N, 5.90; found: C, 75.54; H, 9.08; N, 5.74.

3.9. DAC–BH_3 SMe_2 + cis-3-Hexene to Obtain **10**

An excess of *cis*-3-hexene (ca. 0.05 mL) was added to a stirred solution of **1a** (57.1 mg, 0.1262 mmol) in dichloromethane (2.0 mL). The mixture was stirred for 3 h at ambient temperature, whereupon the volatiles were removed under reduced pressure to afford **10** as a white solid (0.0581 g, 0.1224 mmol, 97% yield). Single crystals suitable for single crystal X-ray diffraction were grown using a slow evaporation of saturated benzene solution of product **10**. mp = 60–64 °C. ^{1}H NMR (C_6D_6, 499.86 MHz): δ 0.63 (m, 3H), 0.72 (t, J = 7.25 Hz, 3H), 0.80–1.17 (m, 7H), 1.80 (s, 6H), 2.08–2.12 (m, 12H), 2.16 (m, 3H), 3.67 (dt, J_d = 31.24 Hz, J_t = 20.99 Hz, 2H), 6.77 (s, 2H), 6.79 (s, 2H). ^{13}C NMR (C_6D_6, 125.70 MHz): δ 14.02, 16.47, 17.81, 17.86, 19.01, 20.84, 20.90, 22.72, 22.98, 24.61, 24.73, 25.94, 26.01, 26.04, 26.11, 31.34, 33.46, 46.26, 53.36, 129.53, 129.60, 129.70, 129.88, 134.20, 134.23, 134.68, 136.73, 136.83, 138.80, 142.34, 168.36, 176.58. ^{11}B NMR (C_6D_6, 160.37 MHz): δ 55.26 (br s). HRMS (CI): $[M + H]^+$ calcd for $C_{30}H_{44}N_2O_2B$: 475.3496; found: 475.3498. Anal. Calcd for $C_{30}H_{43}N_2O_2B$: C, 75.94; H, 9.13; N, 5.90; found: C, 76.16; H, 9.10; N, 5.87.

3.10. DAC–BH_3 SMe_2 + trans-3-Hexene to Obtain **10**

An excess of *trans*-3-hexene (ca. 0.04 mL) was added to a stirred solution of **1a** (12.03 mg, 0.0266 mmol) in dichloromethane (2.0 mL). The mixture was stirred for 22 h at ambient temperature whereupon the volatiles were removed under reduced pressure to afford **10** as a white solid in quantitative yield. mp = 58–62 °C. ^{1}H NMR (C_6D_6, 499.86 MHz): δ 0.63 (m, 3H), 0.72 (t, J = 7.25 Hz, 3H), 0.78–1.19 (m, 7H), 1.79 (s, 6H), 2.08–2.12 (m, 12H), 2.16 (m, 3H), 3.67 (dt, J_d = 31.24 Hz, J_t = 20.74 Hz, 2H), 6.76 (s, 2H), 6.79 (s, 2H). ^{13}C NMR (C_6D_6, 125.70 MHz): δ 14.02, 16.46, 17.79, 17.84, 19.01, 20.85, 20.90, 22.71, 22.97, 24.60, 24.72, 25.92, 25.99, 26.02, 26.09, 31.33, 33.44, 46.28, 53.33, 129.57, 129.61, 129.71, 129.87, 134.15, 134.18, 134.65, 136.76, 136.86, 138.76, 142.27, 168.45, 176.53. ^{11}B NMR (C_6D_6, 160.37 MHz): δ 53.71 (br s). HRMS (CI): $[M + H]^+$ calcd for $C_{30}H_{44}N_2O_2B$: 475.3496; found: 475.3497. Anal. Calcd for $C_{30}H_{43}N_2O_2B$: C, 75.94; H, 9.13; N, 5.90; found: C, 76.24; H, 9.10; N, 5.79.

3.11. DAC–BH_3 SMe_2 + 1-Octene + Cyclohexene

An excess 1:1 molar mixture of 1-octene and cyclohexene (ca. 0.03 mL) was added dropwise to a stirred solution of **1a** (10 mg, 0.0221 mmol) in dichloromethane (0.7 mL). The mixture was stirred for 12 h at ambient temperature, whereupon the crude reaction mixture was analyzed by ^{1}H NMR spectrometry and low resolution mass spectrometry. LRMS for **6** (ESI): $[M + H]^+$ calcd for $C_{30}H_{42}N_2O_2B$: 473.3; found: 473.3. LRMS for **11** (ESI): $[M + H]^+$ calcd for $C_{38}H_{58}N_2O_2B$: 585.5; found: 585.5. LRMS for **12** (ESI): $[M + H]^+$ calcd for $C_{40}H_{64}N_2O_2B$: 615.5; found: 615.5.

4. Conclusion

In conclusion, we have demonstrated that the DAC–BH_3 adduct **1a** facilitated the hydroboration of a range of olefins. The outcomes of these reactions were found to depend on the substrate employed and have provided additional insight into the underlying mechanism. While terminal olefins underwent hydroboration and afforded the expected organoboranes, the use of internal olefins typically resulted in rapid intramolecular ring-expansion of the putative products. The ring-expansion was modulated through the inclusion of terminal olefins in the corresponding reaction mixtures and afforded organoboranes that contained primary and secondary alkyl groups.

Supplementary Materials: The representative ^{1}H, ^{13}C, and ^{11}B NMR spectra (Figures S1–S31) for the above described complexes as well as details about the single crystal XRD structure of **10** (Table S1) are available online at www.mdpi.com/2073-4344/6/9/141/s1.

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