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Reactions of pentaphenylborole with main group hydrides

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ABSTRACT

The reactivity of the anti-aromatic pentaphenylborole with HBpin (pinacolborane), $HGeEt_3$, and $HSnBu_3$ was investigated. In all cases, the products were 1-bora-cyclopent-3-ene heterocycles resulting from the stereospecific addition of the E–H bond to the borole. Both $HGeEt_3$, and $HSnBu_3$ furnished *syn* products, while the reaction with pinacolborane yielded the *anti*-product. The discrepancy between the products is rationalized by previous studies reported on the reactivity of boroles with dihydrogen.

1. Introduction

The generation of carbon–boron, –tin, and –germanium bonds has emerged as an important sector in synthesis given the utility of these groups for functionalization via coupling reactions [1,2]. The majority of the processes to generate these species are promoted by transition metals [3–5]. The advent of frustrated Lewis pair (FLP) chemistry that takes advantage of a Lewis basic and a Lewis acidic center has brought forth new methodologies that avoid the use of transition metal reagents for these types of transformations [6–14]. Whether the FLP system is intermolecular or intramolecular, two separate atoms are required for this process to induce bond cleavage [9,15–17]. It has recently been realized that boroles are able to activate a variety of bonds without the necessity of an external base [18–29]. This high reactivity is rationalized through the strong Lewis acidic boron center and the anti-aromatic four π-electron ring system [30–37].

Piers showed that boroles **1** and **2** (Fig 1) were capable of activating H_2 on their own without the assistance of an external Lewis base to produce 1-boracyclopent-3-enes (**3**) by introducing hydrogen atoms on the carbon centers adjacent to boron [19,20]. Braunschweig later demonstrated that this reactivity was very similar with triethylsilane, yielding the corresponding silyl functionalized species (**4**) [29]. In light of the interesting reported reactivity of boroles with H_2 and silane, we investigated the reactions of pentaphenylborole with pinacolborane (HBpin), $HGeEt_3$, and $HSnBu_3$. These reagents represent three widely used main group hydrides in synthesis and these studies advance the understanding of elemental–hydrogen bond activation at Lewis acidic boron centers.

2. Materials and methods

2.1. General procedures

Unless specified, all reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in an MBraun double-station glove box. Glassware was oven dried before use. Solvents were dried using a JC Meyer Solvent System with columns filled with solvent appropriate drying agents. Pentaphenylborole was prepared by the literature procedure [31]. Unless specified, all other compounds were obtained from VWR, Fisher Scientific, Alfa Aesar, Strem Chemicals, or Aldrich Chemical Company, tested for purity by NMR spectroscopy and used without further purification. Multinuclear NMR spectra (^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$) were recorded at ambient temperature on Bruker Ascend 400 or 600 instruments. ^1H and $^{13}C\{^1H\}$ spectra were referenced to external $SiMe_4$ *via* residual protons in the deuterated solvents or solvent resonances respectively. $^{11}B\{^1H\}$ NMR spectra were referenced externally to $BF_3{\cdot}OEt_2$. High resolution mass spectra (HRMS) were obtained at the University of Texas at Austin Mass Spectrometry Center on a Micromass Autospec Ultima spectrometer using CI. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo Kα radiation ($\lambda = 0.71073$ Å). Crystals were selected under oil, mounted on micromounts then immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL. Melting points

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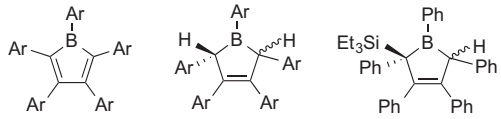

Fig. 1. Structure of boroles and the reaction products with dihydrogen and triethylsilane.

were measured with a Büchi melting point apparatus and are uncorrected.

2.2. Synthesis and characterization of the compounds

anti-**5** Pinacolborane (12.8 mg, 0.100 mmol) was added to a solution of pentaphenylborole (44.4 mg, 0.100 mmol) in CH_2Cl_2 (2 mL) at room temperature and stirred for 3 min. The color changed from dark blue to colorless immediately following the addition. The solvent was removed *in vacuo,* giving a white solid, which was washed with hexanes (2 × 0.3 mL) and dried *in vacuo* to furnish *anti*-**5** as a white powder. Yield (40.2 mg, 70%); mp 117–120 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 12 Hz, 2H), 7.59 (d, J = 12 Hz, 2H), 7.51 (d, J = 12 Hz, 2H) 7.26–6.98 (m, 19H), 4.68 (s, 1H), 1.19 (s, 6H), 1.14 (s, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.8, 143.4, 142.5, 142.4, 140.0, 139.7, 136.2, 132.2, 130.7, 130.3, 130.1, 129.5, 128.5, 128.4, 127.7, 127.4, 127.4, 126.2, 125.2, 125.2, 83.8, 56.2, 25.1, 24.7; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 33.5 (br) the signal from the cyclobora-2-pentene ring was not observed despite extended scan times; FT-IR cm^{-1} (ranked intensity) 2976(15), 1595(9), 1492(7), 1434 (13), 1360(14), 1294(11), 1264(4), 1137(3), 965(6), 750(5), 733 (10), 694(1), 631(12), 559(8), 538(2); HRMS (CI$^+$) for $C_{40}H_{38}B_2O_2$ (M^+), calcd: 572.3058; found: 572.3073.

syn-**6** Triethylgermanium hydride (16.1 mg, 0.100 mmol) was added to a solution of pentaphenylborole (44.4 mg, 100 mmol) in CH_2Cl_2 (2 mL) at room temperature and stirred for 3 min. The color changed from dark blue to colorless immediately following addition. The solvent was removed *in vacuo* giving a white solid which was washed with pentanes (2 × 0.3 mL) and dried *in vacuo* to afford *syn*-**6** as a white powder. Yield (50.7 mg, 83%); mp 145–147 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38–7.33 (m, 5H), 7.28–7.22 (m, 5H), 7.12–6.85 (m, 13H) 6.65 (d, J = 12 Hz, 2H), 4.63 (s, 1H), 0.85–0.81 (m, 9H), 0.69–0.63 (m, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.3, 143.5, 142.9, 141.9, 140.4, 138.9, 135.9, 132.6, 131.3, 130.5, 130.0, 129.5 128.9, 128.3, 127.5, 127.3, 126.5, 126.0, 125.7, 124.7, 67.0, 54.6, 9.9, 6.3; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 79.2 (br); FT-IR cm^{-1}(ranked intensity) 3077 (2), 3044(3), 2871(10), 1574(12), 1459(7), 1430(15), 1374(1), 1168(6), 1075(13), 972(14), 920(9), 909(11), 815(4), 461(8), 422 (5); HRMS (CI$^+$) for $C_{40}H_{31}$BGe (M^+), calcd: 606.2513; found: 606.2534.

syn-**7** A solution of tributyl tin hydride (29.1 mg, 0.100 mmol) in CH_2Cl_2 (5 mL) was added drop wise to pentaphenylborole (44.4 mg, 0.100 mmol) at room temperature until the mixture was no longer blue. The reaction was stirred for another 30 min before the solvent was removed *in vacuo* to give *syn*-**7** as a colorless oil. Yield (58.6 mg, 79%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36–7.23 (m, 10H), 7.12–6.98 (m, 13H), 6.70 (d J = 6.0 Hz, 2H), 4.52 (s, 1H), 1.40–1.14 (m, 12H), 0.81–0.78 (m, 9H), 0.72–0.69 (m, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.9, 143.4, 142.0, 141.3, 139.8, 138.9, 137.7, 136.2, 133.2, 130.9, 130.5, 130.0, 129.3, 128.8, 128.7, 127.5, 127.4, 126.5, 125.9, 125.5, 124.7, 77.9, 77.4, 29.2, 27.5, 13.7, 12.4; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ 71.7 (br); FT-IR cm^{-1}(ranked intensity) 3055(13), 2920(2), 2852(10), 1573(14), 1441(7), 1263(3), 1124 (8), 1072(5), 1028(6), 749(11), 694(1), 595(9), 566(12), 548(15), 517(4); HRMS (CI$^+$) for $C_{46}H_{53}$BSn (M^+), calcd: 736.3262; found: 736.3286.

3. Results and discussion

3.1. Reactions of pentaphenylborole with HBpin, HGeEt$_3$, and HSnBu$_3$

The 1:1 stoichiometric reaction of HBpin with pentaphenylborole (**1**) in CH_2Cl_2 led to a rapid color change from deep blue to colorless, indicating consumption of the borole. Removing the volatiles *in vacuo* and acquiring an ^{1}H NMR spectrum of the redissolved solids in $CDCl_3$ showed resonances consistent with one product. In addition to the aryl protons from the phenyl groups bound to the boracycle, three singlets were observed, integrating in a 6:6:1 ratio with respect to the 25 aryl protons, with two in the aliphatic region for the Bpin methyl groups, and a singlet at 4.68 ppm. The latter singlet is reminiscent of the shift of the protons on the carbon atoms adjacent to boron on the hydrogenated and hydrosilated species (5.14–4.35 ppm) [19,20,29], supporting a hydroborated borole or 1-boracyclopent-3-ene as the product (**5**, Scheme 1). A broad resonance was observed by ^{11}B{^{1}H} NMR spectroscopy at δ 33.5 ppm corresponding to the three coordinate boron atom of the Bpin group [38]. An ^{1}H NOESY NMR experiment did not reveal through space coupling between the hydrogen atom introduced on the boracycle (4.68 pm) with the pinacol CH_3 protons, suggesting an *anti* conformation of the hydroboration product. X-ray diffraction studies on crystals grown by vapour diffusion of pentane into a concentrated Et_2O solution confirmed the identity and stereochemistry as *anti*-**5**. Examination of the crude NMR spectra showed no evidence of the *syn* conformer, only the *anti* product.

The analogous reactions of pentaphenylborole **1** with HGeEt$_3$ and HSnBu$_3$ proceeded in a similar fashion, a noteworthy observation was the rapid disappearance of the blue color of **1** to produce colorless solutions. Removing the solvent *in vacuo* and acquiring ^{1}H NMR spectra of the samples redissolved in $CDCl_3$ showed quantitative reactions for both hydride species in both reactions with singlets at 4.63 and 4.52 ppm for the reactions of HGeEt$_3$ and HSnBu$_3$, respectively. The integration of the singlet was unity with respect to the 25 aryl protons and the aliphatic region corresponded to the proper alkyl protons consistent with 1:1 reactions with pentaphenylborole (15 for HGeEt$_3$ and 27 for HSnBu$_3$). Downfield resonances for both products were observed by ^{11}B{^{1}H} NMR (δ = 79.2 for HGeEt$_3$ and δ = 71.4 for HSnBu$_3$ *c.f.* δ = 66.0 for **1**), both in the region of the hydrogenated and hydrosilated (83.0–78.5 ppm) products, leading to the assignment of the products as the corresponding hydrogermylation and hydrostannation species (**6** and **7**, respectively) [19,20,29]. Acquiring ^{1}H NOESY NMR spectra showed correlations between the singlets for the proton on the α-carbon and the alkyl protons in both **6** and **7**, indicating a *syn* orientation of the proton with respect to the stannyl and germyl moieties (*syn*-**6** and *syn*-**7**). The identity and stereochemistry of *syn*-**6** was confirmed by an X-ray diffraction study on crystals grown by vapour diffusion of pentane into a concentrated Et_2O solution [39].

3.2. X-ray crystallography

Although the reactions with HBpin and HGeEt$_3$ formed exclusively *anti* and *syn* products (*anti*-**5** and *syn*-**6**) respectively, only one enantiomer is in the asymmetric unit, but the other is also present in a 1:1 ratio due to the centrosymmetric space groups ($P\bar{1}$ for *anti*-**5** and $P2_1/c$ for *syn*-**6**). Only one enantiomer of each compound is displayed in Fig. 2 (2*R*,5*S*-*anti*-**5**, 2*R*,5*R*-*syn*-**6**) (see Table 1). In