Enabling and Probing Oxidative Addition and Reductive Elimination at a Group 14 Metal Center: Cleavage and Functionalization of E–H Bonds by a Bis(boryl)stannylene

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ABSTRACT: By employing strongly σ-donating boryl ancillary ligands, the oxidative addition of H2 to a single site SnII system has been achieved for the first time, generating (boryl)2SnH2. Similar chemistry can also be achieved for protic and hydridic E–H bonds (N–H/O–H, Si–H/B–H, respectively). In the case of ammonia (and water, albeit more slowly), E–H oxidative addition can be shown to be followed by reductive elimination to give an N- (or O-)borylated product. Thus, in stoichiometric fashion, redox-based bond cleavage/formation is demonstrated for a single main group metal at room temperature. From a mechanistic viewpoint, a two-step coordination/proton transfer process for N–H activation is shown to be viable through the isolation of species of the types Sn(boryl)2·NH3 and [Sn(boryl)2·(NH3)]2+ and their onward conversion to the formal oxidative addition product Sn(boryl)J(H)(NH3).

INTRODUCTION

Oxidative addition and reductive elimination represent fundamental chemical steps familiar from undergraduate textbooks and key to numerous societal important catalytic processes. The associated Mσ+/Mσ+2 redox shuttle, while facile for noble metals, is not well established for main group systems. This reflects the fact that although oxidative bond activation by subvalent main group systems is well-known (e.g., for 6-valence-electron carbenes), subsequent regeneration of the reduced state via reductive elimination is typically not thermodynamically viable.

With reductive elimination in mind, one potential strategy is to target metallylenes featuring the heavier Group 14 elements, i.e., to exploit metals with intrinsically weaker M–E bonds (and a more favorable Mσ+/Mσ+ potential). The thermodynamic balance between facilitating reductive elimination and maintaining the capability for oxidative addition is a fine one, however; diarylgermynes (Ar2Ge:) have been reported to react with E–H bonds via oxidative addition to give GeIV products, but the corresponding stannynes react via a concerted exchange process, releasing arene and leading to the formation of SnII systems containing Sn–E linkages (E = H, NH2, OR etc.). To date—while addition to distannynes (RSnSnR) has been reported—no experimental evidence exists for the oxidative addition of the archetypal E–H bond (i.e., that in H2) at a mononuclear SnII system to give the corresponding SnIV dihydride.

We hypothesized that the SnII/SnIV redox couple might be manipulated to promote oxidative addition by the use of more strongly σ-donating ancillary ligands. Thus, given the fact that boryl ligands (−BX2) are known to be extremely strong σ-donors (to greater extent even than hydride, alkyl or aryl donors), we targeted oxidative bond activation by boryltin(II) systems. In addition, with the kinetics of E–H oxidative addition in mind, it has been reported that the energy gap between the metallylene singlet ground state and triplet excited state (ΔEσ) is inversely correlated with reactivity. The very strong σ-donor capabilities of boryl substituents are hypothesized to raise the energy of the metallylene HOMO, and so reduce the HOMO/LUMO separation (and thus the related singlet–triplet gap). As such, from a kinetic as well as a thermodynamic perspective, (boryl)SnII systems were perceived as being potential candidates for the activation of E–H bonds.

In the current study we demonstrate that by targeted choice of ancillary substituents, SnII systems can be synthesized that are capable of a range of oxidative addition processes, relevant not only to H2, but also to protic and hydridic E–H bonds. Mechanistically, through the isolation of potential intermediate species we establish experimentally the viability of a two-step activation process for ammonia, involving initial coordination at the metal center, followed by N-to-Sn proton transfer. In addition, in the cases of NH3 and H2O, this net oxidative addition process can be shown to be followed by reductive elimination to give an N- (or O-)borylated product, thus providing demonstration (in stoichiometric fashion) of redox-based bond cleavage/formation at a main group metal.
General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. THF was refluxed over potassium–sodium alloy and distilled prior to use. NMR spectra were measured in CD2Cl2, which was dried over potassium, distilled under reduced pressure and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. 1H and 13C NMR spectra were referenced to external Et4SiBF4. Assignments were confirmed using two-dimensional 1H–1H COSY and 1H–13C HSQC experiments. Chemical shifts are quoted in ppm and coupling constants in Hz.

EXPERIMENTAL SECTION

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Sn(B(NDippCH)2)2(H) (SiH5). 4a. A degassed solution of 1 (95 mg, 0.106 mmol) in C6H6 (2 mL) was exposed to an atmosphere of silane. After 5 min of stirring at 20 °C the yellow-green color disappeared, and all volatiles were removed in vacuo and the residue was mixed with hexane (3 × 5 mL). The extract was evaporated to dryness, and the resulting light-brown solid washed with a small amount of cold hexane and dried in vacuo yielding colorless crystalline 4a (76 mg, 0.082 mmol, 77%). Anal. found (calcld. for C52H74B2N4Sn): C, 67.65 (67.48); H, 8.38 (8.28); N, 6.21 (6.05) %. 1H NMR (CD2Cl2): δ = 7.19 (4 H, t, J = 7.7 Hz, p-H of Ar), 7.09 (8 H, d, J = 7.7 Hz, m-H of Ar), 6.16 (4 H, s, with 119/117Sn satellites) [J(Sn-H) = 9.5 H, NCH3), 3.21 (4 H, septet, J = 6.83 Hz, CHMe3), 2.92 (4 H, septet, J = 6.83 Hz, CHMe3), 2.27 (3 H, d, J = 3.83 Hz, with 119/117Sn satellites) [J(Sn-H) = 39.9 Hz and 1H] satellites [J(Sn-H) = 191.2 Hz, SiH], 1.66 (1 H, quartet, δ = 3.83 Hz, with 119/117Sn satellites) [J(Sn-H) = 1223 and 1281 Hz, SnH4], 0.16–1.13 (48 H, four overlapping doublets, CHMe3). 13C NMR (CD2Cl2): δ = 146.17 (o-C of Ar), 145.74 (o-C of Ar), 140.61 (iso-C of Ar), 127.93 (p-C of Ar), 124.28 (m-C of Ar), 127.33 (m-C of Ar), 123.28 (119/117Sn satellites) [J(Sn-C) = 32.9 Hz, NCH3), 28.92 (CHMe3), 28.47 (CHMe3), 25.96 (CHMe3), 25.89 (CHMe3), 24.31 (CHMe3), 22.80 (CHMe3), 11B [1H (CD3): δ = 27.9. 11B [1H (CD3): δ = 108.8. 1H NMR (CD2Cl2) δ = 7.19 (4 H, t, J = 7.7 Hz, p-H of Ar), 7.05–7.11 (8 + 3 H, m, m-H of Ar and m- and p-H of Ph), 6.15 (4 H, s, with 119/117Sn satellites) [J(Sn-H) = 9.4 Hz, NCH3), 3.86 (2 H, d, J = 3.69 Hz, with 1H [J(Sn-H)] = 0.0767. CCDC ref: 1055215.

Phenylsilane (10.8 mg, 12.3 µL, 0.010 mmol) was added to a solution of 1 (75 mg, 0.084 mmol) in CD2Cl2 (0.7 mL). Almost immediately the yellow-green color disappeared and 1H NMR spectrum showed clean formation of a single product (excess PhSiH3 was also present). The mixture was transferred into a two-section crystallization tube and volatiles removed in vacuo. The residue was dissolved in hexane (1 mL) and the tube sealed under a vacuum. The solution was slowly concentrated at room temperature while large colorless blocks formed. The resulting crystals were washed with a small amount of cold hexane and dried in vacuo yielding 4b (59 mg, 0.059 mmol, 70.1%). Anal. found (calcld. for C52H74B2N4SiSn): C, 69.79 (69.54); H, 8.18 (8.05); N, 5.47 (5.59) %. 1H NMR (CD2Cl2): δ = 7.36 (2 H, m, o-H of Ph), 7.21 (4 H, t, J = 7.7 Hz, p-H of Ar), 7.05–7.11 (8 + 3 H, m, m-H of Ar and m- and p-H of Ph), 6.15 (4 H, s, with 119/117Sn satellites) [J(Sn-H) = 9.4 Hz, NCH3), 3.86 (2 H, d, J = 3.69 Hz, with 119/117Sn satellites) [J(Sn-H)] = 6.88 Hz and 3H satellites [J(Sn-H)] = 190.3 Hz, SiH2Ph), 3.17 (4 H, septet, J = 6.89 Hz, CHMe3), 2.96 (4 H, septet, J = 6.88 Hz, CHMe3), 1.64 (1 H, t, J = 3.69 Hz, with 1H [J(Sn-H)] = 119/117Sn satellites) [J(Sn-H)] = 1252 Hz, SnH3), 1.12 (12 H, d, J = 6.88 Hz, CHMe3), 1.08 (12 H, d, J = 6.88 Hz, CHMe3), 0.94 (12 H, d, J = 6.88 Hz, CHMe3). 13C NMR (CD2Cl2): δ = 146.30 (o-C of Ar), 145.91 (o-C of Ar), 140.86 (iso-C of Ar), 137.19 (119/117Sn satellites) [J(Sn-C) = 12.9 Hz, o-C of Ph), 133.18 (119/117Sn satellites) [J(Sn-C) = 8.6 Hz, iso-C of Ph), 128.75 (p-C of Ph), 127.94 (p-C of Ar), 127.61 (m-C of Ph), 124.25 (m-C of Ar), 123.75 (m-C of Ar), 123.57 (119/117Sn satellites) [J(Sn-C) = 32.6 Hz, NCH3), 28.91 (CHMe3), 28.44 (CHMe3), 26.11 (CHMe3), 25.96 (CHMe3), 24.07 (CHMe3), 23.00 (CHMe3). 11B [1H (CD3): δ = 28.1. 11B [1H (CD3): δ = 63.1 (with 119/117Sn satellites) [J(Sn-Si) = 409.4 and 428.5 Hz. Crystallographic data (for 4b): C52H74B2N4SiSn, M = 1001.79, a = 12.5270(4) Å, b = 12.6173(5) Å, c = 21.1768(8) Å, α = 79.50(5)°, β = 89.40(3)°, γ = 60.70(9)°, triclinic, P1, V = 258.2(2) Å3, Z = 2, R1 for 10834 [data intensity I > 2σ(I)] unique reflections = 0.0614, wR1 (all 10774 unique reflections) = 0.0767. CCDC ref: 1055215.

Sn(B(NDippCH)2)2(H) (SiH5). 4a. A degassed solution of 1 (95 mg, 0.106 mmol) in C6H6 (2 mL) was exposed to an atmosphere of silane. After 5 min of stirring at 20 °C the yellow-green color disappeared, and all volatiles were removed in vacuo and the residue was mixed with hexane (3 × 5 mL). The extract was evaporated to dryness, and the resulting light-brown solid washed with a small amount of cold hexane and dried in vacuo yielding colorless crystalline 4a (76 mg, 0.082 mmol, 77%). Anal. found (calcld. for C52H74B2N4Sn): C, 67.65 (67.48); H, 8.38 (8.28); N, 6.21 (6.05) %.
warm hexane and storing the concentrated extract at 4 °C. This yielded clear blocks, which were washed with a small amount of cold hexane and dried in vacuo turning into a white powder (26 mg, 0.027 mmol, 23.5%). Anal. found (calcld. for C34H63B2N4Sn: C, 62.51 (63.85); H, 8.02 (8.76); N, 7.16 (7.25)%). 1H NMR (CD2Cl2, δ 6.19 (4 H, t, J = 7.4 Hz, p-H of Ar); 7.16 (8 H, d, J = 7.4 Hz, m-H of Ar + C6D5H). 6.22 (4 H, s, with 119/117Sn satellites) signals of Sn−H); 6.5 Hz, NCH3), 3.30 (4 H, septet, J = 6.83 Hz, CHMe3), 3.17 (4 H, septet, J = 6.83 Hz, CHMe3), 2.14 (2 H, br s, BH2), 1.73 (9 H, s, NMe3), 1.12−121 (48 H, four overlapping doublets, CHMe2 + C of hexane), 1.11 (1 H, br s, with 119/117Sn satellites) signals of (Sn−H); 893.9 and 936.2 Hz, SnH), 0.88 (6 H, Me of hexane). 13C{1H} NMR (CD2Cl2): δ 146.71 (Sn(−C)); 146.54 (o-C of Ar), 146.22 (ipso-C of Ar), 127.19 (p-C of Ar), 123.86 (m-C of Ar), 123.78 (m-C of Ar), 123.05 (119/117Sn satellites) signals of Sn(−C); 24.2 Hz, NCH3, 54.42 (119/117Sn satellites) signals of Sn(−C)); 36.3 Hz, NMe3), 31.92 (CH of hexane), 28.57 (CHMe3), 28.53 (CH2SnMe2), 26.82 (CHMe3), 26.35 (CHMe3), 23.76 (CHMe3), 23.48 (CHMe3), 23.01 (CH of hexane), 14.31 (Me of hexane). 11B[1H] (C6D6); δ 31.9 (3-coordinate boron), −8.26 (BH2NMe3). Crystallographic data (for C); C34H63B2N4Sn: M = 966.43, a = 14.1360(2) Å, b = 16.8914(2) Å, c = 25.9139(4) Å, β = 99.1667(12)°, monoclinic, P21/c, V = 6108.47(15) Å3, Z = 4, R = 0.0671 for data intensity I > 2σ(I) unique reflections =0.0412, wR2 (all 1721 unique reflections) = 0.0505, CCDC ref: 1055216.

SnB(NDippCH)2[A]9H) (OH). 6]. To a solution of 1 (108 mg, 0.121 mmol) in C6H6 (2 mL) was added dropwise wet benzene (prepared by stirring dry, deoxygenated benzene (20 mL) with excess water (1 mL)) until the color change from yellow-green to light brown was complete (ca. 9 mL). All volatiles were removed in vacuo and the residue was dried for 2 h at 20 °C. The solid was redissolved in dry benzene and the solution was reacted to give HB(NDippCH)2, HOB− with 119/117Sn satellites1. The solid was redissolved in dry benzene and the solution was exposed to an atmosphere of ammonia and storage of the mother liquor produced a second crop of slightly less pure compound (total: 33 mg, 0.036 mmol, 65%). 1H NMR (CD2Cl2, ref: internal SiMe3), δ 7.06 (4 H, t, J = 7.6 Hz, p-H of Ar), 6.97 (8 H, d, J = 7.6 Hz, m-H of Ar), 6.25 (4 H, s, NCH3), 3.62 (4 H, br, CHMe3), 3.25 (4 H, br, CHMe3), 1.11 (48 H, br, CHMe3), 0.27 (3 H, br s, NH3). 13C[1H] NMR (CD2Cl2, ref: internal SiMe3): δ 146.47 (br, o-C of Ar), 142.02 (ipso-C of Ar), 127.29 (p-C of Ar), 124.07 (br, m-C of Ar), 122.82 (NCH3), 25.79 (br, CHMe3), 23.95 (v br, CHMe3). 11B[1H] (C6D6): δ 45.1. Crystallographic data (for 1NH3): C52H74B2N4OSn, M = 909.50, a = 19.4712(2) Å, b = 14.5386(2) Å, c = 18.7150(2) Å, β = 105.3864(2)°, monoclinic, P21/c, V = 5176.39(7) Å3, Z = 4, R = 0.0986 for data intensity I > 2σ(I) unique reflections =0.0745, wR2 (all 11614 unique reflections) = 0.1023. CCDC ref: 1055211.

Onward Reaction of 1NH3. A sample of 1NH3 was monitored by in situ multinuclear NMR spectroscopy while maintained at 20 °C. For 4−5 h, revealing the formation of two metal-free products: the known compound HB(NDippCH)2,13 and H2NB(NDippCH)2 (identified by comparison of its 1H NMR spectral signals with those of independently prepared sample (see SI)). Although tin metal was also observed to be formed, we were also able to isolate small (but reproducible) quantities of a tin cluster species identified solely on the basis of X-ray crystallography as nido-Sn12[B(NDippCH)3]2 and nido-Sn12[B(NDippCH)3]2 (confirmed by X-ray diffraction). Further crystallization at −30 °C gave needle crystals containing both HB(NDippCH)2, and H2NB−(NDippCH)2.

SnB(NDippCH)2[A]9H) (BuNH2), 1BuNH2. To a solution of 1 (27 mg, 0.030 mmol) in C6H6 (1 mL) was added excess BuNH2 (10 μL, 0.096 mmol) resulting in immediate color change from yellow−green to bright orange. Volatiles were removed in vacuo, the residue was extracted with hexane (1 mL) into a crystallization tube to remove the black precipitate of tin metal. The resulting solution was concentrated and stored at 4 °C for 2 d producing a very small quantity of black (brown in thin layer) block-like crystals of distorted hexagonal shape (1:4 mixture of Sn10/Sn11 clusters). Similar (by X-ray diffraction) crystals were isolated reproducibly from our subsequent experiments in very low yield. Further crystallization at −30 °C gave needle crystals containing both HB(NDippCH)2, and H2NB−(NDippCH)2.

SnB(NDippCH)2[A]9H) (BuNH2), 1BuNH2. To a solution of 1 (27 mg, 0.030 mmol) in C6H6 (1 mL) was added excess BuNH2 (10 μL, 0.096 mmol) resulting in immediate color change from yellow−green to bright orange. Volatiles were removed in vacuo, the residue was extracted with hexane (1 mL) into a crystallization tube to remove the black precipitate of tin metal. The resulting solution was concentrated and stored at 4 °C for 2 d producing a very small quantity of black (brown in thin layer) block-like crystals of distorted hexagonal shape (1:4 mixture of Sn10/Sn11 clusters). Similar (by X-ray diffraction) crystals were isolated reproducibly from our subsequent experiments in very low yield. Further crystallization at −30 °C gave needle crystals containing both HB(NDippCH)2, and H2NB−(NDippCH)2.

Sn(NC5H5)2[A]9H) (BuNH2), 1BuNH2. To a solution of 1 (27 mg, 0.030 mmol) in C6H6 (1 mL) was added excess BuNH2 (10 μL, 0.096 mmol) resulting in immediate color change from yellow−green to bright orange. Volatiles were removed in vacuo, the residue was extracted with hexane (1 mL) into a crystallization tube to remove the black precipitate of tin metal. The resulting solution was concentrated and stored at 4 °C for 2 d producing a very small quantity of black (brown in thin layer) block-like crystals of distorted hexagonal shape (1:4 mixture of Sn10/Sn11 clusters). Similar (by X-ray diffraction) crystals were isolated reproducibly from our subsequent experiments in very low yield. Further crystallization at −30 °C gave needle crystals containing both HB(NDippCH)2, and H2NB−(NDippCH)2.

SnB(NDippCH)2[A]9H) (BuNH2), 1BuNH2. To a solution of 1 (27 mg, 0.030 mmol) in C6H6 (1 mL) was added excess BuNH2 (10 μL, 0.096 mmol) resulting in immediate color change from yellow−green to bright orange. Volatiles were removed in vacuo, the residue was extracted with hexane (1 mL) into a crystallization tube to remove the black precipitate of tin metal. The resulting solution was concentrated and stored at 4 °C for 2 d producing a very small quantity of black (brown in thin layer) block-like crystals of distorted hexagonal shape (1:4 mixture of Sn10/Sn11 clusters). Similar (by X-ray diffraction) crystals were isolated reproducibly from our subsequent experiments in very low yield. Further crystallization at −30 °C gave needle crystals containing both HB(NDippCH)2, and H2NB−(NDippCH)2.
Reaction of \(1\) NH\(_4\) with \(\text{K}[\text{B}(\text{C}_6\text{F}_5)_2]:\) Isolation of \(\text{SnB}(\text{NDippPch})_2\) \(\text{H}[(\text{NH})_2]\). To a solution of \(1\) NH\(_4\) (160 mg, 0.175 mmol) in benzene (2 mL) was added solid \(\text{K}[\text{B}(\text{C}_6\text{F}_5)_2]\) (162 mg, 0.225 mmol). Upon stirring at 20 °C the color of the mixture gradually changed from orange to light brown. After 1 h the mixture was filtered and the filtrate was evaporated in vacuo. A sample of the resulting crystalline material (21 mg) contained ca. 70% \(\text{Sn}[(\text{NDippPch})_2]\) \((\text{H})_2\) obtained by crystallization from methylcyclohexane at 4 °C. After 1.5 h the mixture was precipitated by addition of \(\text{NH}_3\) (252 mg, 0.276 mmol). Volatiles were removed in vacuo, and the orange precipitate was washed with hexane (2 mL), dried, and redissolved in benzene (5 mL) at 20 °C. After stirring for 5 min a deep yellow solution was obtained. Volatiles were removed in vacuo leading to the solution undergoing a color change to brown, and yellow crystalline material to precipitate. A small amount of the concentrated supernatant solution was sealed in a crystallization tube and stored at 4 °C, producing yellow blocks suitable for X-ray crystallography. Washing of the crystalline product with cold hexane resulted in rapid darkening, therefore a small sample for spectroscopic characterization was prepared by crystallization from cyclohexane at 4 °C. The sample showed very broad resonances for Dipp substituents at 20 °C, which started to resolve at \(-10\) °C, however, further cooling resulted in precipitation. The 1H NMR (\(\text{C}_6\text{D}_6\), CDCl\(_3\); ref.: internal \(\text{SiMe}_4\)) \(\delta = 7.01–7.19\) (12 H, br s, p- and m-H of \(\text{Ar}\)), 6.08 (4 H, s, NCH), 3.05 (8 H, br s, CHMe), 1.20 (48 H, br, CHMe), 2.09 (2 H, br s, NH\(_2\)). \(\text{B}[\text{H}](\text{C}_6\text{D}_6)_2\); \(\delta = 41.4\). Attempts to obtain reliable 13C NMR data for \(9\) were frustrated by its low solubility in compatible solvents. Crystallographic data for \(9\) (\(\text{C}_6\text{H}_5\)) \((\text{NDippPch})_2\); \(\text{SnB}(\text{NH})_2\). Tin satellites for the SnH peak \((\text{SnH})\) \(\delta = 9.9\) Hz, CHN), 4.80 (br t, \(\delta = 19.1937(3)\) Å, \(\beta = 117.1098(3)\) °), monoclinic, \(P\) \(2_1\); \(V = 123.52(2)\) Å, \(Z = 8\), \(R_2\) for 10623 [data intensity \(I > 2\sigma(I)\)]. See SI for the run files for frequency calculations, which contain coordinates for the optimized geometries of the model complexes \(\text{MXy}^{+}\) and \(\text{M}\text{Xy}^{-}\).

X-ray Crystallography.

X-ray diffraction data were collected at 150 K using either a Nonius Kappa CCD or Oxford Diffraction (Agilent) SuperNova A diffractometer. Structures were solved with SuperFlip and refined by full-matrix least using CRYSTALS. Any disorder was modelled as per the CIF and hydrogen atoms were treated in the usual manner. Where the structure contained large solvent accessible voids comprising weak, diffuse electron density, the discrete Fourier transforms of the void regions were treated as contributions to the background of the calculated structure factors using PLATON. SQUEEZE integrated within the CRYSTALS software.

Computational Details. DFT calculations were performed using the Amsterdam Density Functional (ADF) Package Software 2012.\(^{15a–e}\) Unrestricted calculations were performed using the Vočko–Wilk–Nussair local density approximation with exchange from Becke,\(^{15d}\) and correlation corrections from Perdew (BP).\(^{15b}\) Slater-type orbitals (STOs)\(^{15f}\) were used for the triple-\(\zeta\) basis set with an additional set of polarization functions (TZP). The large frozen core basis set approximation was applied with no molecular symmetry. The general numerical integration was 6. Relativistic effects were addressed using the scalar Zeroth Order Regular Approximation (ZORA).\(^{15g–m}\) No significant imaginary frequencies were observed for the optimized geometry of the model complexes \(\text{MXy}^{+}\) and \(\text{M}\text{Xy}^{-}\). See SI for the run files for frequency calculations, which contain coordinates for the optimized geometries of model complexes.

RESULTS AND DISCUSSION

Computational Screening. The singlet–triplet energy separation (\(\Delta E_{st}\)) has previously been shown to be of key importance in determining activation barriers in the oxidative addition of \(\text{E}–\text{H}\) bonds at metallene centers.\(^{5a,10}\) With this in mind, we set out to probe (via DFT methods) the scope for tuning this gap in stannylene and related systems by variation in the peripheral substituents. These studies reveal that the incorporation of silyl, phosphido, or better still boryl substituents should lead to values for \(\Delta E_{st}\) of <15 kcal mol\(^{-1}\) (Table 1), while the use of amido substituents, in particular, leads to significant stabilization of the singlet state (\(\Delta E_{st} > 21\) kcal mol\(^{-1}\)). Such findings are in line with the notion that strongly \(\pi\) electron-donating groups reduce the LUMO gap through destabilization of the HOMO,\(^{16}\) and the fact that ligands based around relatively electropositive atoms such as boron or silicon are among the strongest \(\sigma\)-donors currently available to the synthetic chemist.\(^{8}\) Moreover, in contrast to the destabilization of the LUMO (and widening of the HOMO–LUMO gap) effected by \(\pi\)-donor substituents such as amido groups, it would also be expected that the moderate \(\pi\)-acceptor properties of the boryl ligand would, if anything, reduce the HOMO–LUMO gap, and hence also \(\Delta E_{st}\).

The effect of net charge was also considered, given the isobal relationship between formally anionic boryl and...
charge-neutral N-heterocyclic carbene ligands, with the finding that preferential stabilization of the HOMO in the NHC-ligated cation leads to an enhanced magnitude of $\Delta E_{st}$ for bis(boryl)-stannylene and—silylene systems were also evaluated (and shown to possess relatively low-lying triplet states), although in our hands such systems have yet to be accessed synthetically.\textsuperscript{17}

As such, boryl-stannylene complexes were considered to be a logical starting point for experimental studies, offering a workable compromise between accessibility and reactivity.

**Reactivity toward E–H Bonds (E = H, B, Si).**

Diamido-stannylene complexes have previously been shown to be unreactive toward H\textsubscript{2}.\textsuperscript{16} Given the predictions of enhanced reactivity associated with the incorporation of boryl substituents, the reactions of dihydrogen with (amido)borylstannylene 2 and homoleptic bis(boryl) stannylene 1 were therefore investigated (Scheme 1).\textsuperscript{30} Consistent with DFT predictions, we find that oxidative addition of H\textsubscript{2} at the tin center in 1 is facile, occurring steadily at room temperature to give the corresponding bis(boryl)tin(IV) dihydride 3. By contrast, under analogous conditions 2 is unreactive toward dihydrogen, consistent with a significantly higher barrier to H–H bond activation.\textsuperscript{19,20}

Characterization of 3 has been achieved by standard spectroscopic, analytical and crystallographic techniques; particularly diagnostic is the new NMR signal at $\delta_{\text{H}} = 2.22$ ppm due to the SnH\textsubscript{2} unit, for which both $^{117/119}$Sn satellites can be resolved: $^{117}$Sn–H = 1277 Hz; $^{119}$Sn–H = 1337 Hz. Consistently, the molecular structure determined by single crystal X-ray diffraction (Figure 1) features two tin-bound hydrogen atoms in the difference Fourier map, and a significantly widened B–Sn–B angle compared to bis(boryl)-stannylene precursor 1 [135.6(1) vs 118.8(3)\textdegree]. Similar phenomena have previously been observed in the oxidative addition of dihydrogen to lighter group 14 analogues [e.g., 109.7(1) and 120.1(1)\textdegree, respectively, for a (boryl)amidosilylene and the corresponding Si(IV) dihydride].\textsuperscript{9a,23} In similar fashion, the B–Sn–B angle measured for Sn[B(NDippCH\textsubscript{2})\textsubscript{2}]Cl\textsubscript{2} [which can be synthesized through the reaction of 1 with Ph\textsubscript{3}CCl or UCl\textsubscript{4} (SiCl\textsubscript{4})] shows a comparable widening [136.3(1)\textdegree]. Presumably, these observations reflect the shortening of the Sn–B bonds on oxidation from Sn\textsuperscript{II} to Sn\textsuperscript{IV} [e.g., 2.242(2), 2.246(2) \textalpha \textsubscript{3} for 3, cf. 2.290(8) (mean) for 1] and the consequent need to widen the B–Sn–B angle to minimize the repulsive interactions between the sterically very demanding boryl substituents.

While oxidative cleavage of dihydrogen at isolated carbene, silylene and germeylene compounds has been reported previously,\textsuperscript{5,22–25} to our knowledge the transformation of 1 to 3 represents the first example of simple oxidative addition of H\textsubscript{2} to a monometallic Sn\textsuperscript{IV} system to generate a Sn\textsuperscript{V} product. This process appears to be irreversible, and no hint of H–H or B–H elimination is observed from samples of 3 upon storing for several days at room temperature.

The presence of a relatively small singlet–triplet gap also permits the activation of a range of other E–H bonds by 1, including hydric systems such as B–H and Si–H bonds. Thus, silanes such as PhSiH\textsubscript{3} or SiH\textsubscript{4} itself, and boranes such as Me\textsubscript{3}NBH\textsubscript{3} undergo E–H oxidative addition to generate the corresponding silyl- or boryltin(IV) hydrides in moderate to good yield (4a, 4b, 5; Scheme 2).\textsuperscript{26,27} To our knowledge, the
oxidative addition of Si–H and B–H bonds of this sort to give SnIV products has no precedent.26

**Scheme 2. Oxidative Addition of Hydridic E–H Bonds to 1 to Give Silyl and Boryl SnIV Species 4 and 5**

Here too, the appearance of the respective Sn–H resonance in the 1H NMR spectrum is diagnostic of the addition process. Thus, for example, in the case of 4a, formed by the activation of SiH₂, the signal in question is a quartet [δ = 1.66 ppm, J(1H–1H) = 3.8 Hz] with tin satellites [J(117Sn–1H) = 1223 Hz; J(119Sn–1H) = 1281 Hz], while the corresponding doublet SiH₃ resonance shows coupling to both silicon and tin [δ = 2.27 ppm, J(29Si–1H) = 191.2 Hz; J(117/119Sn–1H) = 39.9 Hz]. In similar fashion, the analogous signals for the tin- and silicon-bound hydrogens in 4b are a triplet [J(1H–1H) = 3.7 Hz, with 117/119Sn satellites: J(117Sn–1H) = 1197 Hz; J(119Sn–1H) = 1252 Hz] and a lower field doublet [with 29Si and 117/119Sn satellites J(29Si–1H) = 190.3 Hz; J(117/119Sn–1H) = 64.5 Hz]. In the case of 5, H–H couplings cannot be resolved, presumably due to broadening by the quadrupolar 11B nucleus of the -BH₂·NMes group; the presence of two distinct 11B environments is clearly signaled, however, by resonances at δB = 31.9 (for the three-coordinate boryl substituent) and −8.3 ppm (for the four-coordinate base-stabilized boryl ligand). In addition, for both 4b and 5, structural authentication has proved possible by single crystal X-ray diffraction, which yields the heavy atom skeleton together with likely hydrogen atom positions from the difference Fourier map (Figure 1).

Interestingly, while the structure of 4b features the wide B–Sn–B angle [137.0(1)°] characteristic of other SnIV systems (such as 3 and SnB(NDippCH₂)₂Cl₂), 5 possesses a much narrower angle at the metal center [114.4(1)°] and somewhat longer Sn–B(heterocycle) bonds [2.274(2), 2.284(2) Å cf. 2.242(2), 2.246(2) Å for 3]. The bond to the -BH₂·NMes ligand is of similar length [2.272(3) Å] despite the higher coordination number at B(3) and is therefore clearly best described as a simple 2-center, 2-electron covalent bond (cf. 2.23 Å for the sum of the respective covalent radii).28 We therefore attribute the narrower geometry of the bis(boryl)tin backbone in 5 to the higher steric demands of the relatively bulky -BH₂·NMes ligand (cf. H in 3) in association with the short Sn–E distance (cf. SiH₂Ph in 4b). An alternative description of 5 as a donor/acceptor adduct formed between a stannylene Lewis acid and Me₃N·BH₃ (acting as an essentially unactivated σ(BH) donor) appears unlikely on the basis of the short Sn–B separation and the large Sn–H coupling constant (ca. 900 Hz).29

**Reactivity toward Protic E–H Bonds: Water.** The activation of protic E–H linkages by 1 has also been investigated, with both O–H and N–H bonds being shown to be amenable to oxidative addition. In contrast to compounds 3–5, however, the resulting SnIV products are prone to further reaction leading to B–E reductive elimination (E = O, N).

In the case of water, the hydroxytin(IV) hydride SnB(NDippCH₂)₂(H) (OH), 6, resulting from the oxidative addition of one O–H bond can be isolated in very good yield (85%, Scheme 3) and characterized by multinuclear NMR, X-ray crystallography and elemental microanalysis. As in the cases of H–H, B–H and Si–H oxidative addition products, the resulting Sn–H linkage is characterized in solution by large satellite couplings to 117/119Sn [J(117Sn–1H) = 1385 Hz; J(119Sn–1H) = 1456 Hz], while the (sharper) SnOH resonance can be resolved into a doublet [J(H–1H) = 1.4 Hz] with longer range couplings to tin [J(117/119Sn–1H) = 24.6 Hz].

While the oxidative addition of water to a single main group metal center is very rare, precedent does exist for SnIII, with Pörschke and co-workers reporting the synthesis of Sn(CH₂(SiMe₃)₂)₂(H) (OH) from the corresponding stannylene as long ago as 1998.30a,b The molecular structures of these two systems are similar, featuring Sn–O distances of 1.977(2) (for 6; Scheme 3) and 1.984(1) Å; however, while Sn(CH₂(SiMe₃)₂)₂(H) (OH) aggregates into centrosymmetric dimers via pairs of OH···O hydrogen bonds, 6 is mononuclear in the solid state, presumably reflecting the greater steric bulk of the ancillary boryl ligands. The wide B–Sn–B angle measured for 6 [138.7(1)°] is consistent with those reported for 3, 4b and SnB(NDippCH₂)₂Cl₂.

In contrast to the SnIV compounds formed by the oxidative addition of hydridic E–H bonds, however, 6 undergoes further reaction at elevated temperatures. Thus, refluxing in hexane leads to the formation of equimolar amounts of HB(NDippCH₂) and HOB(NDippCH₂)₂ together with tin metal. This chemistry is thought to be initiated by the reductive elimination of the strong B–O bond from 6 and appears closely related to the onward reactivity of the corresponding ammonia activation product (vide infra).

**Reactivity toward Protic E–H Bonds: Ammonia.** The oxidative addition of N–H bonds in ammonia represents a high profile challenge in synthetic chemistry in part because of the dearth of transition metal systems capable of effecting such a transformation,30 and the relevance of N–H activation to a number of potentially important industrial processes.31 Thus, the reactivity of 1 toward NH₃ has also been explored (Scheme 4).32

![Scheme 3. Oxidative Addition of the O–H Bond in Water to 1 to Give Hydroxy SnIV Hydride 6](image-url)
Addition of excess ammonia to a benzene solution of 1 rapidly yields a compound of composition \( 1\cdot\text{NH}_3 \), which is characterized by a marked downfield shift in the \( \text{NH}_3 \) resonance, from \( \delta_{\text{H}} = -0.17 \) (free \( \text{NH}_3 \)) to 0.32 ppm (isolated \( 1\cdot\text{NH}_3 \)), indicating that the excess \( \text{NH}_3 \) has effectively displaced \( \text{Dipp} \). The presence of the \( \text{NH}_3 \) in the spectrum is further supported by the appearance of two broad resonances for the Dipp methine protons at 20 ppm, which become more prominent on cooling below 0 \( ^\circ \text{C} \). The \( 1\cdot\text{NH}_3 \) is labile toward further reaction and our initial attempts to obtain single crystals were unsuccessful. With this in mind we also synthesized the tert-butylamine adduct \( 1\cdot\text{NH}_3\cdot\text{Bu} \) through the corresponding reaction of 1 with \( \text{BuNH}_2 \) and additionally characterized this system by standard spectroscopic and crystallographic techniques (Figure 2).

From a structural perspective, both \( 1\cdot\text{NH}_3 \) and \( 1\cdot\text{NH}_3\cdot\text{Bu} \) can be shown to feature the N-donor coordinated essentially planar \( \text{Sn} \) unit, which is itself largely unperturbed from that found in the free stannylene [e.g., for \( 1\cdot\text{NH}_3 \), \( \angle \text{N}(2)-\text{Sn}(1)-\text{B}(3/33) = 92.4(1), 94.6(1); \angle \text{B}(3)-\text{Sn}(1)-\text{B}(33) = 119.3(1) \) for \( 7 \)]: \( \angle \) values are consistent with descriptions of these systems as Lewis acid/base adducts formed by interaction of the amine lone pair with the formally vacant \( \pi^* \) orbital at the \( \text{Sn} \) atom.

The behavior of \( 1\cdot\text{NH}_3 \) in solution is found to be strongly dependent on the concentration of free ammonia present. Thus, while isolated single crystalline samples react slowly (\(<50\%\) conversion to a mixture of 7, \( \text{H}_2\text{NB(NDippCH)}_2\cdot\text{Bu} \) for \( 44 \) h at 20 \( ^\circ \text{C} \)), the presence of a 2-fold excess of ammonia leads to more rapid onward reaction with little of the adduct remaining after 21 h under otherwise analogous conditions. The spectroscopic properties of \( 1\cdot\text{NH}_3 \) are also dependent on the presence of additional free ammonia in solution. Thus, isolated crystalline samples of the adduct display two broad resonances for the Dipp methine protons at 20 \( ^\circ \text{C} \), which sharpen on cooling below 0 \( ^\circ \text{C} \), and which form one broad signal at 50 \( ^\circ \text{C} \). This observation is ascribed to slow rotation about the \( \text{Sn} \cdots \text{B} \) bonds in \( 1\cdot\text{NH}_3 \). The presence of an additional free ammonia molecule is consistent with the sharp septet being observed for the Dipp methine protons at 20 \( ^\circ \text{C} \).

Following coordination of \( \text{NH}_3 \), N–H bond cleavage then occurs, generating the amidinot(IV) hydride \( \text{Sn}((\text{NDippCH})_2)_2(\text{H})(\text{NH}_3) \) (7), analogous to the (hydroxy)tin hydride \( \text{Sn}((\text{NDippCH})_2)_2(\text{OH}) \) isolated from the reaction of 1 with water. The formation of the phosphidotin(IV) hydrides by the oxidative addition of \( \text{P} \cdots \text{H} \) bonds to diaryl stannylenes has also been reported recently. Spectroscopically, such an (amido)hydride species is consistent with the pattern of \( ^{1} \text{H} \) NMR resonances observed in situ [\( \delta_{\text{H}} = 4.80 \) (1H, \( \text{SnH} \)), -1.90 ppm (2H, \( \text{SnNH}_2 \))]. These can be compared to shifts of \( \delta_{\text{H}} = 6.13 \) (1H, \( \text{SnH} \)), -2.09 ppm (1H, \( \text{SnOH} \)) for 6, and \( \delta_{\text{H}} = 5.22 \) (1H, \( \text{SiH} \)), 0.99 ppm (2H, \( \text{SiNH}_2 \)) for the thermally stable (and spectroscopically characterized) silicon (amido)hydride \( \text{Si(SiMe}_2)_3\{\text{N(SiMe}_2)_2\cdot\text{Dipp}\}(\text{H})(\text{NH}_3) \) synthesized via the...
reaction of the acyclic silylene Si(SiMe3)3[N(SiMe3)Dipp] with ammonia (SI).

The apparently comparable rates of formation of 7 (from 1-NH3), and its onward conversion (to H2NB(NDippCH)2 and HB(NDippCH)2) render it impossible to obtain significant amounts of this compound via this route. More rapid conversion of 1-NH3 into 7 can be achieved by employing an alternative acid/base synthetic methodology (vide infra). Single crystals of 7 suitable for X-ray crystallography could be obtained via the Lewis acid (K[B(C6F5)4]) catalyzed isomerization of 1-NH3 (Figure 2). The crystals of 7 so obtained are isomorphous with those of 6, but can be shown unequivocally to contain the (amido)tin hydride on the basis of multinuclear NMR measurements made on single crystalline samples redissolved in C6D6. Moreover, the 1H NMR signals associated with the SnH and SnNH2 units are found at chemical shifts indistinguishable from those measured in situ for the intermediate species in the 1/NH3 reaction.

The onward lability of 7 is in line with (i) previous literature reports describing facile coupling between adjacent metal-bound borane moieties and electron-rich coligands,35 and (ii) the observation that isolated (hydroxy)hydride 6 also undergoes elimination of equimolar quantities of hydro- and hydroxyborane (albeit more slowly). In the case of Sn[B-(NDippCH)2]2(H)(NH2), reductive elimination of the strong B–N bond formed by coupling of π-donor amido and π-acceptor boryl components would represent a thermodynamic driving force, and account for the formation of H2NB(NDippCH)2 and a source of Sn6, which is either precipitated as the metal itself, or trapped by unreacted 1-NH3 to generate the observed small quantities of Sn10 and Sn11-clusters. We favor this ordering of the reductive elimination steps (i.e., B–N formation preceding B–H) on the basis that the SnII amide [Sn{B(NDippCH)2}(NH2)]2 can be shown to be stable with respect to B–N elimination, and thus not a viable intermediate under the conditions employed.

Independent synthesis of a complex of composition [Sn{B(NDippCH)2}(NH2)]2 can be achieved by the reaction of amido(boryl)stannylene 2 with ammonia. In this case conversion proceeds rapidly (<1 min) via a formal acid/base reaction. Thus, protonolysis generates the free amine HNMe2Ph and the dinuclear primary amidostannylene [Sn{B(NDippCH)2}(µ-NH2)]2 (8; Scheme 5), the identity of which has been confirmed crystallographically. Such chemistry, leading as it does to the isolation of a SnII amide, mirrors the reactivity toward ammonia reported by Power and co-workers for diarylstannylene systems.36 Moreover, in line with the mechanistic proposals outlined above, in our hands 8 is found to be essentially inert to B–N reductive elimination.

Classical mechanisms of concerted E–H bond activation at a single transition metal center involve donation of electron density from the E–H σ bonding orbital and back-bonding into the corresponding σ* orbital.1 The activation of H2 by acyclic silylenes is also thought to involve initial interaction of the H–H σ-bonding MO with the pz orbital of the electrophilic silicon center,9f while alternative mechanisms exploiting the strongly nucleophilic carbon-centered lone pair have been advanced for E–H activation by related carbene compounds.24 With regard to the activation of ammonia by metallene systems, an alternative mechanistic pathway which has been proposed computationally,35,34,36 involves a second molecule of NH3 acting as a proton shuttle, in effect transferring H+ to a coordinated ammonia molecule to the Group 14 center. Thus, computational studies from Power and Nagase, Pörschke and Sicilia, for example, all propose that such a mechanism ought to be viable for the activation of ammonia (and indeed water) by low valent Group 14 metal centers.10,6a,b,c,54,56 In the case of ammonia activation by 1, we wondered whether the significantly increased rate of onward reaction of 1-NH3 in the presence of excess ammonia might be explained on the basis of a similar mechanism (Scheme 6). Therefore, with a view to probing the plausibility of such deprotonation at N/ reprotonation at Sn acid/base chemistry we set out to isolate the conjugate base of 1-NH3, and examine its behavior in the presence of ammonium salts (i.e., sources of H+).

In the event, the reaction of K[N(SiMe3)2] with 1-NH3 does indeed lead to deprotonation of the tin-bound ammonia molecule and to the formation of the potassium salt of the [Sn{B(NDippCH)2}(NH2)]− anion. Confirmation of the nature of the product could be obtained crystallographically, with the structure shown to feature centro symmetric dimers in the solid state (9; Figure 3).

Deprotonation is accompanied by a marked shortening of the Sn–N distance [2.088(8) Å cf. 2.355(2) Å for 1-NH3], and [Sn(1)] is also engaged in a contact with the potassium cation [d(Sn···K) = 3.745(2) Å] which is well within the sum of the respective van der Waals radii. This observation is consistent with the presence of significant electron density at the SnII center, and accordingly, reaction of 9 with the dialkylaminium salt [HNNMe2Ph][B(C6F5)4] in C6D6 at 20 °C generates a ~2:1 mixture of [Sn{B(NDippCH)2}(µ-NH2)]2− (7) and 1-NH3. This mixture presumably reflects the kinetics of protonation at Sn and N, since the mixture transforms to yield solely the thermodynamic product (7) after 6 h at 20 °C. As such, the notion of N–H oxidative addition occurring via coordination of

Scheme 6. Potential Proton Shuttling Mechanism for N–H activation in 1-NH3 Involving a Second Molecule of Ammonia

“Molecular structure of 8 as determined by X-ray crystallography. Most hydrogen atoms omitted, and Pr groups shown in wireframe format for clarity; thermal ellipsoids set at the 50% probability level. Key bond lengths (Å) and angles (°): Sn(1)–Sn(2) 2.309(2), Sn(1)–N(3) 2.215(1), Sn(1)–N(3′) 2.227(1), B(1)–Sn(1)–N(3) 90.4(1), B(1)–Sn(1)–N(1′) 92.9(1), N(1)–Sn(1)–N(1′) 80.7(1).
NH₃, followed by N-donor mediated proton transfer, can be shown to have some experimental validity. Finally, we note that the transformation of 1-NH₃ into 7 can also be brought about, cleanly and in catalytic fashion by employing ca. 10 mol % of the solvent-free potassium borate K[B(C₆F₅)₄]. Mechanistically, this process is proposed to occur via Lewis acid sequestration of NH₃ from 1-NH₃ by K⁺, resulting in the presence in solution of a small quantity of species of the type [K(NH₃)₂]⁺. The enhanced acidity of the N–H protons in such species presumably then facilitates isomerization via protonation at tin. Consistent with this hypothesis, the direct conversion of 1-NH₃ to 7 can also be brought about by the addition of a catalytic amount (ca. 5 mol %) of [HNMe₂Ph][B(C₆F₅)₄] (see SI).

**CONCLUSIONS**

In conclusion, we have demonstrated that a bis(boryl) ancillary ligand set can facilitate the oxidative addition of a range of E–H bonds at SnII from both a thermodynamic and a kinetic viewpoint. Moreover, in the case of O–H and N–H bonds, the formation via oxidative addition of a tin-bound σ-donor ligand offers a facile route to E–B bond formation (E = O, N) and re-reduction of the tin center. Thus, a single-center redox-based bond modification process is unequivocally established for a main group metal. From a mechanistic viewpoint, a two-step coordination/proton transfer process for N–H activation is shown to be viable through the isolation of intermediate species of the types Sn(boryl)₂-NH₂ and [Sn(boryl)₂(NH₂)]⁺, and protonation of the latter to give Sn(boryl)₂(·H)(NH₂).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00710.

Additional synthetic/characterizing data, copies of NMR spectra for new compounds, and complete details of DFT calculations (including run files). (PDF)

**Crystal data. (CIF)**

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**Notes**

The authors declare no competing financial interest.

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(19) Consistent with the relative inertness of 2 compared to 1 with respect to oxidative bond formation, [4 + 1] cycloaddition with 2,3-dimethylbutadiene proceeds only under more forcing conditions for 2. Thus, while both systems generate stanna-cyclopentene complexes of the type [(MeCCH2)2Sn(X)2]2, the reaction in the case of 1 proceeds in <5 min at room temperature,20 while that for 2 requires stirring for 2 h (see SI).

(20) Protchenko, A. V.; Dange, D.; Blake, M. P.; Schwarz, A. D.; Jones, C.; Mountford, P.; Aldridge, S. J. Am. Chem. Soc. 2014, 136, 10902–10905.

(21) Similar structural observations have been made by Power and Ragogna on P–H oxidative addition at a diarylstannylene.6c

(22) The first example of dihydrogen activation by a main group system at ambient temperature/pressure was reported as late as 2005: (a) Spiess, G. H.; Fettinger, J. C.; Power, P. P. J. Am. Chem. Soc. 2005, 127, 12232–12233. For other examples of H2 activation by Group 14 alkynes analogues, see ref 7 and (b) Li, J.; Shenk, C.; Goedecke, C.; Frenking, G.; Jones, C. J. Am. Chem. Soc. 2011, 133, 18622–18625.

(23) For H2 activation by main group FLPs, see: (a) Welch, G. C.; San Juan, B. R.; Masuda, J. D.; Stephan, D. W. Science 2006, 314, 1124–1126. (b) Stephan, D. W.; Erker, G. Angew. Chem., Int. Ed. 2010, 49, 46–76.

(24) For H2 activation by carbenes, see ref 3 and Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. Science 2007, 316, 439–441.

(25) For H3 activation by silylenes, see refs 9a and 11.

(26) For previous reports of Si–H and B–H bond activation by carbenoids, see, for example: (a) C. Frey, G. D.; Masuda, J. D.; Donnadieu, B.; Bertrand, G. Angew. Chem., Int. Ed. 2010, 49, 9444–9447. (b) Al: Chu, T.; Korobkov, I.; Nikonov, G. I. J. Am. Chem. Soc. 2014, 136, 9195–9202.