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Synthesis and the Thermal and Catalytic Dehydrogenation Reactions of Amine-Thioboranes

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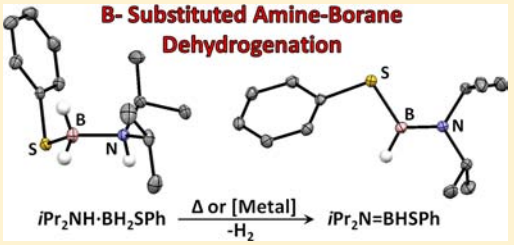
Supporting Information

ABSTRACT: A series of trimethylamine-thioborane adducts, $Me_3N{\cdot}BH_2SR$ (R = *t*Bu [**2a**], *n*Bu [**2b**], *i*Pr [**2c**], Ph [**2d**], C_6F_5 [**2e**]) have been prepared and characterized. Attempts to access secondary and primary amine adducts of thioboranes via amine-exchange reactions involving these species proved unsuccessful, with the thiolate moiety shown to be vulnerable to displacement by free amine. However, treatment of the arylthioboranes, $[BH_2{-}SPh]_3$ (**9**) and $C_6F_5SBH_2{\cdot}SMe_2$ (**10**) with Me_2NH and iPr_2NH successfully yielded the adducts $Me_2NH{\cdot}BH_2SR$ (R = Ph [**11a**], C_6F_5 [**12a**]) and $iPr_2NH{\cdot}BH_2SR$ (R = Ph [**11b**], C_6F_5 [**12b**]) in high yield. These adducts were also shown to be accessible via thermally induced hydrothiolation of the aminoboranes $Me_2N{=}BH_2$, derived from the cyclic dimer $[Me_2N{\text{-}}BH_2]_2$ (**13**), and $iPr_2N{=}BH_2$ (**14**), respectively. Attempts to prepare the aliphatic thiolate substituted adducts $R_2NH{\cdot}BH_2SR'$ (R = Me, *i*Pr; R′ = *t*Bu, *n*Bu, *i*Pr) via this method, however, proved unsuccessful, with the temperatures required to facilitate hydrothiolation also inducing thermal dehydrogenation of the amine-thioborane products to form aminothioboranes, $R_2N{=}BH(SR')$. Thermal and catalytic dehydrogenation of the targeted amine-thioboranes, **11a**/**11b** and **12a**/**12b** were also investigated. Adducts **11b** and **12b** were cleanly dehydrogenated to yield $iPr_2N{=}BH(SPh)$ (**22**) and $iPr_2N{=}BH(SC_6F_5)$ (**23**), respectively, at 100 °C (18 h, toluene), with dehydrogenation also possible at 20 °C (42 h, toluene) with a 2 mol % loading of $[Rh(\mu\text{-}Cl)cod]_2$ in the case of the former species. Similar studies with adduct **11a** evidenced a competitive elimination of H_2 and HSPh upon thermolysis, and other complex reactivity under catalytic conditions, whereas the fluorinated analogue **12a** was found to be resistant to dehydrogenation.



INTRODUCTION

The catalytic dehydrogenation of amine-borane adducts has gained substantial attention in recent years as a result of the large reductions in reaction temperature and increased reaction rates that are possible relative to thermal hydrogen release. Over the past decade the field has grown dramatically, and a wide range of metals and main group species have now been shown to be catalytically active for such processes.[1−20] Research in the area has also been accelerated by the interest in ammonia-borane, $NH_3{\cdot}BH_3$, and related species as potential hydrogen storage and transfer media.[21−28] Furthermore, recently it has also been reported that catalytic dehydrocoupling allows access to poly(alkylaminoboranes), $[RNH{\text{-}}BH_2]_n$, inorganic analogues of polyolefins.[11,29] The dehydrogenation of $NH_3{\cdot}BH_3$ and its derivative borazine, $[HN{\text{-}}BH]_3$, on metallic surfaces have also recently been shown to provide a route to meshes and, significantly, thin films of boron nitride, which may find applications in graphene-based electronic devices.[30]

To date, however, reports of the catalytic dehydrogenation of amine-borane adducts have almost exclusively discussed the reactivity of adducts substituted at nitrogen.[31] These studies have demonstrated that both the thermodynamics of hydrogen release, and the nature of the dehydrogenated products are defined by the choice of substituent(s) at nitrogen.[32−35] In contrast, the dehydrocoupling reactivity of amine-boranes containing heteroatom substitution at boron is virtually unexplored. Research published in the mid 20th century documents the synthesis of amine adducts of thioboranes by various methods, focusing primarily on tertiary amine adducts.[36−38] Mikhailov and co-workers, however, also reported the synthesis of secondary amine-thioborane adducts,[39] and briefly discussed the competitive elimination of hydrogen and the respective thiol from these species when heated to beyond 60 °C.[39] The characterization of the initial adducts and products, however, was limited compared to modern standards with key experimental evidence provided solely by elemental microanalysis and cryoscopic measurements.[39] Of particular relevance, given the current interest in metal-catalyzed dehydrogenation of amine-boranes and their derivatives, is the lack of any reports on the transition metal-catalyzed eliminations of hydrogen from amine-thioboranes. Furthermore, a route to the regeneration of spent ammonia-borane fuel following hydrogen release has recently been reported, employing a B-thiolation process.[40,41] The regeneration initially involves reaction of benzenethiol or benzene-1,2-dithiol with borazine and polyborazylene to produce dithiolated borane adducts of ammonia, making further investigation of B-thiolated amine-borane adducts particularly pertinent.

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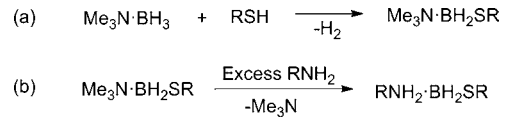
In this paper we present the results of our attempts to prepare monothiolated borane adducts of various amines, and investigations of the dehydrogenation chemistry of the resulting species under thermal and catalytic conditions.

RESULTS AND DISCUSSION

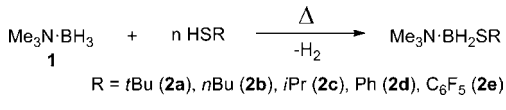
(a). Trimethylamine-Thioborane Adducts, $Me_3N{\cdot}BH_2SR$. *(i). Synthesis of $Me_3N{\cdot}BH_2SR$ (R = tBu [**2a**], nBu [**2b**], iPr [**2c**], Ph [**2d**], and C_6F_5 [**2e**]).* Literature reports of the reaction of $Me_3N{\cdot}BH_3$ (**1**) with aliphatic thiols at high temperature to produce trialkylthioborates provided a potential route to B-thiolated amine-borane adducts.[42] It was postulated that the initial preparation of trimethylamine-thioboranes, $Me_3N{\cdot}BH_2SR$, could then be followed by an amine-exchange process to yield potential dehydrocoupling substrates (Scheme 1).

Scheme 1. Proposed Synthetic Route to Primary Amine-Thioborane Adducts: (a) Initial Synthesis of Trimethylamine-Thioboranes, (b) Subsequent Amine-Exchange to Remove Tertiary Amine Moiety



Utilizing a tertiary amine-borane precursor in this manner also enables temperatures in excess of 100 °C to be employed during the synthesis, conditions under which adducts containing N–H and B–H bonds have been shown to thermally dehydrocouple.[2,22,43] Through a modification of the method of Hawthorne,[42] we were able to prepare a series of monothiolated derivatives of **1** of the form $Me_3N{\cdot}BH_2SR$ in high yield from commercially available starting materials (Scheme 2).

Scheme 2. Generalized Thermal Synthesis of $Me_3N{\cdot}BH_2SR$



The adducts were synthesized via thermolysis of a mixture of amine-borane **1** and the relevant thiol at 100 to 150 °C (Table 1). The adducts $Me_3N{\cdot}BH_2StBu$ (**2a**), $Me_3N{\cdot}BH_2SPh$ (**2d**), and $Me_3N{\cdot}BH_2SC_6F_5$ (**2e**) were isolated as stable, crystalline solids following removal of the solvent under high vacuum, under which conditions residual **1**, a highly volatile solid, and unreacted thiol were also removed. Analysis of these adducts by ^{11}B NMR spectroscopy in $CDCl_3$ solution indicated shifts of −4.2, −3.7, and −1.9 ppm for **2a**, **2d**, and **2e**, respectively, which appeared as triplets, J_{BH} = 100–115 Hz, upon proton coupling. Both the shift and the coupling pattern are consistent with the formation of a new four-coordinate boron environment in each case, with two hydrogen substituents at boron, as expected for monothiolated borane adducts. ^1H and ^{13}C NMR spectroscopy (and ^{19}F NMR spectroscopy in the case of **2e**) also confirmed the successful incorporation of the thiolate moiety into the amine-borane, with chemical ionization mass spectrometry (CI-MS) and elemental microanalysis also consistent with the assigned compositions. Atom connectivity in each case was assigned unequivocally by single crystal X-ray diffraction studies, carried out on crystals grown by sublimation under high vacuum (Figure 1). The respective compounds all crystallize with a single molecule in the asymmetric unit, and are monomeric in nature. The length of the central B–N bond varies slightly with the substituent at boron, with a slight contraction apparent ([**2a**, 1.629(2) Å], [**2d** 1.623(2) Å], and [**2e**, 1.617(2) Å]) as the nominal electron-withdrawing ability of the thiol group increases.[44] The electronic effects of the thiolation appear, however, to be minor in comparison with the steric effect of adding a bulky group at boron, with no overall contraction of the B–N bond apparent relative to the starting material, amine-borane **1** (1.617(6) Å).[45]

Table 1. Selected Properties of the Adducts $Me_3N{\cdot}BH_2SR$ (R = tBu, nBu, iPr, Ph, C_6F_5)

adduct	δ_B (ppm)[a]	melting point (°C)	B–N bond length (Å)
$Me_3N{\cdot}BH_2StBu$ (**2a**)	−4.2	74–75	1.629(2)
$Me_3N{\cdot}BH_2SnBu$ (**2b**)	−1.5		
$Me_3N{\cdot}BH_2SiPr$ (**2c**)	−2.8		
$Me_3N{\cdot}BH_2SPh$ (**2d**)	−3.7	80–81	1.623(2)
$Me_3N{\cdot}BH_2SC_6F_5$ (**2e**)	−1.9	112–113	1.617(2)

[a]All recorded in $CDCl_3$ solution.

Syntheses of $Me_3N{\cdot}BH_2SnBu$ (**2b**) and $Me_3N{\cdot}BH_2SiPr$ (**2c**) were carried out in analogous fashion, with the products isolated as highly moisture sensitive liquids (Table 1). Adduct **2b** could not be purified beyond 95% based on integration of the ^{11}B NMR spectrum, with the impurities postulated to be the multisubstitution products $Me_3N{\cdot}BH(SnBu)_2$ (δ_B 5.6 [d, J_{BH} = 127 Hz]) and $B(SnBu)_3$ (δ_B 58.7 (s) ppm). Adduct **2c** could be obtained more cleanly (~99%), but despite attempted purification of both products by distillation and sublimation under reduced pressure, neither compound provided acceptable elemental microanalysis data.

The multisubstitution observed on reaction with HS*n*Bu and indeed HS*i*Pr at higher temperatures can presumably be explained on the basis of the relative steric encumbrance of the various thiols. In the case of the synthesis of **2a**, for example, the increased steric bulk of HS*t*Bu enabled a clean synthesis of the monosubstituted product, **2a**, at higher temperatures in the presence of a 5-fold excess of thiol.

*(ii). Amine-Exchange Reactions of $Me_3N{\cdot}BH_2SR$ (R = tBu [**2a**], nBu [**2b**], and iPr [**2c**]).* Amine-exchange reactions are well-documented within the amine-borane literature, and serve as a means of transferring the Lewis acidic borane moiety between two amines.[31,46,47] These reactions are understood to occur via nucleophilic substitution at boron, through S_N1 or S_N2 type mechanisms depending on the relative steric encumbrance of the borane moeity.[48–50] Using this method, often over multiple reaction cycles, the substitution of one amine moiety for another can, in many cases, be readily achieved.

It was therefore postulated that treatment of the trimethylamine-thioborane adducts with excess $MeNH_2$ could act as a route to methylamine-thioboranes, of interest as potential dehydrocoupling substrates. However, treatment of the adducts **2a–c**, that is, aliphatic thiolate substituted adducts, with $MeNH_2$ led to unexpected reactivity, with no amine-exchange reaction prevailing. In fact on treatment with excess $MeNH_2$, these adducts proved to be susceptible to nucleophilic displacement of the thiolate moiety by the free amine to

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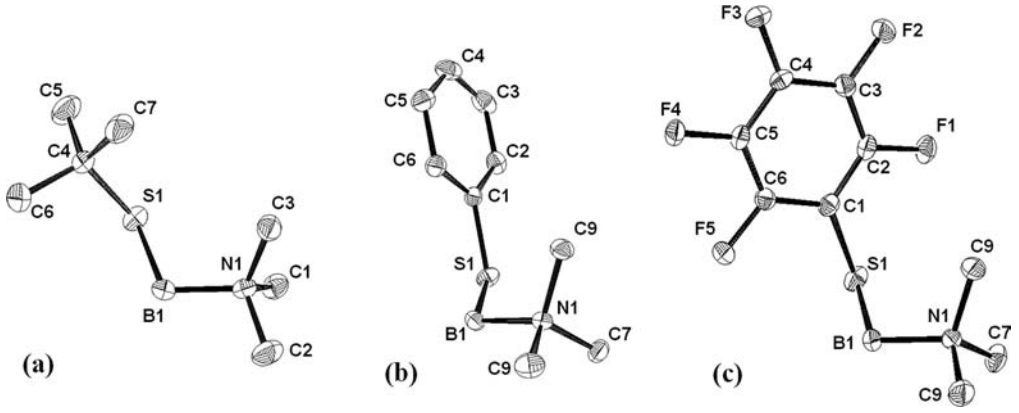

Figure 1. Molecular structures of (a) **2a**, (b) **2d**, and (c) **2e**, with thermal ellipsoids at the 50% probability level. All hydrogen atoms omited for clarity.

produce nonthiolated amine-borane products. For example, upon treatment of a solution of **2a** with a 10-fold excess of $MeNH_2$, ^{11}B NMR spectroscopy indicated the primary products of the reaction with excess amine to be the amine-borane $MeNH_2{\cdot}BH_3$ (**3**) (δ_B −19.3 [q, J_{BH} = 96 Hz]),[2] and the *bis*aminoborane, $HB(NHMe)_2$ (**4**) (δ_B 27.5 [d, J_{BH} = 127 Hz]),[51] in an approximately 1:1 ratio (Scheme 3). The relative integrals of the two products were consistent with a disproportionation mechanism leading to their formation. It is postulated that the reaction proceeds via initial attack of the amine at the boron center, liberating the thiolate moiety into solution. Identical reactivity was observed upon treatment of **2b** and **2c** with $MeNH_2$.

Scheme 3. Attempted Amine-Exchange of Adducts 2a−c with $MeNH_2$

$Me_3N{\cdot}BH_2SR$ —(10 $MeNH_2$, −NMe_3, −HSR)→ $MeNH_2{\cdot}BH_3$ (**3**) + $HB(NHMe)_2$ (**4**)

R = *t*Bu (**2a**), *n*Bu (**2b**), *i*Pr (**2c**)

Repeating the amine-exchange process on adduct **2a** with the secondary amine Me_2NH produced similar results, with the major products $Me_2NH{\cdot}BH_3$ (**5**) (δ_B −14.2 [q, J_{BH} = 96 Hz]) and $(Me_2N)_2BH$ (**6**) (δ_B 28.1 [d, J_{BH} = 129 Hz]), respectively. However, in the cases of **2b** and **2c** as substrates, over 18 h minor quantities of the desired species, $Me_2NH{\cdot}BH_2SR$, appeared to be formed (δ_B −6.4 [t, J_{BH} = 111 Hz, BH_2SnBu] and −5.4 [t, J_{BH} = 111 Hz, BH_2SiPr] ppm respectively) although these proved inseparable from the primary products. This difference in reactivity toward $MeNH_2$ and Me_2NH can be attributed to the increased donor ability of the secondary amine, which may result in more favorable thermodynamics for adduct formation than in the case of $MeNH_2$, where nucleophilic displacement of the thiolate moiety is preferred.

*(iii). Amine-Exchange Reactions of $Me_3N{\cdot}BH_2SPh$ (**2d**) and $Me_3N{\cdot}BH_2SC_6F_5$ (**2e**).* Following the unexpected reactivity of the trimethylamine-thioboranes containing aliphatic thiolates with free amines, analogous experiments were carried out with the thiophenol and pentafluorothiophenol derivatives. It was postulated that the increased electron withdrawing effect of these thiolate groups, particularly in the polyfluorinated case, may lead to a stronger B−N bond, and consequently a reduced tendency to be nucleophilically displaced by free amine, assuming an S_N1 type mechanism. This suggestion was confirmed on treatment of these species with excess $MeNH_2$ solution.

Upon treatment of a tetrahydrofuran (THF) solution of **2d** with a 10-fold excess of $MeNH_2$ at 20 °C, no reaction was observed over 18 h by ^{11}B NMR spectroscopy, with only unreacted starting material present in solution. However, the use of the secondary amine Me_2NH did result in somewhat more successful amine-exchange reactions to produce a species consistent with the formation of $Me_2NH{\cdot}BH_2SPh$ (**11a**), as evidenced by the observation of a triplet in the ^{11}B NMR spectrum at −7.9 ppm of coupling constant 113 Hz. Unfortunately, this reaction also yielded ∼44% conversion to an unknown species by ^{11}B NMR spectroscopy with a chemical shift of −2.5 ppm, appearing as a broad singlet, which proved to be inseparable from the desired product (Scheme 4). A subsequent clean synthesis of the adduct via alternative means (vide infra), however, confirmed the partially successful amine-exchange process in this case. Again this difference in reactivity between Me_2NH and $MeNH_2$ can be attributed to the increased donor ability of Me_2NH, which is likely to produce a more thermodynamically favorable amine-exchange process.

Treatment of **2e** with excess $MeNH_2$ or Me_2NH solution at 20 °C over 18 h produced no reaction with either amine, as evidenced by ^{11}B NMR spectroscopy. It is likely that the increased electron withdrawing effect of the C_6F_5 group is responsible for the reduced reactivity as anticipated. The lack of reactivity toward both amine-exchange or thiolate displacement may indicate that in this case the electron withdrawing effect of the SC_6F_5 group increases the B−N bond strength to the extent that dissociation of the initial adduct, **2e**, to its respective amine

Scheme 4. Amine-Exchange of 2d with 10 equiv of Me_2NH, 20 °C

$Me_3N{\cdot}BH_2SPh$ (**2d**) —(i) 10 Me_2NH, 18 h, 20 °C; (ii) Volatiles Removed; (iii) 10 Me_2NH, 18 h, 20 °C→ $Me_2NH{\cdot}BH_2SPh$ (**11a**, 46%) + $Me_2NH{\cdot}BH_3$ (**5**, 10%) + Unknowns (44%)

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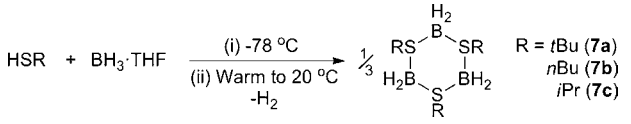
and borane components becomes negligible. This would prevent any amine-exchange via the likely S_N1 mechanism, and may also hinder thiolate displacement, which is also likely to occur via a three-coordinate boron intermediate because of the ready availability of the vacant p-orbital at boron for electron donation.

(b). Thioborane Trimers, $[BH_2-SR]_3$, and Adducts $RSBH_2\cdot SMe_2$. Following the unexpected reactivity of tertiary amine-thioboranes with respect to amine-exchange chemistry, alternative synthetic routes to secondary amine-thioborane adducts were investigated. Two potential routes were pursued, the first via reaction of amines with preformed thioborane trimers or adducts as discussed by Mikhailov, and the second via hydrothiolation reactions of aminoboranes.

*(i). Synthesis of B–S Trimers $[BH_2-SR]_3$ (R = tBu [**7a**], nBu [**7b**], iPr [**7c**], Ph [**9**]) and the Related Adduct $C_6F_5SBH_2\cdot SMe_2$ (**10**).* A series of reports in the mid-20th century document the reaction of liquid diborane and thiols to produce various products including polymeric B–S species, but primarily cyclic trimers of the form $[BH_2-SR]_3$.[37,52,53] Significantly, such trimers have been reported to cleanly yield the amine adduct of the thioborane moiety upon treatment with neat tertiary or secondary amine.[39]

The synthesis of a series of B–S trimers was therefore carried out, using $BH_3\cdot THF$ as a more convenient source of the BH_3 moiety. Addition of neat aliphatic thiols HSR (R = *t*Bu, *n*Bu and *i*Pr) to a solution of $BH_3\cdot THF$ at −78 °C before warming slowly to 20 °C led to the quantitative formation of the trimeric species $[BH_2-StBu]_3$ (**7a**), $[BH_2-SnBu]_3$ (**7b**) and $[BH_2-SiPr]_3$ (**7c**), which appeared as broad triplets in the ^{11}B NMR spectrum, with chemical shifts between −15 and 18 ppm, and coupling constants of ∼100 Hz (Scheme 5). Upon isolation,

Scheme 5. Synthesis of $[BH_2-SR]_3$



7a[54–56] was found to be the only solid product, with **7b** and **7c** both involatile oils. CI-MS in all cases confirmed the formation of the desired trimeric structures, with strong signals for both the molecular ion, and the corresponding monomers, BH_2-SR, observed in each case. Purification of the liquid products by distillation to levels appropriate for elemental microanalysis was not possible because of their involatility under high vacuum and temperature sensitivity, although satisfactory analysis was obtained on the *t*Bu substituted species, which was purified by vacuum sublimation at 50 °C, and also characterized by single-crystal X-ray diffraction (see Supporting Information, section 3b).

Attempted syntheses of the aryl substituted trimers via this method proved to be less successful, with a mixture of products obtained on reaction of $BH_3\cdot THF$ with HSPh or HSC_6F_5. On the basis of existing literature reports[37,57] and our own observations, it was probable that the initial trimeric products of such reactions were cleaved in THF solution to produce simple adducts of the form $RSBH_2\cdot THF$, which subsequently reacted further as evidenced by ^{11}B NMR spectroscopy. Attempts to cleanly isolate the adduct $PhSBH_2\cdot THF$ (**8a**) to confirm this assertion were unsuccessful. Repeating this chemistry with $HSCPh_3$, however, gave a clean reaction over 60 h to furnish $Ph_3CSBH_2\cdot THF$ (**8b**) which was isolated as a colorless solid. Recrystallization of this material from a hexane/THF solution at −40 °C produced large block like crystals suitable for study by X-ray diffraction, which confirmed the expected coordination of a molecule of THF to the thioborane moiety through the oxygen lone-pair (Figure 2).

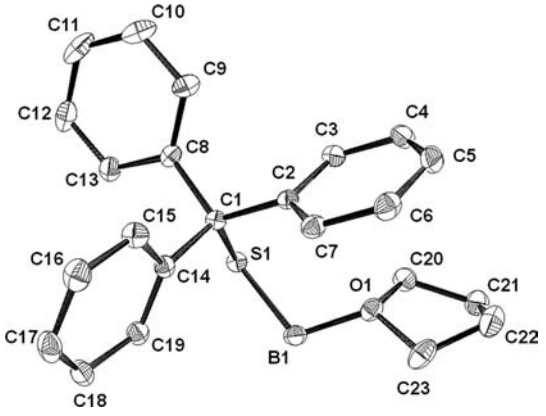


Figure 2. Molecular structure of **8b**, with thermal ellipsoids at the 50% probability level. All hydrogen atoms omitted for clarity.

Because of the apparent decomposition of the THF adducts of $PhSBH_2$ and $C_6F_5SBH_2$ following reaction of HSPh and HSC_6F_5 with $BH_3\cdot THF$, the synthesis of $[BH_2-SR]_3$ (R = Ph (**9**), C_6F_5) was then attempted from $BH_3\cdot SMe_2$ in dichloromethane (DCM). The synthesis of **9** was previously reported via a similar method by Paetzold and co-workers,[57] in hexane solution, and proved equally as facile in DCM at 20 °C. Thioborane **9** was isolated in high yield as a colorless solid, which appeared as a broad triplet in the proton coupled ^{11}B NMR spectrum at −14.2 ppm in CD_2Cl_2. Interestingly, dissolution of this solid in THF at −78 °C appeared to produce the expected THF adduct, **8a**, (δ_B 3.6 [t, J_{BH} = 120 Hz] ppm), which in the absence of free thiophenol or $BH_3\cdot THF$ was stable for at least 1 h at 20 °C.

The synthesis of $[BH_2-SC_6F_5]_3$ was not documented in the literature, and was attempted via an analogous method to that for the thiophenol system. A notably slower reaction occurred to yield complete conversion to a new product, which appeared at −8.2 ppm in the ^{11}B NMR spectrum, and gave a triplet (J_{BH} = 124 Hz) on proton coupling. This product was initially assigned as the expected cyclic trimer $[BH_2-SC_6F_5]_3$. However, upon isolation of the colorless solid product, subsequent multinuclear NMR studies (^1H NMR (CD_2Cl_2) δ_H 2.29 ppm, ^{13}C NMR (CD_2Cl_2) δ_C 22.6 ppm), and CI-MS evidenced the continued presence of an SMe_2 moiety, suggesting in fact the formation of a monomeric dimethylsulfide adduct of the form $C_6F_5SBH_2\cdot SMe_2$ (**10**). It is probable that the increased steric bulk and electron-withdrawing nature of the pentafluorophenyl moiety in this case disfavors the formation of a trimeric product, with coordination of the less sterically demanding, electron-rich SMe_2 moiety quenching the electron deficiency at boron.

*(ii). Reactivity of $[BH_2-SR]_3$ (R = tBu [**7a**], nBu [**7b**], iPr [**7c**], Ph [**9**]), and $C_6F_5SBH_2\cdot SMe_2$ (**10**) with Tertiary and Secondary Amines.* Following the successful synthesis of thioboranes **7a–c** and **9** and dimethylsulfide adduct **10**, the synthesis of amine adducts from these species was investigated. Reaction of trimers **7a–c** and **9**, and adduct **10** with Me_3N in

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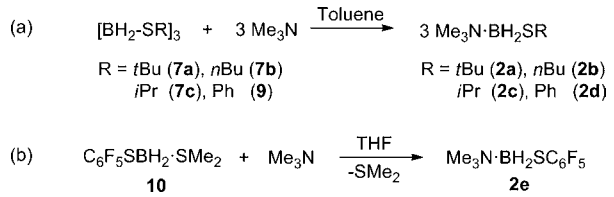
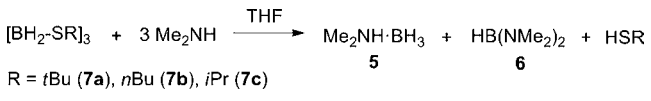
toluene or THF solution at −78 °C cleanly yielded the expected adducts, $Me_3N{\cdot}BH_2SR$, as previously characterized from the thermal syntheses, confirming the applicability of each of these reagents as precursors to amine-thioborane adducts (Scheme 6).[58]

Scheme 6. Synthesis of $Me_3N{\cdot}BH_2SR$ from (a) $[BH_2{-}SR]_3$ and (b) Adduct 10



However, upon treatment of the thioboranes with secondary amines, different reactivity was also observed. In the cases of thioboranes **7a−c**, treatment with a stoichiometric quantity of Me_2NH in THF solution at 0 or −78 °C produced primarily the products associated with disproportionation, as previously discussed, namely, amine-borane **5** and *bis*aminoborane **6** (Scheme 7). Following the previous experiments regarding

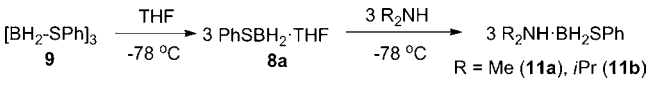
Scheme 7. Reaction of Me_2NH with 7a−c in THF



amine-exchange reactions of $Me_3N{\cdot}BH_2SR$, such disproportionation is not surprising, but is in contrast to published results with regard to the clean synthesis of secondary amine adducts of thioboranes via this method.[39] Altering the conditions to increase dilution produced no change in the reaction products, with those attributed to disproportionation continuing to dominate. Treatment of the trimers **7a−c** with neat Me_2NH or iPr_2NH produced no reaction at ambient temperature.

Attempts to perform the analogous chemistry using the phenyl substituted trimer **9** proved to be significantly more successful as a route to amine-thioborane adducts. Reaction of **9** with Me_2NH in THF at −78 °C produced the desired adduct, $Me_2NH{\cdot}BH_2SPh$ (**11a**), in 91% yield (Scheme 8). The ^{11}B

Scheme 8. Synthesis of $Me_2NH{\cdot}BH_2SPh$ (11a) and $iPr_2NH{\cdot}BH_2SPh$ (11b)



NMR spectrum of the crystalline white solid product in $CDCl_3$ contained a single peak at −7.6 ppm consistent with the expected four-coordinate boron environment, splitting to a triplet on proton coupling ($^1J_{BH}$ = 108 Hz). ^1H and ^{13}C NMR spectra were both consistent with the formation of the desired product, and elemental microanalysis and CI-MS both confirmed the expected composition. Recrystallization of the product at −40 °C from a toluene/hexane mixture produced crystals suitable for X-ray diffraction study, which confirmed the expected atom connectivity (Figure 3a). The compound crystallized as thick colorless plates, in the orthorhombic space group $Pna2_1$, with 4 molecules in the asymmetric unit. The average B−N bond length of 1.607(3) Å is within the

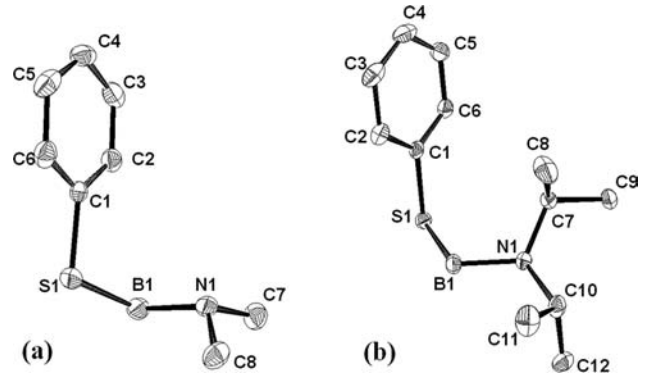


Figure 3. Molecular structures of amine-thioboranes (a) **11a** and (b) **11b**, with thermal ellipsoids at the 50% probability level. All hydrogen atoms omited for clarity.

range expected for a formal B−N single bond in a secondary amine-borane adduct.[45,59−61] Both the nitrogen and boron centers are pseudotetrahedral as would be expected for sp^3 hybridization.

An analogous methodology was used in the preparation of the related adduct $iPr_2NH{\cdot}BH_2SPh$ (**11b**), which was isolated as a white solid in 88% yield from reaction of neat iPr_2NH with a THF solution of **9** at −78 °C (Scheme 8). The ^{11}B NMR spectrum of this compound in $CDCl_3$ contained a single peak, a triplet at −12.3 ppm, with a coupling constant of 100 Hz. ^1H and ^{13}C NMR spectra confirmed the presence of both the iPr_2NH and the BH_2SPh moieties, with further evidence for the composition provided by CI-MS. Subsequent recrystallization of the compound from a toluene/hexane mixture at −40 °C produced large colorless crystals suitable for single crystal X-ray analysis which confirmed the expected connectivity (Figure 3b). The compound was found to crystallize in the monoclinic space group $P2_1/n$ with one molecule per asymmetric unit. The central B−N bond measures 1.625(15) Å, consistent with a single B−N bond in a iPr_2NH adduct,[59] and is slightly increased relative to the analogous Me_2NH adduct. This elongation can be explained by the increased steric bulk of the isopropyl substituents, which are likely to interact more strongly with the substituents at boron.

An attempted synthesis of $Me_2NH{\cdot}BH_2SC_6F_5$ (**12a**) from dimethylsulfide adduct **10** was less successful than with the nonfluorinated analogue. Stoichiometric reaction of Me_2NH and **10** yielded three distinct products, apparent in the ^{11}B NMR spectrum as a triplet at −5.8 ppm (J_{BH} = 115 Hz) [50%], a broad singlet at −2.5 ppm [40%], and a quartet at −14.2 (J_{BH} = 97 Hz) [10%] postulated to be amine-borane **5**. Although the mixture of products could not be separated, the peak at −5.8 ppm was consistent with the formation of the desired adduct **12a** based on the change in chemical shift relative to the related nonthiolated adduct, **5**, and a coupling constant comparable to that for **2e** (J_{BH} = 115 Hz) [The compound was later successfully synthesized via an alternative method, providing spectral data in support of its presence on this case, vide infra].

In contrast, the reaction of **10** with iPr_2NH produced a significantly cleaner reaction, with quantitative conversion to $iPr_2NH{\cdot}BH_2SC_6F_5$ (**12b**) over 1 h at 20 °C based on ^{11}B NMR spectroscopy. The product was isolated as a colorless solid, and possessed a single peak in the ^{11}B NMR spectrum in $CDCl_3$ at −10.5 ppm, which split into a broad triplet on proton coupling. ^1H, ^{13}C, and ^{19}F NMR spectra were also consistent with the assigned structure, suggesting the presence of both iPr_2NH and

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$C_6F_5SBH_2$ moieties. Recrystallization from hexanes at −60 °C produced crystals suitable for X-ray diffraction study, confirming the expected structure based on spectroscopic data (Figure 4). The compound crystallized in the monoclinic

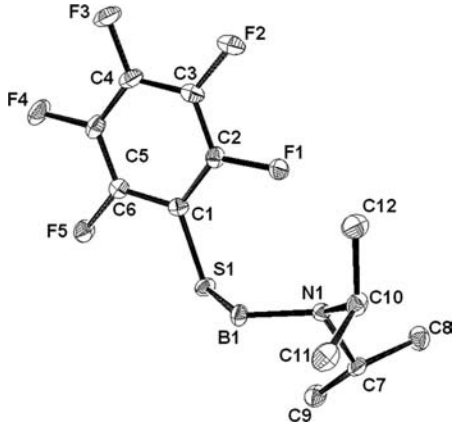

Figure 4. Molecular structure of **12b**, with thermal ellipsoids at the 50% probability level. All hydrogen atoms omited for clarity.

space group $P2_1/c$, with two essentially equivalent molecules per asymmetric unit. The structure was broadly analogous to that of the nonfluorinated analogue **11b**, with effectively no contraction observed in the B−N bond length (1.621(2) Å). The geometries around both boron and nitrogen are both close to tetrahedral, as expected for 4-coordinate, that is, sp^3 hybridized, centers of both elements.

(iii). Hydrothiolation of Secondary Aminoboranes: an Alternative Synthesis of $R_2NH{\cdot}BH_2SR$. A recent publication of Dixon and co-workers that demonstrated the addition of thiols across B−N multiple bonds[40] provided impetus for us to investigate the hydrothiolation of aminoboranes as an alternative route to amine-thioboranes. The synthesis of **12a**, which could not be achieved cleanly by other means, was therefore attempted via this methodology. Heating a toluene solution of the thermally-labile dimer $[Me_2N\text{-}BH_2]_2$ (**13**) in the presence of 2 equiv of HSC_6F_5 to 70 °C led to complete consumption of the aminoborane within 18 h, as evidenced by ^{11}B NMR spectroscopy, with the appearance of a new peak at −5.8 ppm, apparent as a triplet, J_{BH} = 115 Hz, in the proton coupled spectrum. Removal of the solvent furnished the new product as a colorless solid, identified by multinuclear NMR spectroscopy, CI-MS and elemental microanalysis as the desired amine-thioborane **12a** in 82% isolated yield (Scheme 9).

Scheme 9. Synthesis of 12a via Hydrothiolation

$$[Me_2N\text{-}BH_2]_2\ (\mathbf{13}) + 2\ HSC_6F_5 \xrightarrow[70\ ^\circ C,\ 18\ h]{\text{Toluene}} 2\ Me_2NH{\cdot}BH_2SC_6F_5\ (\mathbf{12a})$$

Recrystallization of the solid product from toluene/hexanes at −40 °C produced crystals suitable for an X-ray diffraction study, which confirmed the expected atom connectivity (Figure 5). The compound crystallized in the triclinic space group $P\bar{1}$ as colorless plates, with a single molecule in the asymmetric unit, with a structure again closely related to that of the nonfluorinated analogue **11a**.

The hydrothiolation methodology was readily extended to produce the previously characterized adduct **11a**, and also **11b**/

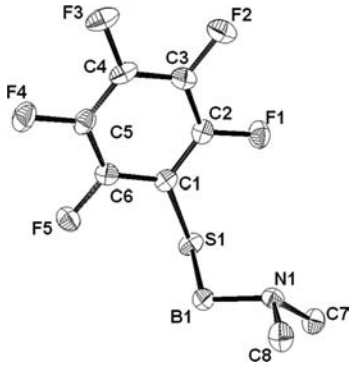

Figure 5. Molecular structure of **12a**, with thermal ellipsoids at the 50% probability level. All hydrogen atoms omited for clarity.

12b, via reaction of the monomeric aminoborane $iPr_2N{=}BH_2$ (**14**) with the respective thiol, in high yield demonstrating its general applicability to this chemistry.

Attempts to utilize this method in the preparation of adducts containing aliphatic thiolates, however, which had proved inaccessible by other methods (vide supra), were unsuccessful. Reaction of **13** with HS*t*Bu, for example, at 60 °C produced a mixture of products, with a peak assigned to the desired adduct $Me_2NH{\cdot}BH_2S$*t*Bu (**15**) (δ_B −7.6 [t, J_{BH} = 111 Hz]) appearing as a minor component of the ^{11}B NMR spectrum of the crude reaction mixture (ca. 8% of products). A significant proportion of the product mixture was assigned as the aminothioborane $Me_2N{=}BH(S$*t*$Bu)$ (**16**) (38%), which appeared as a doublet at 38.6 ppm, J_{BH} = 144 Hz. In this case it appears that the rate of formation of **15** was lower than that of its consumption via thermal dehydrogenation to form **16** (Scheme 10). Reducing

Scheme 10. Attempted Synthesis of Dialkylamine-Thioborane Adducts via Thermolytic Hydrothiolation

$$R_2N{=}BH_2 + HSR' \xrightarrow[\text{Heat}]{k_1} [R_2NH{\cdot}BH_2SR'] \xrightarrow[-H_2]{k_2} R_2N{=}BHSR' \qquad k_2{>}k_1$$

the reaction temperature to 50 °C produced no significant change in product composition, with the rate of both processes dropping at lower temperatures. Similar reactivity was observed on reaction of HS*t*Bu with aminoborane **14** and indeed on reaction of **13** with other aliphatic thiols (e.g., HS*n*Bu, HS*i*Pr). In all cases, therefore, the isolation of the desired amine-thioborane $R_2NH{\cdot}BH_2SR$ was not feasible because of the competitive thermal elimination of hydrogen from the thioborane adduct.

(c). Attempted Synthesis of Primary Amine Adducts of Thioboranes: $RNH_2{\cdot}BH_2SR$. *(i). Reaction of $MeNH_2$ with $[BH_2{-}SR]_3$ (R = tBu [**7a**], nBu [**7b**], iPr [**7c**], and Ph [**9**]) and $C_6F_5SBH_2{\cdot}SMe_2$ (**10**).* Reaction of $MeNH_2$ with B−S trimers **7a**−**c** derived from aliphatic thiols produced identical reactivity to that observed on reaction with Me_2NH in THF at −78 °C. The sole reaction products in this case appear again to be those of disproportionation, namely, $MeNH_2{\cdot}BH_3$ (**3**) and HB(NHMe)$_2$ (**4**), with no evidence of the formation of the desired amine-thioborane adducts (Scheme 11).

To probe the effect of THF on this reaction, an analogous experiment was performed using the liquid amine, nBuNH$_2$, in the absence of solvent. This again led to disproportionation, in this case to yield products assigned by ^{11}B NMR spectroscopy as nBuNH$_2{\cdot}BH_3$ (**17**) (δ_B −20.4 [q, J_{BH} = 94 Hz] ppm)[62] and

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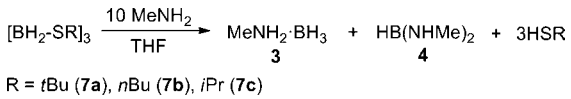
Scheme 11. Reaction of 7a–c with Excess $MeNH_2$ in THF Solution



$(n\text{BuNH})_2\text{BH}$ (**18**) (δ_B 27.3 [d, J_{BH} = 115 Hz] ppm),[51] with no evidence for the formation of a stable thioborane adduct.

Reaction of $MeNH_2$ with the phenyl substituted trimer **9**, however, produced different reactivity. In this case, addition of a solution of $MeNH_2$ to a THF solution of **9** produced rapid conversion to a complex mixture of products by ^{11}B NMR spectroscopy. The major species within the mixture, however, accounted for ~70% of the total soluble boron content, and appeared as a triplet at −11.5 ppm (J_{BH} = 111 Hz). Both the chemical shift and the coupling constant of this species were consistent with the expected amine-thioborane adduct, $MeNH_2{\cdot}BH_2SPh$ (**19**), based upon the analogous secondary amine-thioborane **11a**. Removal of the solvent from the reaction mixture yielded an oily solid, which was immediately triturated with hexanes. Although the resulting solid products could not be further purified in the bulk by sublimation or recrystallization under various conditions, recrystallization from a DCM/hexane mixture at −40 °C fortuitously produced a colorless plate suitable for study by single crystal X-ray diffraction, which confirmed the presence of the desired product, **19** (Figure 6). This compound was found to crystallize

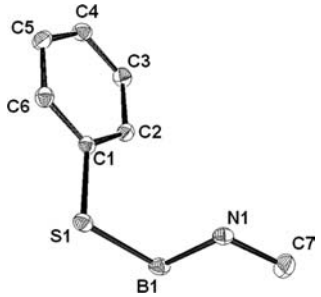


Figure 6. Molecular structure of **19**, with thermal ellipsoids at the 50% probability level. All hydrogen atoms omited for clarity.

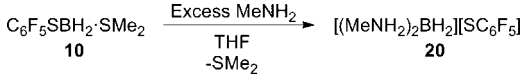
in the orthorhombic space group *Pbca*, and contained a single molecule per asymmetric unit. The substituents at nitrogen and boron were found to be pseudotetrahedral in nature as expected for sp^3 hybridization at both centers. The boron–nitrogen bond length of 1.586(2) Å was of the magnitude expected for a B–N single bond within a primary amine-borane adduct,[45,63] and shows the expected contraction from that of the analogous Me_2NH adduct (B–N: 1.607(3) Å) based on steric arguments.

Although the complete purification of this species could not be achieved, it is likely that the molecular structure demonstrated by X-ray crystallographic study is representative of ~70% of the overall composition, and it is possible to tentatively assign the ^{11}B NMR spectral data by close comparison with that of other similar species. The chemical shift and coupling constant of the major product (δ_B −11.5, J_{BH} = 111 Hz) are within the expected range for the target compound, based on the relative shift between amine-thioborane **11a** (δ_B −7.6, J_{BH} = 108 Hz) and amine-borane **5** (δ_B −14.0)[64] respectively, and the coupling constant of the former compound.

It is postulated that the less well-defined reaction with $MeNH_2$ is due to the reduced donor ability of this amine relative to Me_2NH and iPr_2NH, respectively, which would result in a less favorable adduct forming reaction. This could result therefore in significantly increased levels of competing side reactions, alongside the formation of the desired 1:1 adduct.

Reaction of the related dimethylsulfide adduct, **10**, with excess $MeNH_2$ in THF solution at −78 °C did not yield either the expected amine-thioborane adduct or the previously observed disproportionation products. The product in this case, was found to be the salt $[(MeNH_2)_2BH_2][SC_6F_5]$ (**20**), which was isolated as a colorless solid (Scheme 12). This

Scheme 12. Reaction of $MeNH_2$ and 10 in THF at 20 °C



compound was insoluble in most common NMR solvents, but was completely soluble in d_8-THF producing a poorly resolved triplet in the ^{11}B NMR spectrum at −8.7 ppm, of coupling constant ~90 Hz. The ^{1}H{^{11}B} NMR spectrum was consistent with the assigned structure, with peaks assigned to the Me (δ_H 2.43 ppm) and BH_2 (δ_H 2.03 ppm) environments integrating in a 6:2 ratio. In addition, the ^{13}C and ^{19}F NMR spectra, although broadly uninformative, confirmed the inclusion of a $MeNH_2$ and C_6F_5 moieties, respectively.

Recrystallization of the isolated solid from THF/hexanes at −40 °C produced colorless crystals suitable for X-ray diffraction analysis, which confirmed the product to be salt **20** (See Supporting Information, Section 3a). It is likely that the formation of this compound results from the displacement of the thiolate anion from the borane by nucleophilic attack by the primary amine, although it is unclear why in this case the reaction does not continue to furnish *bis*aminoborane **4** as observed in initial amine-exchange chemistry (vide supra). It is conceivable that the formation of this compound may be due to the increased stability of the $[SC_6F_5]^-$ anion relative to those produced from aliphatic thiols. Interestingly, analogous products, $[(RNH_2)_2BH_2][SR']$, were proposed by Mikhailov and co-workers to result from the treatment of the aliphatically substituted trimers $[BH_2{-}SR']_3$ (R′ = Me, Et) with primary amines, RNH_2 (R = Me, Et),[65] which were not observed in our studies of related species.

It should also be noted that the stoichiometry of the formation of this salt clearly dictates the necessity of an excess of $MeNH_2$, and it was conceivable that the desired product could be formed upon stoichiometric reaction of the amine with adduct **10**. Reaction in this manner, however, yielded only mixtures of the starting material and the salt product based on ^{11}B NMR spectroscopy.

*(ii). Attempted Synthesis of $MeNH_2{\cdot}BH_2SR$ (R = Ph [**19**], C_6F_5) via Hydrothiolation of $[MeNH\text{-}BH_2]_3$ (**21a**) and $[MeNH\text{-}BH_2]_n$ (**21b**).* The lack of a clean synthesis of primary amine-thioborane adducts by other methods led to the investigation of hydrothiolation, as demonstrated for secondary adducts, as an alternative route to these species. Unfortunately however, the reaction of various thiols with the cyclic oligomeric and linear polymeric aminoboranes, $[MeNH\text{-}BH_2]_3$ (**21a**) and [MeNH-

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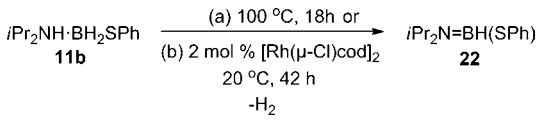
$BH_2]_n$ (**21b**), at elevated temperatures did not lead to thiolated products. The only product of such reactions was *N,N′,N″*-trimethylborazine, $[MeN\text{-}BH]_3$, the reported thermolysis product of both aminoboranes, the formation of which may be enhanced by mild acid catalysis resulting from the presence of the thiol (see Supporting Information, Section 4).

(d). Reactivity of B-Thiolated Adducts with Respect to H_2 Release. *(i). Thermal and Catalytic Dehydrogenation of $iPr_2NH{\cdot}BH_2SPh$ (**11b**) and $iPr_2NH{\cdot}BH_2SC_6F_5$ (**12b**).* Thermal dehydrogenation of $iPr_2NH{\cdot}BH_2SPh$ (**11b**) was investigated initially as a prelude to catalytic studies. A solution of the adduct was, therefore, heated to 100 °C over 18 h in toluene solution. Over this period, ^{11}B NMR spectroscopy demonstrated the growth of a new peak at 37.9 ppm, a doublet of coupling constant 141 Hz, postulated to be due to $iPr_2N{=}BH(SPh)$ (**22**), along with the concomitant consumption of the starting material (Scheme 13a). Upon removal of the volatile components of the reaction mixture, the product was furnished as a colorless oil, which was subsequently recrystallized from hexane solution at −40 °C to yield a colorless solid, which melted at ambient temperature. The ^{11}B NMR spectrum in $CDCl_3$ showed a single peak at 38.7 ppm, a doublet with coupling constant 139 Hz, consistent with a three-coordinate boron environment, with a single hydrogen substituent. The chemical shift in this case was strongly indicative of a monomeric aminothioborane,[66] and was consistent with that observed for the unsubstituted aminoborane analogue $iPr_2N{=}BH_2$ (**14**) (δ_B 35.1 ppm).[2,66] ^1H and ^{13}C NMR spectroscopies indicated the presence of two inequivalent isopropyl environments consistent with the limited rotation around the central B=N bond present in monomeric aminoboranes, and also confirmed the inclusion of a phenyl moiety within the product. Accurate mass CI-MS was also consistent with the assignment of the product as aminothioborane **22**. Adduct **11b** was, therefore, shown to be cleanly dehydrogenated, to produce the monomeric aminothioborane **22** in 59% isolated yield.[67]

Scheme 13. Thermal and Catalytic Dehydrogenation of 11b



Crystallization of the liquid product at −40 °C from hexane solution yielded large colorless plates suitable for single crystal X-ray analysis, confirming the expected atom connectivity in the aminothioborane (Figure 7). The compound was found to crystallize in the monoclinic space group $P2_1/n$, with a single molecule in the asymmetric unit. The core of the molecule is almost perfectly planar, with the angle between the S(1)−B(1)−H(1) and (C7)−N(1)−C(10) planes measuring 0.87°, as generally observed in monomeric aminoboranes.[59,68] Both nitrogen and boron centers are in effectively trigonal-planar environments as expected following sp^3 to sp^2 hybridization at both centers following hydrogen loss. The B−N bond length of 1.385(16) Å shows the expected contraction from that of **11b**, 1.625(15) Å, consistent with the increased bond order associated with the formation of a B−N double bond in this system. To our knowledge, this is the first crystallographic characterization of such an aminothioborane.

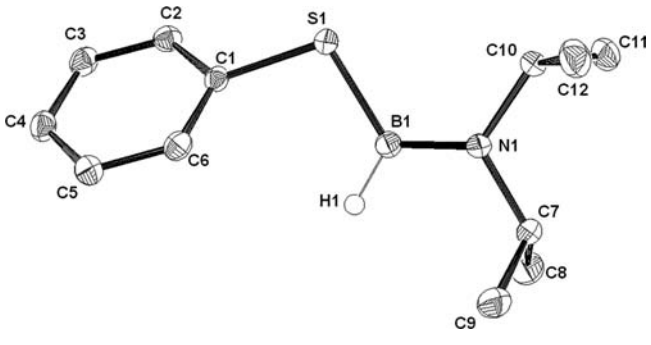


Figure 7. Molecular structure of **22**, with thermal ellipsoids at the 50% probability level. Hydrogens bonded to carbon omited for clarity.

As discussed previously, the employment of transition metal catalysts has been shown to facilitate hydrogen release from simple amine-borane adducts, and it was of interest to investigate similar catalysis in this context. Therefore, we attempted the Rh-catalyzed dehydrogenation of **11b**, using the precursor complex $[Rh(\mu\text{-}Cl)cod]_2$ (cod = 1,5-cyclooctadiene). Using a Rh loading of 2 mol %, the adduct was found to be completely dehydrogenated to produce solely aminothioborane **22** over 42 h at 20 °C (Scheme 13b). In this case, the product could be isolated via sublimation from the catalyst following removal of the volatiles under high vacuum, with multinuclear NMR spectroscopy confirming the identity of the product as that previously characterized.

Analogous thermal dehydrogenation reactions with the perfluorinated analogue, $iPr_2NH{\cdot}BH_2SC_6F_5$ (**12b**), were also observed. Heating a solution of this adduct to 100 °C over 18 h, also led to a relatively clean dehydrogenation to form the monomeric aminothioborane $iPr_2N{=}BH(SC_6F_5)$ (**23**), along with small quantities of aminoborane (**14**) (δ_B 35.1 ppm), suggesting the release of HSC_6F_5 also occurs as a minor pathway. Aminothioborane **23** was isolated as a colorless solid, which showed a single resonance in the ^{11}B NMR spectrum in $CDCl_3$ at 37.0 ppm (d, J_{BH} = 127 Hz), consistent with a three coordinate boron center bound to a single hydrogen substituent. The ^1H and ^{13}C NMR spectra were unremarkable, but were in support of the assigned monomeric structure with resonances consistent with two inequivalent isopropyl groups apparent in both spectra. The $^1H\{^{11}B\}$ spectrum also showed a resonance at 4.84 ppm which integrated to 1 proton, consistent with the single hydrogen environment at boron, and in line with the analogous signal observed for **22** at 5.59 ppm.

Catalytic dehydrogenation of **12b** was also attempted under analogous conditions to those successfully employed in the dehydrogenation of **11b**. Upon treatment of a solution of **12b** with 2 mol % $[Rh(\mu\text{-}Cl)cod]_2$ over 18 h at 20 °C, however, analysis by ^{11}B NMR spectroscopy indicated this adduct was not cleanly dehydrogenated. Over this period, 20% of the initial adduct was consumed to form a mixture of 5 products including $iPr_2NH{\cdot}BH_3$ (δ_B −21.1 ppm) and **14** (δ_B 34.6 ppm), along with a small amount of the desired aminothioborane **23** (δ_B 37.1 ppm) suggesting the presence of several competing side reactions.

*(ii). Thermal and Catalytic Dehydrogenation of $Me_2NH{\cdot}BH_2SPh$ (**11a**) and $Me_2NH{\cdot}BH_2SC_6F_5$ (**12a**).* In contrast to the clean dehydrogenative chemistry observed for **11b**, heating a toluene solution of $Me_2NH{\cdot}BH_2SPh$ (**11a**) to 100 °C over 42 h, appeared to produce a competitive elimination of hydrogen and thiophenol. Analysis of the crude reaction mixture by ^{11}B NMR spectroscopy indicated the major products of the reaction to be $Me_2N{=}BHSPh$ (**24**), (δ_B 39.4

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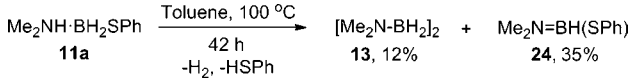
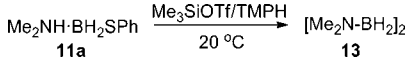
[t, J_{BH} = 153 Hz] ppm, {35%})[69] and cyclodiborazane **13** (δ_B 4.8 [t, J_{BH} = 110 Hz],[2] {12%}), with significant quantities of **11a** remaining unreacted (39%). Continued heating over 68 h led to a mixture containing 41% of **24**, 3% of **13**, and 22% unreacted **11a** remaining (Scheme 14). Separation of the complex mixture of products was, however, unsuccessful, preventing further characterization of novel aminothioborane **24**.

Scheme 14. Thermolysis of 11a at 100 °C, Toluene Solution



This competitive elimination correlates closely with that proposed under similar conditions by Mikhailov,[39] and implies little thermodynamic advantage from elimination of hydrogen rather than thiophenol, despite the release of a gaseous product in the former case. It was therefore of interest to investigate whether the dehydrogenation reaction could be selectively facilitated under catalytic conditions. However, reactions with [Rh(μ-Cl)cod]$_2$, as used for in the successful dehydrogenation of **11b**, and also two further efficient amine-borane dehydrogenation catalysts: IrH$_2$POCOP (POCOP = κ^3-1,3-(OP*t*Bu$_2$)$_2$C$_6$H$_3$])[11] and "Cp$_2$Ti",[6] produced none of the aminothioborane observed thermally, nor indeed aminoborane **13**, the product of thiophenol elimination. However, reaction with the Wilkinson's catalyst analogue, Rh(PHCy$_2$)$_3$Cl[70] (2 mol %, 16 h, toluene) cleanly yielded ~16% of **24**, with no apparent formation of **13**. Allowing this reaction to stir for a further 120 h, however, did not result in a complete conversion to the desired product, which is in fact consumed to produce a new unidentified product at 19 ppm in the ^{11}B NMR spectrum, which remained a singlet on proton coupling. An alternative means of dehydrogenation employing stoichiometric quantities of the frustrated Lewis pair (FLP) Me$_3$SiOTf/2,2,6,6-tetramethylpiperidine[71] (TMPH) was also attempted. Treatment of a toluene solution of **11a**, with a stoichiometric quantity of this FLP at 20 °C, however, resulted in the clean elimination of thiol to produce cyclic diborazane **13** as the major boron containing product (98%), although a trace amount of the aminothioborane **24** was also detected (Scheme 15).

Scheme 15. Reaction of 11a with Me$_3$SiOTf/TMPH



Clearly under these conditions, and indeed on repeating the reaction using **11b**,[72] the elimination of HSPh is more favorable than the elimination of H$_2$ as observed in nonthiolated systems.

The fluorinated adduct, Me$_2$NH·BH$_2$SC$_6$F$_5$ (**12a**), proved to be significantly less reactive toward dehydrogenation. Remarkably, thermolysis of this adduct at 100 °C in toluene solution over 18 h, produced no evidence of small molecule elimination by ^{11}B NMR spectroscopy, with only unreacted **12a** remaining in solution. Repeating the thermolysis at 150 °C in tetraglyme over the same period resulted in complete decomposition of the initial adduct to form a series of unknown products. Catalytic dehydrogenation of **12a** was also attempted using [Rh(μ-Cl)cod]$_2$, Rh(PHCy$_2$)$_3$Cl, and the FLP Me$_3$SiOTf/TMPH respectively, but was not successful.[73]

DISCUSSION

The differing reactivity of the four secondary amine-thioboranes, **11a**/**11b** and **12a**/**12b**, with respect to hydrogen release is likely to be dictated by a combination of steric and electronic effects within the adducts. In a previous computational study, we investigated the thermodynamics of dehydrogenation for a range of amine-borane adducts,[32] including *i*Pr$_2$NH·BH$_3$ (**26**) and Me$_2$NH·BH$_3$ (**5**), unsubstituted analogues to the thiolated adducts studied in this case. The dehydrogenation of **26** to form *i*Pr$_2$N=BH$_2$ (**14**) was calculated to have ΔG = −16.5 kcal/mol, with the analogous reaction for **5** calculated to have ΔG = −11.5 kcal/mol. It is reasonable to suggest, therefore, that upon B-thiolation, a similar relationship may hold, with H$_2$ release from **11b**/**12b** more favorable than in the related methyl substituted species, **11a**/**12a**. Such an assertion is directly in line with experimental results. Furthermore, the observation of the elimination of thiol in the case of thermolysis of **11a** and to a lesser degree **12b** suggests that elimination of HSR is also favorable, and this side reaction would become increasingly significant where the elimination of H$_2$ was not strongly favored. The prevalence of this mode of reactivity in the case of **11a** is again in line with this suggestion.

In the case of **12a** the lack of reactivity at 100 °C or under catalytic conditions evidence an unfavorable elimination of both H$_2$ and HSC$_6$F$_5$. The former may be rationalized by the combination of the presence of Me groups at nitrogen, as discussed above, and the highly electron withdrawing SC$_6$F$_5$ group at boron, both of which are likely to disfavor H$_2$ release.[32] The unfavorable elimination of HSC$_6$F$_5$ is, however, less easily explained. Nevertheless, it is noteworthy that the analogous elimination of HSPh is also sluggish from **11a** (only 12% of cyclodiborazane **13** is formed after 42 h at 100 °C), suggesting subtle effects related to thiol loss may be operational. With regard to the limited catalytic reactivity of the fluorinated adducts, it is likely that the high steric bulk of the thiolate group in this case impairs coordination to the active catalytic centers, thus hampering their action.

SUMMARY

The synthesis of a broad range of amine-thioborane adducts has been developed and detailed investigations of a variety of routes to such species carried out. Thermal dehydrogenation of secondary amine-thioborane adducts has been demonstrated, along with the first example of a metal catalyzed dehydrogenation of such an adduct.

A series of trimethylamine-thioboranes, Me$_3$N·BH$_2$SR (R = *t*Bu [**2a**], *n*Bu [**2b**], *i*Pr [**2c**], Ph [**2d**], C$_6$F$_5$ [**2e**]), have been prepared and characterized. The use of these adducts as precursors to secondary and primary amine-thioboranes via amine-exchange reactions was also investigated, but was found to be unfeasible due to nucleophilic displacement of the thiolate moieties. However, the thioborane trimer [BH$_2$−SPh]$_3$ (**9**) and the dimethylsufide adduct C$_6$F$_5$SBH$_2$·SMe$_2$ (**10**) were found to act as effective precursors to a range of amine-thioboranes. These precursors were found to cleanly form the expected thioborane adducts with Me$_3$N, as characterized via thermal synthesis, but more significantly also formed Me$_2$NH·BH$_2$R (R = Ph [**11a**], C$_6$F$_5$ [**11b**]) and *i*Pr$_2$NH·BH$_2$SR (R = Ph [**12a**],

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C_6F_5 [**12b**]) upon reaction with Me_2NH and iPr_2NH, respectively. All four secondary amine adducts were characterized crystallographically, and as such represent the first structural characterization of this family of compounds.

Studies of the thermal and catalytic dehydrogenation of **11a**/**11b** and **12a**/**12b** evidenced facile hydrogen loss under mild conditions from both diisopropylamine adducts **11b** and **12b**. These adducts were cleanly dehydrogenated at 100 °C to form the monomeric aminothioboranes $iPr_2N{=}BHSR$ (R = Ph [**22**], C_6F_5 [**23**]), with the former adduct also shown to be catalytically dehydrogenated at 20 °C using 2 mol % [Rh(μ-Cl)cod]$_2$. The closely related adduct **11a** was found to competitively eliminate hydrogen and thiol at 100 °C to furnish $Me_2N{=}BH(SPh)$ (**24**) and $[Me_2N\text{-}BH_2]_2$ (**13**) respectively, with Rh-catalyzed dehydrogenation favoring **24** only in the early stages of reaction. The fluorinated analogue, **12a**, could not be cleanly dehydrogenated under thermal or catalytic protocols.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details, crystallographic information and details of additional experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(73) Treatment of toluene solutions of the adducts with 2 mol % of each catalyst over 18 h, however, produced <5% conversion to unknown products, none of which were consistent with the expected aminothioborane, $Me_2N{=}BH(SC_6F_5)$. Treatment of a toluene solution of this adduct with the FLP Me_3SiOTf/TMPH at 20 °C over 18 h, yielded solely cyclic diborazane **13**, again indicating a preferred elimination of the thiolate moiety.