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Efficient Regeneration of Partially Spent Ammonia Borane Fuel

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A necessary target in realizing a hydrogen (H_2) economy, especially for the transportation sector, is its storage for controlled delivery, presumably to an energy producing fuel cell.[1] In this vein, the U.S. Department of Energy's (DOE) Centers of Excellence (CoE) in Hydrogen Storage have pursued different methodologies, including metal hydrides, chemical hydrides, and sorbents, for the expressed purpose of supplanting gasoline's current > 300 mile driving range. Chemical hydrogen storage has been dominated by one appealing material, ammonia borane ($H_3B{-}NH_3$, AB), due to its high gravimetric capacity of hydrogen (19.6 wt %) and low molecular weight (30.7 g mol^{-1}). In addition, AB has both hydridic and protic moieties, yielding a material from which H_2 can be readily released.[2] As such, a number of publications have described H_2 release from amine boranes, yielding various rates depending on the method applied.[3-6] Even though the viability of any chemical hydrogen storage system is critically dependent on efficient recyclability, reports on the latter subject are sparse, invoke the use of high energy reducing agents, and suffer from low yields.[1,7-10] For example, the DOE recently decided to no longer pursue the use of $NaBH_4$ as a H_2 storage material, in part because of inefficient regeneration. We thus endeavored to find an energy efficient regeneration process for the spent fuel from H_2 depleted AB with a minimum number of steps.

Although spent fuel composition depends on the dehydrogenation method,[3,5] we have focused our efforts on the spent fuel resulting from metal-based catalysis, which has thus far shown the most promise. Metal-based catalysts have produced the fastest rates for a single equivalent of H_2 released from AB[4] and up to 2.5 equiv. of H_2 can be produced within 2 hours.[5] While ongoing work is being carried out to tailor the composition of spent AB fuel, we have developed a method for regenerating the predominant product, polyborazylene (PB, Figure 1), resulting from nickel carbene catalyst dehydrogenation.

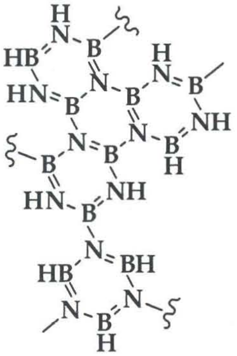
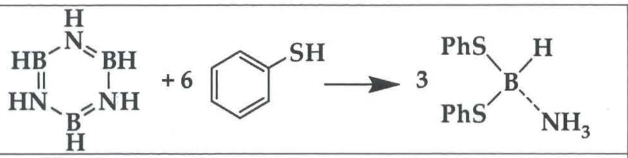
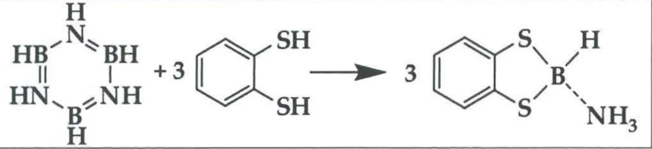


Figure 1 Representative structure of polyborazylene (PB)

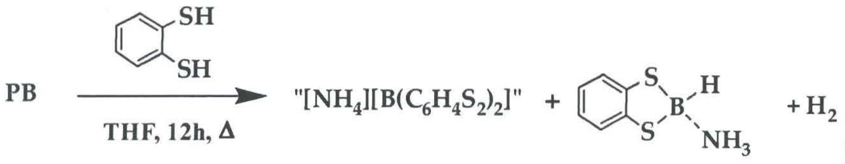
The critical feature of our approach, in contrast to $NaBH_4$ spent fuel regeneration, lies in the use of reagents which avoid the formation of thermodynamically stable B–O bonds and the subsequent need for high energy reducing agents. Thiols appeared attractive since B–S bonds are weaker than analogous B–O bonds and the acidity of the S–H moiety could aid the reaction. On the basis of density functional theory (DFT) calculations (B3LYP exchange-correlation functional and a polarized valence double zeta basis set) for the gas phase coupled with experimental data or estimates of the heats of vaporization, benzenedithiol was predicted to be a better reagent than thiophenol for the initial reaction with borazine, a computational surrogate for PB, where the products are presumed to retain the B–H bond (see Table 1).

Table 1 Estimates of Reaction Energies for Digestion	ΔH (298 K)[a]

	27.4/25.1
	-22.3/0.5

[a] Condensed phase/Gas phase values in kcal/mol

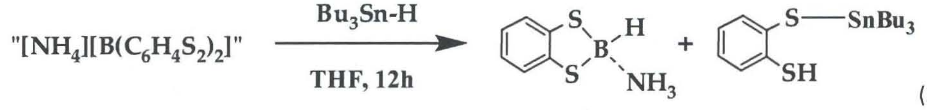
When benzenedithiol and PB were refluxed in THF, consumption of PB was observed by ^{11}B NMR spectroscopy after 12 hours to yield two new resonances. The upfield resonance (δ –5.6, d, $^{1}J_{B\text{-}H}$ = ??) was identified as $(C_6H_4S_2)B{-}H\bullet(NH_3)$ by independent synthesis as well as comparison to a calculated value (see Supplemental Information). The downfield resonance (δ 10.5 ppm, s) exhibits a similar chemical shift value to that of $Li[B(C_6H_4S_2)_2]$,[11] suggesting that $[NH_4][B(C_6H_4S_2)_2]$ is formed. Attempts to make this product independently, via the reaction of $(C_6H_4S_2)B{-}H\bullet(NH_3)$ and benzenedithiol, failed to yield a pure material even under driving conditions (heat and gas removal by freeze/pump/thaw cycles). When $Li[B(C_6H_4S_2)_2]$ was prepared independently according to the literature procedure and checked by ^{11}B NMR, the same resonance (10.5 ppm) was observed, in contrast to that reported (δ 12.1 ppm) in the literature.[11] Both resonances are also observed in the reaction of borazine and benzenedithiol, along with concomitant H_2 formation (see Supplemental Information). This observation suggests that the benzenedithiol reacts with the product $(C_6H_4S_2)B{-}H(NH_3)$ faster than borazine, releasing hydrogen per Scheme 1.



(1)

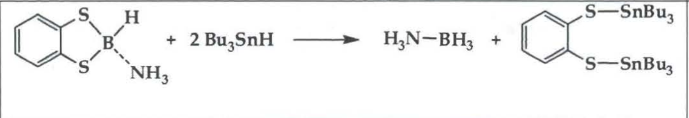
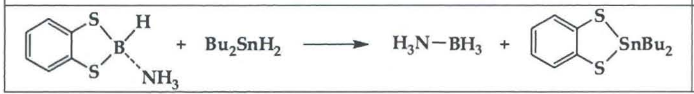
To transform the aforementioned products of scheme 1 into AB, a hydride source is required. Ideally a commercially available hydride source would be desirable, thus Bu_3Sn-H seemed like a good starting point, especially since literature reports suggested a possible Sn-H bond regeneration method via decarboxylation.[12] In a second step, when Bu_3Sn-H is added to the mixture of products of the 1,2-benzenedithiol digestion,

$[NH_4][B(C_6H_4S_2)_2]$ is fortuitously transformed into $(C_6H_4S_2)B–H•(NH_3)$ (Scheme 2). The other product is $C_6H_4SH(S\text{-}SnBu_3)$, as observed by ^{119}Sn NMR and synthesized independently from benzenedithiol and $Bu_3Sn\text{-}H$. Thus in two steps, we have converted PB into a single new boron containing product.

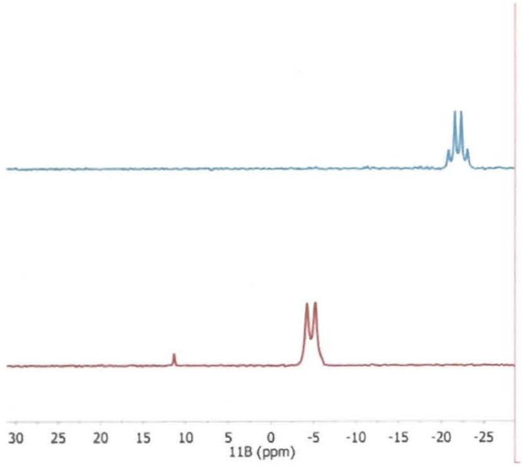


(2)

The subsequent replacement of the dithiolate ligand in $(C_6H_4S_2)B–H•(NH_3)$ with hydride to regenerate AB has thus far proved difficult. A series of hydride sources were screened, all of which either over-reduced the boron to borohydride or didn't react at all. We hypothesized that overcoming the chelate effect of the dithiolate ligand in the first reaction shown in Table 2 might be a substantial problem and thus endeavored to examine suitable hydride sources via theory. DFT calculations of the reactions of $Bu_3Sn\text{-}H$ and Bu_2SnH_2 (shown in in Table 2) were consistent with this hypothesis and predicted that Bu_2SnH_2 should react more favorably on the basis of thermodynamics. Experiments subsequently confirmed that $(C_6H_4S_2)B\text{-}H•(NH_3)$ was transformed into AB using a slight excess of Bu_2SnH_2 (Figure 4), with concomitant formation of $Bu_2Sn(C_6H_4S_2)$ (Figure 5). The absence of borohydride in this hydride transfer reaction makes this reaction very significant.

Table 2 Estimates of \Reaction Energies for Reduction	ΔH (298 K)[a]
	12.3/2.8
	-4.7/0.8

[a] Condensed phase/Gas phase values in kcal/mol



Comment [bld1]: Probably worth having structures superimposed

Figure 2 Reduction of $(C_6H_4S_2)B–H\ (NH_3)$ with Bu_2SnH_2.
Bottom plot is ^{11}B NMR of $(C_6H_4S_2)B–H\ (NH_3)$, top plot is the AB after reduction

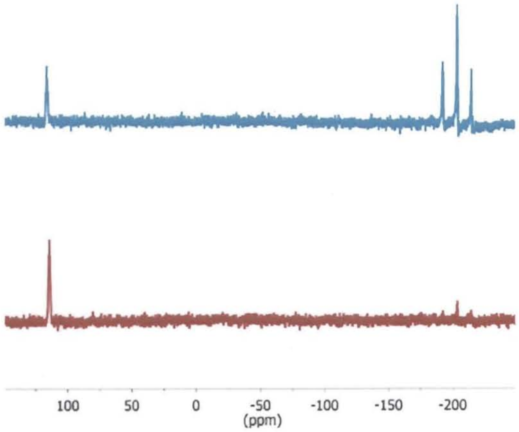
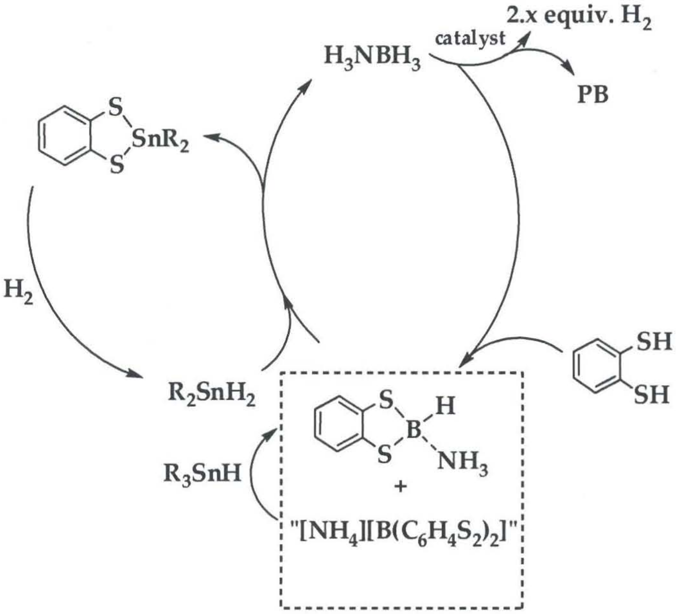


Figure 3 Reduction of $(C_6H_4S_2)B–H\ (NH_3)$ with Bu_2SnH_2. Bottom plot is ^{119}Sn NMR of independently synthesized $Bu_2Sn(C_6H_4S_2)$, top plot shows $Bu_2Sn(C_6H_4S_2)$ and excess Bu_2SnH_2.



Scheme 3 Off-board regeneration scheme for spent ammonia borane

From a practical standpoint, the first step in this regeneration cycle is difficult to optimize because of the apparent side reaction that results in $[NH_4][B(C_6H_4S_2)_2]$ formation. Therefore, to obtain an estimate of the best possible AB yield, excess Bu_3Sn–H was used after the digestion step to both consume unreacted benzenedithiol and to convert any $[NH_4][B(C_6H_4S_2)_2]$ into $(C_6H_4S_2)B$–H•(NH_3). The thermal instability of Bu_2SnH_2 prompted (excess) step-wise addition in the final step to ensure a maximum yield of AB. Using this methodolgy, an overall (isolated) AB yield of 67% was obtained on our first attempt. The complete regeneration cycle is shown in Scheme 3.

To estimate the optimum energetic efficiency for AB regeneration schemes, the following equation has been developed based on the energy of oxidation for 1 mole of H_2 (57.8 kcal) to form H_2O. As part of the DOE CoE in hydrogen storage, we would like to have a method for differentiating (to a first approximation) the various regenerations schemes posited in the literature.

$$\frac{(\text{Equiv. H}_2\text{ stored})(57.8)}{(\text{Equiv. H}_2\text{ used})(57.8)+\sum(\Delta H_{endo})-(\%\text{ heat recovery})\sum(-\Delta H_{exo})}=\mathit{efficiency}$$

Using the aforementioned formula, our regeneration process has a theoretical peak energy efficiency which is higher when compared to the only other peer-reviewed account of AB regeneration (Table 3). We do realize other factors (upscale yield, engineering) will play a profound role in the implementation of any said process on a large scale.

Table 3 Regeneration Process	Efficiency (0% heat recovery)
$NH_4B(OMe)_4 + 3\ H_2 \rightarrow H_3N\text{–}BH_3 + 4\ MeOH$[10]	45 %
$\frac{1}{3}\ B_3N_3H_6 + 2\ H_2 \rightarrow H_3N\text{–}BH_3$	66 %

In conclusion, we have shown that one form of spent AB fuel, polyborazylene, can be regenerated efficiently in one-pot via the stepwise addition of appropriate digesting and reducing agents. Future reports will detail a more complete regeneration cycle, including the recycle of the tin by-product, use of H_2 as the energy source, and improved overall efficiencies.

Acknowledgements

We would like to thank Drs. Troy Semelsberger and Roshan Shrestha for GC characterization of H_2 released during digestion.

References and Notes

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(9.5) See supplemental information for a list of equations used to compare the two regeneration processes

Supplemental Information

Experimental Materials and Methods

General. All reactions were performed under an inert atmosphere, using standard Schlenk line and glovebox techniques. Ethereal solvents and toluene were distilled from Na/benzophenone ketyl radical. ^{1}H, ^{11}B (128 MHz), and ^{119}Sn (149 MHz) NMR spectra were recorded at room temperature (unless otherwise noted) on a Bruker AVANCE 400 MHz spectrometer. ^{1}H spectra were referenced to the residual protons in the solvent and ^{119}Sn NMR was referenced to Me_4Sn. ^{11}B NMR was referenced to BF_3 • etherate placed in a stem coaxial insert (Wilmad). All deuterated solvents were purchased from Cambridge Isotopes (Andover, MA). 1,2-benzenedithiol (96% Acros) was sublimed prior to use and stored cold. 1 M BH_3-THF in THF (Acros) was titrated with a solution of 1,2-benzenedithiol to calculate an accurate concentration. NH_3 in 1,4-dioxanes was used as received from Aldrich Chemical Company. Polyborazylene (PB) was formed by the slow decomposition of borazine, received from Gelest. All other reagents were obtained from Acros and used as received. 1,3,2-benzodithiaborole was synthesized *in situ* by a modification of the literature using BH_3 • THF and benzenedithiol.[1] $^{n}Bu_2SnH_2$ was prepared by the literature method, distilled, and stored in the absence of light at -20 °C.[2]

$HB(C_6H_4S_2)$ • NH_3, 1. 1,3,2-benzodithiaborole (0.07 mmol) was combined with 0.5 M NH_3 in 1,4-dioxanes (300 uL, 0.15 mmol) and the solvent was removed *in vacuo* yielding a white solid (0.009 g, 76 %). ^{1}H NMR (THF): δ x.xx. ^{11}B NMR (THF): δ -5.6 (128 Hz). IR (KBr, cm^{-1}) . EA $C_6H_8BS_2$ Calculated: C 42.63, H 4.77, S 37.93. Found: C xx.xx, H x.xx, S xx.xx. Crystals were grown from a hot saturated THF solution.

Comment [bld1]: Bld2_84 is the reference fo 11B NMR chemical shifts, yield from bld2_192.

Reduction of 1 to Ammonia Borane. 1 (x.xx g, x.xx mmol) was dissolved in THF and combined with $^{n}Bu_2SnH_2$ (x.xx g, x.xx mmol). After heating for 30 minutes @ ~ 60 °C, ^{11}B NMR showed clean conversion to ammonia borane (x.xx mmol, x %).

Comment [bld2]: Either mention in text or somewhere else that the uncoordinated species readily reduces; also this material did sublime, bld2-18, so EA might be possible

$^{n}Bu_2Sn(C_6H_4S_2)$, 3. $^{n}Bu_2SnH_2$ (0.168 g, 0.717 mmol) was combined with benzenedithiol (0.102 g, 0.717 mmol) and stirred overnight. The volatiles were removed *in vacuo*, yielding a white solid (0.262 g, 98 %). ^{1}H NMR (C_6D_6): δ 7.5 (m, 2H), 6.7 (m, 2H), 1.5 (m, 3.5H), 1.3 (m, 3.6H), 1.2 (m, 4.4H), 0.8 (t, 6 H). ^{119}Sn NMR (THF): δ 116. IR (KBr, cm^{-1}) EA:

Comment [bld3]: Exp bld2_44

$Na_2(S_2H_4C_6)$ * THF, x. To a suspension of NaH (0.342 g, 14.3 mmol) in THF (10 mL) at -20 °C was added a solution 1,2-benzenedithiol (1.014 g, 7.13 mmol) in THF (10 mL). After stirring for 24 h, the volatiles were removed *in vacuo* to yield a white powder (1.73 g, 94%). Repeated trituration with hexanes, ultra high vacuum, and heating to 70 °C did not change the isolated mass, resulted in the formulation as a THF adduct.[3]

Comment [bld4]: Bld2_174 provided the basis for this synthesis

$(^{n}Bu_3Sn)_2(C_6H_4S_2)$, 4. $^{n}Bu_3SnCl$ (0.252 g, 0.774 mmol) was combined with $Na_2(S_2H_4C_6)$ * THF (0.100 g, 0.387 mmol) in THF (10 mL) and stirred at RT for 12 h. Removal of the solvent and

Comment [bld5]: Bld2_242 and 304 provided the basis for this synthesis extraction with toluene yielded $(^{n}Bu_3Sn)_2(C_6H_4S_2)$ as a colorless oil (0.231 g, 83%). 1H NMR (C_6D_6): δ 7.73 (m, 2H), 6.82 (m, 2H), 1.6 (m, 11H), 1.3 (m, 14 H), 1.2 (m, 11 H), 0.8 (t, 19 H) ^{119}Sn NMR (THF): δ 72.3. (C_6D_6): δ 77.7. IR (KBr, cm^{-1})

$(C_6H_4SH(SSnBu_3))$, x. $^{n}Bu_3SnH$ (0.041 g, 0.141 mmol) was combined with benzenedithiol (0.020 g, 0.141 mmol). After 12 h the ^{1}H NMR indicated consumption of the Sn-H resonance and the ^{119}Sn NMR revealed a single new peak. ^{119}Sn NMR (THF): δ 84.8. IR (KBr, cm^{-1}) EA:

$[NH_4][B(C_6H_4S_2)_2]$ from 1 and 1,2-benzenedithiol. 1 (x.xx g, x.xx mmol), 1,2-benzenedithiol (x.xx g, x.xx mmol), and THF were heated @ ~ 60 °C for several days. ^{11}B NMR indicated a new boron containing species had formed with a new singlet at 10.5 ppm, much larger than is observed by heating **1** alone. A similar shift was observed by Noth for $LiB(C_6H_4S_2)_2$ at 12.1 ppm.[3] When the reaction of $LiBH_4$ and benzenedithiol was repeated, a singlet at 10.5 (referenced to BF_3-etherate) was obtained.

Regeneration of AB from Polyborazylene. PB (0.049 g, 0.61 mmol) was dissolved in THF and combined with 1,2-benzenedithiol (0.260 g, 1.83 mmol). This was heated overnight at 80 °C. ^{11}B NMR indicated consumption of PB and formation of two new peaks corresponding to **1** and $[NH_4][B(C_6H_4S_2)_2]$. Excess Bu_3Sn-H (240 µL, 0.9 mmol) was added to reduce $[NH_4][B(C_6H_4S_2)_2]$ to **1** and convert unreacted benzenedithiol to $^{n}Bu_3Sn(C_6H_5S)$ or $(^{n}Bu_3Sn)_2(C_6H_4S_2)$. This solution was heated to 60 °C before the addition of $^{n}Bu_2SnH_2$ (1020 µL, 4.86 mmol) in four portions over 40 minutes, reducing **1** to AB (0.038 g, 67 %), which was isolated by extraction of with toluene.

Comment [bld6]: Comes from bld3_60

Reaction of Borazine and 1,2-benzenedithiol. Borazine (0.015 g, 0.186 mmol) and 1,2-benzenedithiol (0.080 g, 0.559 mmol) were combined in THF and heated to 65 C overnight. The resulting ^{11}B NMR revealed two resonances, 10.5 ppm (s) and 5.6 ppm (d, 128 Hz). When the headspace gas was sampled from an equivalent reaction by MS, more H_2 gas was detected relative to the control sample (only borazine and solvent).

Computational Approach and Results

Gas phase calculations were carried out with the Gaussian03 program[1] using density functional theory (DFT)[2] with the B3LYP hybrid exchange-correlation functional[3] and the DZVP2 basis set[4], except for Sn where the cc-pVDZ-PP basis[5] set with an effective core potential was used. Condensed heats of formation at 298 K were estimated as follows. ΔH_f of borazine (c-$B_3N_3H_6$, solid) ($\Delta H_f(s) = -123.6$, $\Delta H_f(g) = -115.5$ kcal/mol) was taken from our previous work where the experimental heat of formation in solution plus an estimate for the enthalpy of melting was combined with our accurate calculation of the gas phase heat of formation.[6] The heat of formation of BH_3NH_3 (solid) was taken from experiment ($\Delta H_f(s) = -36.6 \pm 2.4$, $\Delta H_f(g) = -13.5 \pm 1.0$ kcal/mol).[7,8] The heat of formation of benzenethiol (liquid) was taken from Pedley's compilation ($\Delta H_f(l) = 15.22 \pm 0.19$, $\Delta H_f(g) = 26.60 \pm 0.31$ kcal/mol).[9] The heat of formation of benzenedithiol (liquid) was estimated by combining the heat of vaporization for C_6H_5SH with the gas phase heat of formation of o-$C_6H_4(SH)_2$ obtained from an isodesmic reaction scheme

(ΔH_f(l) = 25.4, ΔH_f(g) = 36.7 kcal/mol). The heat of formation of $(C_6H_5S)_2BH(NH_3)$ (liquid) was estimated from a gas phase heat of formation from isodesmic reactions and a heat of vaporization estimated as 21 kcal/mol from the heat of sublimation of BH_3NH_3 (ΔH_f(l) = -1.3 ΔH_f(g) = 19.7 kcal/mol). The heat of formation of $C_6H_4S_2BH(NH_3)$ (liquid) was estimated in a similar way from a gas phase reaction energy and an estimated heat of vaporization of 18 kcal/mol (ΔH_f(l) = -22.9, ΔH_f(g) = -4.9 kcal/mol). The heat of formation of Bu_3SnH (liquid) and Bu_2SnH_2 (liquid) were estimated from the heats of vaporization[10,11] of $Sn(n\text{-}Bu)_4$, $Sn(Et)_4$, and $Sn(Et)_3H$ and gas phase heats of formation from isodesmic reactions ($\Delta H_f(Bu_3SnH,l)$ = -49.0, $\Delta H_f(Bu_3SnH,g)$ = -31.0 kcal/mol; $\Delta H_f(Bu_2SnH_2,l)$ = -27.6, $\Delta H_f(Bu_2SnH_2,g)$ = -11.6 kcal/mol). The heats of vaporization of $C_6H_4(SSnBu_3)_2$ (liquid) and $C_6H_4S_2SnBu_2$ (liquid) were estimated from the $SnBu_4$ and C_6H_5SH heats of vaporization and gas phase heats of reaction ($\Delta H_f(C_6H_4(SSnBu_3)_2,l)$ = -72.1, $\Delta H_f(C_6H_4(SSnBu_3)_2,g)$ = -47.1 kcal/mol; ($\Delta H_f(C_6H_4S_2SnBu_2,l)$ = -18.7, $\Delta H_f(C_6H_4S_2SnBu_2,g)$ = 1.3 kcal/mol). The heat of formation of $NH_4B(C_6H_4S_2)_2$ (s) was estimated from the $\Delta H_f(NH_4^+)$ = 105.9 kcal/mol[7] and $\Delta H_f((C_6H_4S_2)_2B^-)$ in the gas phase from isodesmic reactions and the lattice energy[12] to get the solid salt ($\Delta H_f(NH_4B(C_6H_4S_2)_2,s)$ = 22.5, $U_{L,298K}$ = 106.8, $\Delta H_f((C_6H_4S_2)_2B^-,g)$ = -21.6 kcal/mol).

For the metal regeneration scheme, the heat of formation of $NH_4B(OMe)_4$ (s) was estimated from the $\Delta H_f(NH_4^+)$[7] and $\Delta H_f(B(OMe)_4^-)$ in the gas phase from isodesmic reactions and the lattice energy[12] to get the solid salt ($\Delta H_f(NH_4B(OMe)_4,s)$ = -225.1, $U_{L,298K}$ = 121.1, $\Delta H_f(B(OMe)_4^-,g)$ = -248.8 kcal/mol). The heat of formation of $Al(OMe)_3$ (l) was obtained from isodesmic reactions and the heat of vaporization estimated from that of $Al(OCH(CH_3)_2)_3$ ($\Delta H_f(Al(OMe)_3,l)$ = -221.1, $\Delta H_f(Al(OMe)_3,g)$ = -205.9 kcal/mol). The heat of vaporization was estimated to be 15.2 kcal/mol. The heat of formation of MeOH (l) was taken from Pedley[9] and the heats of formation of the remaining solids from Wagman et al.[11] or the NIST website.[10]

Gas phase heats of formation and total electronic energies are given in Table S1. Isodesmic reaction schemes are given in Table S2. The components for the efficiency calculations are given in Table S3.

Table S1. Energies in a. u. at the B3LYP/DZVP2 level and B3LYP/cc-pVDZ-PP for Sn and gas phase heats of formation at 298.15 K (values in kcal/mol).[a]

Molecule	E_{elec}	E_{ZPE}	$E_{elec} + E_{ZPE} + \Delta E_{thermal} + RT$	ΔH_f°
BH_3NH_3	-83.245581	0.069892	-83.170900	-13.5 ± 1.0[b]
$B_3N_3H_6$	-242.735788	0.093397	-242.636188	-115.5 ± 1.0[c]
C_6H_5SH	-630.485945	0.099171	-630.379497	26.60 ± 0.31[d]
$C_6H_4(SH)_2$	-1028.677429	0.097958	-1028.570223	36.7[e]
$C_6H_4S_2BH$	-1053.003915	0.096232	-1052.899581	12.9[e]
$C_6H_4S_2BHNH_3$	-1109.595872	0.136812	-1109.448688	-4.9[e]
$(C_6H_5S)_2BHNH_3$	-1341.879511	0.238353	-1341.624397	19.7[e]
$(C_6H_4S_2)_2B^-$	-2080.008829	0.168112	-2079.824953	-21.6[e]
$HSnBu_3$	-688.632205	0.372621	-688.237868	-31.0[e]
H_2SnBu_2	-531.333866	0.257324	-531.060909	-11.6[e]
$C_6H_4(SSnBu_3)_2$	-2403.616783	0.815956	-2402.749092	-47.1[e]
$C_6H_4S_2SnBu_2$	-1557.686957	0.326902	-1557.337390	1.3[e]
H_2S	-399.401557	0.015088	-399.382676	-4.9 ± 0.1[f]
$HB(SH)_2$	-813.112910	0.032346	-823.075201	-21.4[g]
CH_3SH	-438.722080	0.046139	-438.671402	-5.46 ± 0.14[f]
CH_4	-40.532964	0.044821	-40.484329	-17.89[f]
NH_3	-56.580955	0.034525	-56.542616	-10.98 ± 0.084[f]
BH_3	-26.618030	0.026124	-26.588071	25.5 ± 0.7[b]
BH_4^-	-27.2663908	0.033328	-27.229156	-13.5 ± 0.7[b]
C_5H_{12}	-197.824039	0.160657	-197.655313	-35.08 ± 0.14[f]
C_2H_6	-79.854039	0.074742	-79.774857	-20.04 ± 0.07[f]
$HSn(CH_3)_3$	-334.735390	0.114512	-334.611014	5.02
$SnBu_4$	-845.930504	0.487921	-845.417743	-52.2
CH_3OH	-115.763090	0.051327	-115.707467	-48.0[d]
$Al(OCH(CH_3)_2)_3$	-824.054045	0.295608	-823.738493	-257.6
$HOCH(CH_3)_2$	-194.4201402	0.108035	-194.305641	-65.19[f]
$Al(OCH_3)_3$	-588.082858	0.126563	-587.943848	-205.9[e]
H_2O	-76.456993	0.021449	-76.431764	-57.7978 ± 0.0096[f]
$B(OH)_4^-$	-328.480811	0.060611	-328.412667	-320.8

Comment [m7]: REFERENCE

Comment [m8]: REFERENCE

Comment [m9]: ERROR BAR

Comment [m10]: REFERENCE

Comment [m11]: REFERENCE

$B(OCH_3)_4^-$	-485.706074	0.171868	-485.520825	-284.8[e]
H_2	-1.1792864	0.010166	-1.165816	0.0

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[a] E_{elec} = electronic energy; E_{ZPE} = zero point energy; $E_0 = E_{elec} + ZPE$; R = gas constant; T = temperature, in this case, at 298.15 K. Note that Bu = $-CH_2CH_2CH_2CH_3$. [b] Ref. 7. [c] Ref. 6. [d] Ref. 9. [e] This work. [f] Ref 10. [g] Ref. X.

Comment [m12]: Grant, Dixon, etc, submitted

Table S2. Gas phase energies of isodesmic and regular reactions used to obtain condensed phase results. Values in kcal/mol at the B3LYP/DZVP2 level and B3LYP/cc-pVDZ-PP for Sn.[a]

Molecule to obtain in condensed phase **Isodesmic or regular reaction**	**ΔH_{rxn} (298 K)**
$C_6H_4(SH)_2$	
$C_6H_5SH + CH_3SH \rightarrow C_6H_4(SH)_2 + CH_4$	-2.3
$C_6H_4S_2BH$	
$HB(SH)_2 + C_6H_4(SH)_2 \rightarrow C_6H_4S_2BH + 2\ H_2S$	-12.2
$C_6H_4S_2BHNH_3$	
$C_6H_4S_2BH + BH_3NH_3 \rightarrow C_6H_4S_2BHNH_3 + BH_3$	21.2
$(C_6H_5S)_2BHNH_3$	
$C_6H_4S_2BHNH_3 + C_6H_5SH + CH_4 \rightarrow (C_6H_5S)_2BHNH_3 + CH_3SH$	10.5
$HSnBu_3$	
$HSn(CH_3)_3 + 3\ C_5H_{12} \rightarrow HSnBu_3 + 3\ C_2H_6$	9.1
H_2SnBu_2	
$2\ HSnBu_3 \rightarrow H_2SnBu_2 + SnBu_4$	-1.8
$C_6H_4(SSnBu_3)_2$	
$C_6H_4(SH)_2 + 2\ HSnBu_3 \rightarrow C_6H_4(SSnBu_3)_2 + 2\ H_2$	-21.8
$C_6H_4S_2SnBu_2$	
$C_6H_4(SH)_2 + H_2SnBu_2 \rightarrow C_6H_4S_2SnBu_2 + 2\ H_2$	-23.8
$(B(C_6H_4S_2)_2)^-$	
$BH_4^- + 2\ C_6H_4S_2BH \rightarrow (C_6H_4S_2)_2B^- + 2\ BH_3$	17.1
$Al(OCH_3)_3$	
$3\ CH_3OH + Al(OCH(CH_3)_2)_3 \rightarrow Al(OCH_3)_3 + 3\ HOCH(CH_3)_2$	0.1
$B(OCH_3)_4^-$	
$B(OH)_4^- + 4\ CH_3OH \rightarrow B(OCH_3)_4^- + 4\ H_2O$	-3.4

Table S3. Equations used to Assess Regeneration Efficiency.

Current Demonstrated Scheme	**ΔH(kcal/mol)**
$\frac{1}{3}\ B_3N_3H_6\ (l) + C_6H_4(SH)_2\ (l) \rightarrow HB(C_6H_4S_2)NH_3\ (l)$	-7.4
$\frac{1}{2}\ HB(C_6H4S_2)NH_3\ (l) + \frac{1}{2}\ C_6H_4(SH)_2\ (l) \rightarrow \frac{1}{2}\ [NH_4][B(C_6H4S_2)_2]\ (s) + \frac{1}{2}\ H_2\ (g)$	10.0
$\frac{1}{2}\ [NH_4][B(C_6H4S_2)_2]\ (s) + \frac{1}{2}\ Bu_3SnH\ (l) \rightarrow \frac{1}{2}\ HB(C_6H4S_2)NH_3\ (l) + \frac{1}{2}\ C_6H_4(SH)(SSnBu_3)\ (l)$	-13.7
$HB(C_6H4S_2)NH_3\ (l) + H_2SnBu_2\ (l) \rightarrow BH_3NH_3\ (s) + (C_6H_4S_2)SnBu_2\ (l)$	-4.7
$(C_6H_4S_2)SnBu_2\ (l) + 2\ H_2\ (g) \rightarrow C_6H_4(SH)_2\ (l) + H_2SnBu_2\ (l)$	16.4
$\frac{1}{2}\ C_6H_4(SH)(SSnBu_3)\ (l) + \frac{1}{2}\ H_2\ (g) \rightarrow \frac{1}{2}\ C_6H_4(SH)_2\ (l) + \frac{1}{2}\ HSnBu_3\ (l)$	3.7
Overall reaction: $\frac{1}{3}\ B_3N_3H_6\ (l) + 2\ H_2\ (g) \rightarrow BH_3NH_3\ (s)$	**4.3**
Sum of exothermicities	*-25.8*
Sum of endothermicities	*30.1*
Efficiency with 0% heat recovery	66%
Efficiency with 20% heat recovery	68%

Table S3. (Cont.)

Regeneration scheme from: Ramachandran, P. V.; Gagare, P. D. *Inorg. Chem.* **2007**, *46*, 7810-7817.	**ΔH(kcal/mol)**
$NH_4B(OMe)_4$ (s) + NH_4Cl (s) + $LiAlH_4$ (s) → NH_3BH_3 (s) + $Al(OMe)_3$ (l) + MeOH (l) + H_2 (g) + LiCl (s) + NH_3 (g)	-68.5
NaCl (s) + electricity → Na (s) + ½ Cl_2 (g)	98.2
½ Cl_2 (g) + ½ H_2 (g) → HCl (g)	-22.1
HCl (g) + NH_3 (g) → NH_4Cl (s)	-42.1
$Al(OMe)_3$ (l) + 3/2 H_2 (g) + electricity → Al (s) + 3 MeOH (l)	49.9
Na (s) + Al (s) + 2 H_2 (g) → $NaAlH_4$ (s)	-27.6
LiCl (s) + $NaAlH_4$ (s) → $LiAlH_4$ (s) + NaCl (s)	2.4
Overall reaction: $NH_4B(OMe)_4$ (s) + 3 H_2 (g) → NH_3BH_3 (s) + 4 MeOH (l)	**-9.7**
Sum of exothermicities	*-160.3*
Sum of endothermicities	*150.5*
Efficiency with 0% heat recovery	45%
Efficiency with 20% heat recovery	50%

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