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Reductive Dechlorination of BCl_3 for Efficient Ammonia Borane Regeneration

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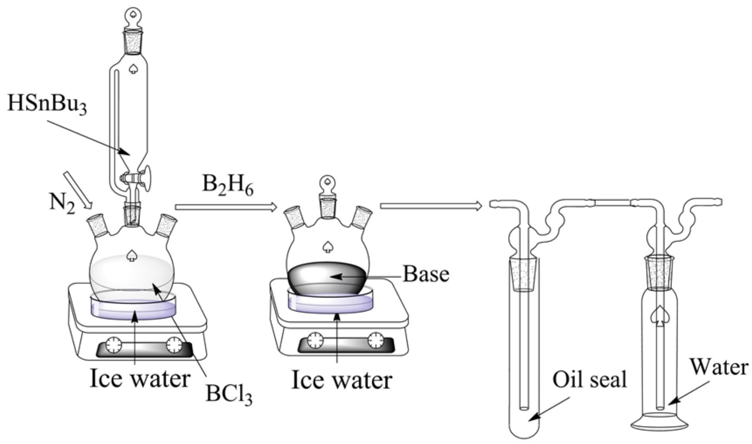

Reactor I **Reactor II**

Fig. S1 A schematic illustration of the preparation of AB. Reactor I and Reactor II correspond to the reactions of eq. (1), eq. (2) and (3), respectively.

$Bu_3SnH + BCl_3 \rightarrow B_2H_6 + Bu_3SnCl$ (1)

$B_2H_6 + 2Et_3N \rightarrow 2Et_3N{\cdot}BH_3$ (2)

$B_2H_6 + 2\ Et_2PhN \rightarrow 2\ Et_2PhN{\cdot}BH_3$ (3)

Thermodynamic Considerations

$$\text{Efficiency} = \frac{(equiv\ H_2\ stored)(57.8)}{(equiv\ H_2\ used)(57.8) + \sum(\Delta H_{endo}) - (\%\ heat\ rercoery)\sum(-\Delta H_{endo})} \quad (4)$$

Table S1 Reaction equations for deriving efficiency.

HCl-Bu_3SnH regeneration scheme	Δ_rH / kcal mol^{-1}
$1/3B_3N_3H_6$ (l) + 4HCl (g) → BCl_3 (g) + NH_4Cl (s) + $1H_2$ (g)	-39.9
NH_4Cl (s) → NH_3 (g) + HCl (g)	42.1
BCl_3 (g) + $3Bu_3SnH$ (l) + Et_2PhN (l) → $Et_2PhN\cdot BH_3$ (l) + $3Bu_3SnCl$	-26.8
$3Bu_3SnCl$ (l) + 3HCOOH (l) → $3Bu_3SnCOOH$ (l) + 3HCl (g)	37.2
$3Bu_3SnCOOH$ (l) → $3Bu_3SnH$ (l) + $3CO_2$ (g)	38.7
$3CO_2$ (g) + $3H_2$ (g) → 3HCOOH (l)	-22.95
$Et_2PhN\cdot BH_3$ (l) + NH_3 (g) → BH_3NH_3 (s) + Et_2PhN (l)	-22.7
total: $1/3B_3N_3H_6$ (l) + $2H_2$ (g) → BH_3NH_3 (s)	+ 5.66
sum of exothermicities:	-112.35
sum of endothermicities:	+118
efficiency with 0% heat recovery: 40 %	
efficiency with 20% heat recovery: 43 %	

The heat of formation ΔH_f (298 K) of $Et_2PhN\cdot BH_3$ was determined by the following reaction of eq. (5). The value of *Δ_rH was -2.52 kcal mol^{-1}.

$Et_2PhN + 1/2B_2H_6 \rightarrow Et_2PhN\cdot BH_3$ (5)

Table S2 Reaction equations for deriving efficiency. [S1]

$HCl-H_2/Ni_3B$ regeneration scheme	Δ_rH / kcal mol^{-1}
$1/3B_3N_3H_6$ (l) + 4HCl (g) → BCl_3 (g) + NH_4Cl (s) + $1H_2$ (g)	-39.9
NH_4Cl (s) → NH_3 (g) + HCl (g)	+42.1
BCl_3 (g) + Et_3N (l) → Et_3NBCl_3 (solv.)	-29.64
Et_3NBCl_3 (solv.) + $3H_2$ (g) + $3Et_3N$ → $Et_3N·BH_3$ (l) + $3Et_3NHCl$ (s)	-89.44
$3Et_3NHCl$(s) → $3Et_3N$ (g) + 3HCl (g)	+145.02
$Et_3N·BH_3$ (l) + NH_3 (l) → NH_3BH_3 (s) + Et_3N (l)	-13.14
heat of condensation of ammonia = -3.15 kal mol^{-1}	-9.46
total: $1/3B_3N_3H_6$ (l) + $2H_2$ (g) → BH_3NH_3 (s)	+ 5.54
sum of exothermicities:	-181.58
sum of endothermicities:	+187.12
efficiency with 0% heat recovery: 35 %	
efficiency with 20% heat recovery: 38 %	

Table S3 Reaction equations for deriving efficiency. [S2]

$C_6H_6S_2$-Bu_3SnH-Bu_2SnH_2 regeneration scheme	Δ_rH / kcal mol^{-1}
$1/3B_3N_3H_6$ (l) + $C_6H_4(SH)_2$ (l) → $C_6H_4S_2BH(NH_3)$ (l)	-6.8
$1/2C_6H_4S_2BH(NH_3)$ (l) + $1/2C_6H_4(SH)_2$ (l) → $1/2[NH_4][B(C_6H_4S_2)_2]$ (s) + $1/2H_2$ (g)	7.0
$1/2[NH_4][B(C_6H_4S_2)_2]$ (s) + $1/2Bu_3SnH$ (l) → $1/2C_6H_4S_2BH(NH_3)$ (l) + $1/2C_6H_4(SH)(SSnBu_3)$ (l)	-12.4
$C_6H_4S_2BH(NH_3)$ (l) + Bu_2SnH_2 (l) → BH_3NH_3 (s) + $C_6H_4S_2SnBu_2$ (l)	-9.7
$C_6H_4S_2SnBu_2$ (l) + $2H_2$ (g) → $C_6H_4(SH)_2$ (l) + Bu_2SnH_2 (l)	21.9
$1/2C_6H_4(SH)(SSnBu_3)$ (l) + $1/2H_2$ (g) → $1/2C_6H_4(SH)_2$ (l) + $1/2Bu_3SnH$ (l)	5.3
$1/3B_3N_3H_6$ (l) + $2H_2$ (g) → BH_3NH_3 (s)	+ 5.4
sum of exothermicities:	-28.9
sum of endothermicities:	34.3
efficiency with 0% heat recovery:	65 %
efficiency with 20% heat recovery:	67 %

Table S4 Reaction equations for deriving efficiency. [S2, S3]

$C_6H_6S_2$-Bu_3SnH-Bu_2SnH_2 regeneration scheme	Δ_rH / kcal mol^{-1}
$1/3B_3N_3H_6$ (l) + $C_6H_4(SH)_2$ (l) → $C_6H_4S_2BH(NH_3)$ (l)	-6.8
$1/2C_6H_4S_2BH(NH_3)$ (l) + $1/2C_6H_4(SH)_2$ (l) → $1/2[NH_4][B(C_6H_4S_2)_2]$ (s) + $1/2H_2$ (g)	7.0
$1/2[NH_4][B(C_6H_4S_2)_2]$ (s) + $1/2Bu_3SnH$ (l) → $1/2C_6H_4S_2BH(NH_3)$ (l) + $1/2C_6H_4(SH)(SSnBu_3)$ (l)	-12.4
$C_6H_4S_2BH(NH_3)$ (l) + Et_2NH (l) → $C_6H_4S_2BH(Et_2NH)$ (l) + NH_3 (g)	1.6
$C_6H_4S_2BH(Et_2NH)$ (l) + $2Bu_3SnH$ (l) → $C_6H_4(SSnBu_3)_2$ (l) + $Et_2NH{\cdot}BH_3$(l)	9.5
$Et_2NH{\cdot}BH_3$(l) + NH_3 (l) → BH_3NH_3 (s) + Et_2NH (l)	-12.3
$1/2C_6H_4(SH)(SSnBu_3)$ (l) + $1/2HCl$ (g) → $1/2C_6H_4(SH)_2$ (l) + $1/2Bu_3SnCl$ (l)	-5
$C_6H_4(SSnBu_3)_2$ (l) + $2HCl$ (g) → $C_6H_4(SH)_2$ (l) + $2Bu_3SnCl$ (l)	-20.2
$5/2Bu_3SnCl$ (l) + $5/2HCOOH$ (l) → $5/2Bu_3SnCOOH$ (l) + $5/2HCl$ (g)	31
$5/2Bu_3SnCOOH$ (l) → $5/2Bu_3SnH$ (l) + $5/2CO_2$ (g)	32.25
$5/2CO_2$ (g) + $5/2H_2$ (g) → $5/2HCOOH$ (l)	-19.125
$1/3B_3N_3H_6$ (l) + $2H_2$ (g) → BH_3NH_3 (s)	+ 5.52
sum of exothermicities:	-75.825
sum of endothermicities:	+81.35
efficiency with 0% heat recovery:	51 %
efficiency with 20% heat recovery:	55 %

Table S5 Reaction equations for deriving efficiency. [S2]

CH_3OH-$LiAlH_4$-NH_4Cl regeneration scheme	Δ_rH / kcal mol^{-1}
$NH_4B(OMe)_4$ (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)	-62.4
NaCl (s) + electricity → Na (s) + 1/2Cl_2 (g)	98.2
1/2Cl_2 (g) + 1/2H_2 (g) → HCl (g)	-22.1
HCl (g) + NH_3 (g) → NH_4Cl (s)	-42.1
$Al(OMe)_3$ (l) + 3/2H_2 (g) + electricity → Al (s) + 3MeOH (l)	45.0
Na (s) + Al (s) + 2H_2 (g) → $NaAlH_4$ (s)	-27.6
LiCl (s) + $NaAlH_4$ (s) → $LiAlH_4$ (s) + NaCl (s)	2.4
$NH_4B(OMe)_4$ (s) + 3H_2 (g) → NH_3BH_3 (s) + 4MeOH (l)	- 8.6
sum of exothermicities:	-154.2
sum of endothermicities:	145.6
efficiency with 0% heat recovery:	46 %
efficiency with 20% heat recovery:	50 %

Table S6 heat of formation $\Delta_f H$.

substance	heat of formation $\Delta_f H$ in kcal/mol	literature
BH_3NH_3 (s)	-36.6 ± 2.4	S1
$B_3N_3H_6$ (l)	-125.9	S1
HCl (g)	-22.06	S1
BCl_3 (g)	-96.31	S1
NH_3 (l)	-6.25	S1
NH_3 (g)	-10.98	S1
NH_4Cl (s)	-75.18	S1
NaOH(aq)	-104.9	S1
H_2O	-68.315	S1
NaCl (aq)	-97.4	S1
N_2 (g)	0	
H_2 (g)	0	
Cl_2 (g)	0	
Bu_3SnH (l)	-45.3	S2
Bu_2SnH_2 (l)	-21.8	S2
$C_6H_6S_2$ (l)	29.7	S2
$(C_6H_5S)_2BH(NH_3)$ (l)	-2.6	S2
$(C_6H_5S_2)_2BH(NH_3)$ (l)	-19.1	S2
$C_6H_4(SSnBu_3)_2$ (l)	-76.7	S2
$C_6H_4S_2SnBu_2$ (l)	-14.0	S2
$C_6H_4(SH)SSnBu_3$ (l)	-23.6	S2
$NH_4B(C_6H_4S_2)$ (l)	24.7	S2
$NH_4B(OCH_3)_4$ (s)	-256.2	S2
$Al(OCH_3)_3$ (s)	-216.1	S2
Et_2PhN (l)	0.43	S4
HCOOH (l)	-101.7	S5
CO_2 (g)	-94.05	S6
B_2H_6 (g)	9.8	S6
N_2H_4	12.1	S7
Et_2NH	-31.31	S8
$Et_2PhN\cdot BH_3$ (l)	-2.52	own experiment

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