Recycle of Tin Thiolate Compounds Relevent to Ammonia-Borane Regeneration.

Supplementary Information

Experimental

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 unless otherwise noted. ^{1}H, and ^{11}B (128 MHz) NMR spectra were recorded at room temperature on a Bruker AVANCE 400 MHz spectrometer. ^{1}H spectra were referenced to the residual protons in the solvent and ^{119}Sn NMR shifts were referenced to $SnMe_4$. *All deuterated solvents were purchased from Cambridge Isotopes (Andover, MA).* *Bu_3SnH (Aldrich), 1,2-benzenedithiol (TCI), 1 M HCl in Et_2O (Aldrich), tributyltin oxide (Aldrich), benzenethiol (Aldrich), Bu_3SnCl (Aldrich), formic acid (Aldrich) were used as received.* *$C_6H_4SH(S\text{-}SnBu_3)$ was prepared by the literature method.*[1] *$[C_6H_4S_2]Na_2$ was prepared by reacting ortho-benzenedithiol with two equivalents of NaH in THF.*

Synthesis of Bu_3SnSPh. Tributyltin oxide (23.6 g, 40 mmol) was combined with benzenethiol (9.3 g, 84 mmol) in toluene (200 mL) and refluxed overnight in a Dean-Stark apparatus. The reaction was allowed to cool to room temperature and then the solvent removed *in vacuo* and the residual oily liquid distilled under reduced pressure (110 ^{o}C, 80 mtorr) to yield Bu_3SnSPh (30.6 g, 97 % yield). δ_H (400 MHz; THF; Me_4Si) 7.50 – 7.31 (2 H, m), 7.20 – 6.99 (3 H, m), 1.65 – 1.40 (5 H, m), 1.40 – 1.21 (6 H, m), 1.21 – 0.96 (6 H, m), 0.96 – 0.76 (9 H, m). δ_H (400 MHz; C_6D_6; Me_4Si) 7.49 (2 H, d, *J* 7.4), 6.96 (3 H, dt, *J* 22.6, 7.1), 1.62 – 1.34 (6 H, m), 1.34 – 1.14 (6 H, m), 1.14 – 0.90 (6 H, m), 0.90 – 0.73 (9 H, m). δ_{Sn} (149 MHz; C_6D_6; Me_4Sn) 77.8.

Reaction of Bu_3SnSPh with HCl. A solution of HCl in Et_2O (3 mL, 1.0 M) was added to Bu_3SnSPh (50 mg, 0.125 mmol) and stirred for 2 hours. The solution was taken to dryness and redissolved in C_6D_6 to show Bu_3SnCl and benzenethiol in 1:1 ratio. δ_H (400 MHz; C_6H_6; Me_4Si) 6.99 - 6.85 (5H, m, Ar-H) 3.07 (1 H, s, SH), 1.59 – 1.47 (6 H, m, CH_2), 1.27 – 1.04 (12 H, m, CH_2), 0.87 – 0.83 (9 H, m, CH_3). δ_{Sn} (149 MHz; C_6D_6; Me_4Sn) 149.

Synthesis of $C_6H_4(S\text{-}SnBu_3)_2$. $[C_6H_4S_2][Na]_2$ (1.84 mmol, 0.478 g) was added to a stirred THF solution of Bu_3SnCl (3.69 mmol, 1.20 g) and stirred overnight. The solution was filtered and the volatiles were removed. The resultant solid was dissolved in hexane, filtered once more and solvent removed under vacuum to yield a colourless oil (1.104 g, 83% yield). δ_H (400 MHz; C_6D_6; Me_4Si) 7.75 (2 H, m, Ar-H), 6.87 – 6.76 (2 H, m, Ar-H), 1.75 – 1.44 (12 H, m, CH_2), 1.42 – 1.10 (24 H, m, CH_2), 1.01 – 0.70 (18 H, m, CH_3). δ_{Sn} (149 MHz; C_6D_6; Me_4Sn) 73.5.

Reaction of $C_6H_4SH(S\text{-}SnBu_3)$ with HCl. A solution of HCl in Et_2O (1.5 mL, 1.0 M) was combined with $C_6H_4SH(S\text{-}SnBu_3)$ (500 mg, 1.16 mmol) and stirred for 1 hour. The resultant solution was taken to dryness to yield a colourless oil which is a mixture of *ortho*-benzenedithiol and Bu_3SnH. δ_H (400 MHz; THF; Me_4Si) 7.28 (2 H, m, Ar-H), 7.12 – 6.83 (2 H, m, Ar-H), 4.36 (2 H, s, SH), 1.92 – 1.45 (12 H, m, CH_2), 1.45 – 1.08 (24 H, m, CH_2), 1.08 – 0.76 (18 H, m, CH_3). δ_{Sn} (149 MHz; THF; Me_4Sn) 102. The oil was washed with Et_2O and taken to dryness, this was repeated three times (3 x 1.0 mL) to leave Bu_3SnCl (410 mg, 83 % yield). δ_H (400 MHz; THF; Me_4Si) 1.86 – 1.45 (6 H, m, CH_2), 1.44 – 1.03 (12 H, m, CH_2), 0.98 – 0.68 (9 H, m, CH_3). δ_{Sn} (149 MHz; THF; Me_4Sn) 102.

Reaction of $C_6H_4(S\text{-}SnBu_3)_2$ with HCl. A solution of HCl in Et_2O (1.0 mL, 1.0 M) was added to $C_6H_4(S\text{-}SnBu_3)_2$ (250 mg, 0.347 mmol) and stirred for 1 hour. The resultant solution was taken to dryness to yield a colourless oil identified as a mixture of *ortho*-benzenedithiol and Bu_3SnH. δ_H (400 MHz; THF; Me_4Si) 7.36 – 7.25 (2 H, m, Ar-H), 7.04 – 6.93 (2 H, m, Ar-H), 4.37 (2 H, s, SH), 1.86 – 1.45 (26 H, m, CH_2), 1.44 – 1.03

(51 H, m, CH_2), 0.98 – 0.68 (39 H, m, CH_3). δ $_{Sn}$ (149 MHz; THF; Me_4Sn) 102. The oil was washed with Et_2O and taken to dryness, this was repeated three times (3 x 1.0 mL) to remove any volatile products resulting in Bu_3SnCl (256 mg, 87 % yield). δ $_H$ (400 MHz; THF; Me_4Si) 1.86 – 1.45 (6 H, m, CH_2), 1.44 – 1.03 (12 H, m, CH_2), 0.98 – 0.68 (9 H, m, CH_3). δ $_{Sn}$ (149 MHz; THF; Me_4Sn) 102.

Synthesis of $Bu_3SnOCH(O)$. Method A. Tributyltin oxide (11.70 g, 19.63 mmol) was combined in Et_2O (100 mL) with formic acid (98 %, 1.55 mL, 41.2 mmol) and stirred at room temperature for 15 minutes. The volatiles were removed *in vacuo* to yield a white oil which was placed under vacuum (2 Torr), resulting in a colourless oil after approximately 15 minutes at room temperature. The oil was steadily heated under vacuum in 5 ^oC increments until the excess formic acid was distilled, resulting in a thick oil. (10.2 g, 78 % yield). **Method B.** To a solution of $^nBu_3SnCl$ (13.07 g, 30.72 mmol) and HOC(O)H (1.41 g, 30.7 mmol) in Et_2O (~100 mL) was added NEt_3 (3.11 g, 30.7 mmol). A white precipitate rapidly formed. The slurry was stirred for 30 minutes and then filtered. The solution was washed with water and dried with Na_2SO_4, followed by the removal of volatiles under reduced pressure to yield $Bu_3SnOC(O)H$ (10.19 g, 30.4 mmol, 99 % yield) δ $_H$ (400 MHz; C_6D_6; Me_4Si) 8.27 (1 H, s, C(O)H), 1.75 – 1.57 (12 H, m, CH_2), 1.43 - 1.33 (6 H, m, CH_2), 1.32 – 1.18 (6 H, m, CH_2), 0.95 (9 H, t, *J* 7.5, CH_3). δ $_C$ (101 MHz; C_6H_6; Me_4Si) 168.6, 28.6, 27.5, 18.8, 14.0. δ $_{Sn}$ (149 MHz; THF; Me_4Si) -13.9.

Conversion of $Bu_3SnOC(O)H$ to Bu_3SnH. Distillation of $Bu_3SnOC(O)H$ (5.0 g, 14.9 mmol) through a column of 3 mm Raschig Rings under reduced pressure (112 °C, 0.3 mmHg) resulted in Bu_3SnH (2.59 g, 8.9mmol, 60 % yield). δ $_{Sn}$ (149 MHz; THF; Me_4Si) -90.3.

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[1] B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus, F. H. Stephens, *Angew. Chem Int. Ed.*, 2009, **48**, 6812.