Supplementary Material (ESI) for Chemical Communications

Siletanylmethyllithium: An Ambiphilic Organosilane

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Supporting Information

Experimental section

All the ^{1}H and ^{13}C NMR spectra were recorded on a Mercury Varian 300 MHz using $CDCl_3$ as deuterated solvent. ^{1}H NMR spectra are reported in ppm (δ) relative to the $CHCl_3$ peak at 7.26 ppm. ^{13}C NMR spectra are reported in ppm (δ) relative to the $CDCl_3$ peak at 77.0 ppm. The IR spectra were recorded on a Perkin Elmer Paragon 1000 FTIR spectrometer on NaCl discs. Low and high resolution mass spectra were performed on a JEOL JMS600 apparatus. The melting points were determined on a Köfler melting point apparatus. Yields refer to isolated material judged to be 95% pure by ^{1}H NMR spectroscopy.

1-(Tributyltin)methyl-1-methylsiletane (1). A solution of tributyltinmethyl iodide (**6**, 5.63 g, 13.1 mmol, 1.0 equiv.) in 10 mL of ethyl ether (Et_2O) was added dropwise to a solution of *t*-BuLi (24 mL, 1.3 M in pentane, 31 mmol, 2.4 equiv.) in 20 mL of ether at –78 ºC. The reaction mixture was maintained at this temperature for 90 min, warmed to 0ºC over 30 min, and then recooled to –78 ºC. The resulting solution was added *via* canula (in portions over 15 min) to a solution of 1-chloro-1-methylsiletane (**3**, 2.29 g, 18.9 mmol, 1.4 equiv.) in 12 mL of THF at –78 ºC. The resulting mixture was stirred for an additional 20 min and then allowed to warm to room temperature over 1 h. The crude product mixture was quenched with 70 mL of saturated NH_4Cl solution and extracted with two portions of hexanes (70 mL and 40 mL). The combined organic phases were washed (70 mL of saturated $NaHCO_3$ solution and 70 mL of saturated NaCl solution),

dried over $MgSO_4$, filtered, and concentrated under reduced pressure to leave a crude oil, which was distilled under vacuum (bp 100–104 C, 0.1 mmHg) to afford 4.10 g (80%) of **1** as a colorless liquid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.12-1.89 (m, 2H), 1.52-1.41 (m, 6H), 1.37-1.25 (m, 6H), 0.96 (apparent t, 4H), 0.90 (t, J = 7.3 Hz, 9H), 0.84 (t, J = 8.0 Hz, $J(^{119}Sn\text{-}^1H)$ = 50.6 Hz, 6H), 0.25 (s, 3H), –0.02 (s, $J(^{119}Sn\text{-}^1H)$ = 64.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.2 ($J(^{119}Sn\text{-}^{13}C)$=19.8 Hz), 27.4 ($J(^{119}Sn\text{-}^{13}C)$=56.5 Hz), 17.5, 17.0 ($J(^{119}Sn\text{-}^{13}C)$=16.5 Hz), 13.7, 10.3 ($J(^{119}Sn\text{-}^{13}C)$=327.0 Hz), 0.5, –6.3. FTIR (thin film, cm^{-1}) 2957, 2926, 1464, 1249, 1119. HRMS (CI^+): Calc'd for $C_{17}H_{38}SiSn$ [M + 1]: 391.1843; Found: 391.1841±0.0005.

1-(Tribenzylsilyl)methyl-1-methylsiletane (8). A solution of *n*-BuLi (0.50 mL, 1.0 M in hexane, 0.50 mmol, 1.2 equiv.) was added over 1 min to a solution of 1-(tributyltin)methyl-1-methylsiletane (**1**, 200 mg, 0.50 mmol, 1.2 equiv.) in 1 mL of THF at –78 °C. The reaction mixture was stirred at –78 °C for 30 min, and then a solution of tribenzylsilyl chloride (140 mg, 0.42 mmol, 1.0 equiv.) in 2 mL of THF was added dropwise over 10 min. The resulting mixture was kept at –78 °C for 2 hours, quenched with water at –78 °C and allowed to warm to room temperature. The quenched reaction mixture was extracted with 10 mL of ethyl ether, and the organics were washed with 10 mL of saturated NH_4Cl solution. The aqueous phase was extracted with 3 mL of ethyl ether. The combined organic phases were washed (10 mL of saturated $NaHCO_3$ solution and 10 mL of saturated NaCl solution), dried over $MgSO_4$, filtered and concentrated under reduced pressure to give 332 mg of the crude oil. The product (**8**) was purified by chromatography 25 g of silica gel (gradient elution with hexane and then 10% toluene/hexane) to afford 95 mg (57 % yield) of a white solid: M.p. = 39–41 °C.

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^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (t, J = 7.6 Hz, 6H), 7.10 (t, J = 7.4 Hz, 3H), 6.96 (d, J = 7.2 Hz, 6H), 2.14 (s, 6H), 2.14-1.92 (m, 2H), 0.97 (apparent t, 4H), 0.23 (s, 3H), –0.03 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.3, 128.6, 128.3, 124.3, 23.6, 18.0, 16.5, 0.76, –0.35. FTIR (thin film, cm^{-1}) 3026, 2926, 1550, 1493. HRMS (CI^{+}): Calc'd for $C_{26}H_{32}Si_2$ [M + 1]: 401.2121; Found: 401.2118±0.0007.