Silylated Cyclohexadienes as New Radical Chain Reducing Reagents: Preparative and Mechanistic Aspects

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Supporting Information

General. ¹H- and ¹³C-NMR spectra: recorded on a Bruker AMX 500, AMX 400, AC 300 or a Varian Gemini 300. Chemical shifts δ in ppm rel. to SiMe₄ as internal standard. TLC: Merck silica gel 60 F₂₅₄ plates; detection with UV or dipping into a soln. of KMnO₄ (1.5 g in 333 mL 1M NaOH) or a soln. of Ce(SO₄)₂·H₂O (10 g), phosphormolybdic acid hydrate (25 g), conc. H₂SO₄ (60 mL), and H₂O (940 mL), followed by heating. FC: Merck or Fluka silica gel 60 (40 – 63 μ m); at *ca.* 0.4 bar. GC: Hewlett Packard 5890 chromatograph using Hewlett Packard HP-5, Macherey-Nagel Optima δ -3, or Supelco γ -DEX 120 columns. Melting points: Büchi 510 apparatus; uncorrected. I.R. spectra: recorded on a Perkin Elmer 782 or Bruker IFS-200 spectrophotometer. MS: Recorded on a VG Tribid, Varian CH7 (EI); IonSpec Ultima, Finnigan MAT TSQ 700 or a Finnigan MAT 95S (ESI) in *m/z* (% of basis peak). SEC: Pump: Merck Hitachi L-6200 A. Columns: Polymer Laboratories PL gel 5 μ m GUARD and MIXED-C. Mobile phase: THF (1 mL/min). Detector: Shodex RI-101. Molar weights and PDI were determined using polystyrene samples of known molecular weight distribution. For data analysis Polymer Laboratories Cirrus GPC Online software (Version 1.0) was used. Solvents were purified by standard methods. Compounds sensitive to air and moisture were handled under argon using Schlenk techniques.

(*tert*-Butyl)(2,6-dimethoxy-1-methylcyclohexa-2,5-dienyl)dimethylsilane (4)

1,5-Dimethoxy-1,4-cyclohexadiene¹ (21 g, 0.15 mol) was dissolved in THF (450 mL). The soln. was cooled to –65 °C. *tert*-butyllithium (94 mL, 1.76M in pentane, 0.165 mol) was

added in 40 min, while the temp. was kept between -60 and -65 °C. The resulting yellow soln. was treated with TMEDA (24.7 mL, 0.165 mol). The soln. was stirred at -65 °C for 90 min and treated with a soln. of TBDMSCl (24.9 g, 0.165 mol) in THF (30 mL) while the temperature was kept below -60 °C. The soln. was allowed to warm to rt (30 min). Stirring was maintained for another 60 min at this temperature. The soln. was cooled to -20 °C over 30 min. Butyllithium (102.5 mL, 1.61M in hexane, 0.165 mol) was added over 30 min. The resulting orange soln. was stirred for another 75 min (-15 to -20 °C) before $(\text{CH}_3\text{O})_2\text{SO}_2$ (15.7 mL, 0.165 mol) was added. After 5 min, the cooling bath was removed and the decolorized reaction mixture was allowed to warm to rt. Pentane (300 mL) and H_2O (100 mL) were added. The org. layer was separated, washed with H_2O (3×100 mL) and brine (20 mL), and dried (MgSO_4). Removal of the solvent *in vacuo* and distillation (*ca.* 85 °C at 1.2 mbar) yielded an oil which crystallized upon standing at 0 °C over night. Washing with methanol afforded, after drying **4** (31.46 g, 78%) as white crystals. Mp: 32 – 33 °C. I.R. (CHCl_3): 2934_s, 2855_s, 1677_s, 1643_w, 1464_m, 1344_m, 1127_s, 1076_m, 977_w cm^{-1} . ^1H -NMR (500 MHz, CDCl_3): 4.46 (*t*, $J = 3.7$ Hz, 2 H, CH); 3.45 (*s*, 6 H, OCH_3); 2.83–2.82 (*m*, 2 H, CH_2); 1.32 (*s*, 3 H, CH_3); 0.85 (*s*, 9 H, $\text{C}(\text{CH}_3)_3$); 0.00 (*s*, 6 H, $\text{Si}(\text{CH}_3)_2$). ^{13}C -NMR (125 MHz, CDCl_3): 158.9 (C), 88.4 (CH), 53.7 (CH_3), 35.7 (C), 27.3 (CH_3), 24.5 (CH_2), 19.8 (CH_3), 19.3 (C), –4.9 (CH_3). MS (EI): 268.2 (15, $[\text{M}]^+$), 253.1 (7, $[\text{M}-\text{CH}_3]^+$), 179.1 (4), 153.1 (29), 152.1 (55), 138.1 (9), 122.1 (21), 121.1 (12), 107.0 (19), 91.0 (11), 89.0 (20), 73.0 (100), 59.0 (16). Anal. calcd for $\text{C}_{15}\text{H}_{28}\text{O}_2\text{Si}$ (268.47): C 67.11, H 10.51. Found: C 67.16, H 10.69.

(2,6-Dimethoxy-1-methylcyclohexa-2,5-dienyl)trimethylsilane (5)

1,5-Dimethoxy-1,4-cyclohexadiene¹ (1 g, 7.1 mmol) was dissolved in THF (30 mL). The soln. was cooled to *ca.* -70 °C. After addition of *tert*-butyllithium (4.9 mL, 1.6M in hexane, 7.9 mmol) and stirring for 1 h, HMPA (1.51 mL, 8.6 mmol) was added, resulting a red soln. After stirring for 10 min at -70 °C, TMSCl (1.0 mL, 7.9 mmol) was added. The red reaction mixture decolorized. After 5 min, the cooling bath was removed and the soln. was allowed to warm to rt and pentane and H_2O were added. The org. layer was separated, washed with H_2O (2 $\times$) and brine, and dried (MgSO_4). After removal of the solvent *in vacuo*, the crude 2,4-dimethoxy-3-trimethylsilyl-1,4-cyclohexadiene (1.53 g, 7.1 mmol) was dissolved in THF (25 mL). The soln. was cooled to *ca.* -70 °C. After addition of butyllithium (4.9 mL, 1.63M in hexane, 7.9 mmol) and stirring for 1 h at -70 °C, HMPA (1.5 mL, 8.6 mmol) was added resulting a red soln. After stirring for 10 min at -70 °C, $(\text{CH}_3\text{O})_2\text{SO}_2$ (0.65 mL, 7.9 mmol) was added. The orange reaction mixture decolorized. After 5 min, the cooling bath was

removed and the soln. was allowed to warm to rt and pentane and H₂O were added. The org. layer was separated, washed with H₂O (2×) and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* and distillation (40 – 41 °C at 0.2 mbar) afforded **5** (1.15 g, 5.1 mmol, 70% over two steps) as a colorless oil. ¹H-NMR (300 MHz, CDCl₃): 4.54 (*t*, *J* = 3.6 Hz, 2 H, CH); 3.48 (*s*, 6 H, OCH₃); 2.83–2.80 (*m*, 2 H, CH₂); 1.30 (*s*, 3 H, CH₃); –0.02 (*s*, 9 H, Si(CH₃)₃). ¹³C-NMR (75 MHz, CDCl₃): 158.4 (C), 88.7 (CH), 54.1 (CH₃), 35.9 (C), 24.5 (CH₂), 16.4 (CH₃), –2.4 (CH₃). Due to its instability, **5** was not further characterized.

(2,6-Dimethoxy-1-methylcyclohexa-2,5-dienyl)dimethyl(1,1,2-trimethylpropyl)silane (6)

1,5-Dimethoxy-1,4-cyclohexadiene¹ (2.72 g, 20 mmol) was dissolved in THF (70 mL). The soln. was cooled to *ca.* –70 °C. After addition of *tert*-butyllithium (14.8 mL, 1.5M in hexane, 22 mmol) and HMPA (4.2 mL, 24 mmol), the resulting soln. was stirred for 1 h at –70 °C. Thexyldimethylchlorosilane (4.3 mL, 22 mmol) was added. After stirring for 1 h at –70 °C, butyllithium (13.5 mL, 1.63M in hexane, 22 mmol) was added. Stirring was continued for 1 h at –70 °C, before (CH₃O)₂SO₂ (4.32 mL, 22 mmol) was added. After 5 min, the cooling bath was removed and the soln. was allowed to warm to rt and pentane and H₂O were added. The org. layer was separated, washed with H₂O (2×) and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* and FC (petrolether) afforded **6** (2.1 g, 33%) as a colorless oil. I.R. (CHCl₃): 3066*w*, 2952*s*, 2904*s*, 2831*m*, 1677*s*, 1643*m*, 1466*s*, 1344*m*, 1123*s* cm^{–1}. ¹H-NMR (400 MHz, CDCl₃): δ = 4.47–4.46 (*m*, 2 H, CH); 3.46 (*s*, 6 H, OCH₃); 2.85–2.81 (*m*, 2 H, CH₂); 1.93 (*septet*, *J* = 6.8 Hz, 1 H, CH); 1.35 (*s*, 3 H, CH₃); 0.80 (*s*, 6 H, C(CH₃)₂); 0.78 (*d*, *J* = 6.8 Hz, 6 H, CH(CH₃)₂); 0.10 (*s*, 6 H, Si(CH₃)₂). ¹³C-NMR (100 MHz, CDCl₃): δ = 159.1 (C), 88.2 (CH), 53.6 (CH₃), 35.9 (C), 32.9 (CH), 26.0 (C), 24.6 (CH₂), 20.6 (CH₃), 18.6 (CH₃), –6.1 (CH₃). MS (EI): 297.3 (<1, [M]⁺), 296.3 (1, [M–H]⁺), 212.2 (19), 153.2 (20), 152.2 (47, [M–Si(CH₃)₂(C₆H₁₃)]⁺), 89.1 (12), 73.1 (100), 59.1 (13), 28.11 (20). Anal. calcd for C₁₇H₃₂O₂Si (296.52): C 68.86, H 10.88. Found: C 68.91, H 10.79.

(2,6-Dimethoxy-1-methylcyclohexa-2,5-dienyl)triisopropylsilane (7)

1,5-Dimethoxy-1,4-cyclohexadiene¹ (4 g, 28 mmol) was dissolved in THF (100 mL). The soln. was cooled to *ca.* –70 °C. After addition of *tert*-butyllithium (20 mL, 1.6M in hexane, 30 mmol) and stirring for 1 h, HMPA (6 mL, 33 mmol) was added, resulting a red soln. After stirring for 10 min at –70 °C, TIPSCl (6.68 mL, 30 mmol) was slowly added. The red reaction mixture decolorized. The soln. was allowed to warm to rt over 30 min. Pentane and

H₂O were added. The org. layer was separated, washed with H₂O (2×) and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* and distillation (140 °C at 0.2 mbar) afforded 2,4-dimethoxy-3-tri(isopropyl)silyl-1,4-cyclohexadiene (7.4 g, 25 mmol, 89%) as a colorless oil. The crude product (3.6 g, 12.3 mmol) was dissolved in THF (50 mL). The soln. was cooled to *ca.* −40 °C. After addition of butyllithium (20 mL, 1.63M in hexane, 30 mmol) and stirring for 2.5 h at −40 to −30 °C, HMPA (5.4 mL, 30.8 mmol) was added resulting a orange soln. After stirring for 15 min at −30 °C, (CH₃O)₂SO₂ (2.93 mL, 30.8 mmol) was added. The reaction mixture decolorized. After 5 min, the cooling bath was removed and the soln. was allowed to warm to rt and pentane and H₂O were added. The org. layer was separated, washed with H₂O (2×) and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* and FC (pentane) afforded **7** (1.46 g, 47 mmol, 38%) as a colorless amorphous solid. I.R. (CHCl₃): 2947_s, 2866_s, 2831_s, 1681_s, 1642_m, 1581_w, 1465_s, 1343_m, 1128_s, 980_m, 882_m cm^{−1}. ¹H-NMR (400 MHz, CDCl₃): 4.47 (*t*, *J* = 3.6 Hz, 2 H, CH); 3.47 (*s*, 6 H, OCH₃); 2.86–2.83 (*m*, 2 H, CH₂); 1.44 (*s*, 3 H, CH₃); 1.26–1.06 (*m*, 3 H, CH(CH₃)₂); 1.09 (*d*, *J* = 6.6 Hz, 18 H, CH(CH₃)₂). ¹³C-NMR (100 MHz, CDCl₃): 159.3 (C), 88.4 (CH), 53.5 (CH₃), 24.9 (CH₂), 21.8 (CH), 19.6 (CH₃), 13.0 (CH). MS (EI): 310.3 (24, [M]⁺), 294.2 (5, [M−CH₃]⁺), 267.2 (12), 251.2 (16), 195.1 (10), 157.2 (41), 153.1 (20), 152.1 (100), 115.1 (47), 87.1 (11). Anal. calcd for C₁₈H₃₄O₂Si (310.55): C 69.62, H 11.03. Found: C 69.43, H 11.16.

(*tert*-Butyl)(2-methoxy-1-methylcyclohexa-2,5-dienyl)dimethylsilane (8)

1-Methoxy-1,4-cyclohexadiene (1.10 g, 10.0 mmol) was dissolved in THF (30 mL) and cooled to *ca.* −70 °C. TMEDA (1.70 mL, 11.3 mmol) and sec-butyllithium (8.73 mL, 1.26M in cyclohexane, 11.0 mmol) were added. The resulting orange soln. was stirred for 70 min at −70 °C and treated with TBDMSCl (1.71 g, 11.3 mmol) in THF (5 mL). After stirring for 1 h at −70 °C sec-butyllithium (8.73 mL, 1.26 M in cyclohexane, 11.0 mmol) was added. Stirring was continued for 1 h at −70 °C before (CH₃O)SO₂ (1.14 mL, 12.0 mmol) was added. After 5 min, the cooling bath was removed and the soln. was allowed to warm to room temperature. The orange mixture decolorized. After 1.5 h MTBE and water were added. The org. layer was separated and the aqueous layer was extracted with MTBE (2x). The combined org. layers were washed with H₂O (2x) and brine, and dried (MgSO₄). Removal of the solvent *in vacuo*, bulb to bulb distillation (205 °C, 0.01 mbar) and FC (pentane) afforded **8** (1.72 g, 72%) as a colorless solid.

Mp: 27 °C. I.R. (Film): 2951_s, 2895_s, 2856_s, 2829_s, 1676_s, 1637_m, 1464_s, 1346_m, 1248_s, 1206_s, 1163_s, 1144_s, 1017_m, 958_m, 834_s, 822_s, 807_s, 764_s, 731_s, 713_m, 672_m, 591_m cm⁻¹. ¹H-NMR (200 MHz, CDCl₃): δ = 5.49–5.47 (*m*, 2 H, CH); 4.43 (*t*, *J* = 3.5 Hz, 1 H, CH); 3.46 (*s*, 3 H, OCH₃); 2.85–2.81 (*m*, 2 H, CH₂); 1.22 (*s*, 3 H, CH₃); 0.88 (*s*, 9 H, C(CH₃)₃); 0.04 (*s*, 3 H, SiCH₃); –0.03 (*s*, 3 H, SiCH₃). ¹³C-NMR (75 MHz, CDCl₃): δ = 159.6 (C), 133.5 (CH), 120.2 (CH), 87.9 (CH), 53.2 (CH₃), 32.4 (C), 27.5 (CH₂), 27.1 (C), 23.1 (CH₃), 19.0 (C), –6.1 (CH₃), –7.1 (CH₃). MS (EI): 238 (20, [M]⁺), 224 (8, [M–CH₃]⁺), 167 (23), 122 (55), 89 (36), 73 (100), 59 (22). HRMS (EI): calcd for C₁₄H₂₆OSi ([M]⁺): 238.1753. Found: 238.1759.

(*tert*-Butyl)(2-methoxy-1-methyl-1,4-dihydronaphthalen-1-yl)dimethylsilane (9)

1,4-Dihydronaphthalene³ (1.21 g, 72% pure, 6.7 mmol) was dissolved in THF (20 mL) and cooled to *ca.* –70 °C. TMEDA (1.03 mL, 6.7 mmol) and *sec*-butyllithium (5.3 mL, 1.39M in cyclohexane, 7.4 mmol) were added. The resulting soln. was stirred for 2 h at –70 °C and treated with TBDMSCl (1.11 g, 7.4 mmol) in THF (10 mL). After 5 min the cooling bath was removed and the reaction mixture was allowed to warm to rt and Et₂O and H₂O were added. The org. layer was separated, washed with H₂O (2×) and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* afforded crude 1-*tert*-butyldimethylsilyl-1,4-dihydronaphthalene, which was dissolved in THF (15 mL) and cooled to 0 °C. Butyllithium (4.27 mL, 1.57M in hexane, 6.7 mmol) was added. The resulting soln. was stirred for 1.5 h at 0 °C and treated with iodomethane (0.42 mL, 6.7 mmol). The reaction mixture was allowed to warm to rt. Stirring was continued for 30 min at this temperature. Et₂O and H₂O were added. The org. layer was separated, washed with H₂O and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* and FC (pentane) afforded **9** (360 mg, 21% over 2 steps) as a colorless oil. I.R. (neat): 3062_w, 3027_m, 2960_s, 2857_s, 2821_m, 1464_s, 1447_m, 1362_w, 1247_s, 986_w, 833_s, 750_s, 693_m, 669_m cm⁻¹. ¹H-NMR (300 MHz, CDCl₃): δ = 7.36–7.17 (*m*, 4 aromat. H); 5.88–5.79 (*m*, 2 H, CH₂); 3.60–3.44 (*m*, 2 H, CH); 1.64 (*s*, 3 H, CH₃); 0.94 (*s*, 9 H, C(CH₃)₃); 0.14 (*s*, 3 H, SiCH₃); 0.00 (*s*, 3 H, SiCH₃). ¹³C-NMR (75 MHz, CDCl₃): δ = 142.2 (C), 135.2 (CH), 132.9 (C), 128.4 (CH), 127.0 (CH), 125.7 (CH), 125.0 (CH), 120.0 (CH), 33.5 (C), 31.2 (CH₂), 28.1 (CH₃), 25.5 (CH₃), 19.2 (C), –6.7 (CH₃), –6.9 (CH₃). MS (EI): 258 (1, [M]⁺), 199 (13), 143 (14), 142 (99), 128 (6), 74 (6), 73 (100), 59 (11). HRMS (EI) calcd for C₁₇H₂₆Si ([M]⁺): 258.1804. Found 258.1806.

(tert-Butyl)(dimethyl)(1-methyl-cyclohexa-2,5-dienyl)silane (10)

1,4-Cyclohexadiene (1.86 mL, 20 mmol) was dissolved in THF (32 mL) and cooled to *ca.* –60 °C. *sec*-Butyllithium (17 mL, 1.3M in cyclohexane, 22 mmol) was added. The resulting soln. was treated with TMEDA (3.08 mL, 20 mmol). The mixture was allowed to warm to –35 °C in 2 h. After addition of TBDMSCl (3.32 g, 22 mmol) in THF (10 mL), the soln. was stirred for 1 h at rt. After cooling to –60 °C, *sec*-butyllithium (17 mL, 1.3M in cyclohexane, 22 mmol) was added. The mixture was allowed to warm to –40 to –35 °C. Stirring was continued for 2 h at this temp. before (CH₃O)₂SO₂ (2.1 mL, 22 mmol) was added. After 5 min, the cooling bath was removed and the mixture was allowed to warm to rt and Et₂O and H₂O were added. The org. layer was separated, washed with H₂O (2x) and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* and distillation (15 mbar, 93 – 95 °C) afforded **10** (2.88 g, 14 mmol, 69%) as a colorless oil. I.R. (CHCl₃): 3007*m*, 2960*s*, 2857*s*, 2821*m*, 1664*w*, 1616*w*, 1471*s*, 1431*w*, 1390*w*, 1362*m*, 1093*w*, 1007*w*, 960*w*, 923*w*, 878*m* cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 5.58–5.50 (*m*, 4 H, CH); 2.73–2.58 (*m*, 2 H, CH₂); 1.16 (*s*, 3 H, CH₃); 0.95 (*s*, 9 H, C(CH₃)₃); –0.02 (*s*, 6 H, Si(CH₃)₂). ¹³C-NMR (100 MHz, CDCl₃): δ = 133.4 (CH), 120.4 (CH), 31.1 (C), 28.1 (CH₃), 26.3 (CH₂), 24.7 (CH₃), 19.1 (C), –7.9 (CH₃). MS (EI): 208.1 (3, [M]⁺), 151.0 (10), 149.0 (46), 135.0 (5), 116.0 (15), 93.0 (12), 73.0 (100), 59.0 (21). HRMS (EI) calcd for C₁₃H₂₄Si ([M]⁺): 208.1647. Found: 208.1654.

Trimethyl(1-methyl-cyclohexa-2,5-dienyl)silane (11)

1,4-Cyclohexadiene (0.94 mL, 10 mmol) was dissolved in THF (16 mL) and cooled to *ca.* –60 °C. *sec*-Butyllithium (8.4 mL, 1.31M in cyclohexane, 11 mmol) was added. The resulting soln. was treated with TMEDA (1.54 mL, 10 mmol). The mixture was allowed to warm to –35 °C in 2 h. After addition of TMSCl (1.39 mL, 11 mmol), the soln. was stirred for 1 h at rt. After cooling to –60 °C, *sec*-butyllithium (8.4 mL, 1.31M in cyclohexane, 11 mmol) was added. The mixture was allowed to warm to –40 to –35 °C. Stirring was continued for 2 h at this temperature before (CH₃O)₂SO₂ (1.04 mL, 11 mmol) was added. After 5 min, the cooling bath was removed and the mixture was allowed to warm to rt and Et₂O and H₂O were added. The org. layer was separated, washed with H₂O (2x) sat. NH₄Cl-soln. and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* and distillation (16 mbar, 53 °C) afforded **11** (1.04 g, 63%) as a colorless oil. I.R. (CHCl₃): 3008*m*, 2957*s*, 2863*m*, 2821*m*, 1662*w*, 1616*w*, 1461*m*, 1432*m*, 1404*w*, 1366*w*, 1333*w*, 1095*w*, 999*w*, 959*m*, 925*m* cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 5.58–5.54 (*m*, 2 H, CH₂–CH); 5.48–5.44 (*m*, 2 H, C–CH); 2.73–2.55 (*m*, 2 H, CH₂); 1.09 (*s*, 3 H, CCH₃); –0.01 (*s*, 9 H, SiCH₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 132.37

(CH), 120.80 (CH), 45.83 (C), 26.52 (CH₂), 22.61 (CH₃), -4.72 (CH₃). MS (EI): 166.2 (<1, [M]⁺), 107.1 (2), 105.1 (2), 93.0 (1), 92.0 (3), 91.0 (2), 79.0 (3), 78.0 (2), 73.0 (21), 59.0 (2), 39.9 (3), 31.9 (29), 27.9 (100), 17.9 (5). Anal. calcd for C₁₀H₁₈Si (166.34): C 72.21, H 10.91. Found: C 71.97, H 10.90.

(*tert*-Butyl)(dimethyl)(9-methyl-9,10-dihydroanthracen-9-yl)silane (12)

9,10-Dihydroanthracene (1.80 g, 10 mmol) was dissolved in THF (40 mL) and cooled to *ca.* -70 °C. Butyllithium (7.4 mL, 1.63M in hexane, 12 mmol) was added dropwise. The resulting suspension was stirred for 1 h at -70 °C and treated with TBDMSCl (1.81 g, 12 mmol) in THF (10 mL). The reaction mixture was allowed to warm to rt and stirred for 1 h at this temperature. The resulting red soln. was cooled to 0 °C and treated with butyllithium (7.4 mL, 1.63M in hexane, 12 mmol). Stirring was continued for 1 h at 0 °C and then iodomethane (0.74 mL, 12 mmol) was added. After stirring for 1 h at rt, Et₂O and H₂O were added. The org. phase was separated, washed with H₂O (2x) and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* and recrystallization (methanol) afforded **12** (2.21 g, 7.2 mmol, 72%) as colorless crystals. Mp: 85 °C. I.R. (CHCl₃): 3068_w, 3008_w, 2960_m, 2930_s, 2858_s, 1603_w, 1476_s, 1448_m, 1391_w, 1029_w, 958_w cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 7.45–7.43 (*m*, 2 aromat. H); 7.26–7.22 (*m*, 4 aromat. H); 7.17–7.13 (*m*, 2 aromat. H); 4.16 (*d*, *J* = 19.0 Hz, 1 H, CH₂); 3.94 (*d*, *J* = 19.1 Hz, 1 H, CH₂); 1.96 (*s*, 3 H, CH₃); 0.65 (*s*, 9 H, C(CH₃)₃); -0.11 (*s*, 6 H, Si(CH₃)₂). ¹³C-NMR (100 MHz, CDCl₃): δ = 142.8 (C), 134.9 (C), 127.8 (CH), 126.0 (CH), 125.7 (CH), 125.0 (CH), 37.2 (CH₂), 27.3 (CH₃), 22.5 (CH₃), 19.4 (C), -5.3 (CH₃). MS (EI): 308.3 (<1, [M]⁺), 293.3 (<1, [M-CH₃]⁺), 193.2 (37), 192.2 (100), 191.2 (16), 178. 2 (26), 73.1 (64), 28.0 (14). Anal. calcd for C₂₁H₂₈Si (308.54): C 81.75, H 9.15. Found: C 81.68, H 9.11.

Trimethyl(9-methyl-9,10-dihydroanthracen-9-yl)silane (13)

According to *Dhar et al.*⁴, 9,10-dihydroanthracene (1.80 g, 10 mmol) was dissolved in THF (40 mL) and cooled to *ca.* -70 °C. Butyllithium (7.4 mL, 1.63M in hexane, 12 mmol) was added dropwise. The resulting suspension was stirred for 1 h at -70 °C and treated with a soln. of TMSCl (1.5 mL, 12 mmol) in THF (10 mL). The reaction mixture was allowed to warm to rt and stirred for 1 h at this temperature. The resulting red soln. was cooled to 0 °C and treated with butyllithium (7.4 mL, 1.63M in hexane, 12 mmol). Stirring was continued for 1 h at 0 °C and then iodomethane (0.74 mL, 12 mmol) was added. After stirring for 1 h at rt, Et₂O and H₂O were added. The org. phase was separated, washed with H₂O (2x) and brine,

and dried (MgSO₄). Removal of the solvent *in vacuo* and recrystallization (methanol) afforded **13** (1.16 g, 43%) as colorless crystals. Mp: 108 °C. I.R. (CHCl₃): 3070_w, 3008_m, 2956_m, 1604_w, 1479_s, 1448_s, 1378_w, 1135_w, 1082_w, 1029_m, 959_w cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 7.35–7.32 (*m*, 2 aromat. H); 7.24–7.20 (*m*, 4 aromat. H); 7.15–7.11 (*m*, 2 aromat. H); 4.13 (*d*, *J* = 19.5 Hz, 1 H, CH₂); 3.95 (*d*, *J* = 19.5 Hz, 1 H, CH₂); 1.83 (*s*, 3 H, CH₃); –0.14 (*s*, 9 H, Si(CH₃)₃). ¹³C-NMR (100 MHz, CDCl₃): δ = 141.4 (C), 133.9 (C), 127.8 (CH), 125.9 (CH), 125.8 (CH), 124.8 (CH), 36.6 (CH₂), 36.1 (C), 20.8 (CH₃), –3.0 (CH₃). MS (EI): 266.3 (5, [M]⁺), 251.3 (3, [M–CH₃]⁺), 193.2 (46), 192.2 (100), 191.2 (22), 178.1 (31), 73.0 (22), 28.0 (10). Anal. calcd for C₁₈H₂₂Si (266.46): C 81.14, H 8.32. Found: C 80.94, H 8.09.

(*tert*-Butyl)(2,6-dimethoxycyclohexa-2,5-dienyl)dimethylsilane (14)

1,5-Dimethoxy-1,4-cyclohexadiene¹ (2.88 g, 21 mmol) was dissolved in THF (50 mL). The soln. was cooled to *ca.* –70 °C. After addition of *tert*-butyllithium (14 mL, 1.6M in hexane, 23 mmol) and stirring for 30 min, HMPA (4.2 mL, 24 mmol) was added resulting a red soln. After stirring for 10 min at –70 °C, TBDMSCl (3.5 g, 23 mmol), dissolved in THF (10 mL) was added. The red reaction mixture decolorized. After 5 min, the cooling bath was removed and the soln. was allowed to warm to rt and pentane and H₂O were added. The org. layer was separated, washed with H₂O (2×) and brine, and dried (MgSO₄). Removal of the solvent *in vacuo* and distillation (0.15 mbar, 62 – 63 °C) afforded **14** (4.13 g, 17.6 mmol, 84%) as a colorless oil. I.R. (CHCl₃): 2999_m, 2954_s, 2856_s, 1680_s, 1649_w, 1463_s, 1440_m, 1355_s, 1139_s, 1029_m, 994_m cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ = 4.49 (*dxd*, *J*₁ = 4.8 Hz, *J*₂ = 2.8 Hz, 2 H, CH); 3.49 (*s*, 6 H, OCH₃); 2.83–2.78 (*m*, 2 H, CH₂); 2.45 (*dxd*, *J*₁ = 6.1 Hz, *J*₂ = 4.0 Hz, 1 H, SiCH); 0.92 (*s*, 9 H, C(CH₃)₃); –0.08 (*s*, 6 H, Si(CH₃)₂). ¹³C-NMR (100 MHz, CDCl₃): δ = 156.1 (C), 88.0 (CH), 53.7 (CH₃), 33.0 (CH), 26.8 (CH₃), 24.7 (CH₂), 17.3 (C), –6.1 (CH₃). MS (EI): 254.2 (90, [M]⁺), 239.2 (41, [M–CH₃]⁺), 197.1 (33), 195.1 (100), 165.1 (41), 139.1 (60), 138.1 (94), 135.1 (65), 73.0 (40). Anal. calcd for C₁₄H₂₆O₂Si (254.44): C 66.09, H 10.30. Found: C 66.10, H 10.30.

(2,6-Dimethyl-1-methylcyclohexa-2,5-dienyl)trimethylsilane (15)

Prepared according to a literature procedure.⁵

The following starting materials were prepared using literature procedures: ***O*-Cyclododecyl-*O*-phenylthionocarbonate**⁶ (table 3, entries 12 and 13); **1,2;5,6-di-*O*-isopropylidene-3-*O*-phenoxythiocarbonyl- α -D-glucofuranoside**⁶ (table 3, entries 14 and 15); **1,2;5,6-di-*O*-isopropylidene-3-*O*-(methylthio)thiocarbonyl- α -D-glucofuranoside**⁷ (table 3, entries 16 and 17).

Reduction of bromoadamantane: representative example (table 1, entry 2)

1-Bromoadamantane (107.5 mg, 0.50 mmol), Si-reagent **4** (174.5 mg, 0.65 mmol) and AIBN (24.5 mg, 0.15 mmol) were dissolved in hexane (2.5 mL) under Ar and heated to reflux. The course of the reaction was monitored by GC. The yield was determined by GC-analysis using tetradecane (130 μ L, 0.50 mmol) as an internal standard. After 5.5 h, the conversion was found to be complete and the yield of adamantane was determined to be 99%.

Barton-McCombie deoxygenation: representative example (table 3, entry 14)

1,2;5,6-Di-*O*-isopropyliden-3-*O*-phenoxythiocarbonyl- α -D-glucofuranoside⁶ (197 mg, 0.50 mmol), Si-reagent **4** (174 mg, 0.65 mmol) and AIBN (25 mg, 0.15 mmol) were dissolved in hexane (2.5 mL) under Ar. The reaction mixture was heated to reflux for 18 h. Removal of the solvent *in vacuo* and purification by FC (Et₂O / pentane 1:10) afforded 3-deoxy-1,2;5,6-di-*O*-isopropylidene- α -D-glucofuranoside (111 mg, 91%) as a colorless solid. The NMR-data are in agreement with those reported in the literature.⁸

Cyclization of 1-iodophenyl allyl ether

1-Iodophenyl allyl ether⁹ (260 mg, 1 mmol), Si-reagent **4** (402 mg, 1.5 mmol), and AIBN (82 mg, 0.5 mmol) were dissolved in hexane (5 mL) under Ar. The reaction mixture was heated to reflux for 10 h. Removal of the solvent *in vacuo* and purification by FC (pentane) afforded 297 mg of a mixture of 3-methyl-2,3-dihydrobenzofurane (0.82 mmol, 82%) and 2,6-dimethoxytoluene (1.23 mmol). The two compounds were not separated. The NMR-data of 3-methyl-2,3-dihydrobenzofurane is in agreement with those reported in the literature.¹⁰

Beckwith-Dowd ring enlargement of methyl 1-bromomethyl-2-oxocyclopentanoate

Methyl 1-bromomethyl-2-oxocyclopentanoate¹¹ (235 mg, 1 mmol), Si-reagent **4** (349 mg, 1.3 mmol), and AIBN (50 mg, 0.3 mmol) were dissolved in hexane (5 mL) under Ar. The reaction mixture was heated to reflux for 7 h. Removal of the solvent *in vacuo* and

purification by FC (Et₂O / pentane 3 : 8) afforded methyl 3-oxocyclohexane-1-carboxylate (76 mg, 0.49 mmol, 49 %) as a colorless oil. The NMR-data are in agreement with those reported in the literature.¹¹

Giese-type addition: representative example (table 4, entry 1)

1-Bromoadamantane (213 mg, 1 mmol), Si-reagent **4** (349 mg, 1.3 mmol), AIBN (49 mg, 0.3 mmol), and acrylonitrile (85 μ L, 1.3 mmol) were dissolved in hexane (3 mL) under Ar. The reaction mixture was heated to reflux for 4 h. Removal of the solvent *in vacuo* and purification by FC (Et₂O / pentane 1 : 30) afforded 3-adamantylpropionitrile **16** (112 mg, 0.59 mmol, 59 %) as a colorless oil. The NMR-data are in agreement with those reported in the literature.¹²

Polymerizations: representative example (table 5, entry 6)

In a Schlenk tube, AIBN (33 mg, 0.203 mmol) and Si-reagent **4** (141 mg, 0.524 mmol) were dissolved in freshly distilled styrene (6 mL, 52.4 mmol). The mixture was degassed with three freeze-thaw cycles. The Schlenk tube was flushed with argon, sealed and heated to 80 °C for 6 h. After cooling to rt, the polymer was dissolved in CH₂Cl₂ and dried at 60 °C (high vacuum, 12 h). Conversion was determined gravimetrically: 93%. The polymer was characterized by SEC (average values of three runs): M_n = 24800. M_w = 51000. PDI = 2.1.

Determination of the Chain Transfer Constant C_x : Four Schlenk-tubes were charged with styrene (1.5 ml, 13.106 mmol) and with Si-reagent **4** (first tube 35 mg, 0.131 mmol, second tube 70 mg, 0.262 mmol, third tube 105 mg, 0.393 mmol, fourth tube 140 mg, 0.524 mmol). A fifth Schlenk-tube was charged only with styrene (1.5 ml, 13.106 mmol) to get the value of M_0 . Every tube was subjected to three freeze-thaw cycles and sealed off under argon. The polymerizations were carried out under an argon atmosphere at 100 °C for 1.5 h. The resulting reaction mixture was dissolved in dichloromethane, poured into an aluminum dish and residual monomer was removed in a vacuum drying cabinet at 60 °C. Conversions were evaluated gravimetrically; molecular weights and polydispersity indices were determined by SEC.

The chain transfer constant C_x was then determined from a Mayo plot of $(1/M_n - 1/M_0)$ as a function of $[4]/[\text{styrene}]$:

$$1/M_n = 1/M_0 + C_x [4]/[\text{Styrene}].^{13}$$

$[4]/[\text{Styrene}]$	Conversion [%]	PDI	$1/M_n$ [mol/g]	$1/M_0$ [mol/g]
0.00	5.3	2.50	-	5.86×10^{-6}
0.01	5.8	2.05	18.8×10^{-6}	5.86×10^{-6}
0.02	5.9	2.04	24.6×10^{-6}	5.86×10^{-6}
0.03	6.1	2.05	25.4×10^{-6}	5.86×10^{-6}
0.04	6.4	1.96	33.6×10^{-6}	5.86×10^{-6}

Linear regression analysis: $C_x = 0.45 \times 10^{-3}$ ($R^2 = 0.96$).

Kinetic studies:

6-Bromohexene (65 mg, 0.4 mmol), Si-reagent **4** (1.072 g, 4 mmol), and AIBN (33 mg, 0.2 mmol) were dissolved in tetradecane (2 mL) under Ar in a pressure stable glass tube. The tube was sealed and heated to 70 °C for 20 min. The ratio methylcyclopentane : 1-hexene was determined by GC-analysis. The yield was determined by GC-analysis using decane (28 mg, 0.2 mmol) as an internal standard. The rate constant k_H for the H-abstraction was determined using the formula

$$\frac{k_{5\text{-exo}}}{k_H} = \frac{[\text{methylcyclopentane}]}{[1\text{-hexene}]} [\text{Si-reagent}]_m$$

with $k_{5\text{-exo}} = 1.07 \times 10^6 \text{ s}^{-1}$ at 70 °C.¹⁴ The kinetic experiment was repeated using different concentrations of Si-reagent **4** (1 – 2M). The reaction was stopped after 20 – 60 min (conversion 16 – 99%).

The rate constant for the reduction of a primary radical with Si-reagent **10** was estimated using the same method.

EPR Spectra: EPR spectra were obtained with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Samples of the substrate (0.3 to 40 mg) and di-*tert*-butyl peroxide (0.01 to 0.1 mL), in 4 mm od quartz tubes were photolysed in the resonant cavity by light from a 500 W super pressure mercury arc lamp. For reactions performed in cyclopropane (up to 0.5 mL), the solution was degassed on a vacuum line using the freeze-pump-thaw technique, and the tube was flame sealed. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker Simfonia

software package. For quantitative measurements, signals were double integrated using the Bruker WinEPR software.

EPR spectra from trimethyl(1-methyl-cyclohexa-2,5-dienyl)silane (11)

Top, No1: Spectrum from ca. 10 mg in neat DTBP at 250 K.

No2: Simulation with $a(1H) = 12.45$, $a(2H) = 8.4$, $a(2H) = 2.4$ G.

No 3 Spectrum at 360 K showing $\text{Me}_2\text{C}^\bullet\text{OSiMe}_3$ radical (central lines).

Bottom, No 4 Spectrum at 335 K with added $t\text{-BuBr}$ showing $t\text{-Bu}^\bullet$ radical (central lines)

EPR spectra from (*tert*-Butyl)(2-methoxy-1-methylcyclohexa-2,5-dienyl)dimethylsilane (8)

Top, A: Spectrum from **8** (ca. 10 mg) with DTBP (10 mg) in cyclopropane at 180 K.

B: Spectrum from **8** in neat DTBP at 340 K showing the $\text{Me}_2\text{C}^\bullet\text{OSiMe}_2\text{Bu-}t$ radical (central lines only) .

Bottom, C: Spectrum at 310 K with added *t*-BuBr showing *t*-Bu $^\bullet$ radical (2 lines including 2nd order structure)

EPR spectra obtained on photolysis of **9** and DTBP

Top A: Spectrum from **9** and DTBP at 240 K

Bottom B: Spectrum from **9** in neat DTBP at 370 K showing the $\text{Me}_2\text{C}^\bullet\text{OSiMe}_3$ radical (central lines only) .

EPR spectra obtained on photolysis of dihydronaphthalene derivative **12**

Top, A: Spectrum for a solution of **12** (10 mg) in DTBP at 240 K

Bottom, B: Simulation with $a(1H) = 12.7$, $a(2H) = 7.6$, $a(2H) = 2.3$, $a(4H) = 1.1$ G

EPR spectra obtained from (2,6-dimethyl-1-methylcyclohexa-2,5-dienyl)trimethylsilane (**15**) with DTBP at 250 K on photolysis with a 500 W Hg arc.

Upper spectrum: experimental.

Lower spectrum: computer simulation with $a(2H) = 2.87$ G, $a(6H) = 7.93$ G, $a(1H) = 12.49$ G, $a(1H) = 23.13$ G, line width 0.7G, mainly Gaussian lineshape.

EPR spectrum from (2,6-dimethyl-1-methylcyclohexa-2,5-dienyl)trimethylsilane (15) in DTBP at 345K.

Upper Spectrum Experimental

Lower Spectrum: Partial fit for simulation with: $a(1H) = 0.71G$, $a(3H) = 2.83 G$, $a(3H) = 10.59 G$, $a(1H) = 26.24 G$, linewidth = 0.4 G.

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