O₂ reactivity with thorium dialkyls supported by amidinate and guanidinate frameworks

Nicholas S. Settineri, Angela A. Shiau and John Arnold*

Department of Chemistry, University of California, Berkeley, and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California, 94720, United States

E-mail: arnold@berkeley.edu

Supporting Information

A.	Experimental Details	S2-S5
B.	NMR Spectra	S6-S21
C.	X-ray Crystallography	S22-S27
D.	Proposed Mechanism	S28
E.	References	S29

A. Experimental Details

General procedures. Unless otherwise stated, all reactions were performed under an atmosphere of dry N₂ using standard Schlenk line techniques or in an MBraun N₂ atmosphere glovebox (<1.0 ppm of O₂/H₂O). All solvents were dried and degassed using a commercially available Phoenix SDS from JC Meyer Solvent Systems. All glassware, syringes, and cannulas were stored in a 140 °C oven for a minimum of 16 h prior to use. Celite was dried in a 140 °C oven for 24 h prior to storage in the glovebox. Deuterated solvents were vacuum-transferred from flasks containing sodium/benzophenone (C₆D₆), degassed with three freeze-pump-thaw cycles, and stored over molecular sieves. ThCl₄(DME)₂,¹ Li(BTBA)(TMEDA),² and Li(TIG)(THF)³ were prepared according to previously reported literature procedures. O₂ gas (99.5% purity) was purchased from Praxair, Inc. and used directly from the cylinder without additional purification. (Trimethylsilyl)methyllithium was purchased from SigmaAldrich as a 1.0 M solution in pentane; solid LiCH₂SiMe₃ was obtained by crystallization from this pentane solution at -40 °C. All other reagents were purchased from commercial sources and used as received. Unless otherwise stated, NMR spectra were collected at ambient temperature on a Bruker AV-300, AVB-400, AV-500, DRX-500 or AV-600 spectrometer. ¹H and ¹³C{¹H} NMR chemical shifts (δ) are reported in ppm and were calibrated to residual solvent peaks. Melting points were determined on an Optimelt SRS instrument using capillary tubes sealed under dry N₂. Elemental analysis samples were sealed under vacuum and analyzed at either the London Metropolitan University or the University of California, Berkeley. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 FTIR spectrophotometer as Nujol mulls pressed between KBr plates.

Th(BTBA)₂Cl(μ -Cl)₂Li(TMEDA) (1): ThCl₄(DME)₂ (2.50 g, 4.52 mmol) was added to a 250 mL Schlenk flask containing a magnetic stir-bar and dissolved in 40 mL of THF. A THF solution (40 mL) of Li(BTBA)(TMEDA) (3.48 g, 9.00 mmol) was slowly added to this stirred solution, resulting in a faint pink solution which was stirred at ambient temperature for 2 h. Volatiles were removed under reduced pressure and the resulting solid was triturated with hexane (2 x 30 mL), and extracted into toluene (75 mL). The solution was filtered away from the colorless LiCl precipitate, concentrated to 20 mL, and stored at -40 °C for 16 h, yielding 1 as large, colorless blocks (3.484 g, 78.1%). ¹H NMR (600 MHz, C₆D₆, 293 K): δ 7.35 (m, 4H, CH_{Ar}), 7.03 (m, 6H, CHAr), 2.07 (s, 12H, NMe2), 1.72 (s, 4H, CH2), 0.34 (s, 36H, SiMe3). ¹³C{¹H} NMR (151 MHz, C₆D₆, 293 K): δ 180.9 (NCN), 142.8 (C_{Ar}), 128.6 (C_{Ar}), 126.8 (C_{Ar}), 56.5 (C_{TMEDA}H₂), 45.8 (NMe₂), 2.8 (SiMe₃). Anal. Calcd for C₃₂H₆₂Cl₃N₆Si₄LiTh (988.6): C, 38.88; H, 6.32; N, 8.50. Found: C, 38.79; H, 6.38; N, 8.42. Mp: 194-202 °C. FTIR (Nujol): 2797 (m), 1291 (m), 1247 (s), 1180 (w), 1160 (w), 1129 (w), 1066 (w), 1034 (m), 1017 (m), 1006 (m), 981 (s), 947 (w), 924 (w), 839 (s), 787 (m), 762 (m), 720 (s), 706 (s), 689 (m), 481 (s), 439 (m). Crystals suitable for singlecrystal X-ray diffraction studies were grown from a concentrated toluene solution stored at -35 °C for 16 h.

Th(BTBA)₂(**CH**₂**SiMe**₃)₂ (2): Solid 1 (3.17 g, 3.21 mmol) was added to a 250 mL Schlenk flask containing a magnetic stir-bar and dissolved in 40 mL of toluene. A toluene solution (60 mL) of LiCH₂SiMe₃ (0.608 g, 6.46 mmol) was slowly added to this stirred solution, resulting in immediate precipitation of a colorless solid. This solution was stirred at ambient temperature for 5 minutes. Volatiles were removed under reduced pressure, and the resulting solid was extracted into hexane (40 mL) and filtered away from the LiCl precipitate. The resulting solution was concentrated to 5 mL and stored at -40 °C for 16 h, yielding 2 as colorless crystals (2.283 g, 76.4%). ¹H NMR (500 MHz, C₆D₆, 293 K): δ 7.31 (m, 4H, *CH*_{Ar}), 7.01 (m, 6H, *CH*_{Ar}), 0.51 (s, 18H, CH₂Si*M*e₃), 0.42 (s, 4H, *CH*₂Si*M*e₃), 0.15 (s, 36H, Si*M*e₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, 293 K): δ 182.5 (NCN), 143.5 (*C*_{Ar}), 128.9 (*C*_{Ar}), 126.2 (*C*_{Ar}), 95.2 (*C*H₂Si*M*e₃), 4.6 (CH₂Si*M*e₃), 2.5 (Si*M*e₃). Anal. Calcd for C₃₄H₆₈N₄Si₆Th (933.5): C, 43.75; H, 7.34; N, 6.00. Found: C, 43.61; H, 7.32; N, 6.16. Mp: 76-77 °C. FTIR (Nujol): 1384 (s), 1248 (s), 1164 (w), 1075 (w), 1003 (m), 994 (m), 975 (s), 919 (m), 838 (s), 785 (s), 759 (s), 744 (m), 714 (s), 604 (w), 479 (m), 439 (w). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated hexane solution stored at -35 °C for 16 h.

Th(BTBA)₂(**OCH**₂**SiMe**₃)₂ (**3**): Solid **2** (0.550 g, 0.589 mmol) was added to a 100 mL Schlenk flask containing a magnetic stir bar and dissolved in hexane (20 mL). The solution was freezepump-thawed once, and the evacuated flask was then filled with O₂ gas (1 atm) via the vacuum manifold of the Schlenk line. The colorless solution was stirred at ambient temperature for 20 minutes. Volatiles were removed under reduced pressure, and the resulting residue was extracted into HMDSO (12 mL). The extract was concentrated to <0.5 mL and placed in a freezer at -35 °C for 16 h, yielding **3** as colorless crystals (0.295 g, 51.8%). ¹H NMR (400 MHz, C₆D₆, 293 K): δ 7.32 (m, 4H, *CH*_{Ar}), 7.06 (m, 6H, *CH*_{Ar}), 4.18 (s, 4H, *CH*₂), 0.27 (s, 18H, *CH*₂Si*Me*₃), 0.18 (s, 36H, Si*Me*₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, 293 K): δ 180.5 (NCN), 144.6 (*C*_{Ar}), 126.2 (*C*_{Ar}), 69.1 (*CH*₂SiMe₃), 2.4 (Si*Me*₃), -3.0 (*CH*₂Si*Me*₃). Anal. Calcd for C₃₄H₆₈N₄Si₆O₂Th (965.5): C, 42.30; H, 7.10; N, 5.82. Found: C, 41.99; H, 6.74; N, 6.15. Mp: 145-150 °C. FTIR (Nujol): 1246 (s), 1087 (m), 1060 (s), 1002 (m), 978 (s), 919 (w), 842 (s), 785 (w), 759 (m), 723 (w), 700 (m), 474 (m). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated HMDSO solution stored at -35 °C for 16 h.

Th(TIG)₂Cl₂(THF) (4): Solid ThCl₄(DME)₂ (0.500 g, 0.902 mmol) was added to a 20 mL scintillation vial containing a magnetic stir-bar and dissolved in THF (10 mL). A THF solution (5 mL) of Li(TIG)(THF) (0.552 g, 1.81 mmol) was then added dropwise to this colorless solution. Over the course of this addition, the reaction mixture turned pale yellow and cloudy; the reaction was stirred at ambient temperature for 16 h. Volatiles were removed under reduced pressure, resulting in a colorless solid, which was then triturated with hexane (3 mL) and extracted into toluene (2 x 5 mL). The solution was filtered through Celite. After volatiles were removed under reduced pressure, the resulting colorless powder was washed with 1 mL diethyl ether (to remove trace amounts of Th(TIG)₃Cl) and dissolved in 2 mL of THF. Storing this concentrated solution at

-40 °C overnight yielded 4 as analytically pure, colorless block crystals (0.390 g, 55.7%). The molecule of coordinated THF could be removed under reduced pressure. ¹H NMR (600 MHz, C₆D₆, 293 K): δ 4.04 (sept, CHMe₂, 4H), 3.64 (m, THF: OCH₂CH₂, 2H), 3.28 (sept, CHMe₂, 4H), 1.50 (d, CHMe₂, 24H), 1.42 (m, THF: OCH₂CH₂, 2H), 1.06 (d, CHMe₂, 24H). ¹³C{¹H} NMR (151 MHz, C₆D₆, 293 K): δ 172.0 (NCN), 68.1 (THF: OCH₂CH₂), 49.5 (CHMe₂), 47.5 (CHMe₂), 25.8 (THF: OCH₂CH₂), 25.7 (CHMe₂), 23.2 (CHMe₂). Anal. Calcd for C₂₆H₅₆Cl₂N₆Th (754.4): C, 41.32; H, 7.47; N, 11.12. Found: C, 41.50; H, 7.36; N, 10.90. Mp: 199 °C (decomp). FTIR (Nujol): 1413 (s), 1324 (m), 1261 (w), 1207 (m), 1180 (w), 1138 (m), 1066 (m), 1019 (m), 800 (s), 722 (m), 665 (w), 513 (w), 460 (w). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated solution of THF stored at -35 °C for 16 h.

Th(TIG)₂(**CH**₂**SiMe**₃)₂ (5): Solid 4 (0.322 g, 0.389 mmol) was added to a 20 mL scintillation vial containing a magnetic stir-bar and dissolved in 10 mL of toluene. The addition of a toluene solution (5 mL) of LiCH₂SiMe₃ (0.074 g, 0.786 mmol) to this solution resulted in the precipitation of a colorless solid. The suspension was further stirred at ambient temperature for 2 h. The reaction mixture was filtered through Celite and the colorless solution was concentrated to 10 mL. Storage of this solution at -35 °C overnight yielded **5** as analytically pure, colorless microcrystals (0.322 g, 96.2%). ¹H NMR (300 MHz, C₆D₆, 293 K): δ 4.11 (sept, *CH*Me₂, 4H), 3.37 (sept, *CH*Me₂, 4H), 1.40 (d, *CHMe*₂, 24H), 1.14 (d, *CHMe*₂, 24H), 0.47 (s, *CH*₂Si*Me*₃, 18H), 0.21 (s, *CH*₂SiMe₃, 4H). ¹³C {¹H} NMR (151 MHz, C₆D₆, 293 K): δ 172.9 (NCN), 91.9 (ThCH₂SiMe₃), 50.1 (*C*HMe₂), 47.2 (*C*HMe₂), 26.2 (*C*H*Me*₂), 23.6 (*C*H*Me*₂), 4.8 (ThCH₂Si*Me*₃). Anal. Calcd for C₃₄H₇₈N₆Si₂Th (858.6): C, 47.53; H, 9.15; N, 9.78. Found: C, 47.65; H, 9.20; N, 10.04. Mp: 128 °C (decomp). FTIR (Nujol): 1317 (m), 1249 (w), 1236 (m), 1208 (m), 1182 (w), 1133 (m), 1122 (m), 1064 (s), 977 (m), 891 (m), 847 (s), 815 (m), 734 (m), 681 (w), 665 (m), 493 (w), 451 (w), 406 (w). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated solution of hexane, stored at -35 °C for 48 h.

Th(TIG)₂(OCH₂SiMe₃)₂ (6): Solid 5 (0.157 g, 0.183 mmol) was added to a 10 mL Schlenk flask containing a magnetic stir-bar and suspended in 5 mL of hexane. The hexane solution was frozen and the N₂ headspace was removed under reduced pressure. After the solution warmed up to room temperature, O₂ (1 atm) was introduced to the flask. The reaction mixture was stirred at ambient temperature for 16 hours, over which the solution became clear. The O₂ atmosphere and remaining volatiles were removed under reduced pressure, resulting in a colorless solid. This solid was dissolved in 1 mL of hexane and the solution was concentrated to ~0.5 mL; storing this solution at -35 °C afforded 6 as analytically pure, colorless block crystals (0.138 g, 88.7%). ¹H NMR (400 MHz, C₆D₆, 293 K): δ 4.22 (s, ThOCH₂SiMe₃, 4H), 4.10 (sept, CHMe₂, 4H), 3.41 (sept, CHMe₂, 4H), 1.41 (d, CHMe₂, 24H), 1.19 (d, CHMe₂, 24H), 0.23 (s, CH₂SiMe₃, 18H). ¹³C{¹H} NMR (151 MHz, C₆D₆, 293 K): δ 169.3 (NCN), 68.7 (ThOCH₂SiMe₃), 49.2 (CHMe₂), 46.8 (CHMe₂), 26.4 (CHMe₂), 23.6 (CHMe₂), -2.9 (ThOCH₂SiMe₃). Anal. Calcd for C₃₄H₇₈N₆Si₂O₂Th (891.3): C, 45.82; H, 8.82; N, 9.43. Found: C, 46.09; H, 8.56; N, 9.27. Mp: 158–161 °C. FTIR (Nujol): 1310

(m), 1244 (m), 1214 (m), 1191 (w), 1136 (w), 1084 (m), 1064 (s), 1019 (m), 856 (s), 722 (m), 670 (m). Crystals suitable for single-crystal X-ray diffraction studies were grown from a concentrated solution of hexane stored at -35 °C for 16 h.

Formation of 6 in the Presence of 1,4-Cyclohexadiene: Three NMR-scale experiments were run simultaneously using 0.020 g portions of **5** (0.023 mmol) in C₆D₆. An internal standard of hexamethylbenzene (3.78 mg, 0.023 mmol) was used for each experiment. (1) 22 μ L of 1,4-cyclohexadiene (0.023 mmol) was added to the first sample. Over the course of 5 days, all peaks corresponding to **5** remained unchanged; a small, insignificant amount of tetramethylsilane (SiMe₄) was generated. (2) After three freeze-pump-thaw cycles, an atmosphere of dry O₂ was introduced to the second sample. The rate of formation of **6** was monitored for 5 days, as judged by the ratio of OCH₂Si**Me**₃:CH₂Si**Me**₃. A small, insignificant amount of SiMe₄ was generated over the course of these 5 days. (3) 22 μ L of 1,4-cyclohexadiene (0.023 mmol) was added to the third sample, along with an atmosphere of dry O₂, following the same freeze-pump-thaw procedure described previously. Over a period of 5 days, the rate of the formation of **6** was significant amount of SiMe₄ was also generated, presumably from the scavenging of C₆H₈ allylic hydrogens by •CH₂SiMe₃. In similar trials, increasing the amount of inhibitor decreased the amount of **6** and increased the amount of SiMe₄ generated, relative to the control.

B. NMR Spectra



Figure S1. ¹H NMR spectrum of Th(BTBA)₂Cl₃Li(TMEDA) (1) at 298 K in C₆D₆. *Toluene



Figure S2. ¹³C{¹H} NMR spectrum of Th(BTBA)₂Cl₃Li(TMEDA) (1) at 298 K in C_6D_6



Figure S3. ¹H NMR spectrum of Th(BTBA)₂(CH₂SiMe₃)₂ (2) at 298 K in C₆D₆



Figure S4. ¹³C{¹H} NMR spectrum of Th(BTBA)₂(CH₂SiMe₃)₂ (2) at 298 K in C_6D_6



Figure S5. ¹H NMR spectrum of Th(BTBA)₂(OCH₂SiMe₃)₂ (3) at 298 K in C₆D₆



Figure S6. ¹³C $\{^{1}H\}$ NMR spectrum of Th(BTBA)₂(OCH₂SiMe₃)₂ (3) at 298 K in C₆D₆



Figure S7. ¹H NMR spectrum of Th(TIG)₂Cl₂(THF) (4) at 298 K in C₆D₆



Figure S8. ${}^{13}C{}^{1}H$ NMR spectrum of Th(TIG)₂Cl₂(THF) (4) at 298 K in C₆D₆



Figure S9. ¹H NMR spectrum of $Th(TIG)_2(CH_2SiMe_3)_2$ (5) at 298 K in C_6D_6



Figure S10. ¹³C{¹H} NMR spectrum of Th(TIG)₂(CH₂SiMe₃)₂ (5) at 298 K in C_6D_6



Figure S11. ¹H NMR spectrum of Th(TIG)₂(OCH₂SiMe₃)₂ (6)at 298 K in C₆D₆



Figure S12. ¹³C $\{^{1}H\}$ NMR spectrum of Th(TIG)₂(OCH₂SiMe₃)₂ (6) at 298 K in C₆D₆



Figure S13. Stacked ¹H NMR spectra of **5** and 1,4-cyclohexadiene at 298 K in C₆D₆ over a period of 5 days with a hexamethylbenzene standard. [‡]One of the 1,4-cyclohexadiene peaks. ^{*}Hexamethylbenzene. ^{Δ}Generated SiMe₄. *Ratio of C*₆Me₆ : SiMe₄ =18 : 0.30.



Figure S14. Stacked ¹H NMR spectra of **5** exposed to dry O₂ at 298 K in C₆D₆ over a period of 5 days with a hexamethylbenzene standard. *Hexamethylbenzene. \triangle Generated SiMe₄. *Ratio of C₆Me₆ : SiMe₄ = 18 : 0.42*.



Figure S15. Stacked ¹H NMR spectra of **5** exposed to dry O_2 in the presence of 1,4-cyclohexadiene at 298 K in C_6D_6 over a period of 5 days with a hexamethylbenzene standard. [‡]One of the 1,4-cyclohexadiene peaks. ^{*}Hexamethylbenzene. ^ΔGenerated SiMe₄. *Ratio of* C_6Me_6 : *SiMe*₄ = 18 : 0.91.



Figure S16. Stacked ¹H NMR spectra of **5** exposed to dry O_2 in the presence of a large excess of 1,4cyclohexadiene at 298 K in C_6D_6 over a period of 40 h. Two bottommost spectra were taken prior to the addition of O_2 and thus verify stability of **5** in the presence of a large excess of 1,4-cyclohexadiene. [‡]1,4cyclohexadiene. ^ΔGenerated SiMe₄.

C. X-ray Crystallography

S21

Crystallographic Procedures. Single-crystal X-ray diffraction experiments were performed at the UC Berkeley CHEXRAY crystallographic facility. Measurements of all complexes were performed on a Bruker APEX-II CCD area detector using Mo K α radiation ($\lambda = 0.71073$ Å). Crystals were kept at 100(2) K throughout collection. Data collection was performed with Bruker APEX2 software (v. 2014.11). Data refinement and reduction were performed with Bruker SAINT (V8.34A). All structures were solved with SHELXT.53.⁴ Structures were refined with SHELXL-2014.⁵ Molecular graphics were computed with Mercury 3.10. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at the geometrically calculated positions and refined using a riding model.

	1	2	c ³ n	4	5	6
Chemical	C32H62Cl3LiN6	$C_{34}H_{68}N_4Si_6Th$	$C_{34}H_{68}N_4Si_6O_2$	$C_{30}H_{64}Cl_2ON_6$	$C_{34}H_{78}N_6Si_2Th$	$C_{34}H_{78}N_6O_2Si_2Th$
formula	$Si_4Th \cdot C_7H_8$		Th	Th		
Formula weight	1080.70	933.49	965.50	827.81	859.24	891.24
Colour, habit	Colorless,	Colorless,	Colorless,	Colorless,	Colorless,	Colorless, block
	block	block	block	block	block	
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P 21/c	P 21/c	P 21/c	P -1	C 2/c	C 2/c
a (Å)	18.8563(10)	26.240(5)	23.380(3)	9.9544(16)	24.340(2)	23.921(5)
b (Å)	12.1439(6)	18.585(5)	9.8979(11)	12.545(2)	11.7801(11)	11.822(2)
c (Å)	23.6059(13)	20.796(5)	20.423(2)	15.474(3)	18.3484(17)	19.372(4)
α (°)	90	90	90	85.589(8)	90	90
β (°)	108.474(2)	113.178(5)	90.519(2)	84.718(8)	123.5780(10)	126.690(6)
γ (°)	90	90	90	72.616(7)	90	90
V (Å ³)	5126.9(5)	9323(4)	4726.0(9)	1833.7(6)	4383.0(7)	4392.8(15)
Ζ	4	8	4	2	4	4
Densitiy (Mg m ⁻	1.400	1.330	1.357	1.499	1.302	1.348
3)						
F(000)	2184	3792	1960	836	1768	1832
Radiation Type	ΜοΚα	MoK _α	MoK _α	MoK _α	MoK _α	MoK _α
μ (mm ⁻¹)	3.190	3.378	3.338	4.242	3.484	3.482
Crystal size	0.12 x 0.10 x	0.10 x 0.10 x	0.18 x 0.13 x	0.05 x 0.02 x	0.10 x 0.10 x	0.10 x 0.10 x 0.05
(mm ³)	0.08	0.10	0.10	0.02	0.10	
Meas. Refl.	76942	61389	97328	78388	67790	68882
Indep. Refl.	9424	16763	8708	6699	4018	4035
R(int)	0.0256	0.0345	0.0419	0.0733	0.0248	0.0317
Einal D indiana	R = 0.0181	R = 0.0285	R = 0.0341	R = 0.0262	R = 0.0137	R = 0.0194
Final K mulces $[I > 2-(I)]$	$R_w = 0.00427$	$R_w = 0.0527$	$R_w = 0.0789$	$R_w = 0.0548$	$R_w = 0.0326$	$R_w = 0.0463$
$[1 \ge 20(1)]$	1.020	1.020	1 1 2 2	1 1 2 4	1 222	1 1 1 0
	1.039	1.037	1.122 2.02 1.07	1.124	1.552	1.110
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}$ (e Å -3)	1.20, -0.30	1.33, -0.90	5.05, -1.07	2.22, -0.34	1.37, -0.81	<i>3.32</i> , - 0.97
(CDC)	1808/80	1808/185	1808/86	1808/87	1808/00	1808/88
	1070407	1070405	1070400	107040/	1070470	1070400



Figure S17. Molecular structure of **1** (thermal ellipsoids drawn at the 50% probability level). Toluene solvent molecule and hydrogen atoms omitted for clarity.



Figure S18. Molecular structure of **2** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms omitted for clarity.



Figure S19. Molecular structure of **4** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms omitted for clarity.



Figure S20. Molecular structure of **5** (thermal ellipsoids drawn at the 50% probability level). Hydrogen atoms omitted for clarity.





S27

Scheme S1. Proposed mechanism for oxygen atom insertion into complexes 3 and 5.

E. References

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S28