SUPPORTING INFORMATION FOR

Convenient Access to the Anhydrous Thorium Tetrachloride Complexes $ThCl_4(DME)_2$, $ThCl_4(1,4\text{-dioxane})_2$ and $ThCl_4(THF)_{3.5}$ and using Commercially Available and Inexpensive Starting Materials

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General Synthetic Considerations

Unless otherwise noted, all reactions and manipulations were performed at 20 ºC in a recirculating Vacuum Atmospheres NEXUS Model inert atmosphere (N_2) drybox equipped with a 40CFM Dual Purifier NI-Train. Glassware was dried overnight at 150 ºC before use. All NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to solvent impurities. Elemental analyses (C, H, Cl and Th) were performed at Columbia Analytical Services in Tucson and Phoenix, AZ. X-ray data were collected using a Bruker APEX2 diffractometer. Structural solution and refinement was achieved using the SHELXL program suite.[1] Details regarding data collection are provided in the CIF files.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich), alumina (Brockman I, Aldrich) and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. All solvents (Aldrich) were purchased anhydrous, dried over KH for 24 h, passed through a column of activated alumina, and stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 (Aldrich) and tetrahydrofuran-d_8 (Cambridge Isotope Laboratories) were purified by storage over activated 4 Å molecular sieves or sodium metal prior to use. $Th(NO_3)_4(H_2O)_5$ was purchased from Merck. Triphenylphosphine oxide, $Na[N(SiMe_3)_2]$, Me_3SiCl, Me_3SiBr, concentrated HCl (37 wt. % in H_2O, 12 M), HCl/diethyl ether (2.0M) were purchased from Aldrich. $(C_5Me_5)MgCl•THF$[2] and $K(O\text{-}2,6\text{-}^tBu_2\text{-}C_6H_3)$[3] were prepared according to literature procedures.

***Caution*:** Natural thorium (primary isotope ^{232}Th) is a weak α-emitter (4.012 MeV) with a half-life of 1.41×10^{10} years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

Synthesis of $ThCl_4(H_2O)_4$ (2)

A 500-mL round-bottom flask was charged with thorium nitrate $Th(NO_3)_4(H_2O)_5$ (20.0 g, 35.1 mmol) and a magnetic stir bar. The solid was then dissolved in concentrated HCl (100 mL) with stirring. In a well-ventilated fume hood, the resulting solution was refluxed for 6 h until no evolution of orange-colored gas was observed and the reaction mixture was colorless (***Caution!*** *Nitrogen oxides are toxic and hazardous gases*). Volatiles were removed under reduced pressure to afford $ThCl_4(H_2O)_4$ (**2**) as a white solid (8.1 g, 18.1 mmol, 100%). ^1H NMR (THF-d_8, 298 K): δ 7.17 (bs, $\nu_{½}$ = 47 Hz; H_2O). Anal. Calcd. for $Cl_4H_8O_4Th$ (mol. wt. 445.91): C, 0.00; H, 1.81. Found: C, <0.2 (not detected); H, 1.56.

Synthesis of $ThCl_4(DME)_2$ (3)

A 500-mL round-bottom Schlenk flask equipped with a magnetic stir bar was charged with $ThCl_4(H_2O)_4$ (**2**) (15.5 g, 34.8 mmol). The solid was dissolved in DME (100 mL) under an argon flow. Using an addition funnel, Me_3SiCl (70 mL, 557 mmol) was added dropwise at room temperature as the reaction is exothermic; upon addition, a crystalline white precipitate forms. The reaction vessel was sealed and the mixture was stirred for 12 h in an 50 °C oil bath. The volume was then concentrated to 20 mL under reduced pressure, leaving a white suspension. The reaction vessel is brought into a drybox. Addition of hexanes (50 mL), followed by filtration over a coarse-porosity fritted filter and drying under reduced pressure afforded $ThCl_4(DME)_2$ (**3**) as a white solid (18.3 g, 33.1 mmol, 95%). ^1H NMR (C_6D_6, 298K): δ 3.76 (s, 6H; OCH_3), 3.33 ppm (s, 4H; OCH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 298K): δ 73.6 (s), 65.8 ppm (s). Anal. Calcd. for $C_8H_{20}Cl_4O_4Th$ (mol. wt. 554.09): C, 17.34; H, 3.64. Found: C, 17.38; H, 3.63.

Synthesis of $ThCl_4(O{=}PPh_3)_3$ (4)

A 125-mL sidearm flask was charged with a magnetic stir bar, $ThCl_4(DME)_2$ (**3**) (1.40 g, 2.52 mmol), triphenylphosphine oxide (2.10 g, 7.55 mmol) and THF (30 mL). The reaction mixture was stirred at room temperature for 6 h. The volatiles were then removed under reduced pressure to give $ThCl_4(O{=}PPh_3)_3$ (**4**) as a white solid (3.05 g, 2.52 mmol, 100%). ^1H NMR (THF-d_8, 298K): δ 7.83 (bs, 18H; Ph), 7.53 (bs, 9H; Ph), 7.43 (bs, 18H; Ph).

Synthesis of $ThCl_4(TMEDA)_2$ (5)

A 20-mL scintillation vial was charged with a stir bar, $ThCl_4(DME)_2$ (**3**) (0.280 g, 0.505 mmol) and THF (3 mL). To the resulting solution, TMEDA (100 µL, 0.667 mmol) was added using a syringe. The reaction mixture was stirred at room temperature for 30 min. The volatiles were then removed under reduced pressure to give $ThCl_4(TMEDA)_2$ (**5**) as a white solid (0.306 g, 0.505 mmol, 100%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported[4] for complex **5**.

Synthesis of $ThBr_4(DME)_2$ (6)

A 20-mL scintillation vial was charged with a stir bar, $ThCl_4(DME)_2$ (**3**) (0.280 g, 0.505 mmol) and toluene (3 mL). To the resulting solution, Me_3SiBr (330 µL, 2.50 mmol) was added using a syringe. The reaction mixture was stirred at room temperature for 48 h. The volatiles were then removed under reduced pressure to give $ThBr_4(DME)_2$ (**6**) as a white solid (0.369 g, 0.505 mmol, 100%). The ^1H NMR spectrum collected in C_6D_6 is consistent with the data previously reported[5] for complex **6**.

Synthesis of $Th(O\text{-}2,6\text{-}^tBu_2\text{-}C_6H_3)_4$ (7)

In a drybox, a 250-mL sidearm flask equipped with a stir bar was charged with $ThCl_4(DME)_2$ (**3**) (5.30 g, 9.57 mmol) and THF (15 mL). A THF (100 mL) solution of potassium 2,6-di-tert-butylphenoxide (9.59 g, 39.2 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 3 h and then filtered through a Celite-padded coarse-porosity fritted-filter. The volatiles were removed under reduced pressure and the resulting off-white solid extracted into 100 mL hot (60 °C) toluene. The solution was collected and the volatile removed under reduced pressure to give $Th(O\text{-}2,6\text{-}^tBu_2\text{-}C_6H_3)_4$ (**7**) as a white solid (9.98 g, 9.47 mmol, 99%). ^1H and $^{13}C\{^1H\}$ NMR spectra collected in C_6D_6 were consistent with the data previously reported[3] for complex **7**.

Synthesis of $[(Me_3Si)_2N]_2Th[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$ (8)

In a drybox, a 250-mL Schlenk flask equipped with a stir bar was charged with $ThCl_4(DME)_2$ (**3**) (4.76 g, 86.0 mmol), $Na[N(SiMe_3)_2]$ (6.30 g, 34.4 mmol) and toluene (100 mL). The reaction vessel was sealed, transferred to a fume hood, and heated in a 110 °C oil bath for 24 h. The volatiles were then removed under reduced pressure and the resulting white solid was extracted with 60 mL hexane and filtered through a Celite-padded coarse-porosity fritted filter. The volume of the collected filtrate was reduced to 10 mL and $(Me_3Si)_2O$ (50 mL) was added. The resulting white suspension was cooled to -35 °C, filtered using a fine-porosity fritted filter, and dried under reduced pressure to give $[(Me_3Si)_2N]_2Th[\kappa^2\text{-}(N,C)\text{-}CH_2Si(CH_3)_2N(SiMe_3)]$ (**8**) as a white solid (5.69 g, 7.99 mmol, 93%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported[6] for complex **8**.

Synthesis of $(C_5Me_5)_2ThCl_2$ (9)

A 250-mL round-bottom Schlenk flask equipped with a magnetic stir bar was charged with $ThCl_4(DME)_2$ (**3**) (5.37 g, 9.70 mmol), $(C_5Me_5)MgCl$•THF (5.70 g, 21.3 mmol) and toluene (70 mL). The reaction vessel was sealed, transferred to a hood, and heated in an 100 °C oil bath for 48 h with stirring. The reaction mixture was cooled to ambient temperature and transferred to a drybox. The solution was heated and filtered while hot through a Celite-padded coarse-porosity fritted filter. The solid collected was washed with 15 mL hot (100 °C) toluene and dried under reduced pressure to give as a white solid $(C_5Me_5)_2ThCl_2$ (**9**) (4.89 g, 8.54 mmol, 88%). The ^1H NMR spectrum collected in C_6D_6 was consistent with the data previously reported[2] for complex **9**.

Synthesis of $ThCl_4(1,4\text{-dioxane})_2$ (10)

In a drybox, a 20-mL thick-walled Schlenk tube equipped with a Teflon valve and a stir bar was charged with $ThCl_4(H_2O)_4$ (**2**) (1.30 g, 2.92 mmol). Next, 1,4-dioxane (4.0 mL), TMSCl (4.0 mL, 31.6 mmol) and a solution of HCl/diethyl ether (4.0 mL, 2.0 M, 8.0 mmol) were added using a syringe. The reaction vessel was sealed and the reaction mixture stirred for 15 h in a 130 °C oil bath. The reaction mixture was then cooled to ambient temperature and tranferred to a drybox. The solution was concentrated to half its original volume (~ 6 mL) and hexane (15 mL) was added. The resulting white suspension was collected over a fine-porosity fritted filter and dried under reduced pressure to give and $ThCl_4(1,4\text{-dioxane})_2$ (**10**) as a white solid (1.57 g, 2.86 mmol, 98%). The insolubility of complex **10** in noncoordinating solvents precluded its characterization using NMR spectroscopy. Dissolution of complex **10** in coordinating solvents (such as THF) leads to the displacement of the 1,4-dioxane ligands. Anal. Calcd. for $C_8H_{16}Cl_4O_4Th$ (mol. wt. 550.06): C, 17.47; H, 2.93; Cl, 25.78; Th, 42.18. Found: C, 17.57; H, 2.63; Cl, 26.0; Th, 38.5.

Synthesis of $ThCl_4(THF)_{3.5}$ (11)

A 20-mL scintillation vial was charged with $ThCl_4$(1,4-dioxane)$_2$ (**10**) (0.500 g, 0.909 mmol) and THF (5 mL). The resulting solution was stirred at room temperature for 10 minutes. The volatiles were removed under reduced pressure affording $ThCl_4(THF)_{3.5}$ (**11**) as a white solid (0.569 g, 0.909 mmol, 100%). ^{1}H NMR (C_6D_6, 298K): δ 3.98 (s, 4H; CH_2O), 1.28 ppm (s, 4H; CH_2CH_2O). Anal. Calcd. for $C_{14}H_{28}Cl_4O_{3.5}Th$ (mol. wt. 626.22): C, 26.85; H, 4.51; Cl, 22.65. Found: C, 27.03; H, 4.53; Cl, 23.0.

References

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