Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Anion-Induced Disproportionation of Th(III) Complexes to Form Th(II) and Th(IV) Products

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Experimental Details

Caution! ^{232}Th is radioactive and is an alpha emitter with a half-life of approximately 1.405x10^{10} years. Samples should be prepared and handled only in laboratories appropriately equipped to handle radioactive materials.

All syntheses and manipulations described below were conducted under argon with rigorous exclusion of air and water using standard glovebox and vacuum line techniques. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred before use. ^{1}H and ^{13}C NMR spectra were recorded on either a CRYO500 MHz or AVANCE600 MHz at 298 K and referenced to residual protio-solvent resonances. UV-visible spectra were collected at 298 K using a Varian Cary 60 Scan UV-visible spectrophotometer or at −80 °C using a Cary 6000i UV-Vis-NIR spectrometer fitted with a Unisoku cryostat. Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR. Electrochemical measurements were collected with a Princeton Applied Research PARSTAT 2273 Advanced Electrochemical System. Data were collected with 200 mM [^{n}Bu$_4$N][PF$_6$] supporting electrolyte in THF and referenced with internal standard (C$_5$Me$_5$)$_2$Fe following previously reported procedures.[6]

2.2.2-Cryptand (crypt, Aldrich) was used as received. 18-Crown-6 (crown, Alfa) was sublimed before use. KH (Sigma) was washed extensively with hexane and toluene to remove oil and dried under vacuum. ^{n}BuLi (Sigma, 2.5 M solution in hexane) was used as received. LiMe (Sigma) and LiCH$_2$SiMe$_3$ were purchased as solutions and the solvent was removed to yield both as a bright white powder which were kept at −35 °C until used. NaN$_3$ and KCl were placed under vacuum at 10^{-5} Torr for 12h before use. KC_8,[1] Cp''_3Th,[2–4] and Cp^{tet}_3Th[5] were synthesized as previously described.

Reaction of Cp''_3Th, KH, and Crypt. Cp''_3Th^{III} (40 mg, 0.046 mmol) and crypt (18 mg, 0.048 mmol) were dissolved in THF (2 mL). KH (2 mg, 0.050 mmol) was added and the solution was stirred for 5 hours. The solution was dried under vacuum and the products were extracted into hexane to afford a pale blue solution. The solvent was removed under vacuum to yield a blue-grey solid (21 mg). The ^1H NMR spectrum in C_6D_6 showed $Cp''_3Th^{IV}H$, Cp''_3Th^{III}, and free crypt. The remaining blue-green solids that did not dissolve in hexane were dissolved in Et_2O, filtered, and dried under vacuum. Crystals were grown from Et_2O/hexane solution at −35 °C and matched the unit cell of $[K(crypt)][Cp''_3Th^{II}]$.[3]

Reaction of Cp''_3Th^{III}, KH, and Crown. Cp''_3Th^{III} (23 mg, 0.027 mmol) and crown (7 mg, 0.027 mmol) were dissolved in THF (2 mL). KH was added and the solution developed a green color as it stirred overnight. The solution was dried under vacuum and extracted into hexane. The remaining blue-green solids were extracted into Et_2O. Both solutions were dried under vacuum. The hexane fraction (16 mg) showed Cp''_3Th^{III} and $Cp''_3Th^{IV}H$ in the ^1H NMR spectrum in a 1:1.1 ratio. $[K(crown)(THF)_2][Cp''_3Th^{II}]$ was identified in the Et_2O fraction (22 mg) by its definitive UV-visible spectrum.[3]

Reaction of Cp''_3Th^{III}, KCl, and Crypt. As described for the KH reaction, Cp''_3Th^{II}, crypt, and KCl were stirred together in THF solution for 2 hours. A dark green color developed. The ^1H NMR spectrum in C_6D_6 of the hexane fraction showed only $Cp''_3Th^{IV}H$. $[K(crypt)][Cp''_3Th^{II}]$ was identified from the Et_2O fraction by UV-visible spectroscopy.

Reaction of Cp''_3Th^{III}, LiMe, and Crypt. Cp''_3Th^{III} (20 mg, 0.023 mmol) and crypt (9 mg, 0.024 mmol) were dissolved in THF (2 mL). LiMe (0.5 mg, 0.023 mmol) was added and the solution turned green after 1 hour. The solution was dried under vacuum. Hexane was added to form a blue solution. This solution was dried under vacuum. The ^{1}H NMR in C_6D_6 showed Cp″$_3$Th^{IV}Me,[10] Cp″$_3$Th^{III}, and free crypt. The remaining green solids that did not dissolve in hexane were dissolved in Et_2O, filtered, and dried under vacuum to yield [Li(crypt)][Cp″$_3$Th^{II}], identified by UV-visible spectroscopy.

Reaction of Cp″$_3$Th^{III}, NaN_3, and Crypt. Cp″$_3$Th^{III} (35 mg, 0.041 mmol) and crypt (15 mg, 0.041 mmol) were dissolved in THF (2 mL) and added to NaN_3 (3 mg, 0.046 mmol). The solution developed a green color as it stirred overnight. The solution was dried under vacuum and extracted into hexane. The remaining blue-green solids were extracted in Et_2O. The hexane fraction was dried under vacuum to yield only Cp″$_3$Th^{IV}N_3 (7 mg, 39%) as a colorless oil. ^{1}H NMR (C_6D_6): δ 6.85 (s, 6H, $C_5H_3(SiMe_3)_2$), 6.81 (s, 3H, $C_5H_3(SiMe_3)_2$), 0.42 (s, 54H, $Si\mathit{Me}_3$) ppm. IR: 2952m, 2895w, 2097s, 1440w, 1374w, 1318w, 1247s, 1204w, 1080w, 921sm, 831s, 790m, 753m, 690w cm^{-1}.

Reaction of Cp″$_3$Th^{III}, $LiCH_2SiMe_3$, and Crypt. Cp″$_3$Th^{III} (25 mg, 0.029 mmol) and crypt (11 mg, 0.029 mmol) were dissolved in THF (2 mL). $LiCH_2SiMe_3$ (3 mg, 0.03 mmol) was added as a solid and the solution quickly turned dark blue-green. The solution was stirred for 2 hours then dried under vacuum. As above, hexane and Et_2O fractions were collected. The ^{1}H NMR spectrum in C_6D_6 of the hexane fraction showed Cp″$_3$Th^{IV}H and Cp″$_3$Th^{III} as the only Cp″-containing compounds present. The Et_2O fraction was dried to yield [Li(crypt)][Cp″$_3$Th^{II}] (29 mg, 81%) identified by UV-visible spectroscopy.[6]

Reaction of Cp″$_3$Th^{III}, ^{n}BuLi, and Crypt. Cp″$_3$Th^{III} (45 mg, 0.052 mmol) and crypt (15 mg, 0.040 mmol) were dissolved in THF (2 mL). ^{n}BuLi (0.2 mL of a 2.5 M solution in hexane, 0.5 mmol) was added via syringe to the stirring solution. The solution immediately turned dark green. The solution was stirred for 5 min then dried under vacuum. The solids were washed with hexane then dissolved in Et_2O, filtered, and dried under vacuum to yield [Li(crypt)][Cp''_3Th^{II}] (41 mg, 66%). The hexane washings were dried under vacuum to yield 21 mg of grey solids. The ^1H NMR spectrum in C_6D_6 showed a single Cp″ environment δ 6.84 (s, 1H, $C_5H_3(SiMe_3)_2$), 6.72 (s, 2H, $C_5H_3(SiMe_3)_2$), 0.41 ppm (s, 18H, $SiMe_3$) that does not match Cp''_3ThH. No resonance was observed above 8 ppm indicative of a Th^{IV}–H. The expected product, $Cp''_3Th(^nBu)$, would likely undergo β–H elimination to form Cp''_3ThH as was observed with Cp''_3ThCl and ^tBuLi.[7]

Reaction of $Cp^{tet}_3Th^{III}$, KH, and Crypt. $Cp^{tet}_3Th^{III}$ (75 mg, 0.13 mmol) and crypt (47 mg, 0.13 mmol) were dissolved in THF (2 mL). This solution was added to KH (7 mg, 0.2 mmol) and stirred for 1 hour. The color of the solution slowly changed from purple to yellow/orange. The solution was dried under vacuum and the products were extracted into toluene. The ^1H NMR spectrum in C_6D_6 showed $Cp^{tet}_3Th^{IV}H$ and free crypt. The remaining solids were dissolved in THF, filtered, and dried. The ^1H NMR spectrum in THF-d_8 showed [K(crypt)][Cp^{tet}] and [K(crypt)][$Cp^{tet}_2Th^{IV}H(\eta^1:\eta^5\text{-}C_5Me_3HCH_2)$].[8] Both compounds were also identified by a unit cell check of single crystals.

Reaction of [K(crown)(THF)$_2$][Cp''_3Th^{II}] with $Cp''_3Th^{IV}Cl$. In one vial, [K(crown)(THF)$_2$][Cp''_3Th^{II}] (10 mg, 0.008 mmol) was dissolved in THF (1 mL) to form a dark blue/green solution. This solution was added via pipet to a second vial containing a colorless solution of $Cp''_3Th^{IV}Cl$ (7 mg, 0.008 mmol) in THF (1 mL). Upon addition, the solution immediately turned deep blue. The solution was stirred for 2 min then dried under vacuum to yield white and blue solids. The solids were redissolved in C_6D_6, filtered, and a ^1H NMR spectrum was obtained. The spectrum showed only Cp''_3Th^{III}, a small amount of Cp''_3ThH, and

18-crown-6 with complete disappearance of Cp''_3ThCl resonances. The solution was dried under vacuum to yield 11 mg of a dark blue solid (theoretical yield of Cp''_3Th^{III} is 14 mg).

***In situ* UV-Visible Spectroscopy.** −80 °C electronic absorption studies of the reaction of Cp''_3Th^{III} and LiMe were performed using a Cary 6000i UV-Vis-NIR spectrometer fitted with a Unisoku cryostat. An initial absorption spectrum was collected followed by addition of excess LiMe (10 equiv) via syringe to a septum capped 1 cm pathlength quartz cell containing a 0.15 mM solution of Cp''_3Th^{III} in THF at -80 °C. The reaction was then followed through collection of absorption spectra (300-700 nm) every 132 seconds until no further change was observed (~ 28 minutes).

Synthesis of $Cp''_3Th^{IV}Me$ from $Cp''_3Th^{IV}Br$. Cp''_3ThBr (100 mg, 0.106 mmol) was dissolved in Et_2O (5 mL). MeLi was added via syringe (0.07 mL of 1.6M solution in THF, 0.112 mmol) and the colorless solution was stirred overnight. Tan precipitate had formed. The solution was dried under vacuum and hexane was added (10 mL). Solids were removed via centrifugation and solvent was removed under vacuum to yield off-white solids of Cp''_3ThMe (64 mg, 69%), identified by ^1H NMR spectroscopy.[10]

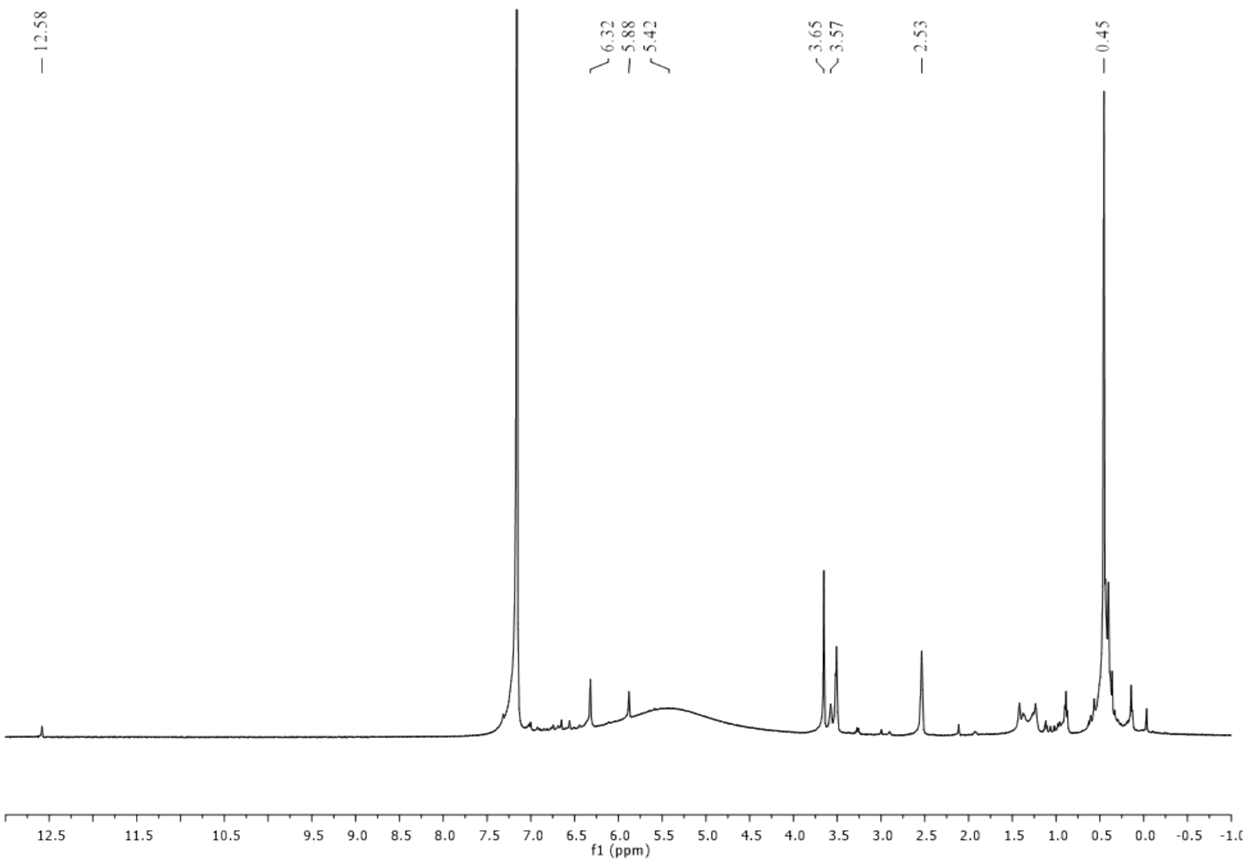

Figure S1: ^{1}H NMR spectrum of the hexane fraction of Cp″$_3$Th + KH + crypt in C_6D_6 after separation of [Cp″$_3$Th]$^{1-}$. Peaks at 12.58, 6.32, 5.88, and 0.45 ppm are assigned to Cp″$_3$ThH,[8] the broad peak at 5.42 ppm is Cp″$_3$Th, and 3.65, 3.57, and 2.53 ppm are free crypt.[9]

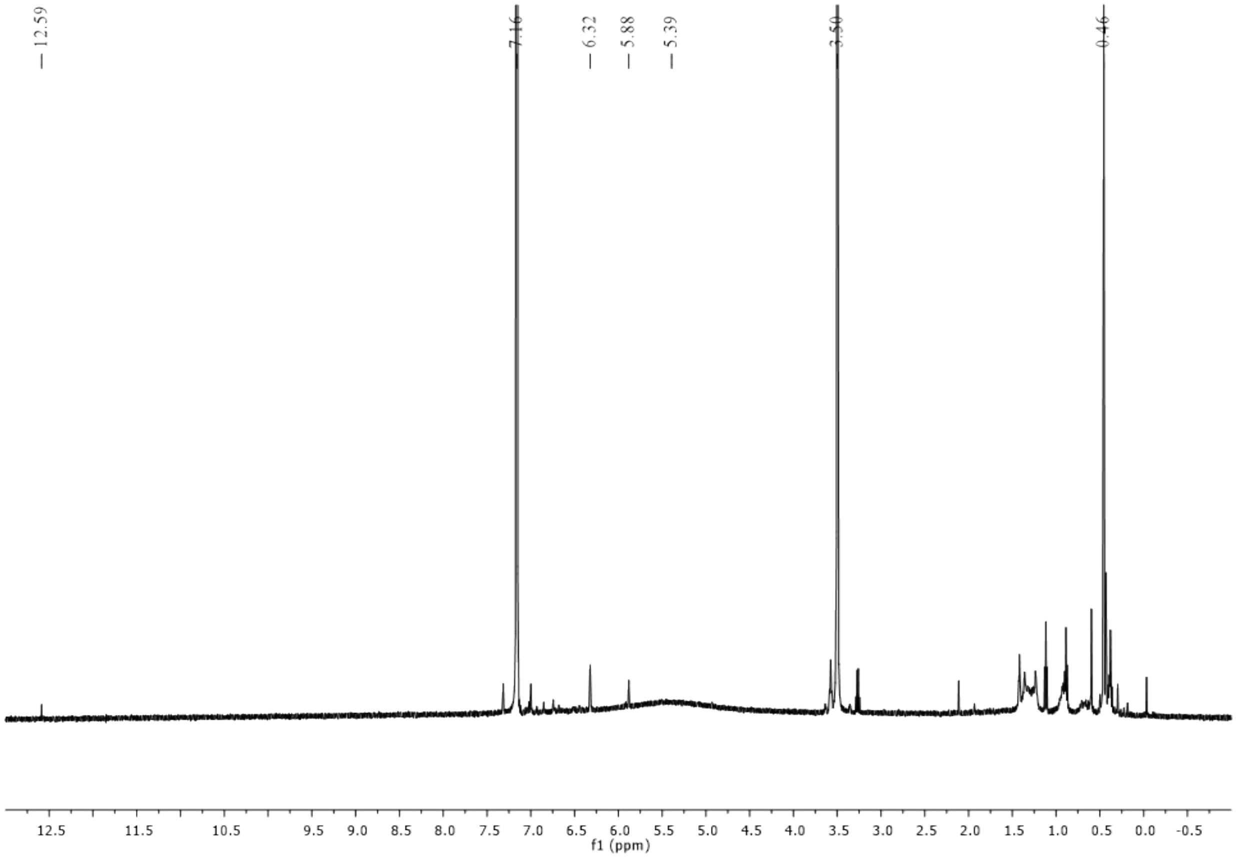

Figure S2: ^{1}H NMR spectrum of the hexane fraction of Cp″$_3$Th + KH + crown in C_6D_6 after separation of [Cp″$_3$Th]$^{1-}$. Peaks at 12.59, 6.32, 5.88, and 0.46 ppm are assigned to Cp″$_3$ThH,[8] the broad peak at 5.39 ppm is Cp″$_3$Th, and 3.50 ppm is free crown.[9]

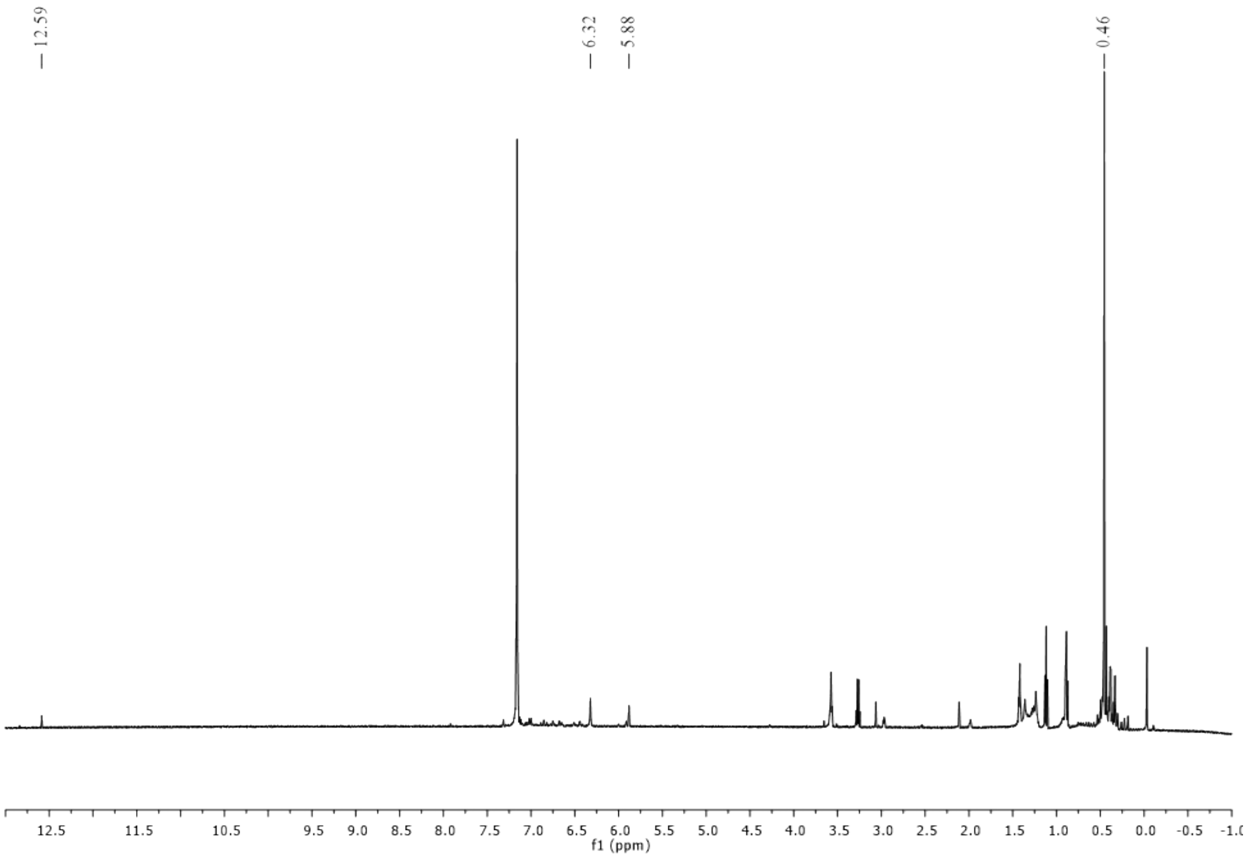

Figure S3: ^{1}H NMR spectrum of hexane fraction of Cp''_3Th + KCl + crypt taken in C_6D_6 after separation of $[Cp''_3Th]^{1-}$. The peaks at 12.59, 6.32, 5.88, and 0.46 ppm are Cp''_3ThH.[8] Most of the other peaks are due to residual solvent (hexane, Et_2O, THF).[9]

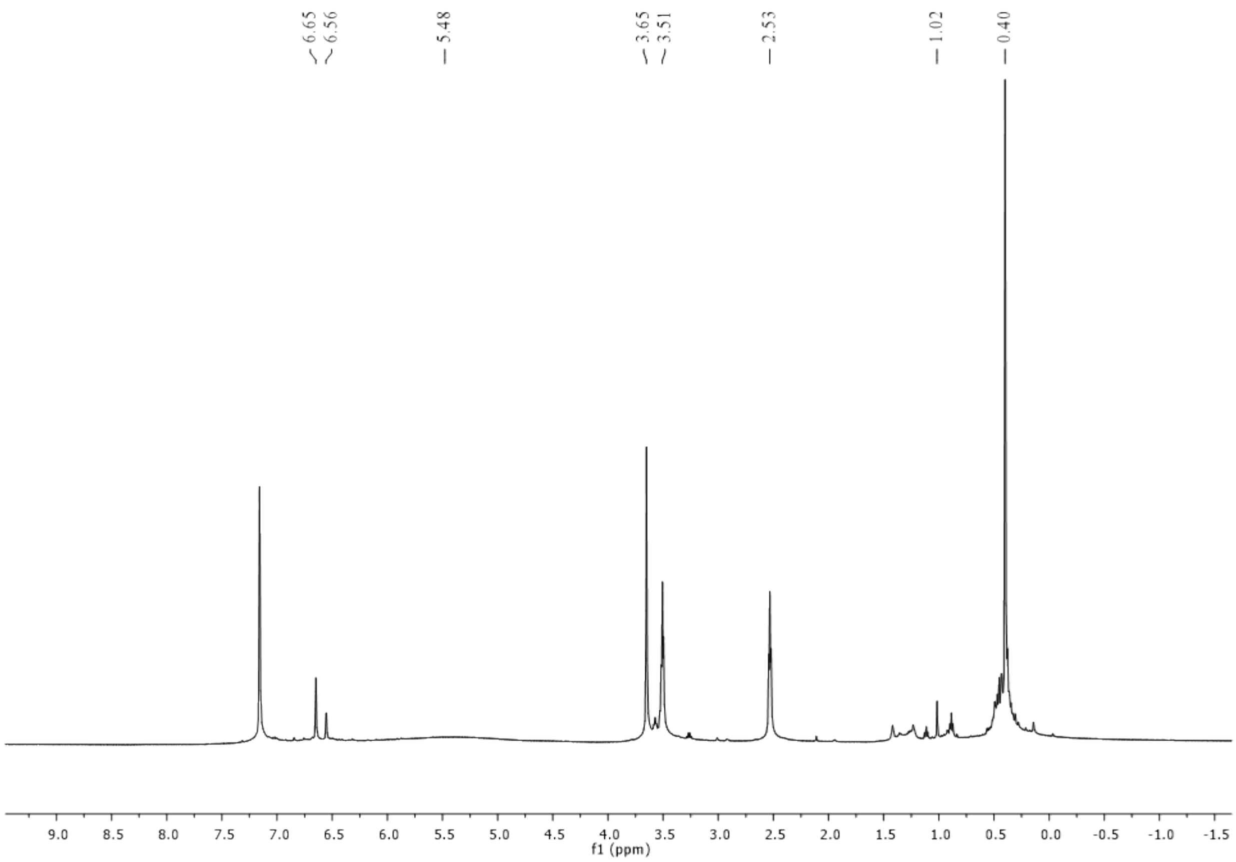

Figure S4: ^{1}H NMR spectrum of the hexane fraction of Cp″$_3$Th + MeLi + crypt taken in C_6D_6 after separation of [Cp″$_3$Th]$^{1-}$. The peaks at 6.65, 6.56, 1.02, and 0.40 ppm are assigned to Cp″$_3$ThMe,[10] the broad peak at 5.48 is Cp″$_3$Th, and the peaks at 3.65, 3.51, and 2.53 are free crypt.

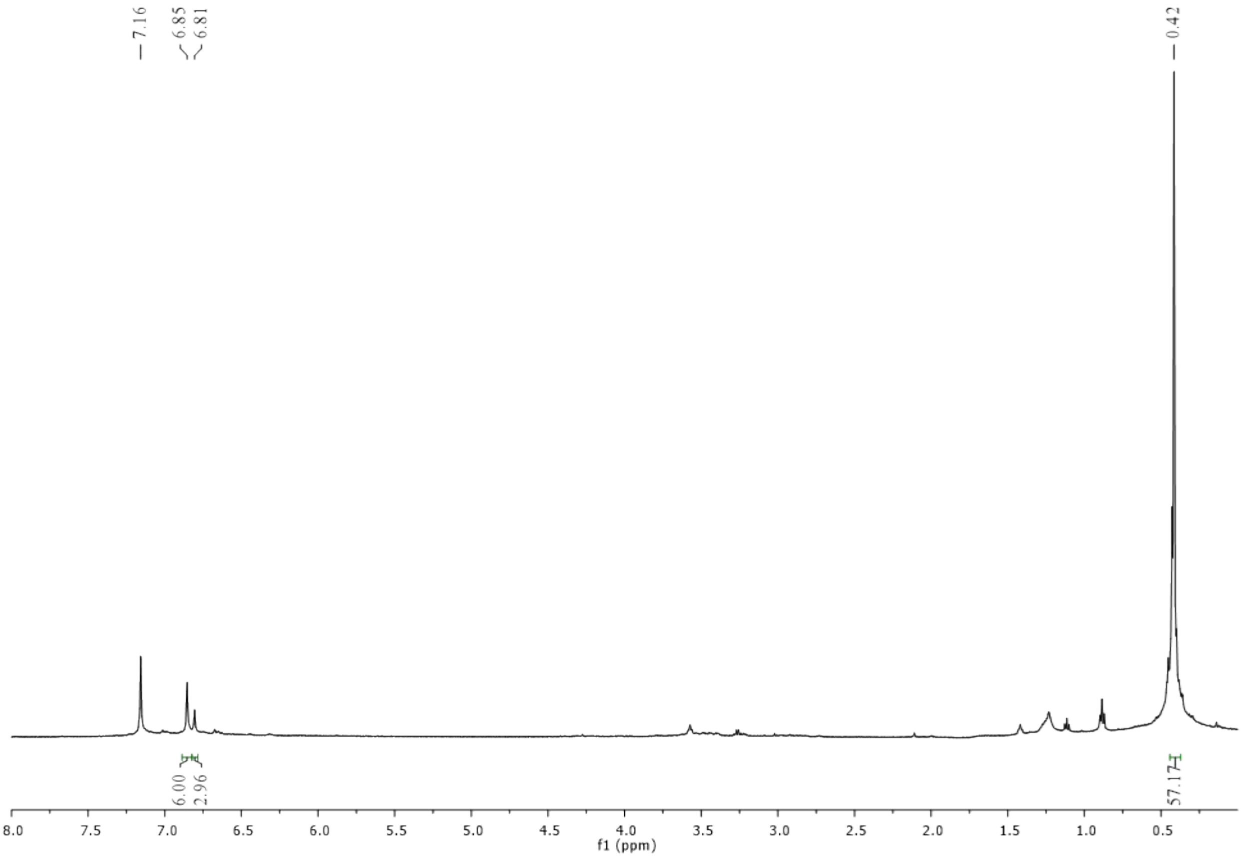

Figure S5: ^{1}H NMR spectrum of Cp''_3ThN_3 in C_6D_6.

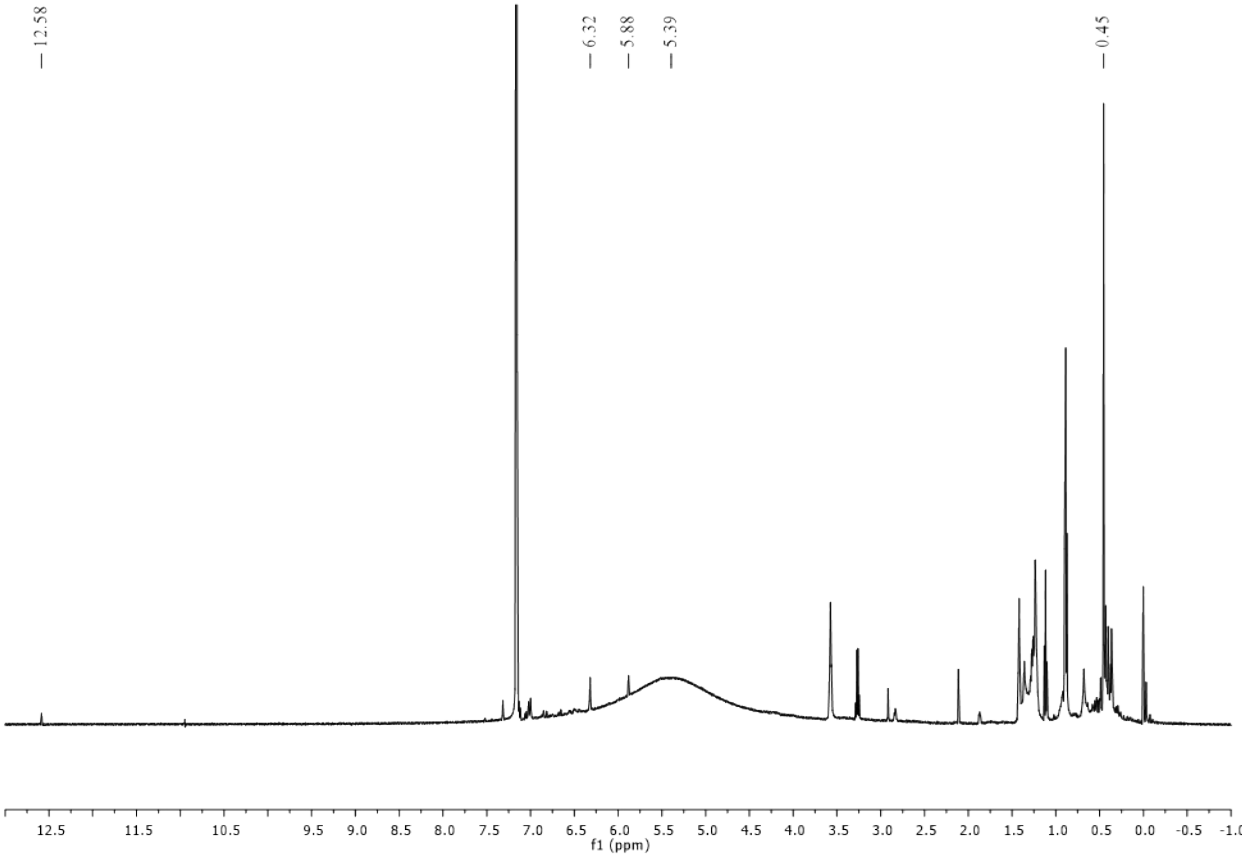

Figure S6: ^{1}H NMR spectrum of the hexane fraction of Cp″$_3$Th + LiCH$_2$SiMe$_3$ + crypt taken in C_6D_6 after separation of [Cp″$_3$Th]$^{1-}$. The peaks at 12.58, 6.32, 5.88, and 0.45 are Cp″$_3$ThH[8] and the broad peak at 5.39 is Cp″$_3$Th. Most of the other peaks are due to residual solvents (hexane, Et$_2$O, THF).[9]

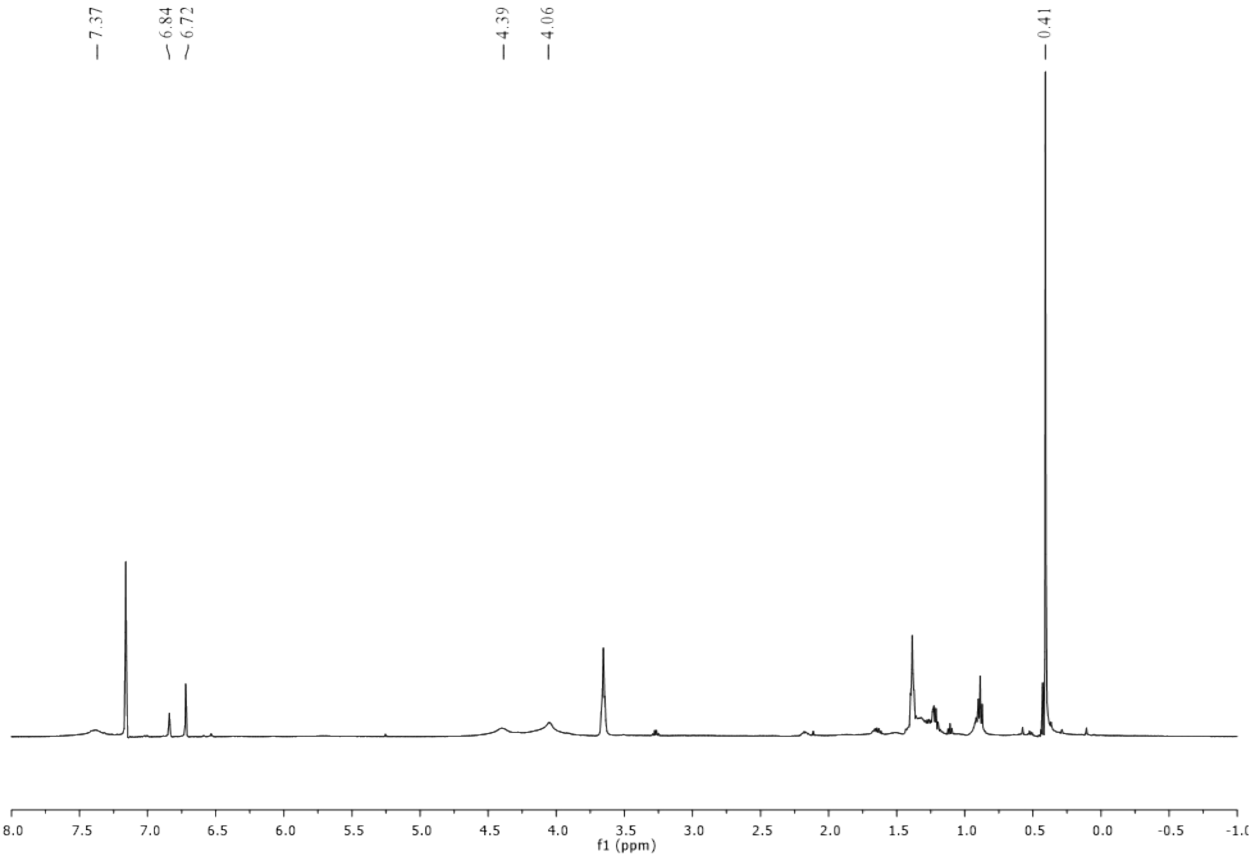

Figure S7: ^{1}H NMR spectrum of the hexane fraction of Cp″$_3$Th + ^{n}BuLi + crypt taken in C_6D_6 after separation of [Cp″$_3$Th]$^{1-}$. The peaks at 6.84, 6.72, and 0.41 are indicative of a single Cp″ environment.

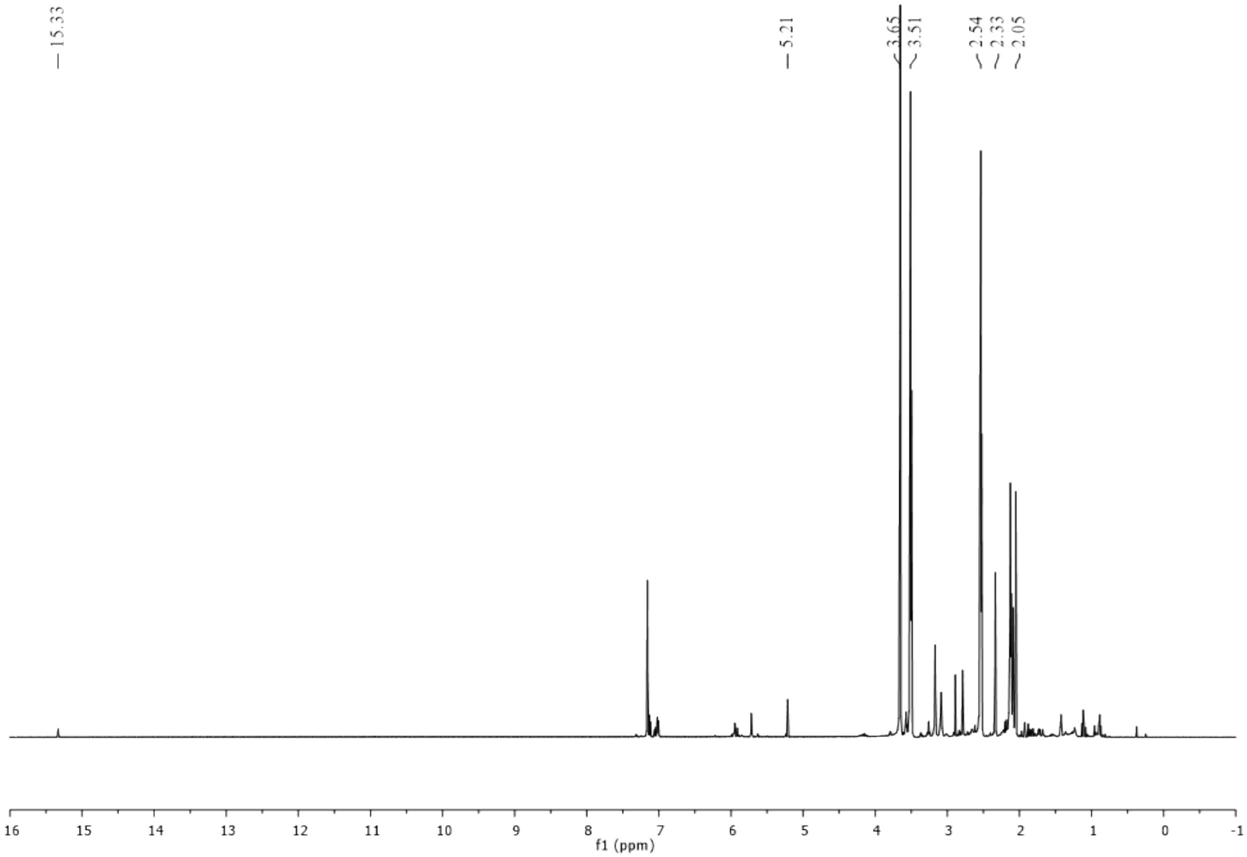

Figure S8: ^{1}H NMR spectrum of the toluene fraction of Cp$^{tet}{}_3$Th + KH + crypt taken in C_6D_6 after separation of [Cp″$_3$Th]$^{1-}$. The peaks at 15.33, 5.21, 2.33, and 2.05 are assigned to Cp$^{tet}{}_3$ThH[8] and the peaks at 3.65, 3.51, and 2.54 are free crypt. Other resonances are due to free solvent (hexane, Et_2O, THF)[9] or unidentified products.

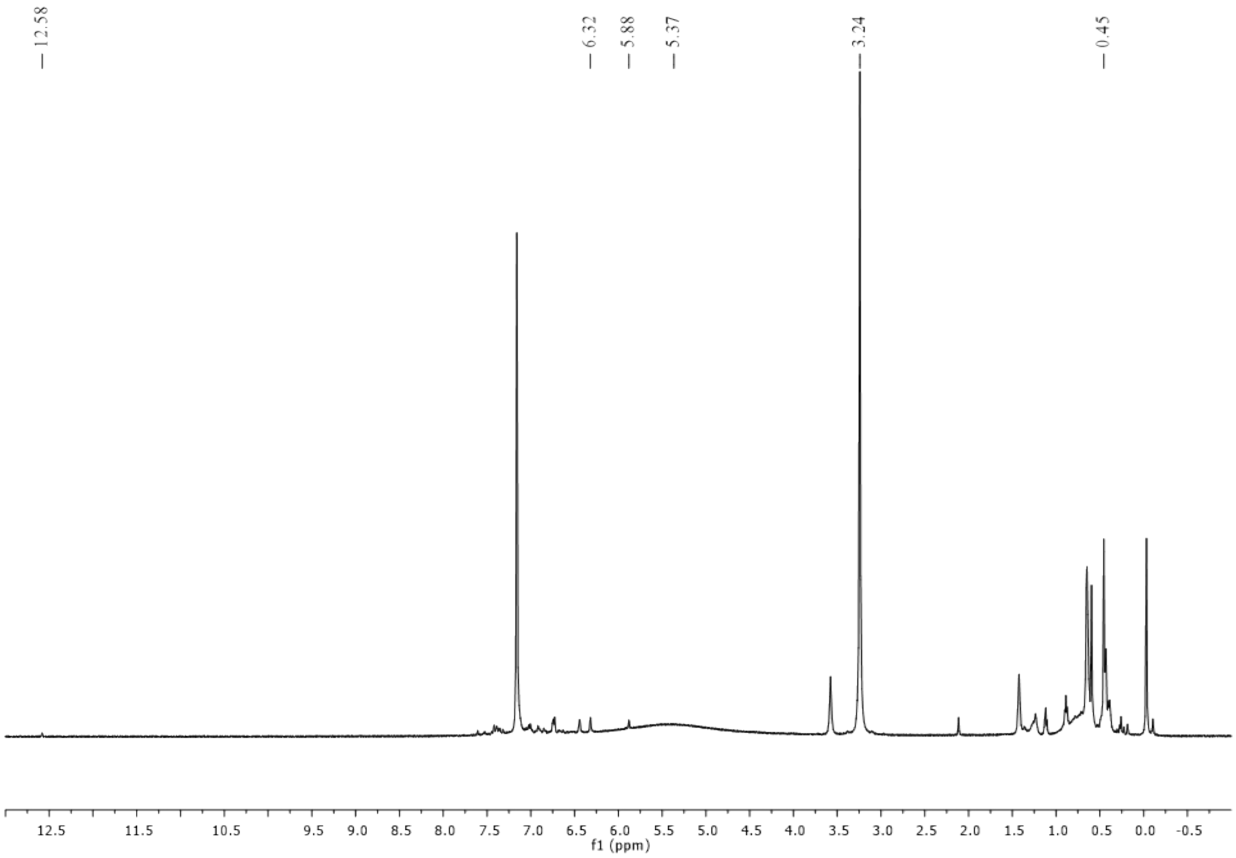

Figure S9: ^{1}H NMR spectrum of [K(crypt)][Cp″$_3$Th] + Cp″$_3$ThCl taken in C_6D_6 after separation of [Cp″$_3$Th]$^{1-}$. The peaks at 12.58, 6.32, 5.88, and 0.45 are Cp″$_3$ThH and the broad peak at 5.37 is Cp″$_3$Th. The resonances for Cp″$_3$ThCl at 6.74, 6.44, and 0.38 ppm were not observed.

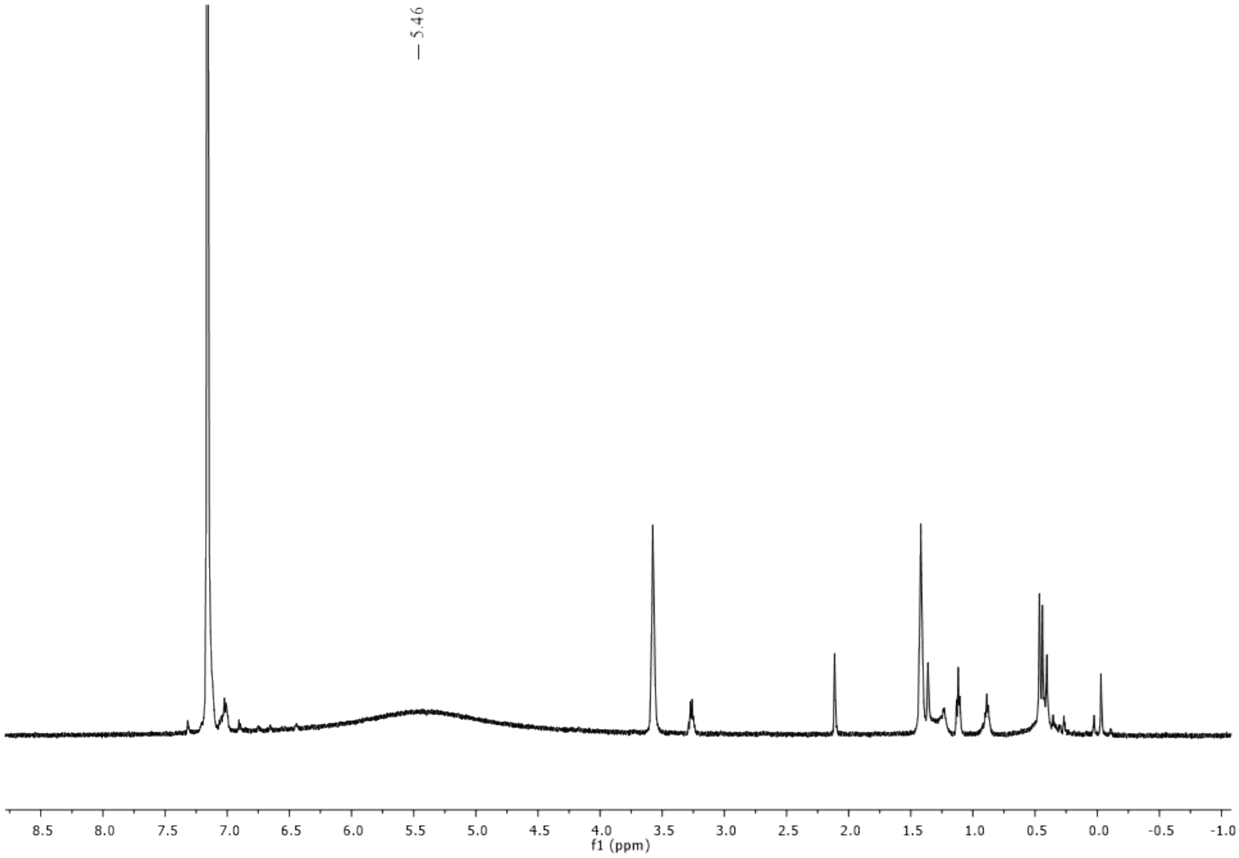

Figure S10: ^{1}H NMR spectrum of Cp″$_3$Th in C_6D_6. Unassigned peaks are due to solvent (C_6D_6, toluene, THF, Et_2O, hexane).[9]

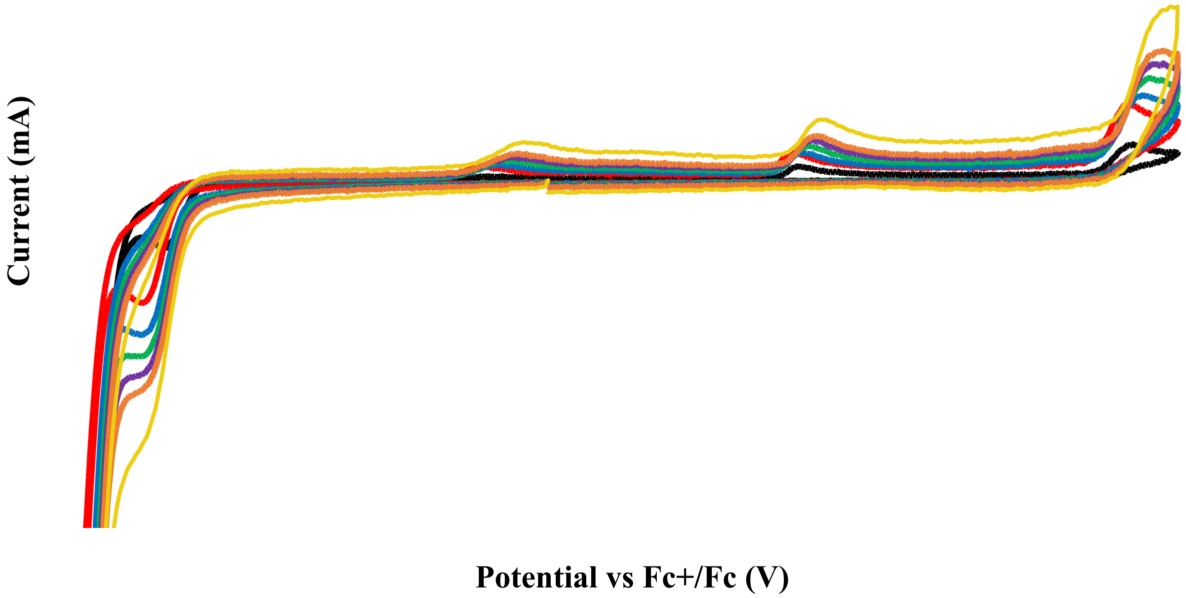

Figure S11: Voltammogram of Cp″$_3$Th^{IV}Me at *v* = 50 (black), 200 (red), 400 (blue), 600 (green), 800 (purple), 1000 (orange), and 2000 mV/s (yellow) in 200 mM [^{n}Bu$_4$N][PF$_6$] / THF.

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