# Synthesis, Structure, and Reactivity of the Sterically Crowded Th^{3+} Complex (C$_5$Me$_5$)$_3$Th Including Formation of the Thorium Carbonyl, [(C$_5$Me$_5$)$_3$Th(CO)][BPh$_4$]

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S *Supporting Information*

ABSTRACT: The Th^{3+} complex, (C$_5$Me$_5$)$_3$Th, has been isolated despite the fact that tris(pentamethylcyclopentadienyl) complexes are highly reactive due to steric crowding and few crystallographically characterizable Th^{3+} complexes are known due to their highly reducing nature. Reaction of (C$_5$Me$_5$)$_2$ThMe$_2$ with [Et$_3$NH][BPh$_4$] produces the cationic thorium complex [(C$_5$Me$_5$)$_2$ThMe][BPh$_4$] that can be treated with KC$_5$Me$_5$ to generate (C$_5$Me$_5$)$_3$ThMe, **1**. The methyl group on (C$_5$Me$_5$)$_3$ThMe can be removed with [Et$_3$NH]- [BPh$_4$] to form [(C$_5$Me$_5$)$_3$Th][BPh$_4$], **2**, the first cationic tris- (pentamethylcyclopentadienyl) metal complex, which can be reduced with KC$_8$ to yield (C$_5$Me$_5$)$_3$Th, **3**. Complexes **1**−**3** have metrical parameters consistent with the extreme steric crowding that previously has given unusual (C$_5$Me$_5$)$^-$ reactivity to (C$_5$Me$_5$)$_3$M complexes in reactions that form less crowded (C$_5$Me$_5$)$_2$M- containing products. However, neither sterically induced reduction nor (η^1-C$_5$Me$_5$)$^-$ reactivity is observed for these complexes. (C$_5$Me$_5$)$_3$Th, which has a characteristic EPR spectrum consistent with a d^1 ground state, has the capacity for two-electron reduction via Th^{3+} and sterically induced reduction. However, it reacts with MeI to make two sterically more crowded complexes, (C$_5$Me$_5$)$_3$ThI, **4**, and (C$_5$Me$_5$)$_3$ThMe, **1**, rather than (C$_5$Me$_5$)$_2$Th(Me)I. Complex **3** also forms more crowded complexes in reactions with I$_2$, PhCl, and Al$_2$Me$_6$, which generate (C$_5$Me$_5$)$_3$ThI, (C$_5$Me$_5$)$_3$ThCl, and (C$_5$Me$_5$)$_3$ThMe, **1**, respectively. The reaction of (C$_5$Me$_5$)$_3$Th, **3**, with H$_2$ forms the known (C$_5$Me$_5$)$_3$ThH as the sole thorium-containing product. Surprisingly, (C$_5$Me$_5$)$_3$ThH is also observed when (C$_5$Me$_5$)$_3$Th is combined with 1,3,5,7-cyclooctatetraene. [(C$_5$Me$_5$)$_3$Th][BPh$_4$] reacts with tetrahydrofuran (THF) to make [(C$_5$Me$_5$)$_3$Th(THF)][BPh$_4$], **2-THF**, which is the first (C$_5$Me$_5$)$_3$M of any kind that does not have a trigonal planar arrangement of the (C$_5$Me$_5$)$^-$ rings. It is also the first (C$_5$Me$_5$)$_3$M complex that does not ring-open THF. [(C$_5$Me$_5$)$_3$Th][BPh$_4$], **2**, reacts with CO to generate a product characterized as [(C$_5$Me$_5$)$_3$Th(CO)][BPh$_4$], **5**, the first example of a molecular thorium carbonyl isolable at room temperature. These results have been analyzed using density functional theory calculations.
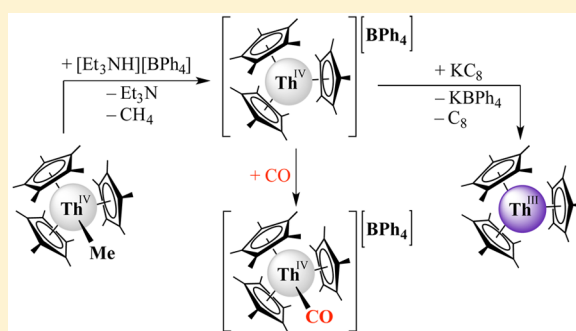
■ INTRODUCTION

Although thorium and uranium are only separated by one element in the periodic table and both are more heavily investigated than the other more radioactive actinides, the chemistry of thorium is less developed compared to that of uranium. Where there are scores of uranium complexes of different types, there are often comparatively few thorium examples despite recent efforts by several groups.[1−9] This is due in part to the limited number of accessible oxidation states of thorium: Th^{4+} is the predominant oxidation state since Th^{3+} is such a strong reductant[10−12] that it is difficult to access[13] and Th^{2+} has only recently been identified.[14] An example of the limited number of Th vs U compounds can be found with the [(C$_5$Me$_5$)$_3$]$^{3-}$ ligand environment. Although there are seven examples with uranium, (C$_5$Me$_5$)$_3$U,[15] (C$_5$Me$_5$)$_3$U(CO),[16] (C$_5$Me$_5$)$_3$U(N$_2$),[17] (C$_5$Me$_5$)$_3$U(NCR),[18] and (C$_5$Me$_5$)$_3$UX[19] (X = F, Cl, Me), there is only one example with thorium,

(C$_5$Me$_5$)$_3$ThH.[20] Addressing this deficiency in the tris- (pentamethylcyclopentadienyl) chemistry of Th vs U has revealed unusual chemistry for both thorium and (C$_5$Me$_5$)$_3$M complexes in general.

With estimates of standard Th^{4+}/Th^{3+} reduction potentials of −3.0 and −3.8 V vs SHE,[10−12] it perhaps was not surprising that it took until 1986 to obtain the first crystallographically characterizable Th^{3+} complex, [C$_5$H$_3$(SiMe$_3$)$_2$]$_3$Th.[21] The difficulty in accessing Th^{3+} is exemplified by the fact that only five additional structures of complexes of Th^{3+} have been subsequently reported over the past 30 years: two other tris(cyclopentadienyl) complexes, [C$_5$H$_3$(SiMe$_2$^{t}Bu)$_2$]$_3$Th[22] and (C$_5$Me$_4$H)$_3$Th,[23] and [K(DME)$_2$]- {[C$_8$H$_6$(SiMe$_2$^{t}Bu)$_2$]$_2$Th},[24] (C$_5$Me$_5$)$_2$[^{i}PrNC(Me)N^{i}Pr]Th,[25]

and $[K(18\text{-crown-}6)(Et_2O)]\{[C_5H_3(SiMe_3)_2]_2Th(\mu\text{-H})_3ThH\text{-}[C_5H_3(SiMe_3)_2]\}$.[26]

An interesting variation of the tris(cyclopentadienyl) complexes listed above is $(C_5Me_5)_3Th$. Such a complex would combine the high reactivity of Th^{3+} with the unusual reactivity conferred by the steric crowding of three pentamethylcyclopentadienyl rings. For many years, it was thought impossible to synthesize $(C_5Me_5)_3M$ complexes[27] since the cone angle of the $(C_5Me_5)^-$ ligand was believed to be 142° and thus three $(C_5Me_5)^-$ ligands would not fit around a metal center.[28] The synthesis of $(C_5Me_5)_3Sm$[29] showed that this class of crowded complexes could be synthesized, and subsequently many $(C_5Me_5)_3M$ complexes, where M = U,[15] La,[30] Ce,[31] Pr,[31] Nd,[32] Sm,[29] Y,[33] and Gd,[33] were isolated and crystallographically characterized. The steric crowding in $(C_5Me_5)_3M$ complexes forces the $(C_5Me_5)^-$ rings to be placed at unusually long distances from the metal, conferring unusual reactivity on the $(C_5Me_5)^-$ ligands. They can act as alkyl ligands via eq 1,

(1)
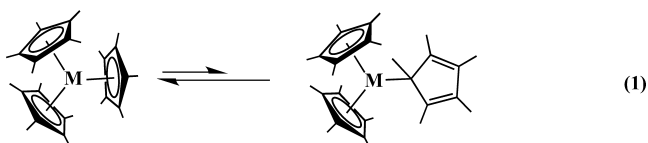
participating in olefin polymerization, CO insertion chemistry, hydrogenolysis, and ring-opening of tetrahydrofuran (THF). They also can effect reduction as shown in eq 2, a reaction

(2)
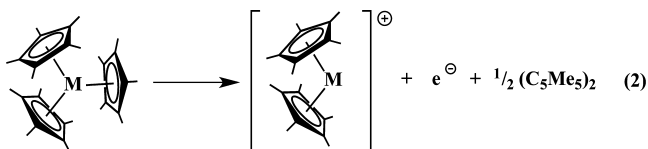
termed sterically induced reduction (SIR).[34] Hence, $(C_5Me_5)_3Th$, if it could be synthesized, could react in a variety of ways including possible multielectron reductions stemming from the combination of SIR with the Th^{4+}/Th^{3+} redox couple. Similar multielectron reductions originating from the combination of SIR and metal-based electrons have been reported from the analogous uranium complex, $(C_5Me_5)_3U$.[35]

Since $(C_5Me_5)_3U$ is known, and thorium is larger than uranium, it should be sterically possible for $(C_5Me_5)_3Th$ to exist, but the difficulty in accessing Th^{3+} made its synthesis a challenge. In addition, it was uncertain if the highly reducing Th^{3+} could coexist with three strongly electron donating $(C_5Me_5)^-$ ligands. Previous attempts to make any type of thorium complex with three pentamethylcyclopentadienyl ligands provided only one example, $(C_5Me_5)_3ThH$,[20] and it was unusual in that it did not react according to eqs 1 and 2.

One conceivable route to the synthesis of $(C_5Me_5)_3Th$ involved the reduction of a cation such as $[(C_5Me_5)_3Th][BPh_4]$ or $[(C_5Me_5)_3Th(THF)][BPh_4]$. These cations could be accessible by protonolysis of the methyl group in $(C_5Me_5)_3ThMe$, if that compound could be synthesized. Previous attempts to make $(C_5Me_5)_3ThMe$ by reacting KC_5Me_5 with the known cation $[(C_5Me_5)_2ThMe][BPh_4]$,[36] synthesized from $(C_5Me_5)_2ThMe_2$,[37] were unsuccessful.[20] We now report conditions that allow the successful preparation of $(C_5Me_5)_3ThMe$ and the subsequent synthesis of $(C_5Me_5)_3Th$ as outlined here. Preliminary studies of the reactivity of $(C_5Me_5)_3Th$ and the other new $(C_5Me_5)_3M$ complexes obtained in the course of its synthesis are also reported.

In addition, the first room temperature stable thorium carbonyl complex has been isolated by reaction of CO with the cationic precursor $[(C_5Me_5)_3Th][BPh_4]$. Although organothorium carbon monoxide chemistry has been studied since the early insertion studies of Marks et al. in the 1970s,[38−42] no molecular thorium carbonyl complexes nor carbonyl complexes of any +4 ions of actinides have been previously reported. The only thorium carbonyl complexes in the literature are Th(CO), $Th(CO)_2$, and $Th(CO)_6$ which were generated in matrix isolation studies at cryogenic temperatures and identified by IR spectroscopy.[43−45] The closest compounds of this type are the tris(cyclopentadienyl) uranium carbonyls $(C_5H_4SiMe_3)_3U$-(CO),[46] $(C_5Me_4H)_3U(CO)$,[47,48] and $(C_5Me_5)_3U(CO)$.[16]

■ EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk, high vacuum line, and glovebox techniques under an argon atmosphere. Solvents were sparged with ultrahigh purity (UHP) argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. C_6D_6 and C_4D_8O were dried over sodium benzophenone ketyl, degassed by three freeze−pump−thaw cycles, and vacuum transferred before use. C_6D_5Cl and C_6H_5Cl were dried with molecular sieves and degassed by three freeze−pump−thaw cycles before use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker GN500 or CRYO500 spectrometers operating at 500 and 125 MHz, respectively, at 298 K unless otherwise noted and were referenced internally to residual protio-solvent resonances. EPR spectra were collected using X-band frequency (9.3−9.8 GHz) on a Bruker EMX spectrometer equipped with an ER041XG microwave bridge. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazyl (DPPH) (g = 2.0036). IR samples were prepared as KBr pellets, or in solution where noted, and analyzed using a Jasco 4700 FT-IR spectrometer. Electronic spectra were collected on a Cary 50 UV−vis spectrometer. Elemental analyses were conducted on a PerkinElmer 2400 Series II CHNS elemental analyzer. $(C_5Me_5)_2ThMe_2$,[37] $[(C_5Me_5)_2ThMe][BPh_4]$,[36] $[Et_3NH][BPh_4]$,[49] and KC_8[50] were prepared according to literature procedures. KC_5Me_5 was prepared in an adaptation of a literature procedure[51] using $KN(SiMe_3)_2$ instead of KH. $KN(SiMe_3)_2$ (Aldrich) was dissolved in toluene and centrifuged, and the supernatant was dried under reduced pressure before use. H_2 (Praxair), ^{12}CO (Praxair, 99.99%,), and ^{13}CO (Aldrich, <5 atom % ^{18}O, 99 atom % ^{13}C) were used as received. MeI and C_8H_8 were dried over molecular sieves and degassed by three freeze−pump−thaw cycles. KH (Aldrich, dispersion in mineral oil) was washed with hexane in an argon-containing glovebox to remove mineral oil before use. Al_2Me_6 (Aldrich, 2.0 M solution in hexanes) was used as received.

$[(C_5Me_5)_2ThMe][BPh_4]$. Note that this synthesis requires extreme purity of the starting materials. $(C_5Me_5)_2ThMe_2$ was recrystallized four times before use. In an adaptation of a literature procedure,[36] solid $[Et_3NH][BPh_4]$ (58 mg, 0.14 mmol) was added to a stirred colorless solution of $(C_5Me_5)_2ThMe_2$ (75 mg, 0.14 mmol) in benzene (15 mL). The white slurry was allowed to react for 2.5 h, during which time it became transparent. Toluene (3 mL) was added and the solvent was removed under reduced pressure to yield an off-white solid. Hexane (10 mL) was added and the mixture was stirred for 20 min. The slurry was centrifuged and the solids were collected and dried to yield $[(C_5Me_5)_2ThMe][BPh_4]$ as an off-white solid (121 mg, 95%). ^1H NMR (C_6D_6):[36] δ 7.85 [m, 8H, o-BPh_4], 7.25 [t, $^3J_{HH}$ = 7 Hz, 8H, m-BPh_4], 7.10 [t, $^3J_{HH}$ = 7 Hz, 4H, p-BPh_4], 1.61 [s, 30H, C_5Me_5], 0.41 [s, 3H, Th-Me].

$(C_5Me_5)_3ThMe$, 1. Solid KC_5Me_5 (84 mg, 0.48 mmol) was added to a stirred solution of $[(C_5Me_5)_2ThMe][BPh_4]$ (207 mg, 0.240 mmol) in toluene (20 mL). The off-white slurry was stirred for 2 days and turned dull yellow. The mixture was centrifuged and the supernatant was filtered to yield a pale yellow solution, which was dried under vacuum to yield white and yellow solids. The yellow component was removed by washing these solids with cold pentane,

and the remaining solids were dried under vacuum to yield **1** as a white solid. X-ray quality crystals were grown from a hot toluene solution cooled to −30 °C (90 mg, 58%). ^{1}H NMR (C_6D_6): δ 2.00 [s, 45H, C_5Me_5], 0.40 [s, 3H, Th-*Me*]. ^{13}C{^{1}H} NMR (C_6D_6): δ 123.95 [C_5Me_5], 56.36 [Th-*Me*], 12.90 [C_5Me_5]. NMR assignments were confirmed with an HMQC experiment. IR: 2969s, 2926s, 2891s, 2850s, 2715m, 1481m, 1431s, 1404m, 1379s, 1364m, 1105m, 1046w, 1013m, 945w, 806w, 727w, 793w, 609m, 591m, 545w, 504m cm^{-1}. Anal. Calcd for $C_{31}H_{48}Th$: C, 57.04; H, 7.41. Found: C, 57.18; H, 7.43.

[(C$_5$Me$_5$)$_3$Th][BPh$_4$], 2, and [(C$_5$Me$_5$)$_3$Th(THF)][BPh$_4$], 2-THF. In a glovebox free of coordinating solvents, solid [Et$_3$NH][BPh$_4$] (29 mg, 0.068 mmol) was added to a stirred colorless solution of crystalline **1** (46 mg, 0.070 mmol) in toluene (20 mL). The white slurry began to turn pink after 20 min and was left to react for 15 h, during which time the color became more intense. The mixture was centrifuged and the supernatant was removed. The solids were washed with toluene and dried to yield **2** as an analytically pure salmon-colored solid (60 mg, 90%). ^{1}H NMR (C_6D_5Cl): δ 7.97 [m, 8H, *o*-B*Ph*$_4$], 7.24 [t, $^3J_{HH}$ = 7 Hz, 8H, *m*-B*Ph*$_4$], 7.10, [t, $^3J_{HH}$ = 7 Hz, 4H, *p*-B*Ph*$_4$], 1.85 [s, 45H, C_5Me_5]. ^{13}C{^{1}H} NMR (C_6D_5Cl): δ 137.07 [*o*-B*Ph*$_4$], 133.88 [C_5Me_5] 126.00 [*m*-B*Ph*$_4$], 122.05 [*p*-B*Ph*$_4$], 12.96 [C_5Me_5]. IR: 3055m, 3034m, 2999m, 2878m, 2962m, 2911m, 2965m, 2853m, 1591w, 1478m, 1442m, 1377w, 1260w, 1240w, 1184w, 1153w, 1062w, 1042w, 1030w, 843w, 742s, 733s, 710s, 706s, 611w, 601m cm^{-1}. Anal. Calcd for $C_{54}H_{65}BTh$: C, 67.78; H, 6.85. Found: C, 67.87; H, 6.87. In a glovebox containing coordinating solvents, X-ray quality crystals of the THF adduct, **2-THF**, were obtained by pentane vapor diffusion into a concentrated THF solution of **2** at −15 °C. ^{1}H NMR (C_4D_8O): δ 7.30 [m, 8H, *o*-B*Ph*$_4$], 6.87 [t, $^3J_{HH}$ = 7 Hz, 8H, *m*-B*Ph*$_4$], 6.72 [t, $^3J_{HH}$ = 7 Hz, 4H, *p*-B*Ph*$_4$], 2.19 [s, 45H, C_5Me_5]. ^{13}C{^{1}H} NMR (C_4D_8O): δ 136.99 [*o*-B*Ph*$_4$], 133.29 [*m*-B*Ph*$_4$], 125.56 [*p*-B*Ph*$_4$], 121.68 [C_5Me_5], 13.77 [C_5Me_5]. NMR assignments were confirmed with HMQC experiments.

Synthesis of [(C$_5$Me$_5$)$_3$Th][BPh$_4$], 2, from (C$_5$Me$_5$)$_3$ThH. Solid [Et$_3$NH][BPh$_4$] (6 mg, 0.01 mmol) was added to a stirred colorless solution of (C$_5$Me$_5$)$_3$ThH (10 mg, 0.016 mmol) in toluene (10 mL). After the resulting white slurry was stirred for 6 h, it became a pink slurry. The mixture was centrifuged and the solids were washed with toluene. The solids were dried to yield **2** as a salmon-colored powder (12 mg, 80%) identified by ^{1}H NMR spectroscopy.

(C$_5$Me$_5$)$_3$Th, 3. Solid **2** (60 mg, 0.063 mmol) was dissolved in THF (20 mL) and KC$_8$ (13 mg, 0.096 mmol) was added. The pale yellow solution immediately turned dark purple. The solution was allowed to react for 20 min before being filtered and dried under reduced pressure to yield purple and white solids. The purple solids were extracted into toluene, filtered, and dried under reduced pressure to yield **3** as a purple solid. Blue X-ray quality crystals were grown from a toluene solution at −35 °C (22 mg, 61%). EPR (toluene, room temperature) g_{iso} = 1.88; (toluene, 77 K) $g_∥$ = 1.97, $g_⊥$ = 1.85. UV–vis (toluene) $λ_{max}$ nm ($ε$, M^{-1} cm^{-1}): 391 (1700), 440 (1100 shoulder), 530 (9500), 569 (4700), 640 (3900). IR: 2967s, 2898s, 2851s, 1500w, 1434s, 1374s, 1359m, 1014w, 800w, 728s cm^{-1}. Anal. Calcd for $C_{30}H_{45}Th$: C, 56.50; H, 7.11. Found: C, 55.98; H, 6.75.

Alternative Synthesis of 3. KC$_8$ (35 mg, 0.26 mmol) was added to a slurry of **2** (97 mg, 0.099 mmol) in benzene (15 mL). The mixture quickly turned purple and was stirred for 3 h before being centrifuged and the supernatant was filtered. The solids were washed three times with toluene (3 mL each), centrifuged, and filtered, and the supernatants were combined and dried under reduced pressure to yield **3** as a purple solid. Crystals were grown from a toluene solution at −30 °C (31 mg, 49%).

(C$_5$Me$_5$)$_3$ThI, 4. Trimethylsilyl iodide (8 drops) was added to a stirred colorless solution of **1** (106 mg, 0.162 mmol) in toluene (18 mL). The solution was stirred for 12 h before being filtered and dried under reduced pressure. The solids were washed with cold pentane, the pentane was pipetted away from the solids, and the remainder was dried under reduced pressure to yield **4** as a white crystalline solid (95 mg, 77%). Crystals of **4** were grown from toluene at −30 °C, but were not suitable for X-ray diffraction. ^{1}H NMR (C_6D_6): δ 2.13 [s, 45H, C_5Me_5]. ^{13}C{^{1}H} NMR (C_6D_6): δ 128.20 [C_5Me_5], 14.29 [C_5Me_5].

IR: 2966s, 2926s, 2900s, 2853s, 1484w, 1431m, 1378m, 1364w, 1107w, 1013w, 728m cm^{-1}. Anal. Calcd for $C_{30}H_{45}ITh·1.5(C_7H_8)$: C, 53.88; H, 6.36. Found: C, 53.74; H, 6.90.

Reaction of (C$_5$Me$_5$)$_3$Th, 3, with Iodomethane. Excess iodomethane (1 drop) was added to a stirred purple solution of **3** (12 mg, 0.019 mmol) in toluene (5 mL). The solution immediately became colorless and was stirred for 15 min before being filtered and dried under reduced pressure to yield a white solid (11 mg). The solid contained an approximate 2:3 mixture of **1** and **4** as the only organothorium products identifiable by ^{1}H and ^{13}C NMR spectroscopies. This corresponds to 0.006 mmol of **1** and 0.009 mmol of **4** with an overall yield of 75% based on thorium. Crystallization in toluene at −30 °C gave a 1:1 mixture of **1** and **4** based on ^{1}H NMR spectroscopy of the crystals. X-ray analysis of the crystals also revealed a mixture of **1** and **4**, but the data were not of high enough quality to determine the relative amounts of each compound.

Reaction of (C$_5$Me$_5$)$_3$Th, 3, with I$_2$. Elemental iodine (2.5 mg, 0.020 mmol) was added to a stirred purple solution of **3** (11 mg, 0.017 mmol) in toluene (5 mL), and within seconds the purple solution faded to colorless. The reaction was stirred for 5 min before being filtered and dried under reduced pressure to yield (C$_5$Me$_5$)$_3$ThI, **4**, as a white solid (9 mg, 70%), as identified by ^{1}H NMR spectroscopy.

Reaction of (C$_5$Me$_5$)$_3$Th, 3, with PhCl. In a J-Young NMR tube, PhCl (16 mg, 0.14 mmol) was added to a purple solution of **3** (7 mg, 0.011 mmol) in C_6D_6 (0.7 mL). Upon mixing, the solution immediately became pale yellow. ^{1}H NMR spectroscopy after 20 min confirmed that a reaction had taken place as a new C_5Me_5 resonance was observed at 2.08 ppm. The solution was mixed periodically for 3 days while being monitored by ^{1}H NMR spectroscopy. No further changes in the NMR spectrum were observed. After 3 days, the solution was filtered and dried under reduced pressure to yield what was presumably (C$_5$Me$_5$)$_3$ThCl as a white solid (7 mg, 95%). ^{1}H NMR (C_6D_6): δ 2.08 [s, 45H, C_5Me_5]. ^{13}C{^{1}H} NMR (C_6D_6): 127.50 [C_5Me_5], 13.26 [C_5Me_5]. When this white solid was treated with iodotrimethylsilane, complex **4** was obtained cleanly in 80% yield similar to the reaction of (C$_5$Me$_5$)$_3$ThMe with iodotrimethylsilane described above. Incomplete combustion was observed in multiple elemental analyses, but the CH ratios of $C_{30}H_{42.3}$ and $C_{30}H_{41.5}$ vs calcd $C_{30}H_{45}$ were found.

Synthesis of (C$_5$Me$_5$)$_3$ThH from [(C$_5$Me$_5$)$_3$Th][BPh$_4$], 2, and KH. Potassium hydride (6 mg, 0.2 mmol) was added to a pink slurry of **2** (10 mg, 0.010 mmol) in toluene (15 mL). After the mixture was stirred for 12 h, the resulting white slurry was centrifuged and filtered. The supernatant was dried under reduced pressure to yield (C$_5$Me$_5$)$_3$ThH as a white solid (6 mg, 92%) as determined by ^{1}H NMR spectroscopy.[20]

Reaction of (C$_5$Me$_5$)$_3$Th, 3, with H$_2$. Solid **3** (7 mg, 0.01 mmol) was dissolved in C_6D_6 (0.6 mL) and transferred to a J-Young NMR tube. The tube was sealed, removed from the glovebox, and attached to a high-vacuum line. The solution was degassed with one freeze–pump–thaw cycle and H$_2$ (1 atm) was added. ^{1}H NMR spectroscopy was then used to monitor the formation of the known (C$_5$Me$_5$)$_3$ThH product.[20] After 34 days, the solution had turned from purple to colorless, indicating the reaction had reached completion. The ^{1}H NMR spectra showed only the formation of (C$_5$Me$_5$)$_3$ThH during this time, with no other discernible decomposition products. The sample was brought back into an argon-containing glovebox and dried under reduced pressure to yield (C$_5$Me$_5$)$_3$ThH as a white solid (6 mg, 86%).

Reaction of (C$_5$Me$_5$)$_3$Th, 3, with C$_8$H$_8$. Solid **3** (9 mg, 0.01 mmol) was dissolved in C_6D_6 (0.6 mL). C$_8$H$_8$ (1 drop) was added to the stirred solution, which immediately turned from purple to pale yellow. Analysis by ^{1}H NMR spectroscopy revealed only the presence of (C$_5$Me$_5$)$_3$ThH and unreacted C$_8$H$_8$. The solution was brought back into an argon-containing glovebox, dried under reduced pressure, washed quickly with cold pentane, and dried again under reduced pressure to yield (C$_5$Me$_5$)$_3$ThH as a white solid (8 mg, 78%). In a stoichiometric reaction, C$_8$H$_8$ (2.5 μL, 0.022 mmol) was added by syringe to **3** (12 mg, 0.018 mmol) in C_6D_6 (0.7 mL). The color changed on contact to yellow. (C$_5$Me$_5$)$_3$ThH (10 mg, 0.015 mmol, 83%) was isolated and identified by ^{1}H NMR spectroscopy.

Reaction of $(C_5Me_5)_3Th$, 3, with Al_2Me_6. Al_2Me_6 (1 drop, 2.0 M in hexane) was added to a stirred purple solution of **3** (12 mg, 0.019 mmol) in toluene (5 mL). The purple solution immediately turned colorless and gray solids (presumably aluminum metal) formed. The mixture was stirred for 5 min before being centrifuged and filtered. The colorless supernatant was dried under reduced pressure to yield $(C_5Me_5)_3ThMe$, **1**, as a white solid (9 mg, 75%), as identified by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies.

Reaction of 2 with ^{13}CO in C_6D_5Cl. In a glovebox containing coordinating solvents, **2-THF** (28 mg, 0.023 mmol) was dissolved in C_6D_5Cl (0.7 mL) in a J-Young NMR tube, which was then sealed, removed from the glovebox, and attached to a high-vacuum line. The solution was degassed with one freeze–pump–thaw cycle and CO (1 atm) was added. A color change from orange to golden yellow was observed within minutes with agitation. An analogous procedure was employed when using ^{12}CO. ^1H NMR (C_6D_5Cl): δ 7.95 [m, 8H, *o*-BPh_4], 7.23 [t, $^3J_{HH}$ = 7 Hz, 8H, *m*-BPh_4], 7.08 [t, $^3J_{HH}$ = 7 Hz, 4H, *p*-BPh_4], 1.75 [s, 45H, C_5Me_5]. $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 200.34 [Th–CO], 137.10 [BPh_4], 129.25 [C_5Me_5], 125.96 [BPh_4], 122.04 [BPh_4], 12.65 [C_5Me_5]. NMR assignments were confirmed with an HMQC experiment. The δ 200.34 resonance in the ^1H coupled ^{13}C NMR spectrum was identical to that in the $^{13}C\{^1H\}$ NMR spectrum; i.e., no "OCH" products are observable. IR (C_6H_5Cl): 2141 cm^{-1} (CO).

Reaction of 2 with ^{13}CO in C_4D_8O. In an argon-containing glovebox, **2-THF** (4 mg, 0.003 mmol) was dissolved in C_4D_8O (0.7 mL) in a J-Young NMR tube, which was then sealed, removed from the glovebox, and attached to a high-vacuum line. The solution was degassed with one freeze–pump–thaw cycle and CO (1 atm) was added. A color change from colorless to golden yellow was observed within minutes with agitation. An analogous procedure was employed when using ^{12}CO. ^1H NMR (C_4D_8O): δ 7.29 [m, 8H, *o*-BPh_4], 6.85 [t, $^3J_{HH}$ = 7 Hz, 8H, *m*-BPh_4], 6.70 [t, $^3J_{HH}$ = 7 Hz, 4H, *p*-BPh_4], 2.01 [s, 45H, C_5Me_5].

X-ray Data Collection, Structure Determination, and Refinement. Crystallographic details for $(C_5Me_5)_3ThMe$, **1**, $[(C_5Me_5)_3Th(THF)][BPh_4]$, **2-THF**, and $(C_5Me_5)_3Th$, **3**, are summarized in the Supporting Information (SI).

Computational Details. Density functional theory (DFT) calculations were performed using the TPSS meta-generalized gradient approximation (meta-GGA) functional[52] and its hybrid variant TPSSh[53] together with Grimme's D3 dispersion correction.[54] Scalar-relativistic effective core potentials (ECPs)[55] and corresponding valence basis sets[56] were used for actinides, while polarized valence triple-ζ basis sets def2-TZVP[57] were used for the other atoms. Solvent effects were included within the continuum solvation model COSMO.[58] A full description of the computational methods is summarized in the SI.

RESULTS AND DISCUSSION

$(C_5Me_5)_3ThMe$. The reaction of multiply recrystallized $(C_5Me_5)_2ThMe_2$ with $[Et_3NH][BPh_4]$ provides samples of the known $[(C_5Me_5)_2ThMe][BPh_4]$ complex[36] suitable for reaction with KC_5Me_5 to make $[(C_5Me_5)_3ThMe]$, **1**, according to eq 3. Complex **1** can be obtained in >70% yield and displays

$$[(C_5Me_5)_2ThMe][BPh_4] \xrightarrow[- KBPh_4]{+ KC_5Me_5} \quad (3)$$
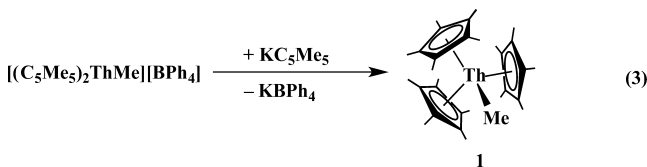
an unexceptional ^1H NMR spectrum in C_6D_6 with resonances at 2.00 and 0.40 ppm in a 45:3 ratio. Complex **1** is surprisingly stable in solution, as crystals can be formed from heating a toluene solution to 90 °C for 1 h followed by cooling to −30 °C.

Complex **1** crystallizes in the same $P6_3/m$ space group as $(C_5Me_5)_3ThH$,[20] $(C_5Me_5)_3UX$ (X = F,[19] Cl,[19] Me[59]), and $(C_5Me_5)_3Ln$ (Ln = La,[30] Ce,[31] Pr,[31] Nd,[32] Sm,[29] Y,[33] Gd[33]) (Figure 1). The (ring centroid)−Th−(ring centroid) angles in
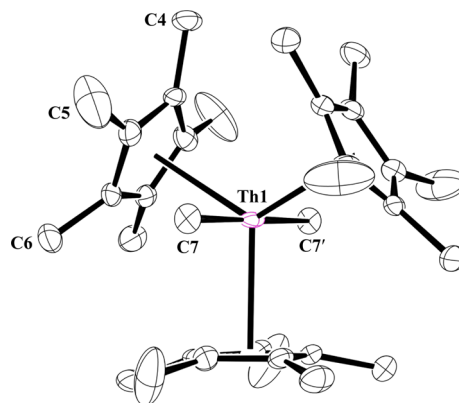

Figure 1. Molecular structure of $(C_5Me_5)_3ThMe$, **1**, with the disorder in the methyl carbon, C7, shown. Thermal ellipsoids are drawn at the 50% level and hydrogen atoms have been omitted for clarity.

1 are rigorously 120°, and, like other known $(C_5Me_5)_3AnX$ structures,[19,20] the methyl ligand is disordered above and below the plane defined by the metal and the three ring centroids. The 2.620 Å Th−(ring centroid) distance in **1** is nearly identical to the 2.613 Å distance in the only other thorium analogue, $(C_5Me_5)_3ThH$. The analogous 2.518 Å distance in $(C_5Me_5)_2ThMe_2$[37] is evidence of the more crowded nature of $(C_5Me_5)_3ThMe$ versus complexes with only two $(C_5Me_5)^-$ groups. The 2.676(15) Å Th−Me distance in **1** is also much longer than the 2.471(8) and 2.478(9) Å distances in $(C_5Me_5)_2ThMe_2$.[37] The displacements of the three unique methyl carbon atoms (C4, C5, and C6) out of the plane of the cyclopentadienyl ring are 0.49, 0.33, and 0.23 Å, respectively, with the former being greater than the 0.48 Å minimum value previously observed for complexes that undergo unusual reactivity like the alkyl reactivity and sterically induced reduction shown in eqs 1 and 2.[34]

$[(C_5Me_5)_3Th][BPh_4]$, 2. A colorless toluene solution of **1** reacts with $[Et_3NH][BPh_4]$ over 15 h to form $[(C_5Me_5)_3Th]$-$[BPh_4]$, **2**, as a salmon-colored solid in 90% yield, eq 4. Although **2** is insoluble in nonpolar solvents, its ^1H NMR spectrum was obtainable in C_6D_5Cl. Resonances for $(C_5Me_5)^-$ and $(BPh_4)^-$ are observed in the appropriate ratio.

$$\underset{\mathbf{1}}{} \xrightarrow[\substack{- CH_4 \\ - Et_3N}]{+ [Et_3NH][BPh_4]} \underset{\mathbf{2}}{[\quad][BPh_4]} \quad (4)$$
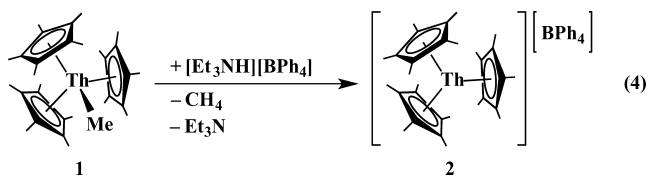
Dissolution of **2** in THF caused an immediate color change of the salmon-colored solids to form a colorless solution of the THF adduct, $[(C_5Me_5)_3Th(THF)][BPh_4]$, **2-THF**, which was identified by X-ray crystallography (Figure 2) and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies in C_4D_8O. Complexes **2** and **2-THF** are the first cationic $(C_5Me_5)_3M$ complexes ever isolated. Complex **2** can also be synthesized by protonation of the hydride ligand in $(C_5Me_5)_3ThH$ with $[Et_3NH][BPh_4]$ to
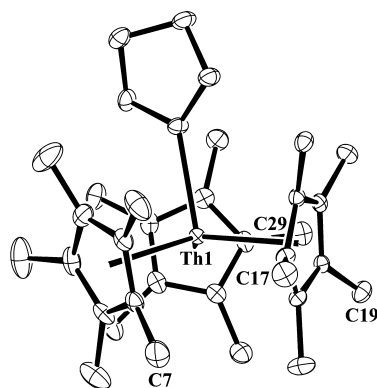
Figure 2. Molecular structure of the cationic component of $[(C_5Me_5)_3Th(THF)][BPh_4]$, **2-THF**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, the $[BPh_4]^-$ anion, and cocrystallized THF have been omitted for clarity.

form **2**, which can be converted back to $(C_5Me_5)_3ThH$ with KH (Scheme 1).

Scheme 1. Interconversion Reactions between $(C_5Me_5)_3ThH$ and $[(C_5Me_5)_3Th][BPh_4]$, 2
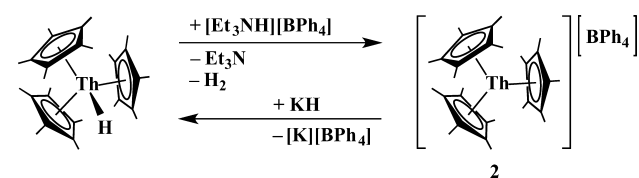
Unlike **1** and all the other $(C_5Me_5)_3MX$ and $(C_5Me_5)_3ML$ examples crystallographically characterized to date, the neutral THF ligand in **2-THF** is not disordered about the metal center and the three rings bend back to accommodate this larger ligand. The sum of (ring centroid)−Th−(ring centroid) angles around thorium in **2-THF** is 353.9°. It is the first tris(pentamethylcyclopentadienyl) metal complex of any kind that adopts a structure similar to the tris-(tetramethylcyclopentadienyl) complexes $(C_5Me_4H)_3UX$ (X = NO,[60] CO,[47,48] CNC_6H_4-p-OMe,[47] THF,[17] Cl,[61] and I[62]) which have distorted tetrahedral structures in which the sum of the (ring centroid)−M−(ring centroid) angles is significantly less than 360°. Unlike **1** and $(C_5Me_5)_3ThH$, whose Th−(ring centroid) distances (2.620 and 2.613 Å, respectively) are all identical due to symmetry, **2-THF** has three unique Th−(ring centroid) distances: 2.599, 2.635, and 2.626 Å. Like **1** and $(C_5Me_5)_3ThH$, however, the ^1H NMR spectrum of **2-THF** shows only one resonance for the $(C_5Me_5)^-$ methyl groups. The signals for the bound THF are indistinguishable from free THF, suggesting fast exchange is occurring. The 2.520(2) Å Th−O distance is within the 2.455(4)−2.628 Å range of less

crowded $[(C_5Me_5)_2ThMe(THF)]^{+63}$ and $[(C_5Me_5)_2ThMe(THF)_2]^{+36}$ complexes.

Due to the asymmetry of **2-THF**, all 15 methyl groups have unique displacements out of the planes of the cyclopentadienyl rings. Three of the methyl groups, C17, C19, and C29, have unusually large displacements of 0.57, 0.59, and 0.52 Å, respectively. These are greater than the 0.48 Å minimum value observed for complexes that undergo the unusual cyclopentadienyl reactions shown in eqs 1 and 2.[34] Previously, the largest observed displacement was 0.54 Å.[34] Interestingly, the three methyl groups showing maximum displacement are not spread evenly over the three cyclopentadienyl rings as is seen in all other $(C_5Me_5)_3MX$ and $(C_5Me_5)_3ML$ complexes where the sum of the (ring centroid)−Th−(ring centroid) is 358−360°. Instead, two methyl groups on one cyclopentadienyl ring, C17 and C19, and one on a second ring, C29, have the largest displacements. The third cyclopentadienyl ring has a maximum methyl displacement of 0.44 Å (C7).

$(C_5Me_5)_3Th$. Addition of potassium graphite to a colorless THF solution of **2-THF** or a benzene slurry of **2** causes a rapid color change to dark purple and generates the Th^{3+} complex $(C_5Me_5)_3Th$, **3** (Scheme 2). Surprisingly, this complex was stable enough to be identified by X-ray crystallography (Figure 3).
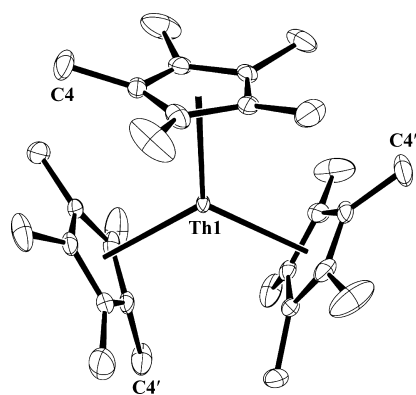

Figure 3. Molecular structure of $(C_5Me_5)_3Th$, **3**. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

Samples of $(C_5Me_5)_3Th$, **3**, were often found to be contaminated with $(C_5Me_5)_3ThH$, which is consistent with the high reactivity of **3** described below. This hydride contaminant can be removed from impure samples of **3** by treatment with $[Et_3NH][BPh_4]$ in a reaction similar to eq 4. Pure **3** can be extracted with toluene from $[(C_5Me_5)_3Th][BPh_4]$, **2**. This purification method is possible because $[Et_3NH][BPh_4]$ does not react with **3**. In this regard, $(C_5Me_5)_3Th$ differs from $(C_5Me_5)_3Ln$ complexes which react with $[Et_3NH][BPh_4]$ to form less crowded $[(C_5Me_5)_2Ln][BPh_4]$ products.[31]

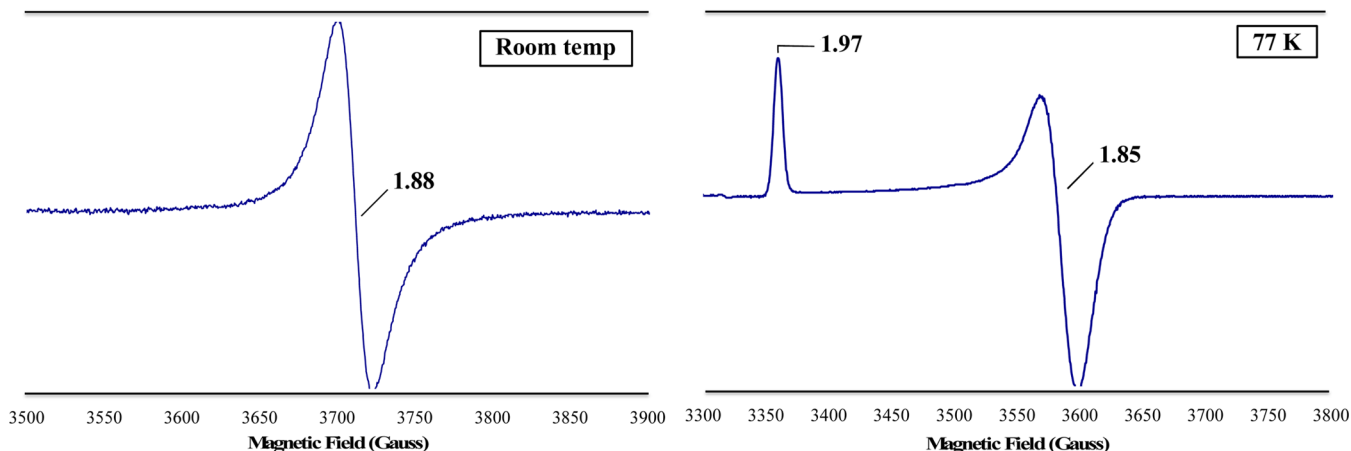**Scheme 2. Formation of $(C_5Me_5)_3Th$, 3**
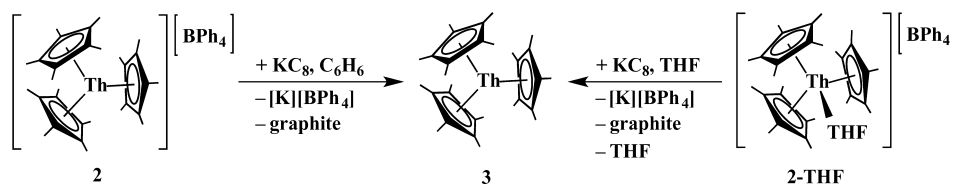
Figure 4. EPR spectrum of $(C_5Me_5)_3Th$, **3**, in toluene at room temperature with $g_{iso} = 1.88$ (left) and at 77 K with $g_\parallel = 1.97$ and $g_\perp = 1.85$ (right).

Spectroscopic Analysis of $(C_5Me_5)_3Th$, 3. Complex **3** shows an isotropic EPR signal at room temperature (Figure 4) with $g_{iso} = 1.88$, which is consistent with a thorium-based radical and a $6d^1$ ground state.[22−26] Theoretical calculations corroborate this assignment by predicting the highest occupied molecular orbital (HOMO) of **3** to be a d_{z^2}-like orbital (Figure S8). The line shape and the g_{iso} value are similar to those of other known monometallic Th^{3+} complexes: 1.916 for $[K(DME)_2]\{Th[\eta^8-C_8H_6(SiMe_2{}^tBu)_2]_2\}$,[24] 1.910 for both $[C_5H_3(SiMe_2{}^tBu)_2]_3Th$[22] and $[C_5H_3(SiMe_3)_2]_3Th$,[22] 1.871 for $(C_5Me_5)_2Th[{}^iPrNC(Me)N^iPr]$,[25] and 1.92 for $(C_5Me_4H)_3Th$.[23] The mixed-valent bimetallic hydride complexes $[K(18\text{-}crown\text{-}6)(Et_2O)]\{[C_5H_3(SiMe_3)_2]_2ThH_2\}_2$[26] and $[K(18\text{-}crown\text{-}6)(THF)][(C_5Me_5)_2ThH_2]_2$[26] also have similar line shapes and g_{iso} values of 1.89 and 1.88, respectively, at room temperature. At 77 K, complex **3** displays an axial EPR signal with $g_\parallel = 1.97$ and $g_\perp = 1.85$ (Figure 4), which is also consistent with the monomeric examples above, but differs from the rhombic signals displayed at low temperatures for the bimetallic species.

The optical spectrum for $(C_5Me_5)_3Th$ is similar to that of $[C_5H_3(SiMe_3)_2]_3Th$[22] in that each contains three maxima between 450 and 650 nm. $(C_5Me_5)_3Th$ has a much larger extinction coefficient of 9500 M^{-1} cm^{-1} ($\lambda_{max} = 539$ nm) vs 5100 M^{-1} cm^{-1} ($\lambda_{max} = 654$ nm) for $[C_5H_3(SiMe_3)_2]_3Th$ (Figure 5). In comparison, the tetramethylcyclopentadienyl Th^{3+} complex $(C_5Me_4H)_3Th$, which is structurally more similar to **3** than $[C_5H_3(SiMe_3)_2]_3Th$, is reported to have an extinction coefficient of 7100 M^{-1} cm^{-1} at $\lambda_{max} = 522$ nm. The strong absorptions in the visible region for Th^{3+} complexes have been attributed in the past to transitions from a $6d^1$ ground state to higher lying f orbitals.[24,25]

Complex **3** crystallizes in the same $P6_3/m$ space group as **1** and all the other $(C_5Me_5)_3M$ complexes listed above except **2-THF**. Like those complexes, it has three rigorously 120° (ring centroid)−Th−(ring centroid) angles. The 2.607 Å Th−(ring centroid) distance of **3** is similar to the 2.620 Å distance of **1**, the 2.620 Å average distance in **2-THF**, and the 2.613 Å distance in $(C_5Me_5)_3ThH$. The similarity in distances parallels the trend with other Th^{3+} d^1 complexes vs their Th^{4+} analogues. It has previously been observed that adding an electron to an f element in a d orbital has much less effect on bond distances than adding an electron to an f orbital (see Table S1).[14,24,25,64−68] However, it is also seen that the 2.581 Å U−(ring centroid) distance of $5f^3$ $(C_5Me_5)_3U$[15] is only slightly
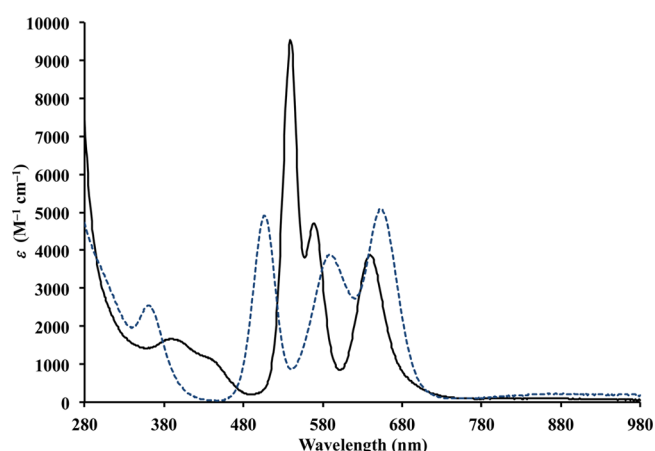

Figure 5. UV−visible spectra of $(C_5Me_5)_3Th$, **3** (black solid line), in toluene and $[(C_5H_3(SiMe_3)_2]_3Th$[22] (blue dotted line) in THF.

longer than the 2.560 and 2.551 Å distances in the $5f^2$ $(C_5Me_5)_3UF$ and $(C_5Me_5)_3UCl$ complexes, respectively. The 2.607 Å Th−(ring centroid) distance of **3** is significantly longer than those in the other tris(cyclopentadienyl) Th^{3+} complexes: 2.53, 2.52, and 2.55 Å for $[C_5H_3(SiMe_2{}^tBu)_2]_3Th$,[22] $[C_5H_3(SiMe_3)_2]_3Th$,[22] and $(C_5Me_4H)_3Th$,[23] respectively, which is consistent with the greater steric crowding expected for three $(C_5Me_5)^-$ rings. The maximum methyl displacement out of the plane of the cyclopentadienyl ring, C4, in **3** is 0.52 Å, i.e. greater than the 0.48 Å minimum value observed for complexes that undergo unusual reactivity shown in eqs 1 and 2.[34]

**Reactivity of the $(C_5Me_5)_3Th$-Containing Complexes.** The new crystallographically characterized tris-(pentamethylcyclopentadienyl)thorium complexes, **1**, **2-THF**, and **3**, have the metrical parameters consistent with the steric crowding necessary to show the unusual $(C_5Me_5)^-$ reactivity in eqs 1 and 2. Each of these complexes has methyl substituent displacements from the cyclopentadienyl ring greater than the 0.48 Å cutoff that defined a minimum for reactivity in a survey of 49 lanthanide and actinide complexes of the $(C_5Me_5)^-$ ligand.[34] However, it must be noted that this reactivity was not observed with $(C_5Me_5)_3ThH$.[20] This was the only previously characterized $(C_5Me_5)_3M$-containing complex that was an exception to the 0.48 Å reactivity guideline. Hence, this sterically crowded hydride did not reduce 1,3,5,7-cyclo-

octatetrane (C_8H_8) or PhX (X = Cl, Br, I), substrates that had been observed to react with other $(C_5Me_5)_3M$ complexes.[19,31,35]

Like $(C_5Me_5)_3ThH$, neither $(C_5Me_5)_3ThMe$, **1**, nor $[(C_5Me_5)_3Th(THF)][BPh_4]$, **2-THF**, nor $[(C_5Me_5)_3Th-[BPh_4]$, **2**, which is presumably also sterically crowded, reacts with PhCl or C_8H_8. Hence, the observed crowding does not confer reactivity on these new Th^{4+} complexes. The fact that **2** reacts with THF to make the adduct, **2-THF**, is another example. All other $(C_5Me_5)_3M$-containing complexes ring-open THF. It would have been expected that the high charge of Th^{4+} in **2** coupled with the fact that the complex has an overall plus charge would be especially effective at polarizing the THF for ring-opening. Evidently, formation of the η^1-C_5Me_5 intermediate presumed to be responsible for the ring-opening[31,69] is not favorable in this case. The η^5 to η^1 transformation could be inhibited by the high charge on the metal and its large size since $(C_5Me_5)_3La$ is not as reactive in THF ring-opening as complexes of the smaller lanthanides.[31] However, $(C_5Me_5)_3La$ has a 2.642 Å M−(ring centroid) distance larger than the 2.599−2.626 Å distances in **2-THF** and it still ring-opens neat THF. Hence, it may be the combination of factors that lead to the stability to THF.

$(C_5Me_5)_3Th$ Reactivity. Like **1**, **2**, and **2-THF**, $(C_5Me_5)_3Th$, **3**, also does not display the special $(C_5Me_5)^-$ reactivity of eqs 1 and 2. It does display reactivity, but this reactivity is associated with the +3 oxidation state and not the steric crowding. In contrast to eqs 1 and 2 that form products with only two pentamethylcyclopentadienyl ligands and less steric crowding, **3** reacts to make *more* sterically crowded tris(pentamethylcyclopentadienyl) products as described below. These reactions are well within the norm of reactivity for An^{3+} complexes with smaller ligand sets, but they are exceptional in these cases since they make such sterically crowded products.

Reactivity with MeI. Complex **3** reacts with MeI to form not only the halide, $(C_5Me_5)_3ThI$, **4**, but also the methyl complex, $(C_5Me_5)_3ThMe$, **1**, in a 2:3 mixture, respectively (eq 5). Complex **4** could be obtained as a pure compound by

$$2 \quad \text{[structure 3]} \xrightarrow{\text{+ MeI}} \text{[structure 1, Me]} + \text{[structure 4, I]} \quad (5)$$
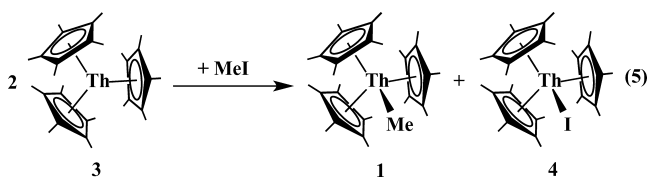
reaction of the mixture of **1** and **4** with Me_3SiI and was identified by ^1H and $^{13}C\{^1H\}$ NMR, as well as by elemental analysis. Complex **4** can also be made from reaction of Me_3SiI with both **1** and $(C_5Me_5)_3ThH$. The MeI reduction reaction, eq 5, is consistent with Th^{3+} reactivity, but no sterically induced reduction is observed according to eq 2 since the products retain the three $(C_5Me_5)^-$ ligands. No evidence for a bis(pentamethylcyclopentadienyl) complex such as $(C_5Me_5)_2Th(Me)I$ was observed by NMR spectroscopy.

Reactivity with I_2. Complex **4** can also be cleanly generated by reaction of **3** with elemental iodine, eq 6, and isolated in a 70% yield as identified by ^1H NMR spectroscopy. No evidence for the formation of $(C_5Me_5)_2ThI_2$[70] was observed by NMR spectroscopy. The reduction of I_2 by the insoluble Th^{3+} complex, $(C_5H_5)_3Th$, has been previously reported to form $(C_5H_5)_3ThI$.[71] Complex **4** shows remarkable stability for such a

$$\text{[structure 3]} \xrightarrow{+ \frac{1}{2}(I_2)} \text{[structure 4, I]} \quad (6)$$
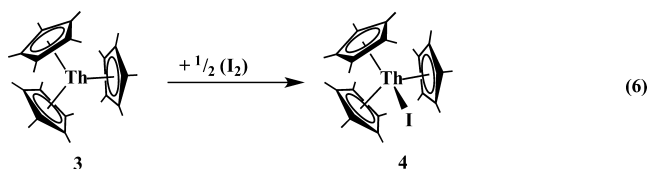
crowded complex; in contrast to $(C_5Me_5)_3UBr$ and $(C_5Me_5)_3UI$, which decompose in 2 min at 60 °C and 3 h at room temperature, respectively,[19] $(C_5Me_5)_3ThI$ does not show any decomposition in C_6D_6 at 65 °C for 24 h. Complex **4** also does not react with PhCl or C_8H_8.

Reactivity with PhCl. Complex **3** was also treated with PhCl to test whether $(C_5Me_5)_3ThCl$ would form via a metal-based one-electron process, or if $(C_5Me_5)_2ThCl_2$ would form with excess PhCl via sterically induced reduction in a reaction analogous to that of $(C_5Me_5)_3U$ with PhCl: 1 equiv of PhCl reacts quickly with $(C_5Me_5)_3U$ to form $(C_5Me_5)_3UCl$ and 2 equiv of PhCl reacts over several days to form $(C_5Me_5)_2UCl_2$.[19] Complex **3** reacts immediately with PhCl to produce a diamagnetic product which displays a ^1H NMR resonance for $(C_5Me_5)^-$ at 2.08 ppm and is postulated to be $(C_5Me_5)_3ThCl$, eq 7. No evidence for the formation of $(C_5Me_5)_2ThCl_2$[37] was

$$\text{[structure 3]} \xrightarrow{+ \text{PhCl}} \text{[structure, Cl]} \quad (7)$$
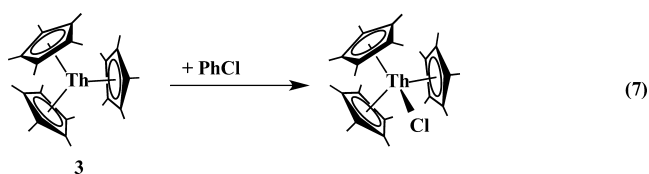
observed, even after mixing for several days with excess PhCl. When the product of eq 7 was treated with Me_3SiI, it cleanly formed $(C_5Me_5)_3ThI$ in 80% yield. This is chemical evidence for formulating the eq 7 product as $(C_5Me_5)_3ThCl$. $(C_5Me_5)_3ThH$ and **1** react similarly with Me_3SiI to form $(C_5Me_5)_3ThI$, but no reaction of **1** with Me_3SiCl is observed over 24 h.

Reactivity with Al_2Me_6. $(C_5Me_5)_3Th$ reacts with Al_2Me_6 to form $(C_5Me_5)_3ThMe$, **1**, in 75% yield, as determined by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies, according to eq 8. Gray

$$\text{[structure 3]} \xrightarrow[\text{− Al}]{+ Al_2Me_6} \text{[structure 1, Me]} \quad (8)$$
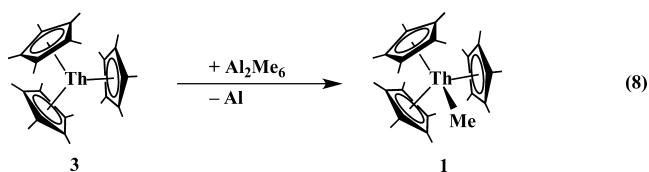
insoluble material, presumed to be aluminum metal, is also formed. Reduction of Al_2Me_6 compounds by organometallic complexes to form M−Me products along with aluminum metal has been previously observed in reactions that have been shown to go through $M-(AlMe_4)$ intermediates.[72,73] Al_2Me_6 has also been shown to react with alkali metals to form $M(AlMe_4)$ (M = K, Rb, Cs) products.[74] However, no Th−$(AlMe_4)$ complexes were isolated or observed in this reaction. The thorium reaction differs from the reaction of $(C_5Me_5)_3Sm$ with Al_2Me_6 which forms $[(C_5Me_5)_2Sm]_2[(\mu-Me)_2Al(C_5Me_5)-Me]_2$.[75] Since Sm^{3+} is not a strong reductant like Th^{3+}, analogous chemistry is not expected.

Formation of $(C_5Me_5)_3ThH$. 1,3,5,7-Cyclooctatetraene is another substrate that is typically reduced by $(C_5Me_5)_3M$ complexes.[31,35] For example, $(C_5Me_5)_3U$ reduces C_8H_8 to

$[(C_5Me_5)(C_8H_8)U]_2(\mu\text{-}C_8H_8)$.[35] The thorium analogue, $[(C_5Me_5)(C_8H_8)Th]_2(\mu\text{-}C_8H_8)$, is known from the reaction of $[(C_5Me_5)_2ThH_2]_2$ with C_8H_8,[76] so an analogous reaction with $(C_5Me_5)_3Th$ thorium might be expected. However, $(C_5Me_5)_3Th$ does not react with C_8H_8 to form a $(C_8H_8)^{2-}$ product. Upon addition of a stoichiometric amount of C_8H_8 to a benzene solution of **3**, a color change from blue to yellow occurs within minutes that is consistent with a Th^{3+} to Th^{4+} transformation. The only product observed in the yellow solution is $(C_5Me_5)_3ThH$. The identity of $(C_5Me_5)_3ThH$ was confirmed by ^{1}H and ^{13}C NMR spectroscopies and by X-ray crystallography. No byproducts were observed by ^{1}H NMR spectroscopy that would indicate the source of the hydride. When the reactions were run in deuterated solvents, the hydride $(C_5Me_5)_3ThH$ was observed and not the deuterium analogue. The facile formation of $(C_5Me_5)_3ThH$ from **3** is consistent with the formation of the hydride as an impurity in the synthesis of **3**. There are evidently nonobvious sources of $(C_5Me_5)_3ThH$ from **3**. Complicated thorium hydride chemistry, including the formation of the structurally similar $[C_5H_3(SiMe_3)_2]_3ThH$ as a unpredicted reaction product, has been observed previously.[26]

The hydride product, $(C_5Me_5)_3ThH$, can also be obtained from the reaction of $(C_5Me_5)_3Th$ with H_2 in C_6D_6. The initially purple solution turned completely colorless after 34 days at room temperature under 1 atm H_2, and $(C_5Me_5)_3ThH$ was identified by ^{1}H NMR spectroscopy, eq 9, and collected in an

(9)
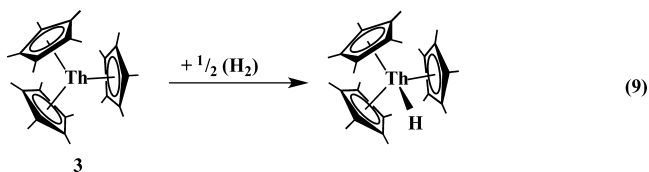
86% yield. In contrast, the less reducing $(C_5Me_5)_3U$ does not react with H_2 under analogous conditions. The $(C_5Me_5)_3Th$ reaction displays unusual kinetic behavior as monitored by ^{1}H NMR spectroscopy. Although the final yield is high, only about 1/3 of the product forms in the first 19 days. The rate increases as the reaction proceeds such that the remaining 2/3 of the yield comes in the last 15 days (see the SI for kinetics plot). This result is surprising since $(C_5Me_4H)_3Th$ did not react appreciably with H_2 before decomposition.[26] Hence it appears that $(C_5Me_5)_3Th$ is more stable in solution than $(C_5Me_4H)_3Th$, but $(C_5Me_5)_3Th$ is more reactive with H_2 than $(C_5Me_4H)_3Th$. $(C_5Me_5)_3ThMe$, **1**, was also treated with H_2 in an attempt to form $(C_5Me_5)_3ThH$ by hydrogenolysis, but no reaction was observed in C_6D_6 over 4 days.

All of the $(C_5Me_5)_3Th$ reactions listed above involve reduction by Th^{3+} rather than any $(C_5Me_5)^-$ related reactions. Consistent with this, **3** does not engage in other $\eta^1\text{-}(C_5Me_5)$ alkyl reactions typical for $(C_5Me_5)_3M$ complexes. For example, it does not ring-open THF as observed for $(C_5Me_5)_3U$[17] and the lanthanide analogues[31] and it does not polymerize ethylene like the $(C_5Me_5)_3M$ complexes (M = U,[15] Ce,[31] Pr,[31] Nd,[31] Sm[31]).

Isolation of a Thorium Carbonyl Complex. The fact that $[(C_5Me_5)_3Th][BPh_4]$, **2**, forms the base adduct $[(C_5Me_5)_3Th\text{-}(THF)][BPh_4]$, **2-THF**, raised the possibility that **2** could react with CO to form a cationic analogue of $(C_5Me_5)_3U(CO)$,[16] namely, $[(C_5Me_5)_3Th(CO)][BPh_4]$, **5**, as shown in eq 10. When solid **2** was treated with 60 psi of CO in a solvent free

(10)
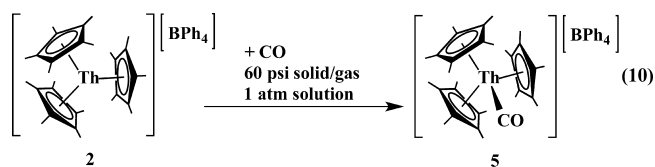
reaction,[77] the initially salmon-colored solid turned pale orange. IR spectroscopy of a KBr pellet of the solids revealed an absorption at 2131 cm^{-1}. In comparison, the cationic d^0 transition metal complex of similar composition, $[(C_5H_5)_3Zr\text{-}(CO)][BPh_4]$, displays an absorption at 2150 cm^{-1}.[78] A similar reaction with [13]CO resulted in an identical color change and an IR spectrum containing an absorption at 2083 cm^{-1}. ^{1}H NMR spectroscopy revealed that the solid-state reaction gave a mixture, so the reaction was examined in solution.

When 1 atm of CO gas was added to a solution of **2** in C_6D_5Cl, the color changed from orange to golden yellow (see SI) and a new $(C_5Me_5)^-$ ^{1}H NMR resonance was observed at 1.75 ppm (vs 1.85 ppm for **2**). The $(C_5Me_5)^-$ resonances in the ^{13}C{^{1}H} NMR spectrum shifted upfield and a broad resonance at 200.4 ppm attributable to a carbonyl ligand was observed when a sample was prepared from [13]CO ([13]CO in C_6D_5Cl resonates at 184.4 ppm). In comparison, the carbonyl in $[(C_5H_5)_3Zr(CO)][BPh_4]$ resonates at 206.9 ppm.[78] The fact that only one [13]CO resonance is observed when **2** was charged with excess CO indicated that exchange was occurring. Variable temperature NMR studies revealed no decoalescence down to -40 °C. IR spectroscopy of the solution revealed an absorption at 2141 cm^{-1} consistent with a CO stretch. A similar reaction with [13]CO resulted in an identical color change and an IR spectrum containing an absorption at 2094 cm^{-1}. This is all consistent with formation of $[(C_5Me_5)_3Th(CO)][BPh_4]$, **5** (eq 10).

When a THF solution of **2-THF** was charged with 1 atm of CO, the $(C_5Me_5)^-$ ^{1}H NMR resonance shifted from 2.19 to 2.01 ppm suggesting that CO could compete for the thorium center even in the presence of neat THF. The ^{13}C{^{1}H} NMR spectrum of **2-THF** charged with [13]CO in C_4D_8O showed a CO resonance shifted to 185.13 ppm.

Complex **5** decomposes when exposed to vacuum, as determined by ^{1}H NMR, IR, and UV−visible spectroscopies (see SI). However, no decomposition was seen for at least 24 h after the CO atmosphere in a J-Young tube containing a C_6D_5Cl solution of **5** was replaced with argon.

Bonding in the Thorium Carbonyl Complex. Since the observed ν_{CO} for **5** is slightly lower than the 2143 cm^{-1} value for free CO,[79] some π back-bonding appears to be occurring in this complex. If no π back-bonding were present in this d^0f^0 complex, a ν_{CO} higher than 2143 cm^{-1} would be expected because the σ bonding orbital for the OC → M interaction is antibonding with respect to CO.[80] This has been observed for main group compounds[81−86] and closed-shell d^8 and d^{10} transition metal complexes.[87−90] Moreover, since cationic metal carbonyl complexes display ν_{CO} values higher than those of the corresponding neutral species,[88,90] the cationic nature of **5** could also contribute to increasing ν_{CO}. Since both effects should raise ν_{CO} higher than 2143 cm^{-1} and a lower value is observed, π back-bonding must be present. This conclusion is corroborated by the ^{13}C{^{1}H} NMR data for **5**: the CO resonance occurs at 200.4 ppm, shifted downfield from the 184.4 ppm value for free CO in C_6D_5Cl. Downfield ^{13}C NMR shifts have been attributed to metal to CO back-bonding, while

upfield shifts are characteristic of complexes with predominant OC → M σ interactions.[80,88] Since the electron configuration of Th in **5** is formally $5f^0 6d^0$, the π back-bonding could originate from ligand-based orbitals, as previously postulated[91] for $(C_5Me_5)_3U(CO)$,[16] $(C_5H_4SiMe_3)_3U(CO)$,[46] and $(C_5Me_4H)_3U(CO)$.[47,48] This is supported by the computational analyses described below.

DFT calculations suggest that the highest six occupied orbitals of $[(C_5Me_5)_3Th]^+$ transform according to the irreducible representations a′, a″, e′, and e″ under the pseudo-C_{3h} symmetry of this molecule and mainly consist of linear combinations of $(C_5Me_5)^-$ HOMOs,[92] as illustrated in Figure 6 and Figures S9−S11.
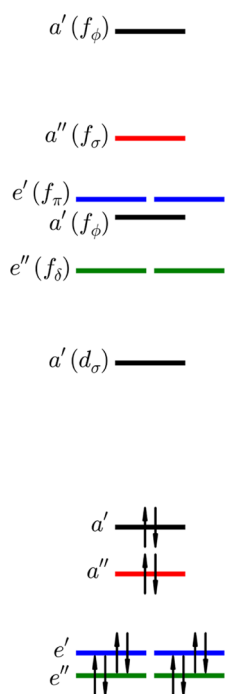

Figure 6. Energy level diagram for frontier orbitals of $[(C_5Me_5)_3Th]^+$ under pseudo-C_{3h} symmetry. Irreducible representations a′, a″, e′, and e″ are color-coded by black, red, blue, and green, respectively. The HOMO−LUMO gap is scaled by 1/3 to save space.

The frontier unoccupied orbitals have predominantly Th 5f and 6d character. In $[(C_5Me_5)_3Th(CO)]^+$, the HOMO of CO forms a dative σ bond with the empty d_σ and f_σ orbitals, while the doubly degenerate CO π^* lowest unoccupied molecular orbitals (LUMOs) participate in π back-bonding with the ligand-based e″ orbitals of the $[(C_5Me_5)_3Th]^+$ fragment

through $6d_\pi$ admixture (Figure 7). The computed TPSSh value of ν_{CO}, 2083 cm^{-1}, agrees with the experimental ν_{CO} for **5** in solution, 2141 cm^{-1}, within the typical error margin of DFT calculations.[93] In addition, the computed −46 cm^{-1} ^{13}C isotope shift for $[(C_5Me_5)_3Th(^{13}CO)]^+$ matches the experimental shift of −47 cm^{-1} (see SI for details).

The ν_{CO} for **5** is significantly higher than the values observed for the uranium carbonyl complexes $(C_5Me_5)_3U(CO)$,[16] $(C_5H_4SiMe_3)_3U(CO)$,[46] and $(C_5Me_4H)_3U(CO)$[47,48] in KBr pellets, 1922, 1969, and 1880 cm^{-1}, respectively. DFT calculations on $(C_5Me_5)_3U$ show that the frontier singly occupied molecular orbitals, Figure S13, are of $5f_\phi$ and $5f_\pi$ character. Thus, in $(C_5Me_5)_3U(CO)$, the U $5f_\pi$ orbitals can donate extra electron density into the CO π^* LUMO,[47,94,95] whereas back-donation only arises from ligand-based orbitals in $[(C_5Me_5)_3Th(CO)]^+$. Moreover, compared to the uranium carbonyl complexes, the higher +4 formal charge of Th in **5** lowers the energies of the frontier orbitals, leading to stronger σ bonding and weaker π back-bonding. These effects result in a ν_{CO} shift of around −200 cm^{-1} from $[(C_5Me_5)_3Th(CO)]^+$ to its U^{3+} analogues. A theoretical study comparing $F_4U(CO)$ with $F_3U(CO)$ predicted a similar shift from the U^{4+} complex to the U^{3+} complex.[94]

To investigate the contribution of the Th 5f orbitals to Th−CO bonding, calculations were carried out on the cationic d^0 transition metal complex, $[(C_5H_5)_3Zr(CO)]^+$,[78] whose ν_{CO} and carbonyl ^{13}C NMR shift are similar to those of **5**. The computed TPSSh ν_{CO} for $[(C_5H_5)_3Zr(CO)]^+$ is 2108 cm^{-1}, in reasonable agreement with the experimental value of 2150 cm^{-1}. The occupied frontier orbitals of $[(C_5H_5)_3Zr(CO)]^+$ resemble those of **5**, Figures S14−S17, except no f character is present in the former. These calculations corroborate that the Th−CO bonding is mainly due to the Th 6d admixture in the ligand-based orbitals and is not strongly affected by the Th 5f orbitals.

■ CONCLUSION

Despite the difficulty in accessing Th^{3+} complexes and the potential problem that three electron-donating $(C_5Me_5)^-$ groups might add too much electron density to such a reducing ion, it has been possible to synthesize and crystallographically characterize $(C_5Me_5)_3Th$, **3**. Several additional tris-(pentamethylcyclopentadienyl) thorium complexes were isolated this study, namely $(C_5Me_5)_3ThMe$, **1**, $[(C_5Me_5)_3Th]$-$[BPh_4]$, **2**, $[(C_5Me_5)_3Th(THF)][BPh_4]$, **2-THF**, $(C_5Me_5)_3ThI$, **4**, and $(C_5Me_5)_3ThCl$. Surprisingly, none of these complexes reacts to relieve the steric crowding imposed by the three pentamethylcyclopentadienyl rings and $(C_5Me_5)_3Th$ reacts only via Th^{3+} reduction pathways to make sterically more
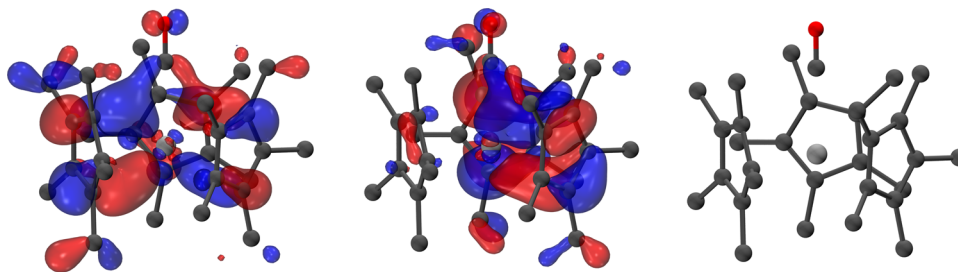

Figure 7. Doubly degenerate HOMO-3 of $[(C_5Me_5)_3Th(CO)]^+$ (left and center), which originate from the e″ ligand-based orbitals of $[(C_5Me_5)_3Th]^+$. A contour value of 0.035 is used. For clarity, the ball-and-stick model is also shown (right), and hydrogen atoms are omitted.

crowded complexes. The previous correlation that $(C_5Me_5)_3M$ complexes with a methyl displacement from the cyclopentadienyl ring greater than 0.48 Å showed unusual reactivity, which was based on 49 examples, must now be rewritten. Although **1**, **2-THF**, and **3** all have crystallographically defined displacements greater than 0.48 Å, they do not participate in the special $(C_5Me_5)^-$ reactions characteristic of $(C_5Me_5)_3M$ complexes. Previously, $(C_5Me_5)_3ThH$ was the only exception. Now there are four. It is clear that the methyl displacement criterion alone is not sufficient to predict reactivity particularly with thorium.

$[(C_5Me_5)_3Th(THF)][BPh_4]$, **2-THF**, is the first crystallographically characterized cationic $[(C_5Me_5)_3M]^+$ complex and the first $(C_5Me_5)_3M$ of any kind that adopts a distorted tetrahedral structure rather than the trigonal planar arrangement of rings found in all other examples. It is also a unique $(C_5Me_5)_3M$ complex in that it does not ring-open THF. The cationic $[(C_5Me_5)_3Th][BPh_4]$, **2**, has allowed the isolation of the first molecular example of a thorium carbonyl complex, characterized as $[(C_5Me_5)_3Th(CO)][BPh_4]$, **5**. These complexes show that the chemistry of thorium can be very different from that of uranium and the lanthanides, even in analogous systems that were thought to be well-defined. The small f contribution to bonding in **5** is reminiscent of the d^2f^0 complex, $\{[C_5H_3(SiMe_3)_2]_3Th\}^-$,[14] and suggests that, depending on the coordination environment, thorium can behave either as an f-block element or as a d-block transition metal. It is therefore important to continue to explore the chemistry of thorium and make such comparisons, as the anomalies and differences may provide clues to help us better understand f element chemistry in general.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10826.

> Photograph of solutions of **2** and **5**, IR spectra for **5**, X-ray diffraction data, atomic coordinates, complete bond distances and angles for compounds **1**, **3**, and **2-THF**, and computational details (PDF)
>
> Crystallographic information for **1**, CCDC Number 1484179 (CIF)
>
> Crystallographic information for **3**, CCDC Number 1484180 (CIF)
>
> Crystallographic information for **2-THF**, CCDC Number 1484181 (CIF)
>
> Cartesian coordinates of DFT optimized structures (TXT)

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Notes

The authors declare no competing financial interest.

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