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Reactivity of Organothorium Complexes with TEMPO

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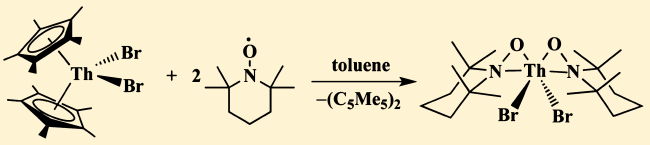
Supporting Information

ABSTRACT: Reactions of the 2,2,6,6-tetramethylpiperidin-1-oxyl radical (TEMPO) with thorium metallocenes have been examined to investigate both the radical reaction patterns for organothorium complexes and the coordination chemistry of TEMPO with thorium. $(\eta^5\text{-}C_5Me_5)_2ThMe_2$ reacts with 2 equiv of TEMPO to generate 1-methoxy-2,2,6,6-tetramethylpiperidine (Me-TEMPO) and $(\eta^5\text{-}C_5Me_5)_2ThMe(\eta^1\text{-TEMPO})$, which contains a $TEMPO^-$ anion coordinated to thorium through oxygen only. $(\eta^5\text{-}C_5Me_5)_2Th(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)$, synthesized from $(\eta^5\text{-}C_5Me_5)_2ThBr_2$ and $(C_3H_5)MgBr$, reacts with 2 equiv of TEMPO to form 1-(2-propen-1-yloxy)-2,2,6,6-tetramethylpiperidine (allyl-TEMPO) and $(\eta^5\text{-}C_5Me_5)_2Th(\eta^1\text{-}C_3H_5)(\eta^1\text{-TEMPO})$. Although bis(TEMPO) metallocenes were not obtained in these reactions, the methyl group in $(\eta^5\text{-}C_5Me_5)_2ThMe(\eta^1\text{-TEMPO})$ is reactive with 1 equiv of CuBr to form $(\eta^5\text{-}C_5Me_5)_2ThBr(\eta^1\text{-TEMPO})$. The bis(TEMPO) metallocene $(\eta^5\text{-}C_5Me_5)_2Th(\eta^1\text{-TEMPO})_2$ is accessible in the reaction of $[(\eta^5\text{-}C_5Me_5)_2ThH_2]_2$ with 4 equiv of TEMPO. In contrast, $(\eta^5\text{-}C_5Me_5)_2ThBr_2$ reacts with 2 equiv of TEMPO by loss of C_5Me_5 to form $(C_5Me_5)_2$ and $(\eta^2\text{-TEMPO})_2ThBr_2$, in which the $TEMPO^-$ anions bind through oxygen and nitrogen. The bromide ions in $(\eta^2\text{-TEMPO})_2ThBr_2$ can be replaced by an additional 2 equiv of TEMPO in the presence of 2 equiv of KC_8 to form the per(TEMPO) complex $Th(\eta^1\text{-TEMPO})_2(\eta^2\text{-TEMPO})_2$. $ThBr_4(THF)_4$ reacts with TEMPO to form $ThBr_4(THF)_2(\eta^1\text{-TEMPO})$, which contains an oxygen-bound TEMPO radical. The Th^{3+} complex $(\eta^5\text{-}C_5Me_4H)_3Th$ is oxidized in the presence of TEMPO, without ligand loss, to afford the Th^{4+} species $(\eta^5\text{-}C_5Me_4H)_3Th(\eta^1\text{-TEMPO})$. The reactions show that TEMPO can react with organothorium complexes in several ways including coordination, anion substitution, and cyclopentadienyl replacement.



INTRODUCTION

The reactions of actinide complexes with radicals are of general interest because nuclear waste stream remediation chemistry involves radiolytically generated radical species. The radical reactivity of actinides has been heavily studied in aqueous solution,[1−5] but less attention has been paid to radical reactions in nonaqueous solution. The actinide metallocenes $(C_5Me_5)_2AnX_2$ (An = Th, U; X = halide, pseudohalide, alkyl, etc.) offer a unique opportunity to study actinide radical chemistry in a well-defined coordination environment. The bis(pentamethylcyclopentadienyl) ancillary ligand set provides stability, solubility, and crystallinity that usually allows reactivity to occur at the An−X bonds and often leads to crystalline products that can be characterized by X-ray crystallography.

Reported here are reactions of thorium metallocenes with a commonly used organic radical, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), to establish a baseline of reactivity for radicals with organoactinides. Thorium was chosen because it has a very stable 4+ oxidation state and the chemistry should be less complicated by redox reactions than that of uranium, which can be isolated in the 2+, 3+, 4+, 5+, and 6+ oxidation states. TEMPO has proven to be a valuable radical reagent in many applications in organic chemistry and biochemistry[6−11] and has been shown to bind to main-group[12,13] and s-block elements,[14] as well as transition metals,[15−26] in several coordination modes. The use of TEMPO in f-element chemistry is more limited and was found in only two reports in the literature. A samarium TEMPO complex, $[(\eta^1\text{-}ONC_5H_6Me_4)_2Sm(\mu\text{-}\eta^1\text{:}\eta^2\text{-}ONC_5H_6Me_4)]_2$, was synthesized from the reaction of TEMPO with $(\eta^5\text{-}C_5Me_5)_3Sm$,[27] and TEMPO delivers an oxo ligand to uranium in its reaction with $U[N(SiMe_3)_2]_3$.[28,29]

EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk-line and glovebox techniques under an argon or a dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents (Cambridge Isotope Laboratories) were dried over a NaK alloy, degassed by three freeze−pump−thaw cycles, and vacuum-transferred before use. ^1H NMR spectra were recorded on Bruker DR400, GN500, and CRYO 500 MHz spectrometers (^{13}C NMR spectra on the 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protiosolvent resonances. IR samples were prepared as KBr pellets and analyzed using a Varian 1000 FT-IR Scimitar series spectrometer. Elemental analyses were conducted on a PerkinElmer 2400 series II CHNS elemental analyzer. $ThBr_4(THF)_4$ (THF = tetrahydrofuran),[30] $(\eta^5\text{-}C_5Me_5)_2ThBr_2$,[31] $(\eta^5\text{-}C_5Me_4H)_3Th$,[32] $[(\eta^5\text{-}C_5Me_5)_2ThH_2]_2$,[33] and KC_8[34] were prepared according to the literature. $(\eta^5\text{-}C_5Me_5)_2ThMe_2$[33] was prepared in a procedure modified from the literature in which $(\eta^5\text{-}C_5Me_5)_2ThBr_2$ was used in lieu of the analogous dichloride complex, toluene was used instead of diethyl ether as a solvent, and the precursors were allowed to react for 3 days. $(CH_2CHCH_2)MgCl$ was

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purchased from Sigma-Aldrich (2.0 M in THF) and used as received. TEMPO (98%, Sigma-Aldrich) was sublimed before use.

(η^5-$C_5Me_5)_2$Th(Me)(η^1-TEMPO) (1). A red solution of TEMPO (110 mg, 0.704 mmol) in toluene (2 mL) was slowly added by pipet to a stirred pale-yellow solution of (η^5-$C_5Me_5)_2ThMe_2$ (181 mg, 0.340 mmol) in toluene (18 mL). The resulting orange-yellow solution was stirred for 12 h and dried under vacuum to yield a mixture of yellow and white solids. ^{1}H NMR spectroscopy revealed the presence of 1-methoxy-2,2,6,6-tetramethylpipridine (Me-TEMPO)[35] as a byproduct that could be separated upon crystallization. Colorless X-ray-quality crystals of **1** were grown from a hexane solution at −30 °C (140 mg, 60%). ^{1}H NMR (C_6D_6): δ 2.08 (s, 30H, $C_5\mathit{Me}_5$), 1.39 (m, 4H, $ONC_5\mathit{H}_6Me_4$), 1.24 (m, 2H, $ONC_5\mathit{H}_6Me_4$), 1.14 (s, 12H, $ONC_5H_6\mathit{Me}_4$), 0.43 (s, 3H, *Me*). ^{13}C NMR (C_6D_6): δ 123.70 (C_5Me_5), 57.60, 40.49, 31.62, 22.71, 17.01, 12.21 ($C_5\mathit{Me}_5$). IR: 3711w, 2969s, 2926s, 2865s, 2727w, 1470m, 1442m, 1378m, 1354m, 1262w, 1240w, 1181w, 1132m, 1104w, 1044w, 996m, 962s, 946m, 876w, 794m, 682s, 640w. Anal. Calcd for $C_{30}H_{51}NOTh$: C, 53.48; H, 7.63; N, 2.08. Found: C, 53.36; H, 7.44; N, 2.07.

(η^5-$C_5Me_5)_2$Th(η^1-C_3H_5)(η^3-C_3H_5) (2). C_3H_5MgCl (265 μL of a 2.0 M solution in THF, 0.530 mmol) was slowly added over 5 min to a colorless solution of (η^5-$C_5Me_5)_2ThBr_2$ (167 mg, 0.252 mmol) in THF (10 mL). The reaction mixture turned pale-yellow upon addition. After stirring for 25 min, the mixture was dried under vacuum to yield a mixture of yellow and white solids. The mixture was then extracted with three 5 mL aliquots of hexane, which were combined, centrifuged, filtered, and dried under vacuum. The extraction was repeated a second time to yield **2** as a yellow powder (117 mg, 80%). Colorless X-ray-quality crystals of **2** were grown from a hexane solution at −15 °C. **2** can also be crystallized from Et_2O or from pentane at −30 °C. ^{1}H NMR (C_6D_6): δ 6.11 (quin, 1H, $CH_2\mathit{C}HCH_2$), 2.93 (d, $^3J_{HH}$ = 11 Hz, 4H, $\mathit{CH}_2CHCH\mathit{H}_2$), 1.85 (s, 30H, $C_5\mathit{Me}_5$). ^{13}C NMR (C_6D_6): δ 122.60 (C_5Me_5), 83.62 (CH_2CHCH_2), 75.35 (CH_2CHCH_2), 12.16 ($C_5\mathit{Me}_5$). IR: 3060w, 2978m, 2906s, 2859s, 2728w, 2362w, 1591s, 1510w, 1437m, 1380s, 1246w, 1211w, 1193w, 1019m, 960m, 936m, 809s, 712m, 633w. Anal. Calcd for $C_{26}H_{40}Th$: C, 53.41; H, 6.90. Found: C, 52.73; H, 6.86.

(η^5-$C_5Me_5)_2$Th(η^1-C_3H_5)(η^1-TEMPO) (3). A red solution of TEMPO (62 mg, 0.40 mmol) in toluene (3 mL) was slowly added by pipet to a stirred pale-yellow solution of **2** (113 mg, 0.193 mmol) in toluene (10 mL). The resulting orange solution was allowed to mix for 12 h, by which time it had returned to a pale-yellow color. The solution was dried under vacuum to yield a tacky pale-yellow solid. ^{1}H NMR spectroscopy revealed the presence of 1-(2-propen-1-yloxy)-2,2,6,6-tetramethylpiperidine (allyl-TEMPO) as a byproduct (δ 5.88 m, 5.29 d, 5.04 d, 4.37 d, 1.49 m, 1.31 m, 1.23 s, 1.17 s),[6] which was removed upon crystallization. Colorless X-ray-quality crystals of **3** were grown from a hexane solution at −15 °C (71 mg, 52%). **3** can also be crystallized in pentane at −30 °C. ^{1}H NMR (C_6D_6): δ 6.67 (m, 1H, $CH_2\mathit{C}HCH_2$), 3.29 (d, $^3J_{HH}$ = 12 Hz, 4H, $\mathit{CH}_2CHCH\mathit{H}_2$), 2.08 (s, 30H, $C_5\mathit{Me}_5$), 1.38 (m, 4H, *m*-$ONC_5\mathit{H}_6Me_4$), 1.23 (m, 2H, *p*-$ONC_5\mathit{H}_6Me_4$), 1.15 (s, 12H, $ONC_5H_6\mathit{Me}_4$). ^{13}C NMR (C_6D_6): δ 124.33 (C_5Me_5), 90.35 (CH_2CHCH_2), 78.74 (CH_2CHCH_2), 59.27, 40.30, 30.25, 17.14, 11.83 ($C_5\mathit{Me}_5$). IR: 3713w, 3072w, 2975s, 2926s, 2868s, 1596s, 1447s, 1398m, 1371m, 1357m, 1297w, 1261w, 1238w, 1181w, 1131m, 1085w, 1026w, 993m, 960s, 942s, 836m, 793m, 681s, 640s, 554m. Anal. Calcd for $C_{32}H_{53}NOTh$: C, 54.92; H, 7.63; N, 2.00. Found C, 54.38; H, 7.52; N, 1.84.

(η^5-$C_5Me_5)_2$Th(η^1-TEMPO)$_2$ (4). A red solution of TEMPO (210 mg, 1.34 mmol) in toluene (4 mL) was slowly added by pipet to a stirred yellow solution of [(η^5-$C_5Me_5)_2ThH_2]_2$ (328 mg, 0.325 mmol) in toluene (15 mL). Visible gas evolution occurred in the resulting orange solution. The solution was allowed to mix for 12 h, at which point it had returned to a yellow color. The solution was dried under vacuum to yield a yellow oil. Colorless X-ray-quality crystals of **4**·$^1/_2$toluene were grown from a toluene solution at −30 °C (224 mg of **4**·$^1/_2$toluene, 55%). ^{1}H NMR (C_6D_6): δ 2.27 (s, 30H, $C_5\mathit{Me}_5$), 1.49 (m), 1.40 (s), 1.25 (s), 1.11 (s). ^{13}C NMR (C_6D_6): δ 126.15 (C_5Me_5), 59.82, 59.46, 41.61, 41.53, 35.06, 34.58, 21.38, 17.65, 13.18 ($C_5\mathit{Me}_5$). IR: 2998s, 2969s, 2935s, 2872s, 2727m, 1606w, 1496m, 1471s, 1447s, 1370s, 1356s, 1296w, 1261m, 1236m, 1211w, 1182m, 1132s, 1084m, 1045m, 993m, 954s, 927s, 874m, 849w, 788s, 729s, 680s, 632s. Anal. Calcd for $C_{38}H_{66}N_2O_2Th{\cdot}0.5C_7H_8$: C, 57.89; H, 8.19; N, 3.25. Found: C, 57.79; H, 8.06; N, 3.36.

(η^5-$C_5Me_5)_2$ThBr(η^1-TEMPO) (5). CuBr (25 mg, 0.17 mmol) was added to a stirred colorless solution of **1** (88 mg, 0.13 mmol) in toluene (8 mL). The mixture was stirred for 16 h and became dark, presumably from copper metal formation. The mixture was centrifuged and filtered to remove solids, and the solvent was removed under vacuum to yield **5** as a white microcrystalline solid (90 mg, 93%). Colorless X-ray-quality crystals of **5** were grown from a toluene solution at −30 °C. ^{1}H NMR (C_6D_6): δ 2.17 (s, 30H, $C_5\mathit{Me}_5$), 1.35−1.15 (m, $ONC_5\mathit{H}_6Me_4$). ^{13}C NMR (C_6D_6): δ 126.26 (C_5Me_5), 61.00, 59.50, 41.25, 40.68, 22.01, 17.78, 17.71, 21.75 ($C_5\mathit{Me}_5$), 21.45 ($C_5\mathit{Me}_5$). IR: 2967s, 2932s, 2910s, 2868s, 2728w, 1466m, 1441m, 1379s, 1357m, 1261w, 1239w, 1206w, 1180w, 1132m, 1089w, 1057w, 1042w, 1023w, 990w, 957s, 942s, 876m, 795s, 728w, 683s, 642m. Anal. Calcd for $C_{29}H_{48}BrNOTh$: C, 47.16; H, 6.65; N, 1.90. Found: C, 47.48; H, 6.55; N, 1.68.

(η^5-$C_5Me_4H)_3$Th(η^1-TEMPO), 6. A red solution of TEMPO (28 mg, 0.179 mmol) in toluene (3 mL) was added dropwise via pipet to a stirred dark-purple solution of (η^5-$C_5Me_4H)_3Th$ (106 mg, 0.178 mmol) in toluene (35 mL). The solution, which was colorless by the end of the addition, was allowed to mix for an additional 10 min before being dried under vacuum. The resulting dull-orange solid was extracted with hexane, centrifuged, filtered, and dried under vacuum to yield a white solid (108 mg, 81%). Colorless X-ray-quality crystals of **6** were grown from a toluene solution at −25 °C. ^{1}H NMR (C_6D_6): δ 6.21 (s, 3H, $C_5Me_4\mathit{H}$), 2.25 (s, 18H, $C_5\mathit{Me}_4H$), 2.17 (s, 18H, $C_5\mathit{Me}_4H$), 1.43 (m, 4H, *m*-$ONC_5\mathit{H}_6Me_4$), 1.36 (m, 2H, *p*-$ONC_5\mathit{H}_6Me_4$), 1.29 (s, 12H, $ONC_5H_6\mathit{Me}_4$). ^{13}C NMR (C_6D_6): δ 125.57 (C_5Me_4H), 122.55 (C_5Me_4H), 121.69 (C_5Me_4H), 59.67, 42.25, 32.54, 23.63, 17.40, 14.99 ($C_5\mathit{Me}_4H$), 14.31 ($C_5\mathit{Me}_4H$), 13.12 ($C_5\mathit{Me}_4H$). IR: 3649w, 2963s, 2918s, 2867s, 2725w, 1585w, 1550w, 1481m, 1443s, 1380m, 1373m, 1360m, 1330w, 1261w, 1219w, 1181w, 1137m, 1089w, 1020m, 916m, 875w, 781s, 675m, 632m, 598m. Anal. Calcd for $C_{36}H_{57}NOTh$: C, 57.51; H, 7.64; N, 1.86. Found: C, 57.59; H, 7.75; N, 1.83.

(η^2-TEMPO)$_2$ThBr$_2$ (7). In a glovebox containing coordinating solvents such as THF, a red solution of TEMPO (95 mg, 0.61 mmol) in toluene (3 mL) was slowly added by pipet to a stirred colorless solution of (η^5-$C_5Me_5)_2ThBr_2$ (200 mg, 0.302 mmol) in toluene (18 mL). Transient purple and maroon colors were sometimes observed in these reactions before the solution became yellow. After 12 h, a white insoluble material was sometimes observed and removed by filtration. Removal of the solvent from the filtrate gave a yellow crystalline solid, which was washed with hexane and dried under vacuum to yield **7** as a white powder (182 mg, 85%). Colorless X-ray-quality crystals were grown from a hot toluene solution that was cooled to −15 °C (121 mg, 57%). When this reaction was performed in a glovebox free of coordinating solvents, the reaction products were often more complicated and crystalline material was not always obtained in significant quantities. ^{1}H NMR (C_6D_6): δ 1.84 (s), 1.73 (s), 1.59 (s, $ONC_5H_6\mathit{Me}_4$), 1.48−1.09 (m, $ONC_5\mathit{H}_6Me_4$), 0.89 (s, $ONC_5H_6\mathit{Me}_4$). ^{13}C NMR (C_6D_6): δ 70.44, 62.96, 61.59, 60.98, 39.89, 38.70, 38.25, 32.01, 28.36 (br), 22.78, 20.17, 17.70, 17.16. IR: 3008s, 2976s, 2941s, 2855s, 2756w, 2701w, 2663w, 1741w, 1604w, 1474s, 1467s, 1378s, 1360s, 1336w, 1303w, 1258m, 1245m, 1235m, 1214m, 1179m, 1131s, 1083m, 1060m, 1015s, 972m, 924m, 884w, 784m, 735m. Anal. Calcd for $C_{18}H_{36}Br_2N_2O_2Th$: C, 30.69; H, 5.15; N, 3.98. Found: C, 30.58; H, 5.08; N, 3.66.

ThBr$_4$(THF)$_2$(η^1-TEMPO) (8). Solid TEMPO (35 mg, 0.22 mmol) was slowly added to a concentrated colorless solution of $ThBr_4(THF)_4$ (197 mg, 0.225 mmol) in toluene (2.5 mL). The solution immediately turned yellow, and yellow precipitate started to form near the end of the addition. After 10 min, the mixture was filtered, and the solvent volume was reduced under vacuum. Yellow X-ray-quality crystals of **8**·toluene were grown from a toluene solution at −30 °C (64 mg of **8**·toluene, 40%). IR: 2974s, 2946s, 2891m, 2878m, 1609w, 1457m, 1397w, 1383w, 1366m, 1340s, 1240s, 1165w, 1121w, 1067w, 1038w,

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Table 1. X-ray Data and Collection Parameters for 1−4

compound	1	2	3	4
empirical formula	$C_{30}H_{51}NOTh$	$C_{26}H_{40}Th$	$C_{32}H_{53}NOTh$	$C_{38}H_{66}N_2O_2Th\cdot{}^1/_2C_7H_8$
temperature (K)	103(2)	143(2)	143(2)	88(2)
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$Pbca$
a (Å)	15.5819(7)	16.733(1)	16.830(1)	13.3034(7)
b (Å)	11.1657(5)	17.651(1)	10.0546(6)	17.3503(9)
c (Å)	17.3224(7)	17.077(1)	19.350(1)	33.922(2)
α (deg)	90	90	90	90
β (deg)	105.021(1)	109.9246(7)	112.4316(6)	90
γ (deg)	90	90	90	90
volume (Å^3)	2910.8(2)	4742.0(5)	3026.5(3)	7829.9(7)
Z	4	8	4	8
ρ_{calcd} (Mg/m^3)	1.537	1.638	1.536	1.461
μ (mm^{-1})	5.143	6.297	4.950	3.844
R1[a] [$I > 2.0\sigma(I)$]	0.0149	0.0205	0.0199	0.0330
wR2[a] (all data)	0.0374	0.0493	0.0417	0.0716

[a]R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. X-ray Data and Collection Parameters for 5−9

compound	5	6	7	8	9
empirical formula	$C_{29}H_{48}BrNOTh$	$C_{36}H_{57}NOTh$	$C_{18}H_{36}Br_2N_2O_2Th$	$C_{24}H_{42}Br_4N\ O_3Th$	$C_{36}H_{72}N_4O_4Th$
temperature (K)	103(2)	88(2)	173(2)	143(2)	143(2)
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$Pbca$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a (Å)	15.5047(7)	18.790(1)	15.284(2)	23.373(2)	11.7106(6)
b (Å)	11.0815(5)	18.064(1)	10.585(1)	22.786(2)	16.4966(9)
c (Å)	17.4222(8)	18.853(1)	14.279(2)	11.7290(8)	19.989(1)
α (deg)	90	90	90	90	90
β (deg)	104.5528(5)	90	94.817(2)	92.9552(9)	90
γ (deg)	90	90	90	90	90
volume (Å^3)	2897.4(2)	6399.2(8)	2301.9(5)	6238.2(7)	3861.5(4)
Z	4	8	4	8	4
ρ_{calcd} (Mg/m^3)	1.693	1.561	2.032	2.011	1.474
μ (mm^{-1})	6.546	4.688	9.963	9.928	3.902
R1[a] [$I > 2.0\sigma(I)$]	0.0156	0.0188	0.0206	0.0318	0.0172
wR2[a] (all data)	0.0381	0.0407	0.0481	0.0695	0.0381

[a]R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

1004s, 963w, 924w, 852s, 833s, 793w, 733w, 668w, 643w. Anal. Calcd for $C_{17}H_{34}Br_4O_3NTh$: C, 23.96; H, 4.02; N, 1.64. Found: C, 24.70; H, 4.01; N, 1.59.

Th(η^1-TEMPO)$_2$(η^2-TEMPO)$_2$ (9) from 7. A colorless solution of **7** (121 mg, 0.172 mmol) in THF (6 mL) and a red solution of TEMPO (54 mg, 0.346 mmol) in THF (2 mL) were chilled to −30 °C. The solutions were removed from the freezer and immediately combined. KC_8 (46 mg, 0.34 mmol) was then slowly added to the mixture. The mixture quickly turned dark with the formation of graphite. The solution was allowed to mix for 45 min before centrifugation. The opalescent supernatant was then filtered repeatedly to remove particulates, and the solution was dried under vacuum. The product was then extracted with toluene (18 mL), filtered, and dried under vacuum to yield a white solid (127 mg, 86%). Colorless X-ray-quality crystals of **9** were grown from a toluene solution at −25 °C. ^{1}H NMR (C_6D_6): δ 1.61 (m, 4H, *m*-ONC$_5$*H*$_6$Me$_4$), 1.45 (s, 12H, ONC$_5$H$_6$*Me*$_4$), 1.37 (m, 2H, *p*-ONC$_5$*H*$_6$Me$_4$). ^{13}C NMR (C_6D_6): δ 60.81 (*o*-ONC$_5$H$_6$Me$_4$), 40.56 (*m*-ONC$_5$H$_6$Me$_4$), 22.00 (ONC$_5$H$_6$*Me*$_4$), 18.02 (*p*-ONC$_5$H$_6$Me$_4$). IR: 3011s, 2966s, 2937s, 2870s, 2675w, 1468s, 1371s, 1355s, 1300w, 1260m, 1242m, 1211m, 1180m, 1132s, 1083w, 1055w, 1043s, 1000s, 964s, 944s, 926m, 876w, 792s, 716w, 677s, 631s. Anal. Calcd for $C_{36}H_{72}O_4N_4Th$: C, 50.45; H, 8.47; N, 6.54. Found: C, 50.58; H, 8.51; N, 6.39.

9 from ThBr$_4$(THF)$_4$. Solid TEMPO (243 mg, 1.55 mmol) was added to a stirred solution of $ThBr_4(THF)_4$ (332 mg, 0.379 mmol) in THF (10 mL). KC_8 (222 mg, 1.64 mmol) was added over 3 min. The mixture immediately turned black with the formation of graphite. The mixture was allowed to react for 1 h before being centrifuged and filtered to remove black solids. The solids were washed with 5 mL of THF followed by 5 mL of toluene. Both washes were combined with the original pale-yellow supernatant and dried under vacuum. The resulting white and brown solid was extracted with toluene, filtered, and dried to yield **9** as a white solid (0.270 g, 83%). ^{1}H NMR spectroscopy confirmed the product as **9**. Colorless X-ray-quality crystals of **9** were grown from a toluene solution at −30 °C (173 mg, 53%).

X-ray Data Collection, Structure Determination, and Refinement. Crystallographic details for compounds **1**−**9** are summarized in Tables 1 and 2 and in the Supporting Information.

RESULTS

(η^5-C$_5$Me$_5$)$_2$ThMe(η^1-TEMPO), 1. (η^5-C$_5$Me$_5$)$_2$ThMe$_2$ reacts with 2 equiv of the TEMPO radical in toluene to cleave a Th−Me bond and form **1** (eq 1). Reactions with only 1 equiv of TEMPO consume only half of the starting material and give the same products but in half the yield. Heating **1** to 75 °C in

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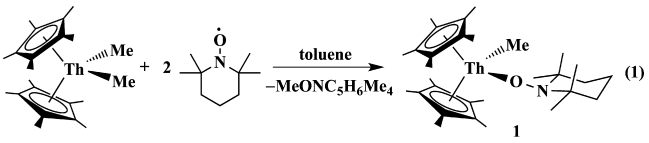


the presence of excess TEMPO also gave only **1** as the product. ^{1}H NMR spectroscopy revealed resonances consistent with Me-TEMPO as a byproduct.

Complex **1** was definitively identified by X-ray crystallography, which revealed that it is an $(\eta^1$-TEMPO$)^-$ complex (Figure 1). Obtaining suitable elemental analytical data on $(\eta^5$-$C_5Me_5)_2$ThMe(TEMPO) and the other TEMPO complexes in this study was problematic. At least two crystallizations and multiple analyses were necessary before elemental analytical data matching that of the expected calculated values were observed.

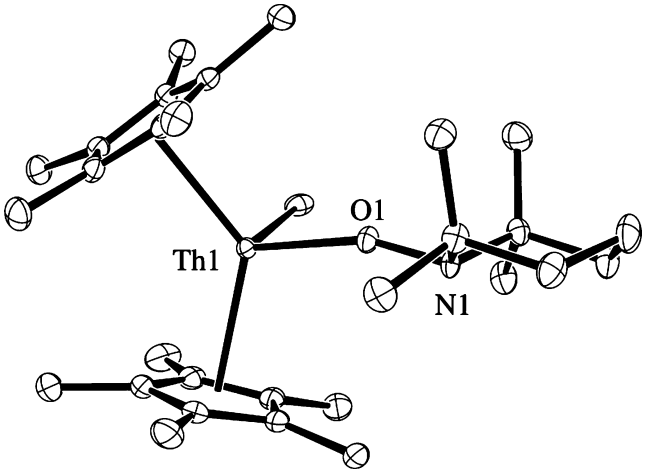
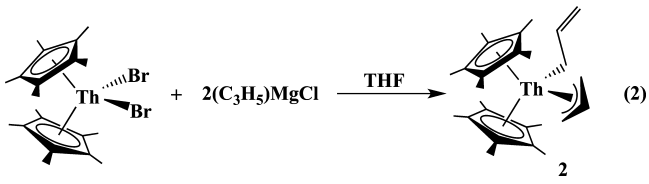


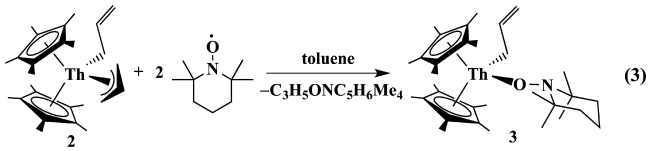
Figure 1. Thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity.

The metrical parameters of the $[(\eta^5$-$C_5Me_5)_2$ThMe$]^{1+}$ part of complex **1**, i.e., the 2.546 and 2.578 Å Th−(η^5-C_5Me_5 ring centroid) distances (Table 3) and the 2.519(2) Å Th−C(Me) length are slightly larger than the 2.518 Å Th−(C_5Me_5 ring centroid) and 2.471(8) and 2.478(9) Å Th−C(Me) distances in $(\eta^5$-$C_5Me_5)_2$ThMe$_2$,[36] which could reflect the larger size of the TEMPO$^-$ anion versus Me$^-$. Consistent with this, the 130.5° (C_5Me_5 ring centroid)−Th−(C_5Me_5 ring centroid) angle in **1** is smaller than the 133.9° analogue in $(\eta^5$-$C_5Me_5)_2$ThMe$_2$. The 2.131(1) Å Th−O(TEMPO) distance is similar to the 2.154(8) Å Th−O(diolate) distance in $[(\eta^5$-$C_5Me_5)_2$Th(μ-$O_2C_2Me_2]_2$.[37] The 1.437(2) Å O−N distance in **1** is typical for a TEMPO$^-$ anion, as are the two 108.9(1)° O−N−C angles.[16,17,21,23,25,27] The sum of the angles around nitrogen, 336.4°, is consistent with a pyramidal geometry about the nitrogen in a fully reduced TEMPO$^-$ anion.[16,17,21]

$(\eta^5$-$C_5Me_5)_2$Th(η^1-C_3H_5)(η^3-C_3H_5), 2, and $(\eta^5$-$C_5Me_5)_2$Th-(η^1-C_3H_5)(TEMPO), 3. To allow examination of TEMPO reactions with a second example of $(C_5Me_5)_2ThR_2$ beyond R = Me, the allyl analogue of $(\eta^5$-$C_5Me_5)_2$ThMe$_2$, namely, **2**, was synthesized from $(\eta^5$-$C_5Me_5)_2$ThBr$_2$ and 2 equiv of (C_3H_5)-MgBr (eq 2). Crystals of **2** are isomorphous with the uranium analogue[38] and have an identical unusual solid-state structure with one η^1-allyl and one η^3-allyl ligand, i.e., $(\eta^5$-$C_5Me_5)_2$Th(η^1-C_3H_5)(η^3-$C_3H_5)_2$ (Figure 2), in each of the two molecules in the unit cell. The bond distances are slightly longer throughout the molecule compared to the uranium complex, which is consistent with the larger ionic radius of thorium.[39] If the η^1/η^3 structure observed for uranium is due to steric crowding that prevents η^3/η^3 coordination, this situation still exists with the larger thorium.



2 reacts with TEMPO in a manner analogous to that of $(\eta^5$-$C_5Me_5)_2$ThMe$_2$, yielding **3**, found by X-ray crystallography to contain both TEMPO and allyl ligands in an η^1-coordination mode (eq 3 and Figure 3). The ^{1}H NMR spectrum of **3** does not contain an η^1-allyl pattern, which indicates that the ligand is fluxional in solution at room temperature. No change in the spectrum was observed down to −90 °C. Like eq 1, reactions of **2** with 1 equiv of TEMPO consume only half of the starting material and give the same products but in half the yield.



As shown in Table 3, the metrical parameters of the $[(\eta^5$-$C_5Me_5)_2$Th(η^1-TEMPO$)]^+$ parts of **1** and **3** are quite similar. Also, the 2.519(2) Å Th−Me distance in **1** is similar to the 2.552(2) Å Th−C(η^1-allyl) distance in **3**. The 130.6° (C_5Me_5 ring centroid)−Th−(C_5Me_5 ring centroid) angle in **3** is smaller than the 134.2° and 134.8° angles in **2**.

$(\eta^5$-$C_5Me_5)_2$Th(η^1-TEMPO)$_2$, 4. In contrast to the reactions of the methyl and allyl metallocenes that form mono(TEMPO) complexes **1** and **3**, the hydride complex $[(\eta^5$-$C_5Me_5)_2$Th$H_2]_2$[33] generates the bis(TEMPO) metallocene **4** (eq 4 and Figure 4). Both TEMPO$^-$ anions bind through oxygen in this product. Gas bubbles are observed to form in solution during this reaction, which are presumably hydrogen because no evidence for an H-TEMPO[35] analogue of the R-TEMPO byproduct described above was observed by NMR spectroscopy. Attempts to form **4** from **1** or **3** with excess TEMPO were unsuccessful as were reactions of **1** and **3** with hydrogen to generate a "$(\eta^5$-$C_5Me_5)_2$ThH(TEMPO)" complex that could be an intermediate on the way to **4**. Similarly, reactions of $[(\eta^5$-$C_5Me_5)_2$Th$H_2]_2$ with 1 equiv TEMPO per thorium center resulted in the formation of **4** in half the yield, while consuming only half of the starting material. No evidence of the formation of a "$(\eta^5$-$C_5Me_5)_2$ThH(TEMPO)" complex was observed. The ^{1}H NMR spectrum of **4** is complicated, and the ^{13}C NMR spectrum showed a doubling of the TEMPO peaks, suggesting that there is some nonequivalence between the TEMPO moieties on the NMR time scale. The ^{1}H NMR

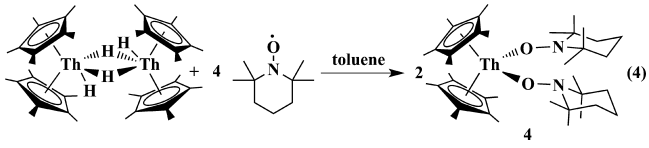


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Table 3. Selected bond distances (Å) and angles (deg) for $(\eta^5\text{-}C_5Me_5)_2Th(Me)(\eta^1\text{-}TEMPO)$, 1, $(\eta^5\text{-}C_5Me_5)_2Th(\eta^1\text{-}C_3H_5)(\eta^1\text{-}TEMPO)$, 3, $(\eta^5\text{-}C_5Me_5)_2Th(\eta^1\text{-}TEMPO)_2$, 4, $(\eta^5\text{-}C_5Me_5)_2ThBr(\eta^1\text{-}TEMPO)$, 5, $(\eta^5\text{-}C_5Me_4H)_3Th(\eta^1\text{-}TEMPO)$, 6, $(\eta^2\text{-}TEMPO)_2ThBr_2$, 7, $ThBr_4(THF)_2(\eta^1\text{-}TEMPO)$, 8, and $Th(\eta^1\text{-}TEMPO)_2(\eta^2\text{-}TEMPO)_2$, 9

	Th−Cnt	Th−O	O−N	Th−O−N	O−N−C	C−N−C
1	2.578	2.131(1)	1.437(2)	161.4(1)	108.9(1)	118.6(1)
	2.546				108.9(1)	
3	2.548	2.129(2)	1.448(2)	163.01(1)	108.4(2)	118.8(2)
	2.577				108.1(2)	
4					109.1(3)	117.7(3)
	2.625	2.167(2)	1.447(4)	157.2(2)	109.3(3)	
	2.601	2.172(3)	1.440(4)	155.8(2)	108.7(3)	117.1(3)
					109.6(3)	
5	2.567	2.113(1)	1.444(2)	162.2(1)	108.5(1)	118.7(2)
	2.535				109.1(1)	
6	2.630	2.179(2)	1.461(2)	158.6(1)	110.2(2)	116.4(2)
	2.685				110.4(2)	
	2.666					
7	N/A				109.2(3)	118.7(3)
		2.192(2)	1.445(4)	84.0(2)	109.3(2)	
		2.197(2)	1.444(4)	84.4(2)	109.6(2)	118.8(3)
					108.8(2)	
8	N/A	2.313(3)	1.291(5)	174.8(3)	115.2(4)	127.2(4)
					115.3(4)	
9	N/A				108.8(2)	117.1(2)
					107.0(3)	
		2.267(2)	1.445(3)	85.8(1)	108.3(2)	117.5(2)
		2.245(2)	1.450(3)	88.3(1)	108.3(3)	
		2.173(2)	1.447(3)	160.8(2)	109.1(2)	118.1(2)
		2.166(2)	1.444(3)	165.8(2)	109.2(2)	
					108.2(2)	117.6(3)
					108.4(2)	

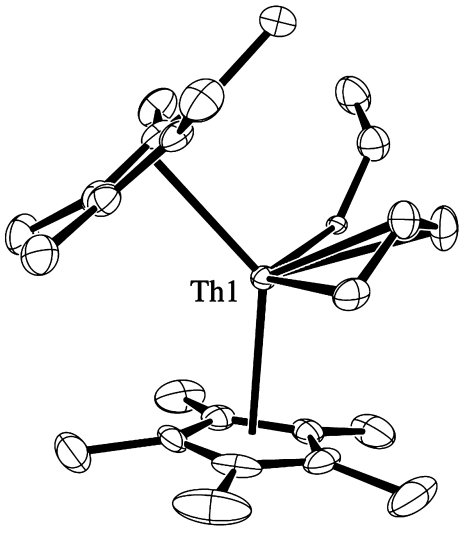

Figure 2. Thermal ellipsoid plot of **2**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity.

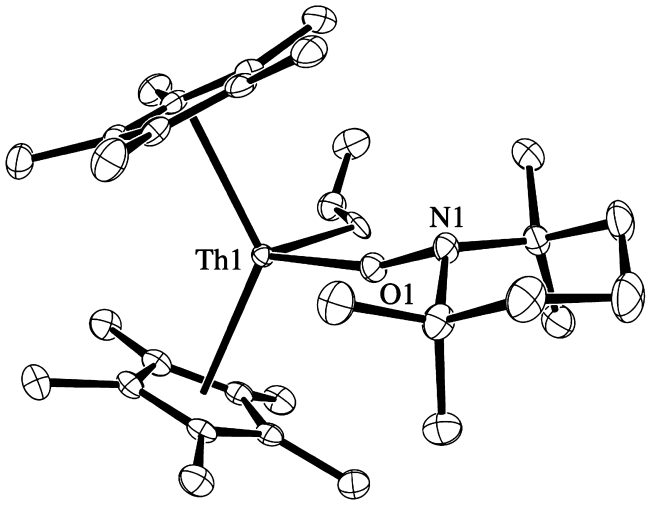

Figure 3. Thermal ellipsoid plot of **3**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity.

spectrum was examined at higher temperature, but a simple spectrum was not obtainable within the temperature range accessible.

The metrical parameters of **4** are presented in Table 3 for comparison. The 2.625 and 2.601 Å Th−(C_5Me_5 ring centroid) distances in **4** are larger than those in **1** and **3**, reflecting the larger size of the $TEMPO^-$ anion compared to Me^- and $allyl^-$. The 126.3° (C_5Me_5 ring centroid)−Th−(C_5Me_5 ring centroid) angle in **4** is smaller than the 130.0° angle in $[(\eta^5\text{-}C_5Me_5)_2ThH_2]_2$, as well as the corresponding angles in **1**−**3**. The 2.167(2) and 2.172(3) Å Th−O(TEMPO) distances in **4** are larger than those in **1** and **3**, while the 1.447(4) and 1.440(4) Å O−N distances in **4** are quite similar. The nitrogen atoms in both $TEMPO^-$ ligands are pyramidal (Table 3), as in **1**−**3**.

$(\eta^5\text{-}C_5Me_5)_2ThBr(\eta^1\text{-}TEMPO)$, 5. Although the methyl group in **1** did not react with extra TEMPO or hydrogen, it

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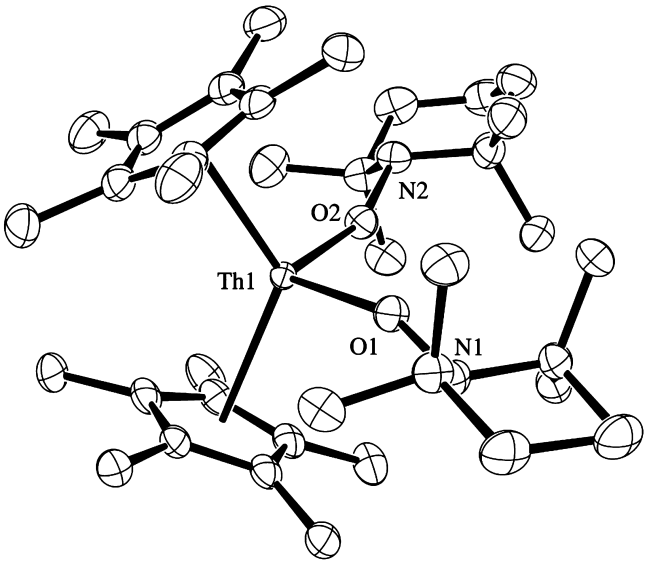
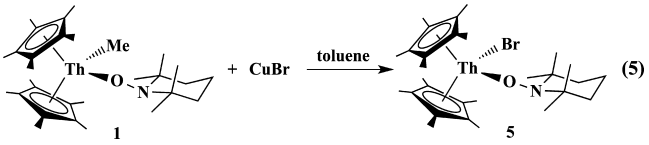


Figure 4. Thermal ellipsoid plot of **4**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity.

did react with 1 equiv of CuBr to form yet another variant of the thorium metallocene TEMPO complex, **5** (eq 5). Complex



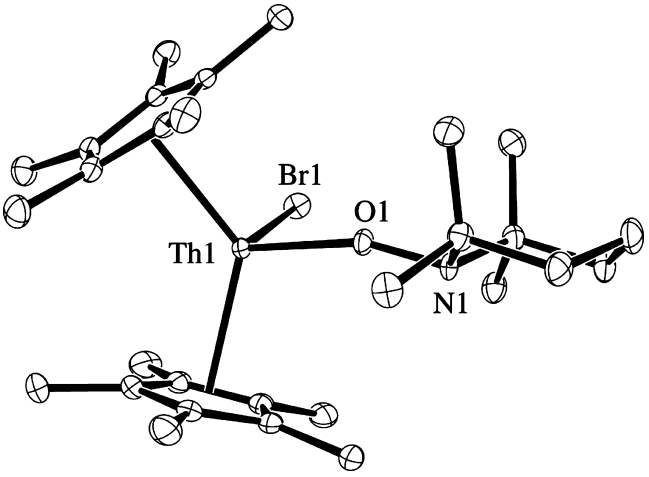
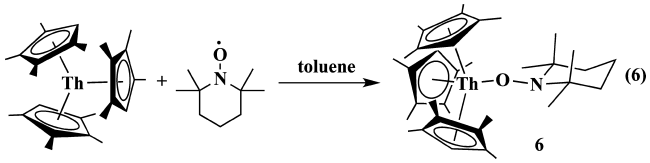


Figure 5. Thermal ellipsoid plot of **5**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity.

5 was characterized by X-ray crystallography (Figure 5) and has a structure similar to that of the methyl complex **1** (Table 3). The 2.8311(2) Å Th−Br bond distance in **5** is longer than the 2.800(2) Å distance in $(\eta^5\text{-}C_5Me_5)_2ThBr_2$ presumably because of the larger size of the $TEMPO^-$ ligand versus bromide.

$(\eta^5\text{-}C_5Me_4H)_3Th(\eta^1\text{-}TEMPO)$, 6. The Th^{3+} complex $(\eta^5\text{-}C_5Me_4H)_3Th$ was also treated with TEMPO, and this leads to oxidation of the metal and formation of a Th^{4+} complex of the $TEMPO^-$ anion **6** (eq 6). The product of the reaction again was definitively identified by X-ray crystallography (Figure 6).



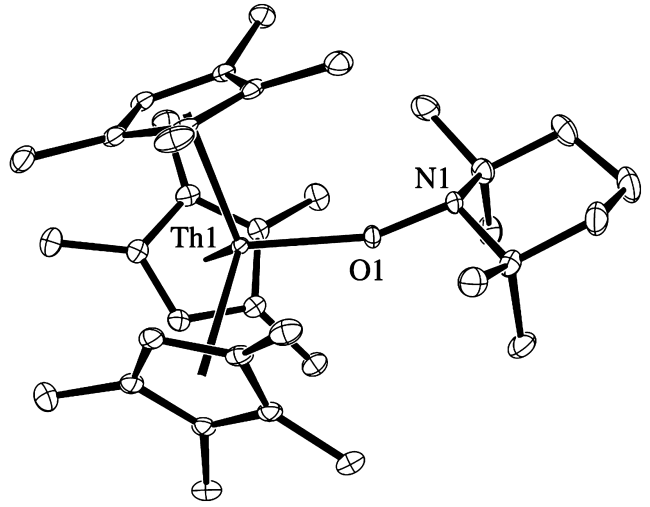
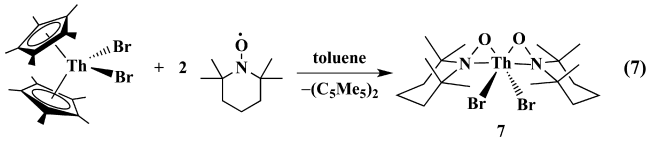


Figure 6. Thermal ellipsoid plot of **6**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity.

The structure of **6** is similar to that of $(\eta^5\text{-}C_5Me_4H)_3ThBr$,[32] but the 2.630−2.685 Å Th−(C_5Me_4H ring centroid) distances in **6** are longer than the 2.567 Å distance in $(\eta^5\text{-}C_5Me_4H)_3ThBr$ and the 112.4°−113.3° (C_5Me_4H ring centroid)−Th−(C_5Me_4H ring centroid) angles are smaller than the 117.7° angle in $(\eta^5\text{-}C_5Me_4H)_3ThBr$. These data are consistent with the larger size of the TEMPO ligand versus bromide.

$(TEMPO)_2ThBr_2$, 7. When $(\eta^5\text{-}C_5Me_5)_2ThBr_2$ was treated with TEMPO as a control reaction, a new TEMPO complex was surprisingly isolated. X-ray crystallography identified the product as **7** (Figure 7). As shown in eq 7, both of the $(C_5Me_5)^-$ ligands of the starting material were lost and $(C_5Me_5)_2$, identified by NMR spectroscopy, was formed as a byproduct.



The crystallographic data for **7** show that the $TEMPO^-$ anions adopt a different binding mode in this thorium TEMPO complex, attaching through both oxygen and nitrogen. Despite this different coordination mode of the TEMPO ligands in **7**, the N−O distances as well as the O−N−C and C−N−C angles, which result in a pyramidal geometry about the nitrogen atoms, are similar to those in **1** and **3**−**5**, where the TEMPO ligands are η^1-bound. The 2.192(2) and 2.197(2) Å Th−O bond lengths in **7** are much shorter than the 2.499(4) and 2.504(4) Å Th−N distances and are slightly longer than the

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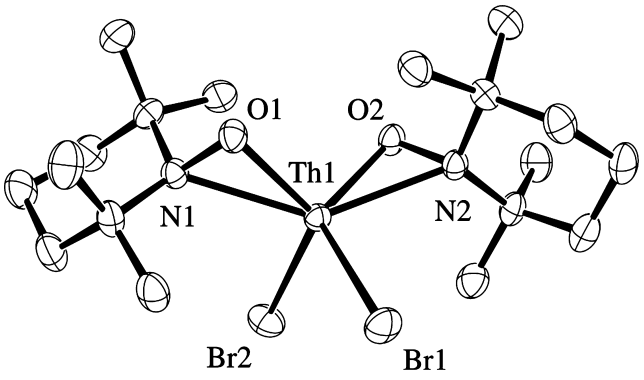


Figure 7. Thermal ellipsoid plot of **7**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity.

Th−O distances in **1** and **3**−**5**. The 2.8366(5) and 2.8514(5) Å Th−Br distances in **7** are similar to the 2.8311(2) Å Th−Br distance in **5**, which are both longer than the 2.800(2) Å distance in $(C_5Me_5)_2ThBr_2$, even though **7** is formally six-coordinate while **5** and $(\eta^5\text{-}C_5Me_5)_2ThBr_2$ are eight-coordinate. This suggests that the two $(\eta^2\text{-TEMPO})^-$ ligands can occupy a coordination environment like two $(C_5Me_5)^-$ ligands.

$ThBr_4(THF)_2(\eta^1\text{-TEMPO})$, 8. Given the surprising result in eq 7, a reaction was examined using $ThBr_4(THF)_4$ as the starting material and 1 equiv of TEMPO. Once again a reaction occurs, and a new product of limited stability can be crystallized. **8** was isolated by crystallization from toluene and identified by X-ray crystallography (Figure 8 and eq 8).

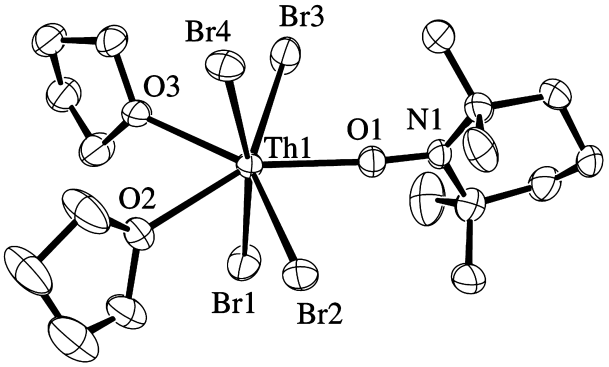
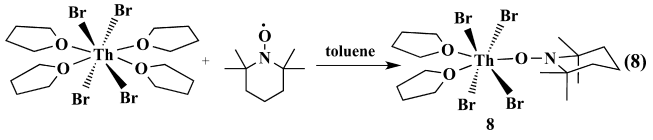


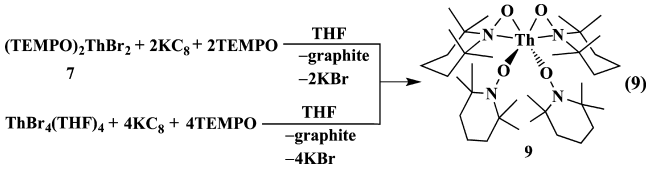
Figure 8. Thermal ellipsoid plot of **8**. Thermal ellipsoids are drawn at the 50% probability level. A second identical molecule, solvent, and all hydrogen atoms have been omitted for clarity.



Reactions with 2 equiv of TEMPO also gave just **8** (identified by X-ray crystallography). The X-ray data showed that the structural features of the TEMPO unit in **8** are distinctively different from those in all of the complexes described above. The 115.2(4) and 115.3(4)° O−N−C angles are larger than the 108−109° angles in the other complexes, and the Th−O−N angle is almost linear: 174.8(3)°. The sum of the angles around the nitrogen, 357.7°, indicates an almost completely planar geometry about the nitrogen. These features are consistent with coordination of TEMPO as a neutral radical,[13−15,18,20,22,24] which is reasonable because Th^{5+} is not a viable oxidation state for thorium. The 1.291(5) Å O−N distance in **8** is very similar to the 1.283(9) Å bond length in the structure of the isolated free radical.[27] This distance is shorter than those in the other complexes presented here, 1.437−1.461 Å, and this is consistent with a higher N−O bond order in the neutral TEMPO ligand in **8**.

Compound **8** has limited stability compared to the other thorium TEMPO complexes described above. Removal of the solvent via reduced pressure leads to some decomposition because the dried solids do not completely redissolve again in toluene, and the addition of THF also leads to decomposition.

$Th(\eta^1\text{-TEMPO})_2(\eta^2\text{-TEMPO})_2$, 9. Considering the apparent stability of bromide ligands in TEMPO reactions, KC_8 was employed to help facilitate their complete removal to make a per(TEMPO) thorium complex. Both **7** and $ThBr_4(THF)_4$ can be transformed into the per(TEMPO) complex **9** (eq 9). The



complex was identified by X-ray crystallography and found to contain two $(\eta^1\text{-TEMPO})^-$ and two $(\eta^2\text{-TEMPO})^-$ ligands (Figure 9). Only one set of TEMPO ^1H NMR resonances is observed at 298 K, indicating that, in solution, fluxional processes are occurring to equilibrate all of the TEMPO ligands.

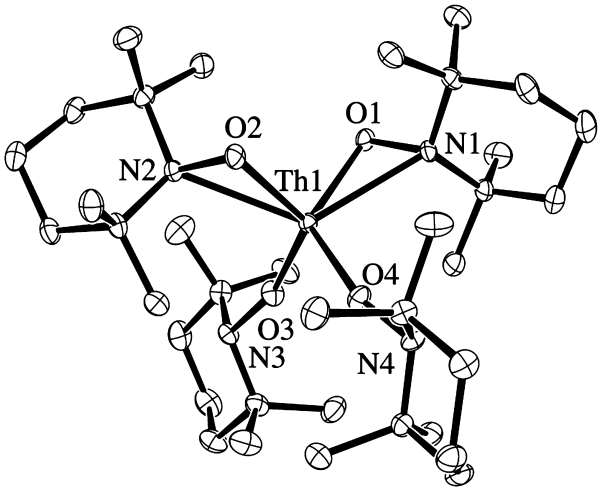


Figure 9. Thermal ellipsoid plot of **9**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms have been omitted for clarity.

The metrical parameters of each type of $TEMPO^-$ ligand in **9** are similar to their analogues in the other thorium complexes described here with anionic TEMPO ligands. Hence, the 2.173(2) and 2.166(2) Å Th−O(η^1-TEMPO) bond lengths in **9** are slightly shorter than the 2.267(2) and 2.245(2) Å Th−O(η^2-TEMPO) distances in **9**. It is interesting to note the structural similarities between **4** and **9**, which differ only by the substitution of two $(C_5Me_5)^-$ ligands with two $(\eta^2\text{-TEMPO})^-$ ligands. The Th−O bond lengths for the η^1-TEMPO ligands in

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each structure are almost identical, as are the N−O bond lengths. The Th−O−N angles are slightly larger on the η^1-TEMPO ligands in **9** than in **4**.

DISCUSSION

TEMPO reacts readily with a variety of thorium metallocenes to form new thorium complexes of the $TEMPO^-$ anion. With the methyl and allyl complexes $(\eta^5\text{-}C_5Me_5)_2ThMe_2$ and $(\eta^5\text{-}C_5Me_5)_2Th(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)$, a single Th−C bond is reactive, and complexes containing just one $TEMPO^-$ anion are formed, $(\eta^5\text{-}C_5Me_5)_2ThMe(\eta^1\text{-TEMPO})$, **1**, and $(\eta^5\text{-}C_5Me_5)_2Th(\eta^1\text{-}C_3H_5)(\eta^1\text{-TEMPO})$, **3**, respectively. With the hydride complex $[(\eta^5\text{-}C_5Me_5)_2ThH_2]_2$, two $TEMPO^-$ anions can be attached to the metal to form $(\eta^5\text{-}C_5Me_5)_2Th(\eta^1\text{-TEMPO})_2$, **4**. With $(\eta^5\text{-}C_5Me_5)_2ThBr_2$, the TEMPO reaction product $(\eta^2\text{-TEMPO})_2ThBr_2$, **7**, is no longer a metallocene, and further substitution is possible to access the per(TEMPO) complex $Th(\eta^1\text{-TEMPO})_2(\eta^2\text{-TEMPO})_2$, **9**. With thorium tetrabromide, the radical complex $ThBr_4(THF)_2(\eta^1\text{-TEMPO})$, **8**, is isolable.

The metrical parameters for the complexes of anionic $TEMPO^-$ are all similar, with the exception of the Th−O−N angle in the η^2 cases, where the angle is much smaller than that in the η^1 complexes. The η^2 coordination does not significantly change the Th−O and O−N bond lengths compared to the η^1 complexes. The structural features of the TEMPO ligand in **8** are significantly different from those in $TEMPO^-$. In **8**, the Th−O−N angle is larger and the TEMPO nitrogen has a planar geometry. Both features are consistent with a neutral adduct.

The detailed mechanisms of these reactions are unknown, and several possibilities are reasonable. One view is to consider the Me^-, $allyl^-$, and H^- ligands formally as reductants that can reduce TEMPO to $TEMPO^-$ in eqs 1, 3, and 4. Precedent for the reduction of TEMPO to $TEMPO^-$ is shown by the reaction of the Th^{3+} complex $(\eta^5\text{-}C_5Me_4H)_3Th$ with TEMPO to form the Th^{4+} product **6** (eq 6). Evidence by ^1H NMR spectroscopy for Me-TEMPO and allyl-TEMPO byproducts is consistent with the trapping of a second equiv of TEMPO (necessary for these reactions to go to completion) by radicals formed by a $R^- \rightarrow e^- + R$ reaction. It is also possible that TEMPO coordinates to thorium, as is observed in the radical complex of thorium tetrabromide **8**, and then inner-sphere electron abstraction and alkyl loss occurs. In the reaction of $[(\eta^5\text{-}C_5Me_5)_2ThH_2]_2$ (eq 4), the observation of a gaseous byproduct suggests that dihydrogen rather than H-TEMPO forms in this case. Consistent with this observation, extra equivalents of TEMPO are not needed in eq 4. This reaction could occur in several ways including pathways involving hydrogen-atom abstraction by TEMPO and protonation of a thorium hydride by H-TEMPO.

The reaction of $(\eta^5\text{-}C_5Me_5)_2ThBr_2$ with TEMPO to form **7** and $(C_5Me_5)_2$ can also be viewed as a redox reaction involving the $(C_5Me_5)^- \rightarrow e^- + C_5Me_5$ half-reaction. Although $(C_5Me_5)^-$ ligands are known to engage in this half-reaction in sterically crowded complexes[40−46] and form $(C_5Me_5)_2$ as a byproduct, this type of reactivity is not common with f-element metallocenes with normal bond distances. In fact, one of the features of $(C_5Me_5)^-$ that makes it such a valuable ancillary ligand is that it is relatively inert. Few routes exist to cleanly remove $(C_5Me_5)^-$ and form new isolable complexes.[47,48] The TEMPO reaction shown in eq 7 evidently provides this type of reactivity. One possible explanation for this reaction is coordination of a TEMPO radical to the thorium metal center, as observed in **8**, which produces a sterically crowded molecule followed by sterically induced reduction.

Given that only one methyl and one allyl ligand react in $(\eta^5\text{-}C_5Me_5)_2ThMe_2$ and $(\eta^5\text{-}C_5Me_5)_2Th(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)$, respectively, whereas both hydrides react in $[(\eta^5\text{-}C_5Me_5)_2ThH_2]_2$ suggests that there may be some steric component to the reaction. Coordination of the TEMPO radical to the thorium is likely to be a prior requirement given the observed coordination of a TEMPO radical to thorium tetrabromide in complex **8**. The structural data consistently show that the $TEMPO^-$ anion is larger than methyl or allyl, so coordination of a second TEMPO radical to **1** and **3** would be sterically more difficult than coordination of the first equiv of TEMPO. This could explain the fact that **1** and **3** do not react further with TEMPO even though the Me^- and $allyl^-$ ligands are capable of TEMPO reduction.

The TEMPO chemistry reported here shows that the TEMPO moiety can be a flexible ligand for coordinating thorium. It can coordinate as an η^1 ligand with steric bulk larger than Me^-, $allyl^-$, and Br^-, as shown by the structures of **1**, **3**, and **5**. However, TEMPO can also coordinate as an η^2 group that can effectively replace $(\eta^5\text{-}C_5Me_5)^-$, as shown in **7** and **9**. Given the inherent size of the $TEMPO^-$ anion and its ability to bind η^1 and η^2, steric influences can be important in determining reaction outcomes. Too few examples are presented here to make broad generalizations, but the utility of the flexibility of TEMPO should be examined further in the future.

CONCLUSION

The three previously described binding modes of TEMPO[15] with transition and alkali metals, namely, η^1-monoanionic, η^2-monoanionic, and η^1-radical coordination, have all been observed with thorium. The TEMPO radical can bind to thorium as a neutral radical, it can replace anionic ligands such as methyl, allyl, hydride, and bromide, and it can formally take the place of the polydentate ligand $(\eta^5\text{-}C_5Me_5)^-$. It is a versatile ligand for thorium that can be used to change the coordination environment and remove $(C_5Me_5)^-$ ligands. Despite the radical nature of these reactions, reproducible reactions are observed with high yields in most cases.

ASSOCIATED CONTENT

Supporting Information

X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles for compounds **1**−**9** (CIF, CCDC 995514−995522, respectively). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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