Synthesis of the First Tris(pentamethylcyclopentadienyl) Hydride Complex, (C$_5$Me$_5$)$_3$ThH

William J. Evans,* Gregory W. Nyce, and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, Irvine, California 92697-2025

Summary: To determine if tris(pentamethylcyclopentadienyl) chemistry could be extended to thorium, the reaction of a cationic organometallic thorium hydride with K(18-crown-6)(C$_5$Me$_5$) was examined and found to produce (C$_5$Me$_5$)$_3$ThH.

Introduction

Although for many years it was believed that it was impossible to assemble three large pentamethylcyclopentadienyl rings around even the largest metals in the periodic table, several examples of (C$_5$Me$_5$)$_3$M complexes have now been identified, including M = Sm,[1] Nd,[2] La,[3] and U.[4] In the uranium case, even more crowded molecules containing an extra ligand have been isolated: (C$_5$Me$_5$)$_3$UX in which X = F, Cl.[5] Formation of analogous thorium (C$_5$Me$_5$)$_3$M or (C$_5$Me$_5$)$_3$MX complexes is more difficult because the uranium syntheses involved U(III) precursors and Th(III) is much less accessible. In fact, only a few Th(III) organometallic compounds have been reported.[6] Consequently thorium has a limited reduction chemistry compared to uranium.

For this reason, sterically crowded (C$_5$Me$_5$)$_3$MZ complexes (Z = monoanionic ligand) of thorium are of interest, since it has been shown that sterically crowded (C$_5$Me$_5$)$_3$M complexes can function as one-electron reductants even if the metal is not redox active. For example, this sterically induced reduction (SIR) chemistry has been observed for both trivalent (C$_5$Me$_5$)$_3$Nd[7] and tetravalent (C$_5$Me$_5$)$_3$UCl,[5] which function as one-electron reductants to form products in the same Nd-(III) and U(IV) oxidation states as the starting materials, e.g., eq 1.


If the appropriately sterically crowded tris(pentamethylcyclopentadienyl) Th(IV) complexes could be synthesized, SIR could provide thorium reduction chemistry without the difficulties inherent in synthesizing Th(III) complexes. To develop SIR chemistry with Th-(IV) in this way, a synthetic route to a (C$_5$Me$_5$)$_3$ThZ complex was needed that did not require Th(III) precursors. This has now been achieved with Z = H to make the first example of a (C$_5$Me$_5$)$_3$MH complex.

Results and Discussion

The synthesis of (C$_5$Me$_5$)$_3$M complexes is difficult due to the steric crowding and the high reactivity of these compounds.[8] In general, all of the known syntheses of (C$_5$Me$_5$)$_3$M complexes appear to involve formation of one highly stable product that drives the reaction and leaves the components [(C$_5$Me$_5$)$_2$M]$^+$ and (C$_5$Me$_5$)$^-$, which then combine to form the desired (C$_5$Me$_5$)$_3$M complex. For example, the four syntheses of (C$_5$Me$_5$)$_3$Sm involve the formation of the stable byproducts (C$_5$Me$_5$)Sm(C$_8$H$_8$),[1] Pb,[9] (C$_5$Me$_5$)$^-$,[4] and KBPh$_4$,[2] eqs 2−5.
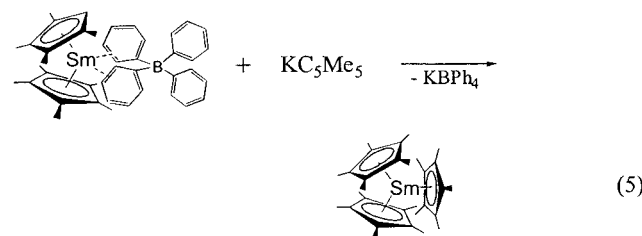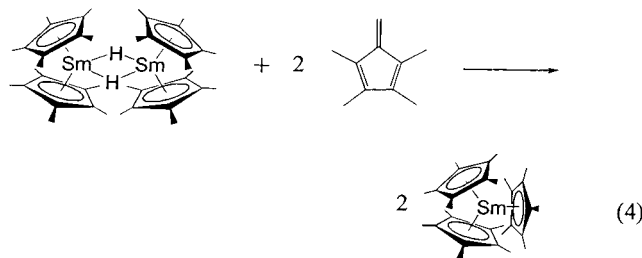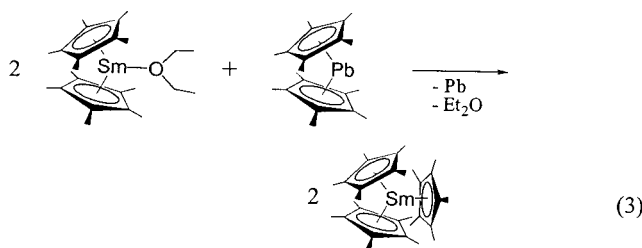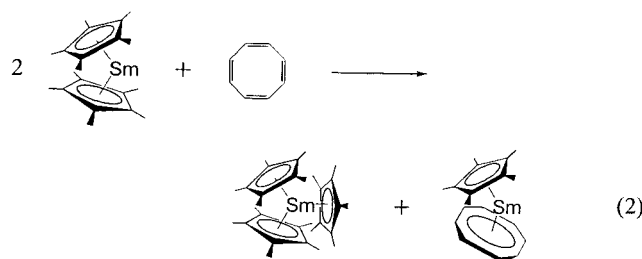
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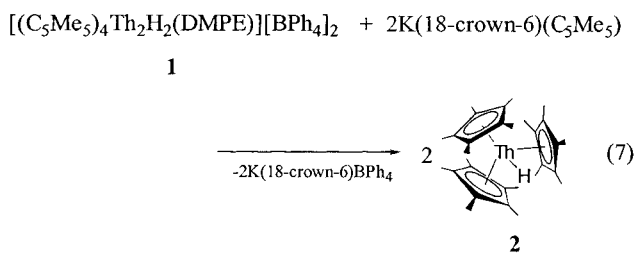
The synthesis of a $(C_5Me_5)_3ThZ$ complex was approached using a variation of eq 5 in which the reactions of $[(C_5Me_5)_2ThZ][BPh_4]$ complexes with KC_5Me_5 were examined. Initially, this reaction was attempted with $[(C_5Me_5)_2ThMe][BPh_4]$.[10] However, the desired product, $(C_5Me_5)_3ThMe$, was not readily isolated. Z = H was then chosen since it was conceivable that $[(C_5Me_5)_2-ThH_2]_2$[11] could undergo protonolysis with $[Et_3NH][BPh_4]$ to yield the requisite cationic precursor $[(C_5Me_5)_2ThH]-[BPh_4]$. Unfortunately, initial attempts to make $[(C_5-Me_5)_2ThH][BPh_4]$ and react it with KC_5Me_5 gave a mixture of products. However, when 1,2-bis(dimethylphosphinoethane) (DMPE) was added to stabilize the desired cationic hydride, success was acheived.

Protonolysis of $[(C_5Me_5)_2ThH_2]_2$ in the presence of DMPE gave a product, **1**, that has analytical data and reactivity consistent with $[(C_5Me_5)_4Th_2H_2(DMPE)]-[BPh_4]_2$,[12] eq 6, although its identity has not been

$$[(C_5Me_5)_4Th_2H_2(DMPE)][BPh_4]_2 \qquad (6)$$

1
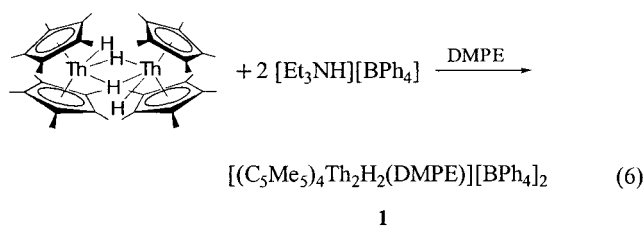
confirmed by X-ray crystallography. Since neither **1** nor KC_5Me_5 is appreciably soluble in benzene, the crown ether compound $K(18\text{-crown-}6)(C_5Me_5)$[13] was used to deliver KC_5Me_5 in soluble form. Over 12 h, a new product, **2**, was isolated as a pale yellow powder in 70% yield.

The ^1H NMR spectrum of **2** contains a $(C_5Me_5)^-$ resonance and a hydride resonance in a 45:1 ratio. The hydride resonance at 15.4 ppm is significantly shifted upfield relative to the 19.2 resonance observed in $[(C_5-Me_5)_2ThH_2]_2$. In addition, irradiation of the $(C_5Me_5)^-$ resonance led to an NOE signal enhancement of the hydride resonance. X-ray crystallography[14] confirmed that **2** was $(C_5Me_5)_3ThH$, eq 7.

$$[(C_5Me_5)_4Th_2H_2(DMPE)][BPh_4]_2 \;+\; 2K(18\text{-crown-}6)(C_5Me_5)$$

1

$$\xrightarrow{-2K(18\text{-crown-}6)BPh_4} \; 2 \quad \qquad (7)$$

2

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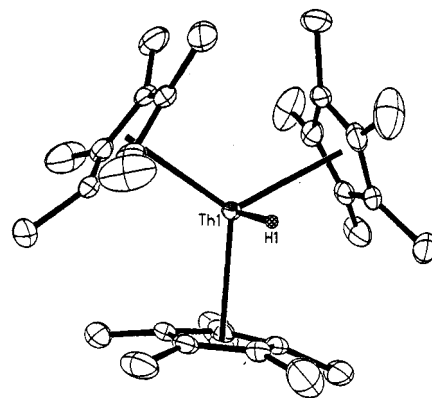

Figure 1. Plot of $(C_5Me_5)_3ThH$, **2**, with thermal ellipsoids drawn at the 50% probability level.

$(C_5Me_5)_3ThD$ was made analogously and showed a ^1H NMR spectrum like that of **2** except that the hydride resonance was not observed. Comparison of the infrared spectra of **2** with that of $(C_5Me_5)_3ThD$ indicated that the ν_{Th-H} stretch was at 1413 cm^{-1}.

Complex **2** crystallizes in the same $P6_3/m$ space group as $(C_5H_5)_3ZrH$[15] and $(C_5Me_5)_3UX$ (X = Cl, F)[5] and has the hydride ligand disordered on either side of the plane defined by thorium and the three $(C_5Me_5)^-$ ring centroids, Figure 1. The 2.87(4) Å $Th-C(C_5Me_5)$ average distance overlaps within the error limits with $M-C(C_5-Me_5)$ average distances in other $(C_5Me_5)_3M$ complexes (M = Sm 2.82(5),[1] Nd 2.86(6),[2] U 2.84(4)[4] Å) and in $(C_5-Me_5)_3UCl$,[5] 2.82(4) Å. The $Th-C$ distances range from 2.845(2) to 2.946(3) Å. The 2.33(13) Å $Th-H$ distance in **2** is similar to the only other $Th-H$ distances in the literature, but the error limits on these numbers preclude detailed comparisons: $(2,6\text{-}^tBu_2C_6H_3O)_6Th_3(\mu_3\text{-}H)_2$-$(\mu\text{-}H)_4$[16] (2.0(1)-2.6(1) Å) and $[(C_5Me_5)_2ThH(\mu\text{-}H)]_2$[11] [2.03(1) (terminal)$-$2.29(3) (bridging) Å].

Preliminary reactivity studies suggest that the chemistry of **2** is surprisingly limited. Solutions of **2** in C_6D_6 show no sign of decomposition after 2 months at room temperature. Unlike $(C_5Me_5)_3M$ complexes of Sm and U, **2** does not reduce 1,3,5,7-cyclooctatetraene or Ph$-$X (X = I, Br, Cl). In contrast to $[(C_5Me_5)_2ThH_2]_2$[17] and $(C_5-Me_5)_3M$ compounds (M = Sm,[18] U,[4] Nd[19]), which readily

(12) The bimetallic DMPE-bridged formulation is suggested because it matches the analytical data best. Comparison with $(C_5Me_5)_2UH$-(DMPE) (Duttera, M. R.; Fagan, P. J.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 865) would suggest a reasonable monometallic alternative. Crystallographic connectivity data obtained on a poorly diffracting crystal of $[(C_5Me_5)_2UCl]_2$(DMPE) indicate that a bridged structure is also possible.
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(14) X-ray quality crystals were grown by slowly cooling a hot toluene solution of **2**. A colorless crystal of approximate dimensions $0.26 \times 0.26 \times 0.30$ mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. Crystal data for **2** at 163(2) K: $C_{30}H_{46}Th$, hexagonal, space group $P6_3/m$, $a = 10.0378(2)$ Å, $c = 15.4285(5)$ Å, $V = 1346.27(6)$ Å^3, $Z = 2$. The molecule was located on a site of 6 symmetry. The hydride atom was disordered and was included with a partial site-occupancy-factor (1/6) to account for an equal distribution over two sites. At convergence, wR2 = 0.0321 and GOF = 1.174 for 54 parameters refined against 801 unique reflections (0.85 Å resolution). As a comparison for refinement against F, R1 = 0.0140 for those data, 774 data with $I > 2.0\sigma(I)$.
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polymerize ethylene, the reaction of **2** under 1 atm of ethylene affords no measurable amount of polymer. These results suggest that adding a fourth ligand to $(C_5Me_5)_3M$ complexes can significantly limit reactivity and may have important implications on the mechanism of sterically induced reduction chemistry.

Experimental Section

General Procedure. All manipulations were performed under a nitrogen or argon atmosphere by glovebox or Schlenk techniques. DMPE was dried over sieves and degassed before use. Benzene and benzene-d_6 were degassed, dried over potassium, and distilled before use. NMR spectra were recorded at 25 °C on a Bruker DRX-400 spectrometer. IR spectra were recorded on an ASI ReactIR 1000. Elemental analyses were performed by Analystische Laboratorien, Lindlar, Germany.

Preparation of $[(C_5Me_5)_4Th_2H_2(DMPE)][BPh_4]_2$, 1. In a THF-free glovebox, $[(C_5Me_5)_2ThH_2]_2$[17] (122 mg, 0.12 mmol) was added to a stirred benzene suspension of $[Et_3NH][BPh_4]$ (101 mg, 0.24 mmol) and DMPE (36 mg, 0.24 mmol). Immediate gas evolution was observed. After the reaction mixture was stirred for 8 h, the solvent was removed by rotary evaporation. The white product was washed with 2 mL of benzene and dried in vacuo to yield **1** as a white powder (192 mg, 89%). IR (cm^{-1}, thin film): 3057m, 3038m, 2961s, 2926s, 2856s, 1583m, 1478m, 1444m, 1428m, 1378w, 1262sh, 1050s, 915m, 892m, 803s, 702s. Anal. Calcd for $Th_2C_{94}H_{118}B_2P_2$: C 62.88, H 6.75. Found: C 62.88, H 6.62.

Preparation of $(C_5Me_5)_3ThH$, 2. In a THF-free glovebox, a benzene solution of $K(C_5Me_5)[18$-crown-6][13] (49 mg, 0.11 mmol) was added to a stirred benzene suspension of **1** (100 mg, 0.012 mmol). The reaction mixture was allowed to stir for 12 h. A white precipitate was removed by centrifugation, and the solvent was removed by rotary evaporation, yielding **2** as a pale yellow powder (50 mg, 70%). IR (cm^{-1}, thin film): 2961s, 2910s, 2856s, 1444m, 1413m (Th$-$H), 1370m, 1258sh, 1096vs, 1015vs, 799vs, 706s, 683s. Anal. Calcd for $ThC_{30}H_{46}$: C 56.32, H 7.41, Th, 36.27. Found: C 56.19, H 7.14, Th, 36.60. ^{1}H NMR (400 MHz, C_6D_6): δ 2.16 (s, C_5Me_5, 45 H), 15.4 (s, 1 H). ^{13}C NMR (100 MHz, C_6D_6): δ 13.2 (C_5Me_5), 124.4 (C_5Me_5).

Supporting Information Available: Tables of crystallographic data for **2** are available free of charge via the Internet at http://pubs.acs.org.

OM010596E

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