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Unique Molecular Structure of the Actinide Hydrido Aryloxide Complex $Th_3(\mu_3\text{-}H)_2(\mu_2\text{-}H)_4(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_6$

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Investigations into the synthesis, reactivity, and structural characterization of metal hydride complexes have led to the development of a major area of organometallic research,[2] due primarily to the numerous catalytic and stoichiometric reactions in which these species are often involved.[3] As recently noted by Chisholm *et al.*,[4] the overwhelming majority of transition metal hydride complexes are supported by soft π-acceptor ligands such as carbon monoxide or phosphine, or π-bound carbocyclic ligands such as cyclopentadienyl, and the number of hydride complexes supported exclusively by π-donating alkoxide or aryloxide ligands is very small, with most of the known examples being based upon Mo, W, or Re metal centers.[4] Early transition metal alkoxide/hydride complexes are limited to the Group 5 species $Ta(OSi\text{-}t\text{-}Bu_3)_3H_2$,[5a] $[M(OSi\text{-}t\text{-}Bu_3)_2H_2]_2$ (M = Nb,[5b] Ta[5a]), $Nb(O\text{-}2,6\text{-}(C_6H_{11})_2C_6H_3)_4H$,[5c] and $Ta(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_3H_2L$ (L = phosphine ligand)[5d] and the titanium derivatives $Ti_4(OEt)_{13}(H)$[6] and $Ti_3(OPh)_6(H)$,[7] which have been proposed only on the basis of reactivity data. During our ongoing investigations into the alkoxide and aryloxide chemistry of the early actinide elements,[8] we have isolated and structurally characterized a thorium polyhydride complex supported solely by aryloxide ligands which possesses a highly unusual molecular geometry. We report here initial details of the synthesis, characterization, and solid-state molecular structure of $Th_3H_6(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_6$.

A THF solution of $ThBr_4(THF)_4$[9] reacts smoothly with 2 equiv of KOAr (Ar = 2,6-*t*-$Bu_2C_6H_3$) to produce $ThBr_2(OAr)_2(THF)_2$ (**1**) as colorless crystals in 67% yield (eq 1). Subsequent alkylation of **1** with 2 equiv of Me_3SiCH_2MgCl allows the

$$ThBr_4(THF)_4 + 2KOAr \xrightarrow[18\ h]{THF} \underset{\mathbf{1}}{ThBr_2(OAr)_2(THF)_2} + 2KBr$$
$$Ar = 2,6\text{-}t\text{-}Bu_2C_6H_3 \qquad (1)$$

isolation of $Th(OAr)_2(CH_2SiMe_3)_2$ (**2**) as colorless crystals in 61% yield after crystallization from toluene (eq 2).[10]

$$\mathbf{1} + 2Me_3SiCH_2MgCl \xrightarrow[dioxane,\ 3\ h]{toluene} \underset{\mathbf{2}}{Th(OAr)_2(CH_2SiMe_3)_2} \qquad (2)$$

A benzene solution of **2** reacts with dihydrogen (1.5 atm) at room temperature over a period of 7 days to produce the dihydride $[ThH_2(OAr)_2]_3$ (**3**) in 33% yield after crystallization (eq 3).[11] Liberation of $SiMe_4$ during the reaction is confirmed

$$2 \xrightarrow[benzene,\ 7\ d]{H_2} {}^{1}/_{3}\underset{\mathbf{3}}{[ThH_2(OAr)_2]_3} + 2SiMe_4 \qquad (3)$$

by ^1H NMR spectroscopy. Formulation of **3** as a trimeric species was suggested by a solution molecular weight determination in benzene solution (isopiestic method, calcd for $[ThH_2(OAr)_2]_3$ 1934, found 2061). Complex **3** shows a singlet resonance in its ^1H NMR spectrum at 20.54 ppm indicative of a thorium hydride species,[12] and this resonance shows only slight broadening upon cooling a toluene-d_8 solution to −90 °C. The IR spectrum of **3** (Nujol mull, KBr plates) displays ν(Th−H) stretches at 1336, 975, and 795 cm^{-1} which are shifted to 954, 705, and 560 cm^{-1}, respectively, upon deuteration (the deuterated sample of **3** was prepared by using deuterium in place of hydrogen in eq 3). In the thorium hydrido complexes $\{[Me_2Si(\eta\text{-}C_5Me_4)_2]Th(\mu_2\text{-}H)_2\}_2$ and $[(\eta\text{-}C_5Me_5)_2Th(\mu_2\text{-}H)(H)]_2$, the bridging thorium hydrides show ν(Th−H) stretches in the region 1285−481 cm^{-1}, while terminal Th−H stretching frequencies were observed at 1404 and 1370 cm^{-1}.[12]

In order to further elucidate the molecular structure of **3**, a single-crystal X-ray diffraction study was undertaken, and an ORTEP plot of the solid-state structure of $Th_3(\mu_3\text{-}H)_2(\mu_2\text{-}H)_4(OAr)_6$ (**3**) is shown in Figure 1.[13] All hydride ligands were located and refined during the structure determination. The overall molecular structure of **3** comprises a triangular arrangement of three thorium metal centers, in which each face of the

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[10] Preparative details for **1** and **2** are presented in the supporting information.

[11] $[ThH_2(OAr)_2]_3$ (**3**): Benzene (10 mL) was added to a 50 mL Kontes flask containing **2** (0.325 g, 0.40 mmol), and a hydrogen atmosphere (1.5 atm) was placed over the solution. The mixture was stirred for 3 days, and then all volatiles were removed *in vacuo*. ^1H NMR spectra of the crude reaction mixture showed the presence of unreacted **2** and two products. Benzene (8 mL) and hydrogen (1.5 atm) were again added to the flask, and the solution was stirred an additional 4 days. All volatiles were removed *in vacuo*, and upon addition of 1 mL of hexane, crystals were deposited. Yield: 0.085 g (33%). ^1H NMR (300 MHz, benzene-d_6): δ 20.54 (s, 2 H, ThH), 7.21 (d, $^3J_{HH}$ = 8 Hz, 4 H, *m*-OAr), 6.79 (t, $^3J_{HH}$ = 8 Hz, 2 H, *p*-OAr), 1.59 (s, 36 H, *t*-Bu). Anal. Calcd for $C_{28}H_{44}O_2Th$: C, 52.17; H, 6.88. Found: C, 52.27; H, 6.75.

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[13] Full details of the structure analysis for **3** may be found in the supporting information. Data were collected on a Siemens P4/PC diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 69 Å). Crystal data for **3** (at −100 °C): monoclinic space group $P2_1/c$, a = 13.571(1) Å, b = 26.610(3) Å, c = 27.510(2) Å, β = 96.716(7)°, V = 9866(2) Å^3, d_{calc} = 1.418 g cm^{-3}, Z = 4. The structure was solved by direct methods and full-matrix least-squares refinement. All non-hydrogen atoms were refined anisotropically, except for two severely disordered hexane solvent molecules in the lattice. Weighting of the low-angle data was used to locate the hydrogen atoms associated with the thorium core, and these hydrogens were refined with isotropic temperature factors fixed at 0.08 Å^2. The final refinement converged to $R1$ = 0.0460 and $R2_w$ = 0.0812.

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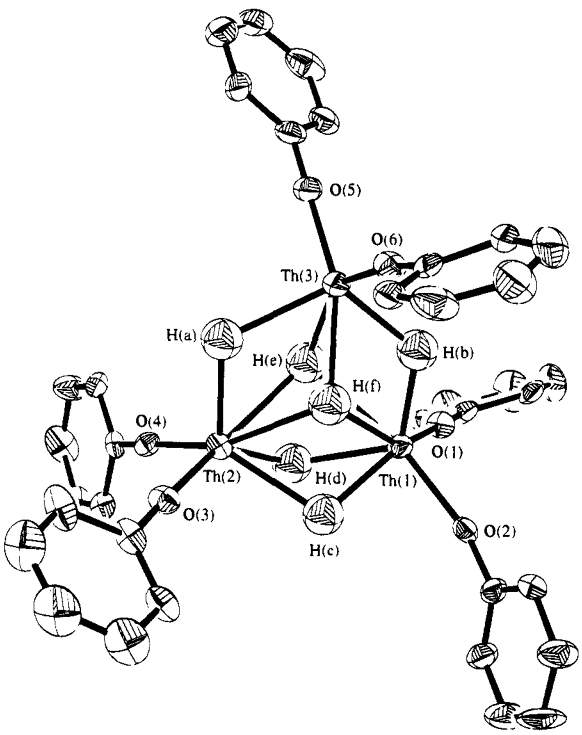

Figure 1. ORTEP representation of the molecular structure of $Th_3(\mu_3\text{-}H)_2(\mu_2\text{-}H)_4(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_6$ (**3**) with *tert*-butyl groups omitted for clarity (thermal ellipsoids at 40% probability). Selected bond distances (Å) and bond angles (deg): Th(1)−Th(2) 3.588(1), Th(1)−Th(3) 3.781(1), Th(2)−Th(3) 3.818(1), Th(1)−O(1) 2.159(7), Th(1)−O(2) 2.143(7), Th(2)−O(3) 2.164(7), Th(2)−O(4) 2.126(7), Th(3)−O(6) 2.127(7), Th(3)−O(5) 2.139(7), Th(1)−H(b) 2.0(1), Th(1)−H(c) 2.2(1), Th(1)−H(d) 2.2(1), Th(1)−H(e) 2.4(1), Th(1)−H(f) 2.6(1), Th(2)−H(a) 2.2(1), Th(2)−H(c) 2.3(1), Th(2)−H(d) 2.3(1), Th(2)−H(e) 2.5(1), Th(2)−H(f) 2.4(1), Th(3)−H(a) 2.3(1), Th(3)−H(b) 2.2(1), Th(3)−H(e) 2.3(1), Th(3)−H(f) 2.3(1), O(2)−Th(1)−O(1) 104.4(2), O(4)−Th(2)−O(3) 107.4(2), O(6)−Th(3)−O(5) 113.5(2), Th(2)−Th(1)−Th(3) 62.34(1), Th(1)−Th(2)−Th(3) 61.30(1), Th(1)−Th(3)−Th(2) 56.36(1).

trimer is capped by a μ_3-H ligand, and each thorium bears two terminal aryloxide ligands. Four μ_2-H ligands bridging the thorium atoms complete the coordination sphere. Two sides of the trimetallic core (which exhibit nonbonding Th−Th distances of 3.781(1) and 3.818(1) Å) are each bridged by a μ_2-H ligand, while the third side is bridged by two μ_2-H ligands and displays an extremely short nonbonding Th−Th distance of 3.588(1) Å (*cf.* Th−Th distance in thorium metal, 3.59 Å).[14] To the best of our knowledge, this is the shortest Th−Th interaction yet seen in a discrete molecular complex, and is significantly shorter than the Th−Th distance of 3.632(2) Å found in the related quadruply-bridged system $\{[Me_2Si(\eta\text{-}C_5Me_4)_2]Th(\mu_2\text{-}H)_2\}_2$.[12b] These short Th−Th distances are attributable primarily to the four bridging hydride interactions which pull the metal centers close together and not to substantial Th−Th bonding interaction.[12b] The relatively large errors associated with the Th−H distances do not allow any meaningful comparisons to be drawn between specific bond lengths within the core, but the range of Th−(μ_2-H) distances (2.0(1)−2.3(1) Å) is entirely consistent with the Th−(μ_2-H) distances of 2.29(3) Å found following a neutron diffraction study of $[(\eta\text{-}C_5Me_5)_2Th(\mu_2\text{-}H)(H)]_2$.[15] Th−($\mu_3$-H) distances of 2.3(1)−2.6(1) Å are slightly longer than the Th−(μ_2-H) bond distances, while Th−O distances of 2.126(7)−2.164(7) Å are directly comparable with those observed in other thorium aryloxide complexes, such as $Th(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_4$ (2.189(6) Å)[8b] and $Th(O\text{-}2,6\text{-}Me_2C_6H_3)_4py_2$ (2.198(6) Å (av)).[8b] Th−O−C angles are almost linear, ranging from 166.6(6) to 179.1(7)°, and are typical of those seen in other transition metal complexes bearing bulky aryloxide ligands.[16]

The molecular geometry of **3** is highly unusual and is worthy of special note. The central $M_3(\mu_3\text{-}H)_2(\mu_2\text{-}H)_4$ core appears to be structurally unprecedented among metal hydride complexes, and we are aware of only three structurally characterized complexes among the later transition metals which feature triply-bridging hydride ligands capping both faces of a trimetallic core.[17] The overall M_3X_{12} moiety may be considered as a derivative of the well-known M_3X_{11} structural type[18] formed by the addition of a single μ_2 ligand along one edge. The resulting $M_3(\mu_3\text{-}X)_2(\mu_2\text{-}X)_4X_6$ geometry appears to be a new structural type of triangular cluster. Preliminary reactivity studies of **3** have revealed modest activity in the catalytic hydrogenation of 1-hexene (1 atm of H_2, 3 turnovers h^{-1}) and slow H−D exchange of the hydride ligands (half-life, ~36 h) when **3** is placed under 1 atm of D_2. Further studies of the reactivity of **3** are in progress.

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Supporting Information Available: Tables of crystal structure determination data, fractional atomic coordinates, bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and full experimental procedures for **1**, **2**, and **3** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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