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Communications

Synthesis and Characterization of Thorium *ansa*-Cyclopentadienyl−Amido Complexes

Jeffery T. Golden, Denis N. Kazul'kin, Brian L. Scott,
Alexander Z. Voskoboynikov, and Carol J. Burns*

Los Alamos National Laboratory, Chemical Division MS J515, Los Alamos, New Mexico 87545

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*Summary: Two new thorium complexes, a tetramer (**1**) of $C_5Me_4Si(Me)_2NPhThCl_2$, and a dimer (**2**) of $Li(Et_2O)_2[C_5Me_4Si(Me)_2N$-t-$BuThCl_3]$, have been synthesized and characterized. In both cases, structural studies reveal the thorium centers may be viewed as having pseudo-octahedral geometry, formally with two dative and two covalent chloride interactions.*

ansa-Cyclopentadienyl−amido complexes are known for the d-transition series and lanthanide metals.[1−3] These molecules, typically known as constrained-geometry catalysts (CGCs), have garnered attention as olefin polymerization catalysts, due to the high activities they display[4−6] and the properties of the polymers they produce.[7,8] In addition, CGCs, especially lanthanide CGCs, find use in polymerization and other catalytic processes.[9−12] Since olefin polymerization catalysts are not typically recovered from industrial processes, actinide metals have little practical application as olefin polymerization catalysts. Nevertheless, constrained-geometry ligands of the general type $CpSi(R)_2NHR'$ can be viewed as electronic analogues for bis(cyclopentadienyl) or *ansa*-cyclopentadienyl ligands, with important changes in the steric environment imposed at the metal by the ligand.[13−15] As such, they may be employed as alternate ligand scaffolds for the actinide metals. Electron-rich ligands are thought to be necessary in order to stabilize U(VI) bis(imido) complexes, although the size of alkylated cyclopentadienyl ligands may contribute to the relative lack of reactivity of these complexes.[16] It is possible that constrained-geometry ligands may be able to stabilize U(VI) bis(imido) functionalities while enhancing their reactivity through a reduction in steric bulk.

Two main strategies have been employed for introducing an *ansa*-cyclopentadienyl-silylamino ligand onto metal complexes.[17] The first method is the double

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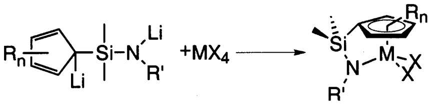
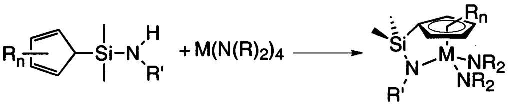
deprotonation of the constrained geometry ligand[18] followed by salt metathesis (eq 1). Alternatively, the ligand may be deprotonated directly by the metal complex with concomitant elimination of small molecules to incorporate the constrained-geometry ligand into the complex (eq 2). Initial work aimed at making uranium *ansa*-cyclopentadienyl—amido complexes using either method was unsuccessful. For this reason, thorium was chosen to gain an understanding of how to synthesize actinide *ansa*-cyclopentadienyl—amido complexes. These molecules are interesting to study in their own right as analogues of the group IV CGCs.



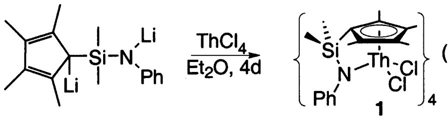
(1)



(2)

In the synthesis of zirconium constrained-geometry complexes, tetrakis(amido)zirconium starting materials give better yields of the corresponding constrained-geometry complexes. However, for our first attempts at making thorium constrained-geometry complexes the first method[18] was chosen, as the metal halide starting materials are more readily available. This methodology resulted in satisfactory isolation of the target compounds.

Synthesis of $C_5Me_4Si(Me)_2NPhThCl_2$ was accomplished by addition of the doubly deprotonated ligand salt to $ThCl_4$ in ether with stirring for 4 days (eq 3).



(3)

After the reaction was begun, a very slight yellowing of the solution was noted, as $ThCl_4$ was slowly taken up into solution and fine powdery lithium salts precipitated from solution. It is difficult to determine, visually, when the reaction is finished, since the starting materials and products are all colorless. However, reaction times of less than 4 days lead to decreased yields. Filtration of the solution through Celite and removal of solvent under reduced pressure afford the complex in 86% crude yield. The crude material is not pure and presumably contains a small amount of the lithium chloride adduct of $C_5Me_4Si(Me)_2NPhThCl_2$ (vide infra). Despite this problem, X-ray-quality crystals were formed by slow evaporation of solvent from an ether/hexane solution of the reaction product. Crystallographic characterization reveals that the complex crystallizes as a tetramer (**1**) with bridging chlorides (Figure 1). One equivalent of hexane cocrystallizes with tetramer **1**. The idealized symmetry of the tetramer is D_2, crystallizing in a tetrahedral space group. A single chloride is bridged between Th(1) and Th(1A) and another between Th(2) and Th(2A), while three chloride bridges between Th(1) and Th(2) and also between Th(1A) and (Th2A) were found. NMR experiments in C_6D_6 reveal that the tetrameric structure is retained in solution as separate peaks for each methyl group on the silyl and cyclopentadienyl moiety (six peaks) in the complex are observed.

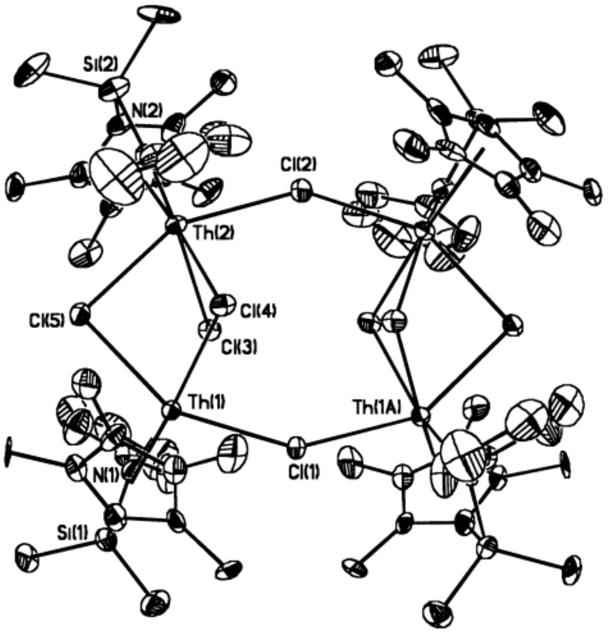
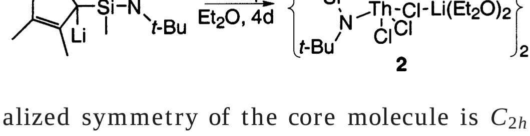


Figure 1. Tetrameric structure of $C_5Me_4Si(Me)_2NPhThCl_2$ (**1**).

While suitable crystals of **1** may be grown by slow evaporation of an ether/hexane solution, in practice, it is more convenient to crystallize **1** from toluene at −35 °C. One equivalent of toluene cocrystallizes with each tetrameric unit ($\mathbf{1}\cdot C_7H_8$). The toluene adduct to the tetramer of **1** does not appear to interfere with any subsequent procedures or characterization.[19]

In an analogous reaction aimed at forming $C_5Me_4Si(Me)_2N$-*t*-$BuThCl_2$, less lithium halide salt was observed from the reaction mixture (by mass) than expected. X-ray-quality crystals of **2** were grown from a concentrated solution of ether at −35 °C. As shown in Figure 2, crystallographic characterization confirmed that while the reaction succeeded at forming a thorium *ansa*-cyclopentadienyl—amido complex, a dimer—$Li_2(Et_2O)_4[C_5Me_4Si(Me)_2N$-*t*-$BuThCl_3]_2$ (**2**) (eq 4)—was formed. The idealized symmetry of the core molecule is C_{2h}. Even though the reaction conditions were the same, the methodology did not produce the salt-free complex as it did in the case of the phenyl analogue. Prolonged exposure of **2** to dynamic vacuum liberates 2 equiv of diethyl ether from the complex to form $Li_2(Et_2O)_2[C_5Me_4Si(Me)_2N$-*t*-$BuThCl_3]_2$ (**2**-2Et$_2$O).[20]



(4)

Despite the differences in the solid-state structure and the chemical disposition of the halide donors, there are structural similarities between the complexes. The solid-state structures indicate that coordination numbers of

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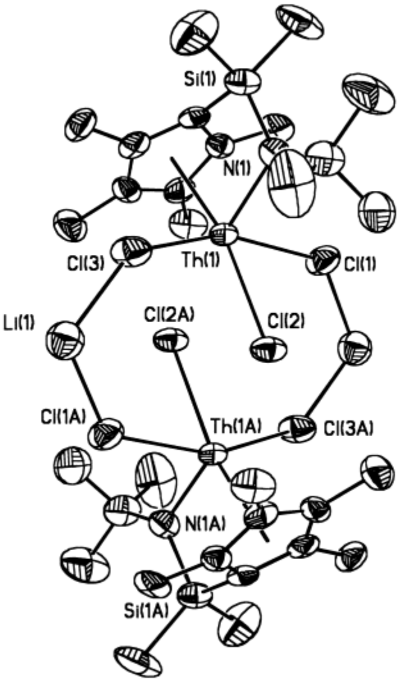

Figure 2. Dimer of ($C_5Me_4Si(Me)_2N$-*t*-Bu)$ThCl_2$·LiCl (**2**). Diethyl ether is omitted for clarity (four coordinated ether molecules).

8 are preferred in both **1** and **2**. The coordination environment of each metal may be regarded as a pseudo-octahedron. The cyclopentadienyl moiety takes an apical position, and the amido functionality resides at a position cis to the cyclopentadienyl moiety in the octahedron. The remaining sites of the octahedron are chlorides. The thorium−Cp-centroid distances are 2.46 and 2.47 Å in the tetramer **1**, while the distance is 2.50 Å in the dimer **2**. The thorium−nitrogen distances are 2.268(9) and 2.238(9) Å for the tetramer **1** and 2.312(6) and 2.320(7) Å in the dimer **2**. In both complexes, each thorium is ligated by four chlorides. Two chlorides lie approximately in the plane formed by the Cp centroid, the thorium center, and the amido functionality, and two chlorides are disposed nearly symmetrically on either side of that plane. In **1** the thorium−chloride distances range between 2.805(3) and 2.874(3) Å, with an average length of 2.839 Å and a median length of 2.840 Å. For dimer **2** the thorium−chloride distances have a maximum length of 2.933(2) Å and a minimum length of 2.756(2) Å. The average thorium−chloride bond length is 2.833 Å, and the median bond length is 2.821 Å. No complexes with a similar chloride binding motif for closely related constrained-geometry complexes were found during a structural database search.[21]

The knowledge gained from this study will help facilitate the synthesis of uranium compounds analogous to **1** or **2**. Extending the idea that lithium can interfere with the synthesis of these thorium constrained-geometry complexes, it is likely that using the dilithiated *ansa*-cyclopentadienyl−amido starting material may have had a detrimental effect upon the attempted synthesis of the analogous uranium complexes. Lithium salts of these ligands may, therefore, be poor starting materials for the synthesis of the uranium analogues.

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Supporting Information Available: Text giving synthetic and spectroscopic data and tables giving X-ray structural data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Crystal data for **1**: $C_{74}H_{106}Cl_8N_4Si_4Th_4$, mol wt 2375.75, tetragonal, $P4_12_12$, $a = 16.521(3)$ Å, $b = 16.521(3)$ Å, $c = 31.814(9)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 8683(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.817$ Mg/m^3, $\lambda = 0.710\,73$ Å, $T = 203(2)$ K, 56 640 measured reflections, 7954 unique, $\mu = 7.171$ mm^{-1}, maximum/minimum transmission 0.2673/0.2007, R1($I > 2\sigma$) = 0.0695, wR2 = 0.0942, GOF (F^2) = 1.592, 425 parameters, final difference map within 2.153 and −1.423 e Å^{-3}. Selected data for **1**·C_7H_8: yield 13.5% (54% by ligand); ^{1}H NMR (C_6D_6, 300 MHz, 21 °C) δ 7.28 (t, $J = 7.8$ Hz, 8H, meta N−Ph), 7.12 (d, $J = 7.2$ Hz, 2H, ortho C_7H_8), 7.04 (t, $J = 6.9$ Hz, 1H, para C_7H_8), 6.99 (d, $J = 7.3$ Hz, 8H, ortho N−Ph), 6.91 (t, $J = 7.1$ Hz, 4H, para N−Ph), 2.11 (s, 3H, methyl C_7H_8), 2.05 (s, 12H, $H_3CC_5(Me)_3$), 1.92 (s, 12H, $H_3CC_5(Me)_3$), 1.88 (s, 12H, $H_3CC_5(Me)_3$), 1.62 (s, 12H, $H_3CC_5(Me)_3$), 0.49 (s, 12H, H_3CSi), 0.37 (s, 12H, H_3CSi); IR (mineral oil mull, KBr plates, cm^{-1}) 1587 (s), 1326 (w), 1294 (m), 1244 (s, br), 1168 (m), 1102 (s), 1068 (m), 1026 (m), 997 (w), 892 (s, br), 835 (s, br), 780 (s, br), 727 (m), 697 (s, sh), 608 (w, sh); mp >250 °C. Anal. Calcd for $C_{75}H_{100}Si_4N_4Th_4Cl_8$: C, 37.82; H, 4.23; N, 2.35. Found: C, 37.70; H, 4.38; N, 2.28.

(20) Crystal data for **2**: $C_{46}H_{94}Cl_6Li_2N_2O_4Si_2Th_2$, mol wt 1486.07, triclinic, $P\bar{1}$, $a = 11.261(3)$ Å, $b = 13.431(3)$ Å, $c = 22.979(5)$ Å, $\alpha = 84.364(4)°$, $\beta = 76.713(4)°$, $\gamma = 74.913(4)°$, $V = 3263.1(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.512$ Mg/m^3, $\lambda = 0.710\,73$ Å, $T = 203(2)$ K, 21 281 measured reflections, 10 985 unique reflections, $\mu = 4.870$ mm^{-1}, maximum/minimum transmission 0.8290/0.5926, R1($I > 2\sigma$) = 0.0486, wR2 = 0.1116, GOF = 1.315, 467 parameters, final difference map within 2.142 and −1.080 e Å^{-3}. Selected data for **2**-2OEt$_2$: yield 43% (by ligand); ^{1}H NMR (C_6D_6, 300 MHz, 21 °C) δ 3.27 (q, $J = 7.4$ Hz, 4H, $O(CH_2CH_3)_2$), 2.53 (s, br, 6H, $C_5(CH_3)_2(CH_3)_2$), 2.30 (s, 6H, $C_5(CH_3)_2$-$(CH_3)_2$), 1.48 (s, 9H, $NC(CH_3)_3$), 1.07 (t, $J = 7.5$ Hz, 6H, $O(CH_2CH_3)_2$), 0.63 (s, 6H, $Si(CH_3)_2$); IR (mineral oil mull, KBr plates, cm^{-1}) 1595 (w), 1405 (s, sh), 1293 (s), 1259 (w, br), 1044 (w, br), 910 (w), 853 (s, br); mp >250 °C. Anal. Calcd for $C_{19}H_{37}SiNThCl_3LiO$: C, 34.12; H, 5.58; N, 2.09. Found: C, 33.38; H, 5.03; N, 2.06.

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