

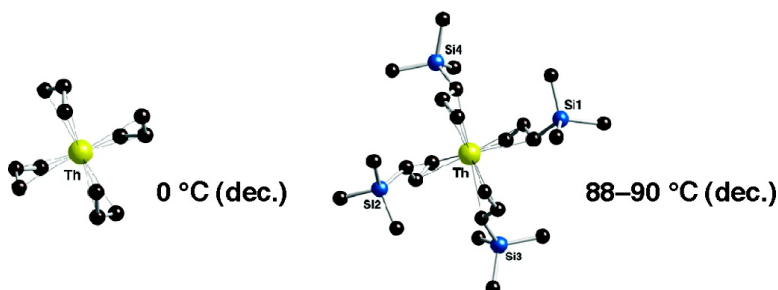
Communication

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Christin N. Carlson, Timothy P. Hanusa, and William W. Brennessel

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Metal Allyl Complexes with Bulky Ligands: Stabilization of Homoleptic Thorium Compounds, $[(\text{SiMe}_3)_n\text{C}_3\text{H}_{5-n}]_4\text{Th}$ ($n = 1, 2$)

Christin N. Carlson,[†] Timothy P. Hanusa,^{*,†} and William W. Brennessel[‡]

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and X-ray Crystallography Facility, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received April 18, 2004; E-mail: t.hanusa@vanderbilt.edu

Although the allyl moiety is widely encountered in synthetic reagents and catalysts,¹ many homoleptic allyl complexes $[\text{C}_3\text{H}_5]_n\text{M}$ are coordinatively unsaturated and highly thermolabile. Allyl ligands with bulky substituents have been used to prepare thermally stable, electron-deficient homoleptic complexes that have no monomeric counterparts with unsubstituted ligands, e.g., $[\pi\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]_2\text{M}$ ($\text{M} = \text{Cr}, 12\text{-e}^-; \text{Fe}, 14\text{-e}^-$).^{2,3} Systematic study of the way that variably substituted ligands affect the properties of known, but marginally stable, complexes could considerably broaden the range of accessible allyl species. Toward this end, we report the synthesis of the first homoleptic actinide allyl complexes that are stable at and above room temperature. These compounds demonstrate the modifications that bulky ligand substituents can make to the structure and solution behavior of the parent allyl species.

Tetra(allyl)thorium was first described by Wilke almost 40 years ago.⁴ Supported on dehydroxylated alumina,⁵ it has been studied as a heterogeneous catalyst for arene hydrogenation⁶ and for the exchange of alkane and cycloalkane C–H bonds with D_2 .⁷ Manipulations of the yellow compound are best conducted below -20°C , as $(\text{C}_3\text{H}_5)_4\text{Th}$ will decompose at 0°C .⁸ In view of its thermal fragility, the properties of its counterparts containing trimethylsilylated ligands are striking. Specifically, the reaction of 4 equiv of $\text{K}[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]$ ⁹ or $\text{K}[1\text{-(SiMe}_3)\text{C}_3\text{H}_4]$ ³ with $\text{ThBr}_4\text{(thf)}_4$ ¹⁰ in THF at -78°C produces the complexes $[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]_4\text{Th}$ (**1**) and $[1\text{-(SiMe}_3)\text{C}_3\text{H}_4]_4\text{Th}$ (**2**), respectively, in high yield (see Supporting Information for details). They are soluble in both aromatic and aliphatic hydrocarbons and do not coordinate THF (¹H NMR spectroscopy). Bright yellow **1** is indefinitely stable at room temperature in the solid state and in solution under an inert atmosphere. It melts at $122\text{--}124^\circ\text{C}$ (dec) and tolerates brief (<5 min) exposure to air without noticeable decomposition. Pale yellow **2** melts with decomposition at $88\text{--}90^\circ\text{C}$; the solid can survive only fleeting (<1 min) contact with air before decomposing. After several weeks under nitrogen at room temperature, solid **2** shows signs of decomposition.

The solid-state structure of **1** was obtained for a crystal grown at -35°C from hexanes solution.¹¹ The complex crystallizes as a monomeric species with the thorium coordinated by four η^3 -allyl ligands in a distorted tetrahedral arrangement (Figure 1); the SiMe_3 groups of all four ligands are in *syn,syn* configurations. The Th–C distances range from $2.617(5)$ to $2.892(5)$ Å, a spread (0.275 Å) similar to that of the Th–C contacts in the slipped indenyl complex $(\eta^3\text{-Ind})_4\text{Th}$ ($2.66(3)\text{--}2.97(4)$ Å; $\Delta = 0.31$ Å).¹² The C_3 planes of the ligands in **1** are tipped away from the metal, and the fold angles¹³ vary from 122.4 to 127.0° (cf. the $120.7\text{--}122.7^\circ$ angles found in the uranium allyl complex $(\text{C}_5\text{Me}_5)\text{U}(2\text{-MeC}_3\text{H}_4)_3$).¹⁴

The solid-state structure of **2** was obtained for a yellow block grown at room temperature from hexanes.¹⁵ It crystallizes as a

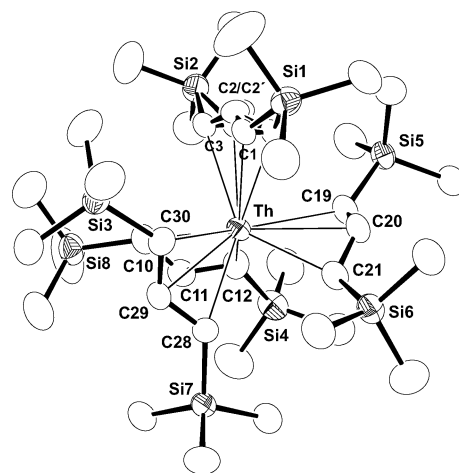


Figure 1. ORTEP of the non-hydrogen atoms of $[1,3\text{-(SiMe}_3)_2\text{C}_3\text{H}_3]_4\text{Th}$. Carbons C1–C3 are disordered over two positions (68:32). Selected bond distances [Å]: Th–C1(C1'), $2.727(7)$ ($2.764(14)$); Th–C2(C2'), $2.817(8)$ ($2.836(14)$); Th–C3(C3'), $2.729(6)$ ($2.750(14)$); Th–C10, $2.892(5)$; Th–C11, $2.856(5)$; Th–C12, $2.617(5)$; Th–C19, $2.869(5)$; Th–C20, $2.865(5)$; Th–C21, $2.660(5)$; Th–C28, $2.731(4)$; Th–C29, $2.815(4)$; Th–C30, $2.707(5)$.

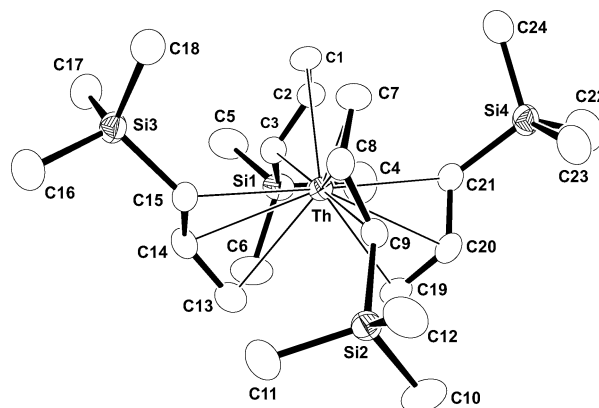


Figure 2. ORTEP of the non-hydrogen atoms of $[1\text{-(SiMe}_3)\text{C}_3\text{H}_4]_4\text{Th}$. Selected bond distances [Å]: Th–C1, $2.679(3)$; Th–C2, $2.797(3)$; Th–C3, $2.746(3)$; Th–C7, $2.731(3)$; Th–C8, $2.795(3)$; Th–C9, $2.692(3)$; Th–C13, $2.723(4)$; Th–C14, $2.803(3)$; Th–C15, $2.720(3)$; Th–C19, $2.707(3)$; Th–C20, $2.806(3)$; Th–C21, $2.719(3)$.

monomer with a more regular geometry than **1** (approximate S_4 symmetry); the thorium is coordinated by four η^3 -allyl ligands, of which all the SiMe_3 groups are in a *syn* configuration (Figure 2). The Th–C bond distances range from $2.679(3)$ to $2.806(3)$ Å; this variation (0.127 Å) is less than half that in **1**. The fold angles in **2** are slightly smaller than those in **1** and cluster in the narrow range of $119.8\text{--}121.4^\circ$; the decrease probably reflects reduced interligand crowding. Compounds **1** and **2** are the first crystallographically

[†] Vanderbilt University.

[‡] University of Minnesota.

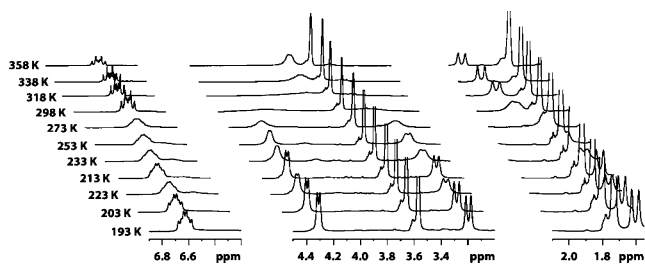


Figure 3. Variable-temperature ^1H NMR ($\text{THF}-d_8$) of $[1-(\text{SiMe}_3)_2\text{C}_3\text{H}_4]_4\text{Th}$. The peaks near δ 3.6 and 1.7 represent residual solvent protons.

characterized examples of thorium allyl complexes and represent the first structurally authenticated neutral $[\pi\text{-R}_n\text{C}_3\text{H}_{5-n}]_4\text{M}$ species.¹⁶

The irregularity observed in the solid-state structure of **1** persists in solution at low temperature. The ligands are not equivalent on the ^1H NMR time scale below room temperature (see Supporting Information for details). For example, at the lowest temperature investigated (-75 °C), four resonances appear for the terminal protons, two as distinct doublets and the other two as broad humps. On warming, further broadening and coalescence occur, and the signals expected for a single type of π -bound ligand appear by 25 °C. They become well defined by 65 °C; i.e., the terminal allylic protons appear as a doublet at δ 3.31 ($J = 15.6$ Hz), the central proton as a triplet at δ 6.89 ($J = 15.6$ Hz), and the SiMe_3 protons as a singlet at δ 0.18. Decomposition products are observed in toluene solution on heating **1** to 75 °C for 10 min.

Stereochemical nonrigidity in solution is also observed with **2** and is less complex than that with **1**. Unlike the latter, but like $(\text{C}_3\text{H}_5)_4\text{Th}$, the four allyl ligands of **2** are equivalent at all temperatures and in both $\text{THF}-d_8$ and toluene- d_8 . At -80 °C (Figure 3), a static π -bound structure is evident. Most diagnostic of this is the observation of two doublets (δ 4.32, $J_{\text{cis}} = 7.6$ Hz; δ 3.21, $J_{\text{trans}} = 14.8$ Hz) for the two terminal (*gem*) allyl protons. These broaden and disappear into the baseline near room temperature and reappear as a single broad, barely resolved doublet (δ 3.76) at 85 °C. This behavior is consistent with averaging of the geminal *syn*, *anti* protons, probably via a $\pi\text{-}\sigma\text{-}\pi$ intramolecular conversion, as has been proposed to occur for the allyl ligands in $(\text{C}_3\text{H}_5)_4\text{Th}$ and $(\text{C}_5\text{H}_5)_3\text{Th}(\text{C}_3\text{H}_5)$.⁸ Use of the two-site exchange formalism¹⁷ provides an estimated ΔG^\ddagger for the conversion of 14.5 ± 1.0 kcal mol^{-1} . Interestingly, this overlaps the value calculated for hydrogen exchange in the parent $(\text{C}_3\text{H}_5)_4\text{Th}$ (14 kcal mol^{-1}).⁶

Even though $(\text{C}_3\text{H}_5)_4\text{Th}$ has not been structurally authenticated, DFT calculations were used to compare its predicted structure with that of **2**. Geometry optimization¹⁸ of $(\text{C}_3\text{H}_5)_4\text{Th}$ using the Th and C coordinates from **2** as a starting point converged to a minimum, with bond distances of 2.695–2.822 Å ($\Delta = 0.127$ Å; $\text{av} = 2.751$ Å) and fold angles for the four ligands of 122.3°; these values are remarkably close to those of the experimental structure of **2**.

The similar energetics for *syn*, *anti* hydrogen rearrangement in $(\text{C}_3\text{H}_5)_4\text{Th}$ and **2**, and the apparently small effect that the mono-(trimethylsilyl)allyl ligand has on the core Th–allyl geometry, suggest that **2** is a good structural and energetic model for the parent complex. The substantial improvement in the thermal stability of $(\text{C}_3\text{H}_5)_4\text{Th}$ by the replacement of only one terminal proton with a SiMe_3 group likely stems not only from the somewhat greater shielding of the metal center by the trimethylsilyl group but also from the restricted fluxional motion of the ligands (only geminal proton averaging is observed). The latter probably inhibits the ease

of ligand coupling reactions, which is a common decomposition mode in homoleptic allyl complexes.¹⁹

In summary, use of trimethylsilylated allyl ligands has permitted the isolation and structural characterization of thermally stable homoleptic π -allyl complexes of thorium. Evidence from NMR spectra and X-ray crystallography suggests that the trimethylsilyl groups cause relatively little perturbation in the essential metal–allyl geometry. The improvement in stability is a likely consequence of the restricted motion of the allyl ligands and the resulting blockage of decomposition pathways. Further investigation of the ramifications of this effect will be important in the design of other sterically stabilized f-element complexes.²⁰

Acknowledgment. The Petroleum Research Fund of the American Chemical Society is thanked for support of this research.

Supporting Information Available: Synthetic and crystallographic details (PDF) and X-ray crystallographic files (CIF) for compounds **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Beckhaus, R. *Synth. Methods Organomet. Inorg. Chem.* **2000**, *9*, 1–52.
- Smith, J. D.; Hanusa, T. P. *J. Am. Chem. Soc.* **2001**, *123*, 6455–6456.
- Carlson, C. N.; Smith, J. D.; Hanusa, T. P.; Brennessel, W. W.; Young, V. G., Jr. *J. Organomet. Chem.* **2003**, *683*, 191–199.
- Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Walter, D. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151–164.
- Eisen, M. S.; Marks, T. J. *J. Mol. Catal.* **1994**, *86*, 23–50.
- Eisen, M. S.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10358–10368.
- Eisen, M. S.; Marks, T. J. *Organometallics* **1992**, *11*, 3939–3941.
- Heteroleptic allyl complexes can be much more robust than their homoleptic counterparts; e.g., $(\text{C}_5\text{H}_5)_3\text{Th}(\text{C}_3\text{H}_5)$ is stable to 210 °C (Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1976**, *98*, 703–710).
- Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *Angew. Chem., Int. Ed.* **1999**, *38*, 217–219.
- Clark, D. L.; Frankcom, T. M.; Miller, M. M.; Watkin, J. G. *Inorg. Chem.* **1992**, *31*, 1628–1633.
- Crystals of $[1,3-(\text{SiMe}_3)_2\text{C}_3\text{H}_4]_4\text{Th}$ are monoclinic, space group $C2/c$, with $a = 41.770(6)$ Å, $b = 12.227(2)$ Å, $c = 20.379(3)$ Å, $\beta = 98.543(2)^\circ$, $V = 10293(2)$ Å³, $Z = 8$, and $\rho_{\text{calc}} = 1.257$ g cm^{-3} for $\text{fw} = 973.79$. Refinement of 8575 reflections collected at the University of Minnesota at 173 ± 2 K with $I > 2.0\sigma(I)$ led to residuals of $R(F^2) = 0.0412$ and $R_w(F^2) = 0.0896$.
- Rebizant, J.; Spirlet, M. R.; Kanellakopoulos, B.; Dornberger, E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1497–1500.
- The fold angle is defined as that between the C_3 allyl plane and the plane passing through the metal atom and the two terminal allyl carbon atoms.
- Cymbaluk, T. H.; Ernst, R. D.; Day, V. W. *Organometallics* **1983**, *2*, 963–969.
- Crystals of $[1-(\text{SiMe}_3)_2\text{C}_3\text{H}_4]_4\text{Th}$ are monoclinic, space group $P2_1/c$, with $a = 11.0558(15)$ Å, $b = 28.104(4)$ Å, $c = 11.1187(15)$ Å, $\beta = 106.960(2)^\circ$, $V = 3304.4(8)$ Å³, $Z = 4$, and $\rho_{\text{calc}} = 1.377$ g cm^{-3} for $\text{fw} = 685.06$. Refinement of 6605 reflections collected at the University of Minnesota at 173 ± 2 K with $I > 2.0\sigma(I)$ led to residuals of $R(F^2) = 0.0257$ and $R_w(F^2) = 0.0537$.
- Anionic $[(\text{C}_3\text{H}_5)_n\text{M}]^-$ molecules have been characterized for La and Ce: (a) Taube, R.; Windisch, H.; Goerlitz, F. H.; Schumann, H. *J. Organomet. Chem.* **1993**, *445*, 85–91. (b) Huang, Z.; Chen, M.; Qiu, W.; Wu, W. *Inorg. Chim. Acta* **1987**, *139*, 203–207.
- Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.
- DFT calculations were performed under S_4 symmetry with Gaussian 03W using the B3PW91 functional, the SDD basis set on Th, and the cc-pVDZ basis set on C and H. The SDD basis is constructed with a quasirelativistic effective core potential that allows the incorporation of scalar relativistic effects in a nonrelativistic calculation. Frequency calculations confirmed that the optimized geometry was a minimum on the potential energy surface ($N_{\text{imag}} = 0$).
- (a) Blom, R.; Swang, O. *Eur. J. Inorg. Chem.* **2002**, 411–415. (b) Jolly, P. W.; Krueger, C.; Schick, K. P.; Wilke, G. *Z. Naturforsch.* **1980**, *35B*, 926–928. (c) Boennemann, H.; Grard, C.; Kopp, W.; Pump, W.; Tanaka, K.; Wilke, G. *Angew. Chem.* **1973**, *85*, 1024–1035.
- Kuehl, C. J.; Simpson, C. K.; John, K. D.; Sattelberger, A. P.; Carlson, C. N.; Hanusa, T. P. *J. Organomet. Chem.* **2003**, *683*, 149–154.

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