

Unprecedented Bending and Rearrangement of *f*-Element Sandwich Complexes Induced by Superbulky Cyclooctatetraenide LigandsVolker Lorenz,<sup>†</sup> Benjamin M. Schmiede,<sup>‡</sup> Cristian G. Hrib,<sup>†</sup> Joseph W. Ziller,<sup>‡</sup> Anja Edelmann,<sup>†</sup> Steffen Blaurock,<sup>†</sup> William J. Evans,<sup>\*,‡</sup> and Frank T. Edelmann<sup>\*,†</sup><sup>†</sup>Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany<sup>‡</sup>Department of Chemistry, University of California, Irvine, California 92697-2025, United States

## Supporting Information

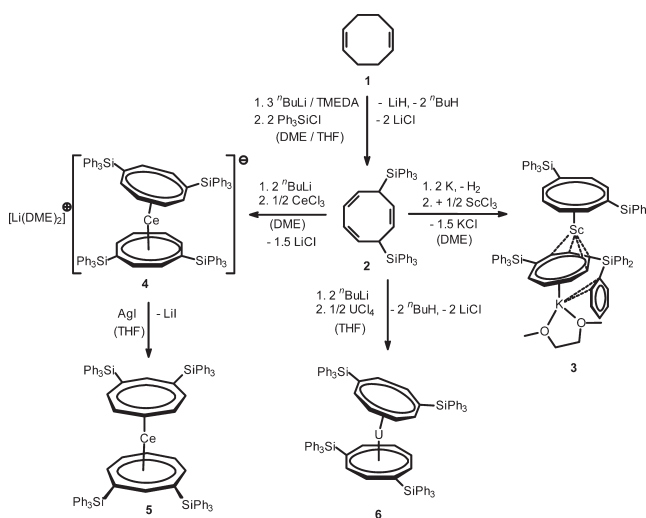
**ABSTRACT:** The use of the superbulky cyclooctatetraenide dianion ligand  $[\text{C}_8\text{H}_6(\text{SiPh}_3)_2]^{2-}$  ( $= \text{COT}^{\text{BIG}}$ ) in organo-*f*-element chemistry leads to unprecedented effects such as the formation of a significantly bent anionic  $\text{Ce}^{\text{III}}$  sandwich complex, a novel cerocene formed by sterically induced  $\text{SiPh}_3$  group migration, as well as the first example of a bent uranocene.

Superbulky ligands such as the perphenylated cyclopentadienyl anion ( $\text{C}_5\text{Ph}_5^-$ ) are known to impart unique properties or coordination geometries on their complexes with main group and transition metals.<sup>1</sup> In homogeneous catalysis, the  $\text{C}_5\text{Ph}_5$  ligand has been reported to enhance stereoselectivity in asymmetric syntheses<sup>2</sup> and increase the activity and selectivity of Cr catalysts in ethylene oligomerization.<sup>3</sup> Spectacular results in organolanthanide chemistry have recently been achieved with the related perarylated ligand  $\text{C}_5(\text{C}_6\text{H}_4^i\text{Bu}-p)_5$  ( $= \text{Cp}^{\text{BIG}}$ ). This ligand was found to induce reduction of a  $\text{Sm}^{\text{III}}$  precursor to the divalent samarocene ( $\text{Cp}^{\text{BIG}}_2\text{Sm}$ ).<sup>4</sup>

Besides the ubiquitous Cp ligands, the cyclooctatetraenide dianion ( $= \text{COT}$ ) and its derivatives play a major role in organo-*f*-element chemistry.<sup>5</sup> In recent years, the use of bulky silyl-substituted COT ligands such as 1,4-bis(trimethylsilyl)cyclooctatetraenide ( $= \text{COT}''$ ) has proven to be highly beneficial in the synthesis of novel sandwich complexes of *f*-elements, including triple- and tetra-decker structures.<sup>6</sup> However, unlike in Cp chemistry, the steric demand of COT ligands has not yet been stretched to the limit. A notable early indication that *f*-element complexes of very bulky COT ligands could have unique properties was the finding that octaphenyluranocene is an air-stable material in contrast to pyrophoric  $\text{U}(\text{COT})_2$ .<sup>7</sup>

We now report that the use of the superbulky 1,4-bis(trimethylsilyl)cyclooctatetraenide ligand ( $= \text{COT}^{\text{BIG}}$ ) leads to unusual coordination geometries and reaction pathways when combined with scandium and *f*-elements. The key precursor, 1,4-bis(trimethylsilyl)cyclooctatriene (**2**), is readily accessible in 50 g quantities and 52% yield by a modification of the synthetic route described for the  $\text{SiMe}_3$  congener (Scheme 1).<sup>6</sup>

An X-ray analysis of **2** (Figure 1) illustrated the large size of the two  $\text{SiPh}_3$  substituents in comparison with the central eight-membered ring. Reactivity studies clearly revealed unique behavior for the “superbulky”  $\text{COT}^{\text{BIG}}$  ligand in combination with

Scheme 1. Synthesis of the  $\text{COT}^{\text{BIG}}$  Complexes **3–6**

scandium and *f*-elements. *In situ* deprotonation of **1** with potassium followed by treatment with anhydrous  $\text{ScCl}_3$  afforded  $[\text{K}(\text{DME})][\text{Sc}(\text{COT}^{\text{BIG}})_2]$  (**3**) as bright orange needles in 67% yield (Scheme 1). X-ray diffraction revealed a slipped  $\eta^4, \eta^8$ -coordination of the  $\text{COT}^{\text{BIG}}$  rings to Sc as well as an  $\eta^2$ - $\pi$ -interaction of a phenyl substituent with potassium (Figure 2 left).  $\eta^4$ -Bonding of a bridging COT ring to scandium is not without precedent and has been observed in  $[\text{Li}(\text{THF})_2][\mu-(\eta^4:\eta^4\text{-COT})\text{Sc}(\text{COT})]$ .<sup>8</sup>

Even more surprising was the structure of the related anionic cerium(III) sandwich complex  $[\text{Li}(\text{DME})_2][\text{Ce}(\text{COT}^{\text{BIG}})_2]$  (**4**) which was prepared by reaction of  $\text{CeCl}_3$  with 2 equiv of  $\text{Li}_2(\text{COT}^{\text{BIG}})$  made *in situ* in DME (Scheme 1, bright green crystals, 66% yield). The single-crystal X-ray analysis (Figure 2) showed that in contrast to all previously reported  $[\text{Ln}(\text{COT})_2]^-$  or  $[\text{Ln}(\text{COT}'')_2]^-$  derivatives,<sup>5,6</sup> the anion in **4** is significantly bent (tilt angle between the eight membered rings:  $15.1^\circ$ ). The 2.78(1) Ce–C(avg) and the 4.111 Å (ring centroid)–(ring centroid) distance in **4** compare quite well with those found in  $[\text{Li}(\text{THF})_4][\text{Ce}(\text{COT})_2]$  [2.74(1) Å; 4.086 Å],<sup>9</sup>  $[\text{Na}(\text{THF})_3][\text{Ce}(\text{COT})_2]$  [2.74(2) Å; 4.099 Å],<sup>9</sup> and  $[\text{Yb}(\text{THF})_6][\text{Ce}\{1,3,6-(\text{Me}_3\text{Si})_3\text{-C}_6\text{H}_5\}_2]_2$  [2.76(7) Å; 4.114 Å].<sup>10</sup> Except for the bending in the  $167.2^\circ$  (ring centroid)–Ce–(ring centroid) angle the common

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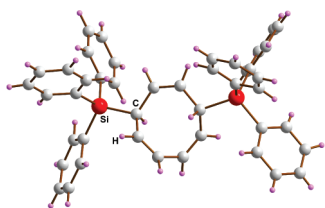


Figure 1. Molecular structure of 2.

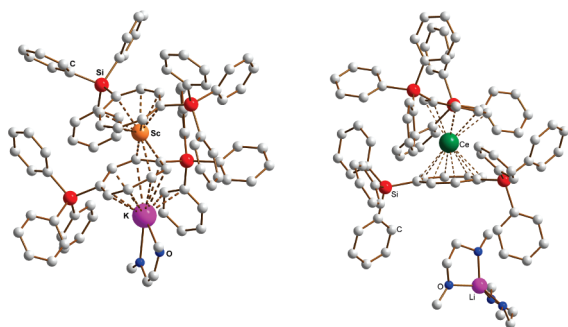


Figure 2. Molecular structures of 3 (left) and 4 (right).

cerocene features in **4** are relatively unchanged compared with those listed above.

Another characteristic worthy of comparison is the deviation of ring substituents out of the plane of the ring.<sup>11</sup> The Si atoms that are closest in space to each other (Si2 and Si3), on opposite C<sub>8</sub> rings, show deviations from the C<sub>8</sub> ring of 0.22 and 0.41 Å respectively, while the largest Si deviations in [Yb(THF)<sub>6</sub>][Ce{1,3,6-(Me<sub>3</sub>Si)<sub>3</sub>C<sub>8</sub>H<sub>5</sub>}<sub>2</sub>]<sub>2</sub>,<sup>10</sup> which contains parallel C<sub>8</sub> rings, are 0.23 and 0.34 Å. Clearly the bending in the (ring centroid)–Ce–(ring centroid) angle of **4** is a result of steric hindrance between opposing phenyl rings of the SiPh<sub>3</sub> substituents.

Anionic bis(COT<sup>−</sup>) sandwich complexes of Ce<sup>3+</sup> can be oxidized to the corresponding neutral cerocenes with the use of suitable oxidizing agents like AgI or allyl bromide.<sup>12</sup> Knowing the bent structure of **4**, it was tempting to see if the bending would increase upon oxidation. AgI oxidation of **4** proceeded smoothly with formation of the neutral cerocene **5** (Scheme 1, dark purple needles, 63%). X-ray diffraction analysis of **5** unexpectedly revealed the presence of strictly coparallel rings, but the molecule now contains the 1,3-isomer of the COT<sup>BIG</sup> ligand! Obviously steric pressure becomes too severe upon oxidation to the neutral cerocene that SiPh<sub>3</sub> group migration is induced for relief. Figure 3 clearly shows the sterically more relaxed and highly symmetrical molecular structure of **5** as a result of this unprecedented rearrangement.

A logical extension of these initial experiments was the synthesis and structural characterization of the corresponding uranocene, U(COT<sup>BIG</sup>)<sub>2</sub> (**6**). Would this compound be bent like the [Ce(COT<sup>BIG</sup>)<sub>2</sub>]<sup>−</sup> anion in **5**, or would SiPh<sub>3</sub> group migration occur again? Treatment of UCl<sub>4</sub> with 2 equiv of Li<sub>2</sub>(COT<sup>BIG</sup>) in THF afforded the dark green uranocene derivative **6** in 58% isolated yield (Scheme 1). An X-ray diffraction study answered the structural question in favor of the first assumption.

The structure of **6** (Figure 4) differs from all previously reported bis(cyclooctatetraenyl) uranium complexes<sup>7,13</sup> in that the rings are not parallel. The 168.7° (ring centroid)–U–(ring centroid) angle makes **6** the first bent uranocene. Comparison of

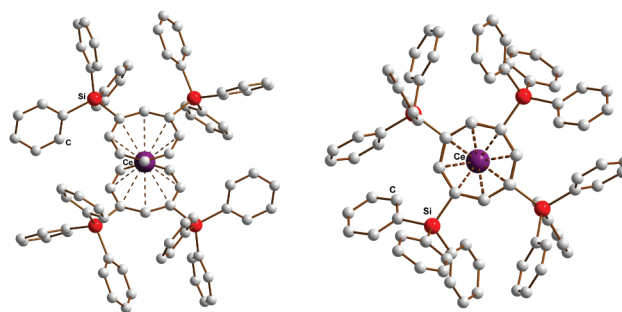
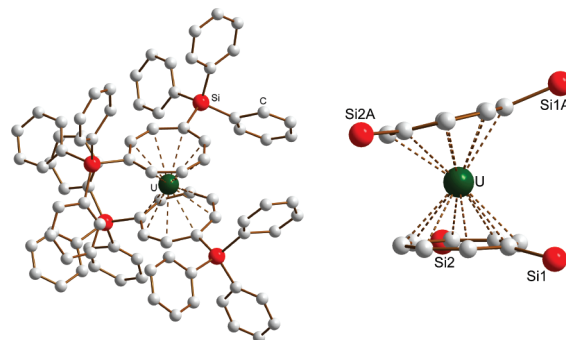


Figure 3. Two different views of the molecular structure of 5.

Figure 4. Molecular structure of 6 (right: SiPh<sub>3</sub> groups omitted).

the 2.649(3)–2.734(2) Å U–C distances, the 2.67(2) Å U–C (avg) distance, and the 3.856 Å (ring centroid)–(ring centroid) distance in **6**, with those in (C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>U [2.635(10)–2.675(11) Å; 2.647(4) Å; 3.847 Å],<sup>2</sup> (C<sub>8</sub>H<sub>4</sub>Ph<sub>4</sub>)<sub>2</sub>U [2.61(2)–2.69(2) Å; 2.65(2) Å; 3.793(3) Å],<sup>7b</sup> and (C<sub>8</sub>H<sub>4</sub>Me<sub>4</sub>)<sub>2</sub>U [2.624(11)–2.688(12) Å; 2.658(6) Å; 3.836(9) Å],<sup>13b</sup> shows that although the U–C distances span a larger range, the average U–C distance and inter-ring spacing are only slightly numerically larger than the analogous values in other uranocenes. Hence, it appears that the bent nature of **6** allows common uranocene structural features to be maintained while providing room for the four large SiPh<sub>3</sub> groups that cannot easily adopt a tetrahedral geometry due to the 1,4-substitution pattern.

As in **4**, the SiPh<sub>3</sub> substituents in **6** are out of the plane of the C<sub>8</sub> ring in this case by 0.20 and 0.32 Å. In contrast, in the sterically bulky (C<sub>8</sub>H<sub>4</sub>Ph<sub>4</sub>)<sub>2</sub>U<sup>7b</sup> the phenyl groups are able to twist slightly with respect to the ring to allow the carbon atoms of the phenyl rings bound to the C<sub>8</sub> ring to still lie in the plane defined by the C<sub>8</sub> ring. This is not possible in **6** with the much larger SiPh<sub>3</sub> substituents.

In summary, we have shown that in sandwich complexes of scandium and *f*-elements the superbulky COT ligand [C<sub>8</sub>H<sub>6</sub>–(SiPh<sub>3</sub>)<sub>2</sub>]<sup>2−</sup> puts such severe steric pressure on the central metal atoms that either significant bending or unprecedented ligand rearrangement is induced. The bent anionic Ce(III) sandwich **4**, the rearranged cerocene **5**, and the bent uranocene **6** are the first of their kind. Both the intriguing COT<sup>BIG</sup> ligand and the newly formed 1,3-bis(triphenylsilyl)cyclooctatetraenide ligand clearly warrant further investigations in this field.

## ■ ASSOCIATED CONTENT

**S** Supporting Information. CIF files giving X-ray structural data for **2**–**6** as well as experimental details on the preparation

and characterization of 2–6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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