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Unprecedented Bending and Rearrangement of f-Element Sandwich Complexes Induced by Superbulky Cyclooctatetraenide Ligands

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S *Supporting Information*

ABSTRACT: The use of the superbulky cyclooctatetraenide dianion ligand $[C_8H_6(SiPh_3)_2]^{2-}$ (= COT^{BIG}) in organo-*f*-element chemistry leads to unprecedented effects such as the formation of a significantly bent anionic Ce^{III} sandwich complex, a novel cerocene formed by sterically induced $SiPh_3$ group migration, as well as the first example of a bent uranocene.

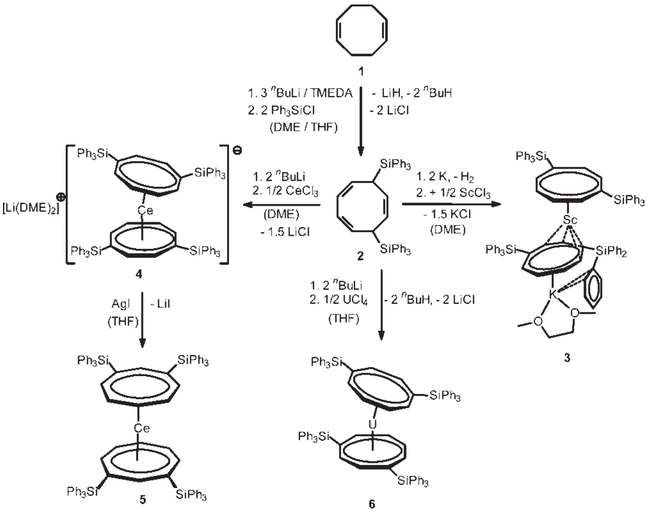
Superbulky ligands such as the perphenylated cyclopentadienyl anion ($C_5Ph_5^-$) are known to impart unique properties or coordination geometries on their complexes with main group and transition metals.[1] In homogeneous catalysis, the C_5Ph_5 ligand has been reported to enhance stereoselectivity in asymmetric syntheses[2] and increase the activity and selectivity of Cr catalysts in ethylene oligomerization.[3] Spectacular results in organolanthanide chemistry have recently been achieved with the related perarylated ligand $C_5(C_6H_4{}^nBu\text{-}p)_5$ (= Cp^{BIG}). This ligand was found to induce reduction of a Sm^{III} precursor to the divalent samarocene $(Cp^{BIG})_2Sm$.[4]

Besides the ubiquitous Cp ligands, the cyclooctatetraenide dianion (= COT) and its derivatives play a major role in organo-*f*-element chemistry.[5] In recent years, the use of bulky silyl-substituted COT ligands such as 1,4-bis(trimethylsilyl)cyclooctatetraenide (= COT″) has proven to be highly beneficial in the synthesis of novel sandwich complexes of *f*-elements, including triple- and tetra-decker structures.[6] 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 $U(COT)_2$.[7]

We now report that the use of the superbulky 1,4-bis(triphenylsilyl)cyclooctatetraenide ligand (= COT^{BIG}) leads to unusual coordination geometries and reaction pathways when combined with scandium and *f*-elements. The key precursor, 1,4-bis(triphenylsilyl)cyclooctatriene (**2**), is readily accessible in 50 g quantities and 52% yield by a modification of the synthetic route described for the $SiMe_3$ congener (Scheme 1).[6]

An X-ray analysis of **2** (Figure 1) illustrated the large size of the two $SiPh_3$ substituents in comparison with the central eight-membered ring. Reactivity studies clearly revealed unique behavior for the "superbulky" COT^{BIG} ligand in combination with scandium and *f*-elements. *In situ* deprotonation of **1** with potassium followed by treatment with anhydrous $ScCl_3$ afforded $[K(DME)][Sc(COT^{BIG})_2]$ (**3**) as bright orange needles in 67% yield (Scheme 1). X-ray diffraction revealed a slipped η^4,η^8-coordination of the COT^{BIG} rings to Sc as well as an η^2-π-interaction of a phenyl substituent with potassium (Figure 2 left). η^4-Bonding of a bridging COT ring to scandium is not without precedent and has been observed in $[Li(THF)_2][\mu\text{-}(\eta^4{:}\eta^4\text{-COT})Sc(COT)]$.[8]

Scheme 1. Synthesis of the COT^{BIG} Complexes 3−6



Even more surprising was the structure of the related anionic cerium(III) sandwich complex $[Li(DME)_2][Ce(COT^{BIG})_2]$ (**4**) which was prepared by reaction of $CeCl_3$ with 2 equiv of $Li_2(COT^{BIG})$ 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 $[Ln(COT)_2]^-$ or $[Ln(COT'')_2]^-$ derivatives[5,6] the anion in **4** is significantly bent (tilt angle between the eight membered rings: 15.1°). 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 $[Li(THF)_4]$-$[Ce(COT)_2]$ [2.74(1) Å; 4.086 Å],[9] $[Na(THF)_3][Ce(COT)_2]$ [2.74(2) Å; 4.099 Å],[9] and $[Yb(THF)_6][Ce\{1,3,6\text{-}(Me_3Si)_3\text{-}C_8H_5\}_2]_2$ [2.76(7) Å; 4.114 Å].[10] Except for the bending in the 167.2° (ring centroid)−Ce−(ring centroid) angle the common

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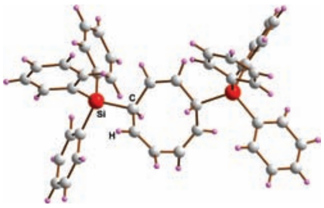

Figure 1. Molecular structure of **2**.

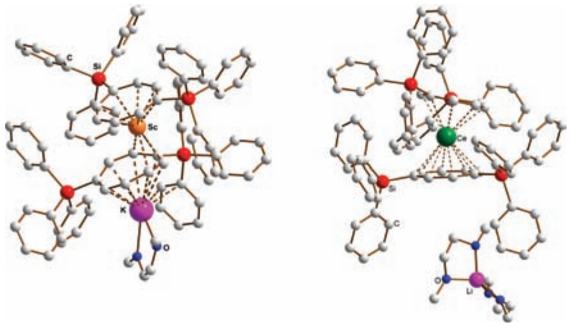

Figure 2. Molecular structures of **3** (left) and **4** (right).

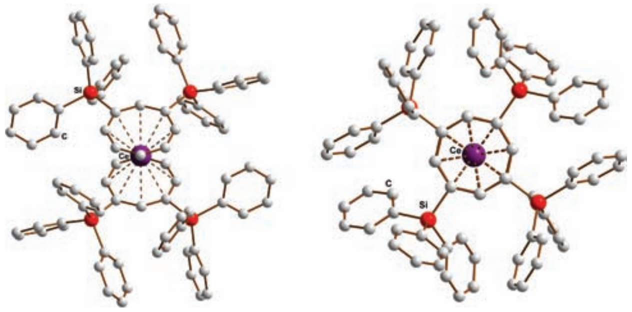

Figure 3. Two different views of the molecular structure of **5**.

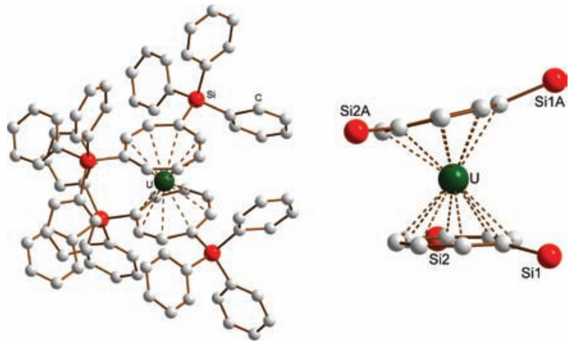

Figure 4. Molecular structure of **6** (right: $SiPh_3$ groups omitted).

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

Another characteristic worthy of comparison is the deviation of ring substitutents out of the plane of the ring.[11] The Si atoms that are closest in space to each other (Si2 and Si3), on opposite C_8 rings, show deviations from the C_8 ring of 0.22 and 0.41 Å respectively, while the largest Si deviations in $[Yb(THF)_6][Ce\{1,3,6\text{-}(Me_3Si)_3C_8H_5\}_2]_2$,[10] which contains parallel C_8 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 $SiPh_3$ substituents.

Anionic bis(COT) sandwich complexes of Ce^{3+} can be oxidized to the corresponding neutral cerocenes with the use of suitable oxidizing agents like AgI or allyl bromide.[12] 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^{BIG} ligand! Obviously steric pressure becomes too severe upon oxidation to the neutral cerocene that $SiPh_3$ 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, $U(COT^{BIG})_2$ (**6**). Would this compound be bent like the $[Ce(COT^{BIG})_2]^-$ anion in **5**, or would $SiPh_3$ group migration occur again? Treatment of UCl_4 with 2 equiv of $Li_2(COT^{BIG})$ 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[7,13] in that the rings are not parallel. The 168.7° (ring centroid)−U−(ring centroid) angle makes **6** the first bent uranocene. Comparison of 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 $(C_8H_8)_2U$ [2.635(10)−2.675(11) Å; 2.647(4) Å; 3.847 Å],[2] $(C_8H_4Ph_4)_2U$ [2.61(2)−2.69(2) Å; 2.65(2) Å; 3.793(3) Å],[7b] and $(C_8H_4Me_4)_2U$ [2.624(11)−2.688(12) Å; 2.658(6) Å; 3.836(9) Å],[13b] 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 $SiPh_3$ groups that cannot easily adopt a tetrahedral geometry due to the 1,4-substitution pattern.

As in **4**, the $SiPh_3$ substituents in **6** are out of the plane of the C_8 ring in this case by 0.20 and 0.32 Å. In contrast, in the sterically bulky $(C_8H_4Ph_4)_2U$[7b] 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_8 ring to still lie in the plane defined by the C_8 ring. This is not possible in **6** with the much larger $SiPh_3$ substituents.

In summary, we have shown that in sandwich complexes of scandium and *f*-elements the superbulky COT ligand $[C_8H_6(SiPh_3)_2]^{2-}$ 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^{BIG} ligand and the newly formed 1,3-bis(triphenylsilyl)cyclooctatetraenide ligand clearly warrant further investigations in this field.

■ ASSOCIATED CONTENT

Ⓢ 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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