One ligand fits all: lanthanide and actinide sandwich complexes comprising the 1,4-bis(trimethylsilyl)cyclooctatetraenyl (≡COT″) ligand†‡

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The series of anionic lanthanide(III) sandwich complexes of the type [Ln(COT)2]− (COT″ = 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion) has been largely extended by the synthesis of eight new derivatives ranging from lanthanum to lutetium. The new compounds [Li(DME)3][Ln(COT)2] (Ln = Y (1), La (2), Pr (3), Gd (4), Tm (6), Lu (8)) and [Li(THF)4][Ln(COT)2] (Ln = Ho (5), Tm (7)) were prepared in good yields following a straightforward synthetic protocol which involves the treatment of LnCl3 with 2 equiv. of in situ-prepared Li2COT in either DME (=1,2-dimethoxyethane) or THF. The neutral actinide sandwich complexes An(COT)2 (An = Th (9), U (10)) and An(COT)22 (COT‴ = 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl dianion; An = Th (11), U (12)) were synthesized in a similar manner, starting from ThCl4 or UC14, respectively. The COT″ ligand imparts excellent solubility even in low-polar solvents as well as excellent crystallinity to all new compounds studied. All twelve new f-element sandwich complexes have been structurally authenticated by single-crystal X-ray diffraction. All are nearly perfect sandwich complexes with little deviation from the coplanar arrangement of the substituted COT″ rings. Surprisingly, all six [Li(DME)3][Ln(COT)2] complexes covering the entire range of Ln3+ ionic radii from La3+ to Lu3+ are isosctructural (space group P6). Compound 10 is the first uranocene derivative for which 13C NMR data are reported.

1. Introduction

Second only to the omnipresent cyclopentadienyl complexes, the dianionic 10π-cyclooctatetraenyl ligand C8H82−, commonly abbreviated as COT, plays an important role in the organometallic chemistry of lanthanides and actinides for almost 50 years. There is a general understanding that the large, flat C8H82− ring is ideally suited for overlapping with the f-orbitals of the large lanthanide and actinide ions. Early work in this area was mainly focused on complexes bearing unsubstituted COT ligands. Scheme 1 shows some prototypical lanthanide COT complexes which are considered milestones in the development of organolanthane chemistry using COT ligands.

Notable are the anionic sandwich complexes K[Ln(COT)2] (A),1 the dimeric half-sandwich mono(cyclooctatetraenyl)-lanthanide chlorides [(COT)Ln(pCl)(THF)]2 (B),2 the mixed-sandwich complexes (COT)LnCp (C),3 and the so-called cerocene, Ce(COT)2 (D).4 The chemistry of such lanthanide COT complexes has already been summarized in several comprehensive review articles.1,2,3,5

In the case of actinides, the discovery of uranocene, U(COT)2 (Scheme 2, An = U), by Streitwieser and Müller-Westerhoff in 1968 had a considerable impact on the development of organoactinide chemistry.11,12 Following the preparation of uranocene, other tetravalent actinidoenes An(C8H8)2 (Scheme 2; An = Th, Pa, Np, Pu) have also been reported.1,12 The bonding in uranocene is considered to be less ionic than in the lanthanide sandwich complexes K[Ln(COT)2] (A) and Ce(COT)2 (D). Uranocene is also significantly more stable than cerocene and the thorium analogue Th(COT)2, which can be explained by a higher degree of covalency due to a stronger participation of the 5f and 6d orbitals in the uranium–cyclooctatetraenyl bonding. Recent work by Ephritikhine and co-workers has demonstrated that the chemistry of actinidoenes continues to produce very interesting results.13 In general, the use of the unsubstituted COT ligand in organolanthane and -actinide chemistry has several disadvantages...
Recent findings by Murugesu and co-workers revealed that some of the anionic [Ln(COT)\textsuperscript{n-}]	extsuperscript{−} sandwich complexes behave as organometallic single-molecule magnets.\textsuperscript{17,20,21,23} Due to the renewed interest in this class of compounds, we carried out a broader investigation on lanthanide and actinide COT\textsuperscript{n-} sandwich complexes. In this contribution we report the synthesis and structural characterization of the new anionic lanthanide sandwich complexes [Li(DME),][Ln(COT)\textsuperscript{n-}] (Ln = Y (1), La (2), Gd (4), Tm (6), Lu (8)) and [Li(THF),][Ln(COT)\textsuperscript{n-}] (Ln = Pr (3), Ho (5), Tm (7)) as well as the neutral actinide sandwich complexes An(COT)\textsuperscript{n+} (An = Th (9), U (10)) and An(COT')\textsuperscript{n+} (An = Th (11), U (12)).

Most recently, after this work had been completed, Murugesu et al. reported the synthesis, structure, and magnetic properties of the closely related uranium(m) sandwich complex [Li(DME),][U(COT)\textsuperscript{n+}] and the isostructural and isoelectronic lanthanide analogue [Li(DME),][Nd(COT)\textsuperscript{n+}]. This work also included the synthesis and structural characterization of the neutral uranocene derivative U(COT)-, although its preparation involved a different synthetic route (\textit{vide infra}).\textsuperscript{27}

2. Results and discussion

The general synthetic protocol for preparing the anionic lanthanide sandwich complexes is outlined in Scheme 3. The synthesis starts with the well-established preparation of 1,4-bis(trimethylsilyl)cycloocta-2,5,7-triene from 1,5-cyclooctadiene according to Cloke \textit{et al.}\textsuperscript{10} The dilithium reagent Li\textsubscript{2}COT\textsuperscript{−} can be conveniently prepared by metalation of 1,4-bis(trimethylsilyl)cycloocta-2,5,7-triene with n-butyllithium,\textsuperscript{19} and the resulting solutions can be used \textit{in situ} for further reactions. However, it is also possible to isolate crystalline adducts of Li\textsubscript{2}COT\textsuperscript{−}, e.g. [Li(TMEDA),][Li(COT)\textsuperscript{−}] (TMEDA = N,N,N',N'-tetramethylethylenediamine),\textsuperscript{10c} [Li(DME),][COT\textsuperscript{−}],\textsuperscript{26c} and [Li(THF),][Li2(COT)\textsuperscript{−}].\textsuperscript{26b} The latter two adducts have been structurally characterized through X-ray diffraction. [Li(TMEDA),][Li(COT)\textsuperscript{−}] was shown to be an inverse sandwich complex with the two Li\textsuperscript{+} ions coordinated to the bridging 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (=COT\textsuperscript{−}) in organo-f-element chemistry.\textsuperscript{14} In many cases, using the bulky COT\textsuperscript{−} ligand did in fact improve the solubility of the products, but occasionally also led to novel molecular structures and coordination geometries.\textsuperscript{7c,10d,14} Typical examples include the unprecedented cluster-centered Pr/Li multidecker sandwich complex of the composition [Pr(COT\textsuperscript{−})\textsubscript{2}][Li2(COT\textsuperscript{−})\textsubscript{2}][Li(THF),][Cl\textsubscript{2}]\textsuperscript{15} as well as the first linear rare-earth metal triple-decker complexes Ln\textsubscript{2}(COT\textsuperscript{−})\textsubscript{3} (Ln = Nd, Gd, Dy, Ho, Er).\textsuperscript{14,16,18} Previously reported anionic lanthanide sandwich complexes comprising [Ln(COT)\textsuperscript{n−}]\textsuperscript{−} anions include the THF solvates [Li(THF),][Ln(COT)\textsuperscript{n−}] with Ln = Y,\textsuperscript{19} Ce,\textsuperscript{19} Pr,\textsuperscript{19} Nd,\textsuperscript{14,19} Sm,\textsuperscript{19} Gd\textsuperscript{17} and Dy\textsuperscript{17} as well as the DME adducts [Li(DME),][Ln(COT)\textsuperscript{n−}] (Ln = Ce,\textsuperscript{14,20} Dy,\textsuperscript{17} Er\textsuperscript{21}) Li(DME)[ Tb(COT)\textsuperscript{−}]\textsuperscript{22} and Li(DME)[Dy(COT)\textsuperscript{−}]\textsuperscript{23} A notable neutral lanthanide sandwich complex containing COT\textsuperscript{−} is the cerocene derivative Ce(COT\textsuperscript{−})\textsuperscript{24} Sterically even more demanding is the 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl dianion ligand (=COT\textsuperscript{−}'), which has also been successfully employed in organolanthanide\textsuperscript{24–26} and -actinide chemistry.\textsuperscript{24,27}

Recent findings by Murugesu and co-workers revealed that some of the anionic [Ln(COT)\textsuperscript{n−}]\textsuperscript{−} sandwich complexes behave as organometallic single-molecule magnets.\textsuperscript{17,20,21,23}
purification was achieved by recrystallization of the crude products from toluene. The DME adducts [Li(DME)]_3[Ln(COT)]_2 (Ln = Y (1), La (2), Pr (3), Gd (4), Tm (6), Lu (8)) were obtained by extraction of the reaction products with toluene followed by recrystallization from DME after addition of n-pentane. The products were isolated in moderate to good yields or upon prolonged storage in the dry-box. In contrast, crystals of the THF adducts [Li(THF)]_4[Ln(COT)]_2 (Ln = Ho (5), Tm (7)) were obtained by extraction of the reaction products with toluene. The molecular structure of the THF adduct [Li(THF)]_4[Ho(COT)]_2 (5) is shown in Fig. 1, and Fig. 2 shows the molecular structure of [Li(DME)]_3[Lu(COT)]_2 (8) as a representative DME adduct.

As can be seen from Table 3, the average Ln–C bond lengths vary between 2.785 Å in the lanthanum complex 2 and 2.609 Å in the lutetium derivative 8. The difference of 0.176 Å can be attributed to the lanthanide contraction. Certainly the most significant result is the finding that all known [Li(DME)]_3[Ln(COT)]_2 complexes (Ln = Y (1), La (2), Ce, Pr, Nd, Gd (4), Dy, Er, Tm (6), Lu (8)) are isostrophic. The same can be said about the series of known [Li(THF)]_4[Ln(COT)]_2 complexes, including the new derivatives [Li(THF)]_4[Ho(COT)]_2 (5) and [Li(THF)]_4[Tm(COT)]_2 (7). The Ctr–Ln–Ctr angles (Ctr = ring centroid) are found to be in the very narrow range between 177.8° for [Li(THF)]_4[Tm(COT)]_2 (7) and 175.9° for

### Table 1 Crystallographic data for 1–6

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Table 2 Crystallographic data for 7–12

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Fig. 1 Molecular structure of [Li(THF)]_{4}Ho(COT)^{8} (5).

Table 3 Selected average bond lengths (Å) and angles (°) of the lanthanide sandwich complexes 1–8. Ctr stands for the COT ring centroids

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Fig. 2 Molecular structure of [Li(DME)]_{2}[Lu(COT)^{8}] (8).
congeners 9 and 10, thorium compound 11 forms bright yellow crystals, while crystals of 12 appear dichroitic red/green. Both complexes are highly soluble in common organic solvents, including hydrocarbons.

All four silyl-substituted actinidocenes 9–12 have been structurally characterized through single-crystal X-ray diffraction. Crystallographic data for 9–12 are summarized in Table 2; selected bond lengths and angles are listed in Table 4. The molecular structures are depicted in Fig. 3 and 4. As can be seen from the structural data listed in Table 4, the overall structural features of all four actinidocene derivatives studied here are very similar. According to the unsymmetrical substitution pattern on the cyclooctatetraenyl rings leading to steric interactions, all complexes show a slight distortion from the ideal linear arrangement with Ctr–M–Ctr angles of about 174°. As expected, evidence for actinide contraction is found which is reflected in ~5 pm shorter M–C as well as in ~7 pm shorter M–Ctr distances in the uranium complexes as compared to the thorium species (Table 5).

In the following, the structural and spectroscopic characterization of 10 as a typical example will be discussed in more detail. The molecular structure of 10 can be clearly described as being of the well-known uranocene type (Fig. 5). Accordingly, in the molecular structure the central uranium atom is placed between the two cyclooctatetraenyl rings with U–Ctr distances of 1.913 or 1.921 Å, comparable to previously reported uranocene derivatives (Fig. 5). However, the trimethylsilyl substituents in 1,4-positions of the cyclooctatetraenyl ring lead to an arrangement in the solid state where on one side of the molecule a stronger steric interaction between the two cyclooctatetraenyl rings results. Si1 and Si4 are found to be in closer steric environment than Si2 and Si3, giving rise to a significant repulsion on this side of the rings. This has an influence on the bond lengths and angles in that the two cyclooctatetraenyl rings do not bind symmetrically to the central uranium atom. The U–C bond distances cover a range between 2.642 and 2.690(4) Å with the longer bond lengths found on the side with the stronger steric interactions, whereas the shortest U–C bond length is observed for U1–C22 with 2.642(4) Å. Accordingly, the two cyclooctatetraenyl rings are not coordinated coplanar with

![Fig. 3](image1.png)

**Table 4** Overview of all known anionic lanthanide sandwich complexes of the type [Li(THF)$_4$][Ln(COT$^{19}$)$_2$] (denoted THF) and [Li(DME)$_3$][Ln(COT$^{19}$)$_2$] (denoted DME). X: compounds described in this work.

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![Scheme 4](image2.png)

**Scheme 4** Synthetic route to the neutral actinidocenes An(COT$^{19}$)$_2$ (An = Th (9), U (10)).

![Scheme 5](image3.png)

**Scheme 5** Synthesis of the neutral actinidocenes An(COT$^{19}$)$_2$ (An = Th (11), U (12)).

![Fig. 4](image4.png)

**Fig. 4** Molecular structures of Th(COT$^{19}$)$_2$ (11) and U(COT$^{19}$)$_2$ (12).

![Table 5](image5.png)

**Table 5** Selected average bond lengths (Å) and angles (°) of the actinide sandwich complexes 9–12. Ctr stands for the COT ring centroids; mean values are given in parentheses.

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<td>M–Ctr</td>
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<td>1.921/1.913 (1.917)</td>
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<td>Ctr–M–Ctr</td>
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</table>

![Fig. 5](image6.png)
respect to the uranium center. This results in a Ctr–U–Ctr angle of 7.0° and a tilt angle between the two ring planes of 7.4° with the opening to the side of Si1/Si4 (Table 4 and Fig. 5). This is further reflected in the corresponding distances between opposing carbon atoms of the two COT rings in the staggered structure. With 4.047 and 4.070 Å the distances C1–C17 and C2–C18 are remarkably longer than those between C5 and C21 or C6 and C22, which are with 3.627 or 3.614 Å significantly shorter. These structural findings clearly show that compound 10 shows typical uranocene structural features but with a significant distortion caused by steric effects due to the trimethylsilyl substituents at the COT rings. A significantly stronger tilting of the two cyclooctatetraenyl rings has been observed in the 1,4-bis(triphenylsilyl)-substituted system where ring-to-ring C–C distances between 3.468 and 4.247 Å and a tilt angle of 11.4° have been found.30

The spectroscopic data of the complexes 9–12 are in good agreement with their structural features. As expected, the IR spectra of 9–12 are all very similar, showing the comparable molecular constitution of these actinocenes. Frequencies arising from the COT ligand increase slightly upon complexation as compared to K₂COT. However, the spectra are more complicated than those of the unsubstituted actinocenes as the SiMe₃-substituents give rise to strong absorptions themselves and cause a distortion from the ideal D₈h-symmetry observed in the actinocenes, leading to a higher number of observed frequencies.31 However, the general congruency of the IR and FIR spectra clearly shows the similarity in the structural features of the complexes 9–12. The other spectroscopic data will be highlighted taking again compound 10 as example. In contrast to the corresponding Th-complex 9, the uranocene derivative 10 exhibits a 5f²-electron configuration causing paramagnetism and an intensely red color in transmission. These findings are confirmed by the UV-vis data (Fig. 6), showing that below 450 nm the absorption of the complex is strongly increasing.
resonance can be clearly assigned to the protons of the SiMe₃ substituents. In the two-dimensional HH-correlated spectrum the resonances at −39.63 and −45.62 ppm (β-position to the SiMe₃-substituents) are assigned to the protons in the (CH)₄-chain of the COT ring, whereas the resonance at −25.20 ppm corresponds to the ring protons positioned between the two trimethylsilyl substituents in 1,4-positions (Fig. 8).

This assignment is in good agreement with the published data where a strong influence of the paramagnetism on the chemical shifts in uranocene derivatives is described. However, in this paper, for the first time, the ¹³C chemical shifts of a uranocene complex are reported. The carbon resonance of the SiMe₃ groups was localized at −3.5 ppm. The proton resonance at −25.20 ppm exhibits a cross peak at 325.9 ppm in the ¹³C frequency, whereas the two coupling H-atoms of the aromatic ring at −39.63 ppm and −45.62 ppm give rise to carbon resonances as well at low field shifts with 293.8 and 270.3 ppm, respectively (Fig. 9). The observation of carbon frequencies at these low fields is in agreement with theoretical predictions.

3. Conclusions

In summarizing the results reported here, the series of anionic lanthanide(III) sandwich complexes of the type [Ln(COT°)]⁻ (COT° = 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion) has been largely extended through the synthesis of eight new derivatives ranging from lanthanum to lutetium. Surprisingly, neither the ionic radius nor the oxidation state of the f-element ion (Ln³⁺/An⁴⁺) have a pronounced influence on the structural features of the compounds [Li(DME)]₃[Ln(COT°)]₂ (1–8; Ln = Y, La, Pr, Gd, Tm, Lu), [Li(THF)]₃[Ln(COT°)]₂ (5, 7; Ln = Ho, Tm), and Ln(COT°)₂ (9, 10; An = Th, U) and An(COT°°)₂ (11, 12; An = Th, U). In all cases the slight deviation from the ideal sandwich structure is in the same range. Through this comparative study anionic sandwich complexes containing the [Ln(COT°)]⁻ anions have now become available for the entire series of rare-earth metals. This should allow for more detailed investigations e.g. of the magnetic properties in the course of future studies.

4. Experimental section

4.1 General procedures

All operations were performed with rigorous exclusion of air and water in oven-dried or flame-dried glassware under an inert atmosphere of dry argon, employing standard Schlenk, high-vacuum and glovebox techniques (MBraun MBLab; <1 ppm O₂, <1 ppm H₂O). THF, DME, toluene, and cyclopentane were dried over sodium/benzophenone and freshly distilled under a nitrogen atmosphere prior to use. All glassware was oven-dried at 120 °C for at least 24 h, assembled while hot, and cooled under high vacuum, prior to use. The starting materials, anhydrous LnCl₃ (Ln = Ce, Nd), ThCl₄, UCl₄, C₈H₈(SiMe₃)₂, Li₂(COT°)₂, and K₂COT°° were prepared according to the published procedures. The NMR spectra were recorded in C₆D₆ or d₈-THF solutions on a Bruker AVANCE 600 (¹H: 600.1 MHz; ¹³C: 150.9 MHz) or a Bruker AVANCE 400 (5 mm WB, ¹H: 400.1 MHz; ¹³C: 100.6 MHz) (Ln compounds), or a Bruker-AVANCE 250 (5 mm TBI, ¹H: 250.1 MHz; ¹³C: 62.5 MHz) (An compounds). ¹H and ¹³C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. IR (KBr) spectra were recorded using a Perkin-Elmer FT-IR 2000 spectrometer. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 2 spectrometer. Mass spectra (EI, 70 eV) were run on a MAT 95 apparatus. Microanalyses of the compounds were performed.
using a Leco CHNS 932 apparatus. Metal analyses were performed via ICP AES.

2.4 Preparation of the anionic lanthanide sandwich complexes 1–8 (general synthetic protocols)

(a) DME solvates [Li(DME)]\([\text{Ln} \cdot \text{C}_8\text{H}_6(\text{SiMe}_3)_2]\] (Ln = Y (1), La (2), Pr (3), Gd (4), Tm (6), Lu (8)). \(\text{Li}_2\text{(COT)}\) was prepared in situ by adding 15.0 mL (24.0 mmol) of a 1.6 M \(n\)-butyllithium solution in \(n\)-hexane at r.t. to a solution of 3.0 g (12.0 mmol) \(\text{C}_6\text{H}_5\text{Li}\) in 150 mL of THF. 6.0 mmol of anhydrous LnCl\(_3\) were added as a solid, the reaction mixture was stirred for 24 h and the solvents were completely removed under vacuum. The solid residue was extracted with 150 mL of toluene. After filtration, the toluene was again completely removed under vacuum and replaced by 30 mL of DME. After addition of the same amount of \(n\)-pentane, the products [Li(DME)]\(\cdot\) [\(\text{C}_6\text{H}_5\text{Li}\)]\(\cdot\) [\(\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}\)] crystallized upon standing at room temperature for a few days.

(b) THF solvates [Li(THF)]\([\text{Ln} \cdot \text{C}_8\text{H}_6(\text{SiMe}_3)_2]\] (Ln = Ho (5), Tm (7)). The reactions were carried out exactly in the same manner as described above. After extraction of the products with toluene and filtration, the volume of the solution was reduced to ~20 mL. The products [Li(THF)]\(\cdot\) [\(\text{C}_6\text{H}_5\text{Li}\)]\(\cdot\) [\(\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}\)] crystallized directly upon standing at room temperature for a few days.

3.1 Elemental analysis calculd. for \(\text{C}_{40}\text{H}_{78}\text{Li}_6\text{O}_6\text{Si}_4\text{Y}\) (\(M = 931.59\) g mol\(^{-1}\)) = C, 51.57; H, 8.44. Found: C, 50.83; H, 8.59%. IR (KBr disc): \(\nu = 3788\) w, 3546 v, 3220 w, 2997 v, 2953 s, 2897 m, 2829 m, 2540 w, 2101 v, 1959 w, 1871 w, 1800 v, 1753 v, 1637 w, 1599 w, 1437 w, 1441 m, 1410 m, 1369 w, 1310 w, 1248 s, 1192 w, 1124 m, 1086 m, 1066 m, 1053 m, 1028 w, 982 w, 933 m, 909 m, 837 v, 782 w, 769 v, 750 m, 717 m, 680 w, 651 s, 636 w, 548 w, 521 w, 451 w, 459 w, 421 w cm\(^{-1}\). NMR data could not be obtained for [Li(DME)]\(\cdot\) [\(\text{C}_6\text{H}_5\text{Li}\)]\(\cdot\) [\(\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}\)] due to the paramagnetic character of the Ga\(^{3+}\)-ion. MS (EI): \(m/z = 637 (4\%), [\text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\) ppm. 29Si NMR (79.5 MHz, \(d_8\)-toluene, 24 °C): \(\delta = 0.55\) ppm. MS (EI): \(m/z = 637 (1\%), [\text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\) ppm. 29Si NMR (79.5 MHz, \(d_8\)-toluene, 24 °C): \(\delta = 0.55\) ppm. MS (EI): 

3.2 Elemental analysis calculated. for \(\text{C}_{40}\text{H}_{78}\text{Li}_6\text{O}_6\text{Si}_4\text{Ho}\) (\(M = 943.27\) g mol\(^{-1}\)) = C, 53.52; H, 8.33. Found: C, 50.50; H, 7.95%. IR (KBr disc): \(\nu = 3469\) w, 3222 w, 2994 m, 2956 s, 2897 m, 2835 v, 2100 v, 1959 w, 1868 w, 1757 v, 1638 w, 1599 w, 1452 w, 1405 v, 1370 w, 1312 w, 1248 s, 1210 v, 1193 w, 1181 v, 1156 w, 1124 w, 1086 m, 1065 m, 1052 m, 1028 w, 981 w, 932 w, 837 v, 783 v, 750 m, 716 m, 690 w, 681 w, 651 w, 565 v, 514 w, 404 v, 478 w, 459 w, 423 w cm\(^{-1}\). NMR data could not be obtained for [Li(DME)]\(\cdot\) [\(\text{C}_6\text{H}_5\text{Li}\)]\(\cdot\) [\(\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}\)] due to the paramagnetic character of the Ho\(^{3+}\)-ion. MS (EI): \(m/z = 662 (5\%), [\text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\) ppm. 29Si NMR (79.5 MHz, \(d_8\)-toluene, 24 °C): \(\delta = 2.31\) ppm. MS (EI): \(m/z = 662 (5\%), [\text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\cdot [\text{Li} \cdot \text{C}_6\text{H}_5\text{Li}]\) ppm. 29Si NMR (79.5 MHz, \(d_8\)-toluene, 24 °C): \(\delta = 2.31\) ppm.
uranium complex

single-crystals were obtained by recrystallization in a closed identical conditions as described for Th led to the formation of $^{10}$THF. Due to the high solubility of all reactants the reactions were treated with 2.05 equiv. of freshly prepared Li$_2$(COT$_8$-pentane (20 mL) was added, yielding an intense yellow solution $^{10}$C NMR (CDCl$_3$): $\delta = 325.9$ (CH$_3$), 293.8, 270.3 (CH), 692, 674w, 651w, 624w, 556w, 503w, 478w, 459w, 427w cm$^{-1}$. $^{1}H$ NMR (CDCl$_3$): $\delta$ = 3.39 (s, 12H, DME), 3.25 (s, 18H, DME), 0.43 (s, 36H, Si(C$_8$H$_6$)).

4.4 Preparation of the actinide sandwich complexes

The two polysilylated actinidocenes 11 and 12 were prepared by treatment of AnCl$_3$ (An = Th, U) with 2 equiv. of K$_2$(COT$^+$)$^2$, following the procedure reported by Edelmann and Kannelakopulos et al. (cf. Scheme 5).$^{24b}$ Bright yellow 11 and dichroitic red/green 12 were isolated in high yields of around 80% after recrystallization from n-pentane.

4.5 Crystal structure determination

The intensity data of the lanthanide sandwich complexes 1–8 were collected on a Stoe IPDS 2T diffractometer with MoK$_\alpha$ radiation. The data were collected with the Stoe XAREA program using $\omega$-scans.$^{19}$ The space groups were determined with the XRED32 program. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on $F^2$ using SHELXL-97.$^{40}$ Data collection parameters are summarized in Tables 1 and 2.

4.3 Preparation of the actinide sandwich complexes

An(COT$^+$)$^2$ (An = Th (9), U (10)) (general synthetic protocol)

$\sim$200 mg of anhydrous AnCl$_4$ (An = Th, U; $\sim$0.5 mmol) were treated with 2.05 equiv. of freshly prepared Li$_2$(COT$^+$) in 25 mL of THF. Due to the high solubility of all reactants the reactions were finished after 2 h stirring at r.t. The solvent was evaporated and n-pentane (20 mL) was added, yielding an intense yellow solution (Th) and a red-green solution for the U complex 10. Filtration and removal of the solvents afforded the crude complexes in $\sim$80% yield. From the yellowish thorium complex 9 (m.p. 135 °C) single-crystals were obtained by recrystallization in a closed ampule at 240 °C under high vacuum. From the oily, crude uranium complex 10, single-crystals grew in the refrigerator during storage at 4 °C for several months. Sublimation under identical conditions as described for Th led to the formation of red crystals in a green oil.

Th$_2$(C$_8$H$_6$(SiMe$_3$)$_2$)$_3$ (9). Elemental analysis calc. for C$_{28}$H$_{48}$Si$_4$Th ($M_e$ = 729.07 g mol$^{-1}$): C, 46.13; H, 6.64; Th, 31.83. Found: Th, 32.0%. IR (KBr disc): $\nu$ = 3063w, 3002m, 2954m, 2895m, 1447w, 1403w, 1382w, 1370w, 1330w, 1302w, 1249w, 1191w, 1051w, 1042w, 1018m, 988m, 964m, 926m, 838vs br, 812m, 806m, 780w, 750s, 720s, 710m, sh, 699w, 661w, 633m, 470w, 347m, 302m, 241m cm$^{-1}$. $^{1}H$ NMR (CDCl$_3$): $\delta$ = 6.86 (m, 12H, CH), 0.60 (br, 36H, CH$_2$) ppm. $^{13}C$ NMR (CDCl$_3$): $\delta$ = 113.1, 112.3, 110.0 (CH), 0.9 (CH$_3$) ppm.

U$_2$(C$_8$H$_6$(SiMe$_3$)$_2$)$_3$ (10). Elemental analysis calc. for C$_{28}$H$_{48}$Si$_4$U ($M_e$ = 735.06 g mol$^{-1}$): C, 45.75; H, 6.58; U, 32.38. Found: U, 31.9%. IR (KBr disc): $\nu$ = 3031w, 2999m, 2956m, 2896m, 1586w, 1445w, 1403w, 1247s, 1081w, 1066w, 1038s, 977m, 940m, 931m, 900m, 838vs, br, 793w, 750s, 742m, 710m, sh, 691w, 651w, 633m, 540w, 502w, 478w, 458w, 422w, 338m, 303m, 283m, 249m cm$^{-1}$. UV-vis (Et$_2$O, $\lambda$, nm ($\epsilon$, cm$^{-1}$ mol$^{-1}$)) = 360, 380, 530, 520, 537, 567, 592(1461), 618(438), 635(195), 691(20), 732(19), 980(17), 1322(4), 1479(7), 1710(1), 1755(1), 1793(1), 1865(6) nm. $^{1}H$ NMR (CDCl$_3$): $\delta$ = −9.99 (36H, CH$_3$), −25.20 (4H, CH), −39.63 (4H, CH), −45.62 (4H, CH) ppm. $^{13}C$ NMR (CDCl$_3$): $\delta$ = 325.9 (CH$_3$), 293.8 (CH$_3$), −3.5 (CH$_3$) ppm.

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