NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Full Paper submitted to *New Journal of Chemistry*

One ligand fits all: Lanthanide and actinide sandwich complexes comprising the 1,4-bis(trimethylsilyl)cyclooctatetraenyl (= COT'') ligand‡

Janek Rausch,[a] Christos Apostolidis,*[b] Olaf Walter,[b] Volker Lorenz,[a] Cristian G. Hrib,[a] Liane Hilfert,[a] Marcel Kühling[a] and Frank T. Edelmann*[a]

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 treatment of $LnCl_3$ with 2 equiv. of *in situ*-prepared Li_2COT'' in either DME (= 1,2-dimethoxyethane) or THF. The neutral actinide sandwich complexes $An(COT'')_2$ (An = Th (**9**), U (**10**)) and $An(COT''')_2$ (COT''' = 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl dianion; An = Th (**11**), U (**12**)) were synthesized in a similar manner starting from $ThCl_4$ or UCl_4, 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 Ln^{3+} ionic radii from La^{3+} to Lu^{3+} are isostructural (space group P-1). Compound **10** is the first uranocene derivative for which ^{13}NMR data are reported.

New Journal of Chemistry Accepted Manuscript

---

[a] *Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany. E-mail: frank.edelmann@ovgu.de.; Fax: +49 391 6712933; Tel: +49 391 6758327*

[b] *European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany. E-mail: christos.apostolidis@ec.europa.eu.*

‡ Electronic supplementary information (ESI) available: CIF files of the X-ray structural data for all compound reported in this work. CCDC 1052366-1052372 (**1-8**) and CCDC 1049924-1049927 (**9-12**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/

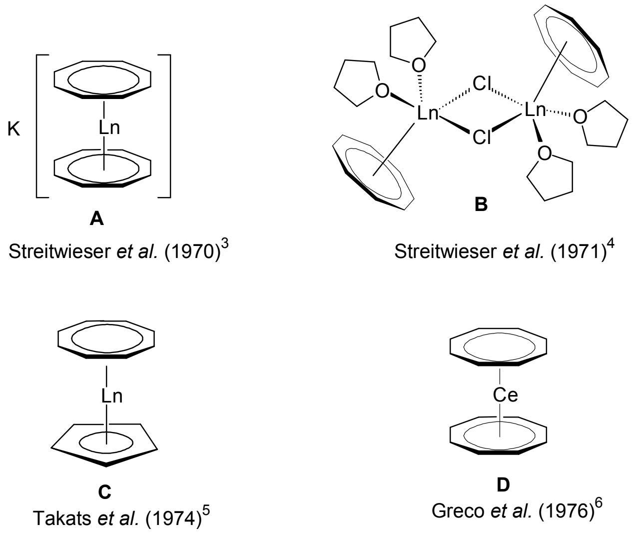
Dedicated to Professor Basil Kanellakopulos on the occasion of his 80th birthday

New Journal of Chemistry Accepted Manuscript

New Journal of Chemistry Accepted Manuscript

1. Introduction

Second only to the omnipresent cyclopentadienyl complexes, the dianionic 10π-cyclooctatetraenyl ligand $C_8H_8^{2-}$, 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 $C_8H_8^{2-}$ ring is ideally suited for overlapping with the *f*-orbitals of the large lanthanide and actinide ions.[1] Early work in this area was mainly focused on complexes bearing unsubstituted COT ligands.[2] Scheme 1 shows some prototypical lanthanide COT complexes which are considered milestones in the development of organolanthanide chemistry with COT ligands. Notable are the anionic sandwich complexes K[Ln(COT)$_2$] (**A**),[3] the dimeric half-sandwich mono(cyclooctatetraenyl)lanthanide chlorides [(COT)Ln(*μ*-Cl)(THF)$_2$]$_2$ (**B**),[4] the mixed-sandwich complexes (COT)LnCp (**C**),[5] and the so-called cerocene, Ce(COT)$_2$ (**D**).[6] The chemistry of such lanthanide COT complexes has already been summarized in several comprehensive review articles.[2,7]



A
Streitwieser *et al.* (1970)[3]

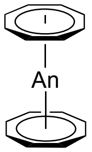
B
Streitwieser *et al.* (1971)[4]

C
Takats *et al.* (1974)[5]

D
Greco *et al.* (1976)[6]

Scheme 1 Prototypical lanthanide COT sandwich and half-sandwich complexes.

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 actinidocenes An(C_8H_8)$_2$ (Scheme 2; An = Th, Pa, Np, Pu) have also been reported.[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 5*f* and 6*d* orbitals in the uranium-cyclooctatetraenyl bonding. Recent work by Ephritikhine and co-workers has demonstrated that the chemistry of actinidocenes continues to produce very interesting results.[13]



An = Th, Pa, U, Np, Pu

Scheme 2 Schematic representation of the neutral actinidocenes $An(C_8H_8)_2$ (An = Th, Pa, U, Np, Pu).

In general, the use of the unsubstituted COT ligand in organolanthanide and -actinide chemistry has several disadvantages in terms of low solubility and/or poor crystallinity. For example, the most important series of precursors in lanthanide COT chemistry, the chloro-bridged mono(COT) dimers $[(COT)Ln(\mu\text{-}Cl)(THF)_2]_2$ (Scheme 1, **B**),[4] lack good solubility even in THF. Moreover, commercially available cyclooctatetraene is very expensive. As a consequence, more soluble alternative starting materials such as $(COT)LnI(THF)_n$ (Ln = Tm, $n = 2$; Ln = La, Ce, Pr, Nd, Sm, $n = 3$)[2,8] and $[(COT)Ln(\mu\text{-}O_3SCF_3)(THF)]_2$ (Ln = Ce, Pr, Nd, Sm)[9] have been reported in the literature, but their use as precursors in organolanthanide chemistry still remains limited.[2] More recently, lanthanide COT chemistry received fundamental new impulses through the use of bulky silyl-substituted cyclooctatetraenyl ligands. The initial idea originated from the pioneering work of Cloke *et al.*, who first employed the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (= COT'') in organo-*f*-element chemistry.[10] In many cases, using the bulky COT'' ligand did in fact improve the solubility of the products, but occasionally also led to novel molecular structures and coordination geometries.[7g,10,14] Typical examples include the unprecedented cluster-centered Pr/Li multidecker sandwich complex of the composition $[Pr(COT'')]_2[Pr_2(COT'')_2]_2Li_2(THF)_2Cl_8$[15] as well as the first linear rare-earth metal triple-decker complexes, $Ln_2(COT'')_3$ (Ln = Nd, Gd, Gy, Ho, Er).[14,16-18] Previously reported anionic lanthanide sandwich complexes comprising $[Ln(COT'')_2]^-$ anions include the THF solvates $[Li(THF)_4][Ln(COT'')_2]$ with Ln = Y,[19] Ce,[19] Pr,[19] Nd,[14,19] Sm,[19] Gd[17] and Dy[17] as well as the DME adducts $[Li(DME)_3][Ln(COT'')_2]$ (Ln = Ce,[14,20] Dy,[17] Er[21]), $Li(DME)Tb(COT'')_2$[22] and $Li(THF)(DME)Dy(COT'')_2$.[23] A notable neutral lanthanide sandwich complex containing COT'' is the cerocene derivative $Ce(COT'')_2$.[24] Sterically even more demanding is the 1,3,6-

New Journal of Chemistry Accepted Manuscript

tris(trimethylsilyl)cyclooctatetraenyl dianion ligand (= COT'''), which has also been successfully employed in organolanthanide[24-26] and -actinide chemistry.[24,27]

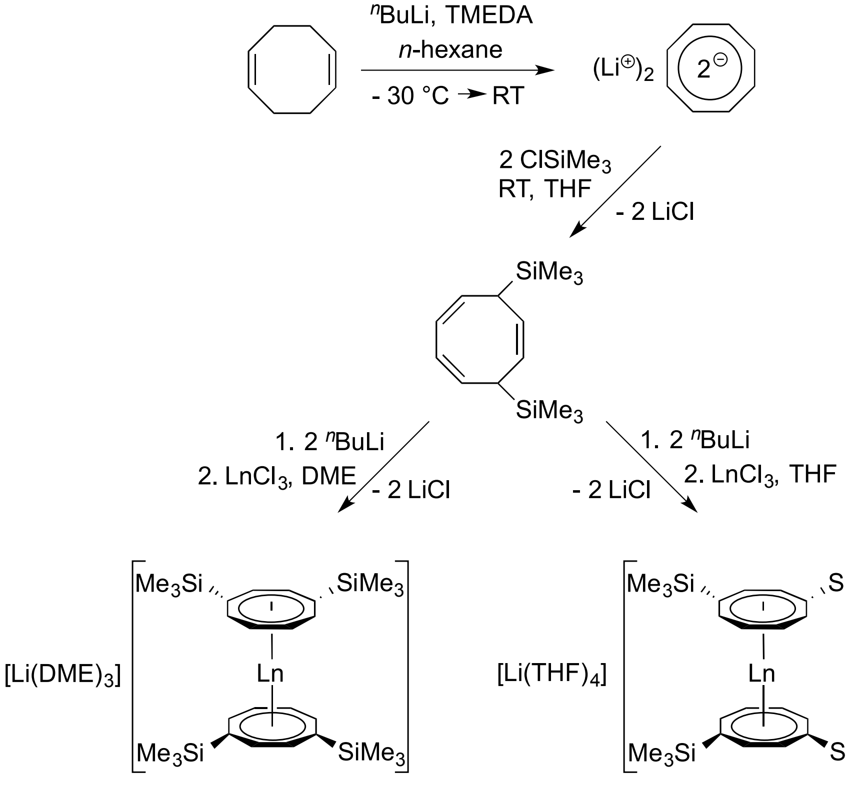
Recent findings by Murugesu and co-workers revealed that some of the anionic $[Ln(COT'')_2]^-$ sandwich complexes behave as organometallic single-molecule magnets.[17,20,21,23] Due to the renewed interest in this class of compounds, we carried out a broader investigation of lanthanide and actinide COT'' sandwich complexes. In this contribution we report the synthesis and structural characterization of the new anionic lanthanide sandwich complexes $[Li(DME)_3][Ln(COT'')_2]$ (Ln = Y (**1**), La (**2**), Gd (**4**), Tm (**6**), Lu (**8**)) and $[Li(THF)_4][Ln(COT'')_2]$ (Ln = Pr (**3**), Ho (**5**), Tm (**7**)) as well as the neutral actinide sandwich complexes $An(COT'')_2$ (An = Th (**9**), U (**10**)) and $An(COT''')_2$ (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(III) sandwich complex $[Li(DME)_3][U(COT'')_2]$ and the isostructural and isoelectronic lanthanide analogue $[Li(DME)_3][Nd(COT'')_2]$. This work also included the synthesis and structural characterization of the neutral uranocene derivative $U(COT'')_2$ (**10**), although its preparation involved a different synthetic route (*vide infra*).[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 et al.[10] The dilithium reagent Li_2COT'' can be conveniently prepared by metalation of 1,4-bis(trimethylsilyl)cycloocta-2,5,7-triene with *n*-butyllithium,[10] and the resulting solutions can be used *in situ* for further reactions. However, it is also possible to isolate crystalline adducts of Li_2COT'', *e.g.* $[Li(TMEDA)]_2(COT'')$ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine),[10c] $[Li(DME)]_2(COT'')$,[28a] and $[Li(THF)_2]_2[Li_2(COT'')_2]$.[28b] The latter two adducts have been structurally characterized through X-ray diffraction. $[Li(TMEDA)]_2(COT'')$ was shown to be an inverse sandwich complex with the two Li^+ ions coordinated to the bridging 1,4-bis(trimethylsilyl)cyclooctatetraene dianion ring in an η^3-allyl-like fashion.[28a] $[Li(THF)_2]_2[Li_2(COT'')_2]$ contains two Li^+ ions sandwiched between two COT'' rings and two $Li(THF)_2^+$ units attached to the outside of the COT'' rings.[28b] In the present study, however, it was found to be more convenient to use *in situ*-prepared THF solutions of Li_2COT'' rather than isolated samples. Accordingly, the anionic lanthanide sandwich complexes **1-8** were prepared by treatment of selected anhydrous lanthanide trichlorides, $LnCl_3$, with 2 equiv. of Li_2COT'' in THF solution as outlined in Scheme 3. In the case of the THF adducts

New Journal of Chemistry Accepted Manuscript

[Li(THF)$_4$][Ln(COT'')$_2$] (Ln = Ho (**5**), Tm (**7**)), 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 (57-75%) in the form of yellow or yellow-green, highly air-sensitive crystalline solids. It has been noted earlier that DME is the solvent of choice for crystallizing these anionic lanthanide sandwich complexes.[14,20] The DME solvates are readily crystallized and the resulting crystals do not lose DME even under vacuum or upon prolonged storage in the dry-box. In contrast, crystals of the THF adducts are less stable with respect to loss of solvent and become opaque upon storing in the dry-box.



Ln = Y (**1**), La (**2**), Pr (**3**), Gd (**4**), Tm (**6**), Lu (**8**)　　Ln = Ho (**5**), Tm (**7**)

Scheme 3 Synthetic route to the anionic lanthanide sandwich complexes **1-8**.

Meaningful NMR spectra could be obtained only for the diamagnetic products [Li(DME)$_3$][Y(COT'')$_2$] (**1**), [Li(DME)$_3$][La(COT'')$_2$] (**2**), and [Li(DME)$_3$][Lu(COT'')$_2$] (**8**) as well as for the paramagnetic praseodymium derivative **3**. In all four cases the ^{1}H and ^{13}C NMR data were in good agreement with the formation of the expected anionic sandwich complexes. The observation of only one signal in the ^{29}Si NMR spectra (**1**: 0.7 ppm, **2**: 0.5 ppm, **3**: -46 ppm, **8**: 0.8 ppm) indicated high purity of the materials. Moreover, the IR spectra

New Journal of Chemistry Accepted Manuscript

of the DME adducts on one hand and the THF adducts on the other hand were found to be almost superimposable. All new complexes were structurally characterized through single-crystal X-ray crystallography. Crystallographic data for **1-8** are summarized in Tables 1 and 2. The most significant bond lengths and angles are listed in Table 3.

Table 1. Crystallographic Data for **1 - 6**.

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{40}H_{78}LiO_6Si_4Y$	$C_{40}H_{78}LaLiO_6Si_4$	$C_{40}H_{78}LiO_6PrSi_4$	$C_{40}H_{78}GdLiO_6Si_4$	$C_{44}H_{80}HoLiO_4Si_4$	$C_{40}H_{78}LiO_6Si_4Tm$
a (Å)	11.445(2)	11.557(2)	11.532(2)	11.428(2)	11.358(2)	11.410(2)
b (Å)	12.219(2)	12.262(3)	12.286(3)	12.216(2)	11.657(2)	12.239(2)
c (Å)	18.477(4)	18.340(4)	18.388(4)	18.406(4)	19.603(4)	18.503(4)
α (°)	99.13(3)	98.83(3)	98.82(3)	98.84(3)	87.12(3)	99.12(3)
β (°)	102.20(3)	102.56(3)	102.49(3)	102.36(3)	82.38(3)	102.17(3)
γ (°)	99.68(3)	98.57(3	99.04(3)	99.44(3)	77.39(3)	100.11(3)
V (Å^3)	2438.7(8)	2461.6(9)	2464.1(9)	2428.0(8)	2509.9(9)	2434.9(8)
Z	2	2	2	2	2	2
formula weight	863.23	913.23	915.23	931.57	957.31	943.25
space group	P-1	P-1	P-1	P-1	P-1	P-1
T (°C)	153(2)	133(2) K	153(2)	133(2)	153(2)	153(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calcd} (g cm^{-3})	1.176	1.232	1.234	1.274	1.267	1.287
μ (mm^{-1})	1.332	1.003	1.124	1.503	1.707	1.959
R(Fo or Fo^2)	0.0467	0.0381	0.0267	0.0333	0.0491	0.0319
R_w(Fo or Fo^2)	0.1018	0.0944	0.0662	0.0883	0.0859	0.0771

New Journal of Chemistry Accepted Manuscript

Table 2. Crystallographic Data for **7** - **12**.

	7	**8**	**9**	**10**	**11**	**12**
Empirical formula	$C_{44}H_{80}LiO_4Si_4Tm$	$C_{40}H_{78}LiLuO_6Si_4$	$C_{28}H_{48}Si_4Th$	$C_{28}H_{48}Si_4U$	$C_{34}H_{64}Si_6Th$	$C_{34}H_{64}Si_6U$
a (Å)	11.358(2)	11.471(2)	9.830(3)	12.6598(12)	20.9990(12)	23.381(3)
b (Å)	11.657(2)	12.051(2)	9.898(3)	20.3542(18	25.1674(15)	21.170(3)
c (Å)	19.603(4)	18.459(4)	17.038(5)	24.645(2)	17.8458(10)	18.125(2)
α (°)	87.12(3)	99.79(3)	79.262(4)	90	90	90
β (°)	82.38(3)	101.72(3)	80.692(4)	90	114.3160(10)	107.923(2)
γ (°)	77.39(3)	100.05(3)	80.891(3)	90	90	90
V (Å^3)	2509.9(9)	2403.6(8)	1.5932(8)	6350.6(10)	8594.7(9)	8536.3(18)
Z	2	2	2	8	8	8
formula weight	961.31	949.29	729.06	735.05	873.43	879.42
space group	P-1	P-1	P-1	Pbca	C2/c	$P2_1/c$
T (K)	153(2)	143(2)	100(2)	173(2)	200(2)	200(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calcd} (g cm^{-3})	1.272	1.312	1.520	1.538	1.350	1.369
μ (mm^{-1})	1.899	2.192	4.845	5.277	3.657	3.991
R(Fo or Fo^2)	0.0390	0.0557	0.0472	0.0238	0.0301	0.0421
R_w(Fo or Fo^2)	0.1015	0.1473	0.1084	0.0838	0.0675	0.1127

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

	Y (**1**)	La (**2**)	Pr (**3**)	Gd (**4**)	Ho (**5**)	Tm (**6**)	Tm (**7**)	Lu (**8**)
Ln-C	2.649	2.785	2.740	2.680	2.607	2.624	2.615	2.609
C-C	1.413	1.414	1.414	1.416	1.414	1.417	1.414	1.412
Si-C	1.865	1.867	1.866	1.867	1.868	1.867	1.868	1.864
Li-O	2.135	2.133	2.134	2.134	1.921	2.135	1.919	2.123
Ln-*Ctr*	1.900	2.084	2.020	1.940	1.873	1.861	1.850	1.845
Ctr-Ln-*Ctr*	176.19	175.59	175.80	175.74	177.6	176.6	177.8	176.86

All eight lanthanide complexes were found to form large crystals quite readily. X-ray quality single-crystals of the DME solvates $[Li(DME)_3][Ln\{C_8H_6(SiMe_3)_2\}_2]$ (Ln = Y (**1**), La (**2**), Pr (**3**), Gd (**4**), Tm (**6**), Lu (**8**) were obtained by recrystallization from solvent mixtures of DME and *n*-pentane (1:1) at room temperature. Single-crystals of the THF adducts $[Li(THF)_4][Ln(COT'')_2]$ (Ln = Ho (**5**), Tm (**7**)) were grown from concentrated solutions in THF at r.t. The molecular structure of the THF adduct $[Li(THF)_4][Ho(COT'')_2]$ (**5**) is shown

New Journal of Chemistry Accepted Manuscript

in Figure 1, and Figure 2 shows the molecular structure of [Li(DME)$_3$][Lu(COT")$_2$] (**8**) as a representative DME adduct.

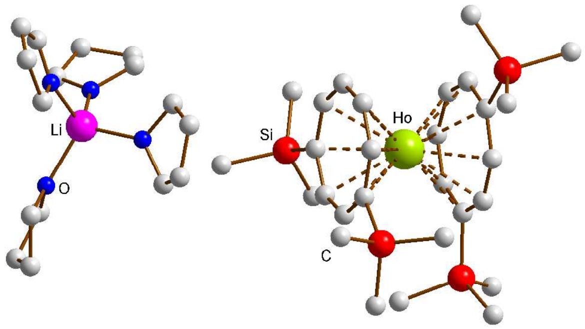


Figure 1 Molecular structure of [Li(THF)$_4$][Ho(COT")$_2$] (**5**).

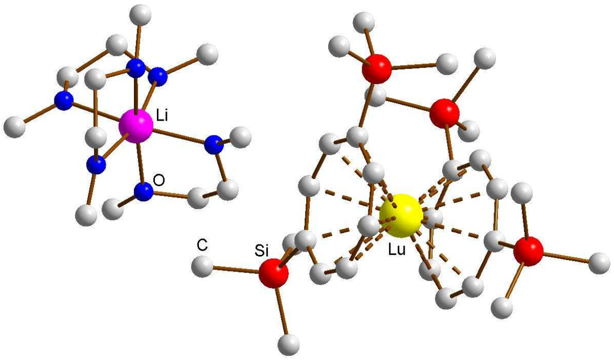


Figure 2 Molecular structure of [Li(DME)$_3$][Lu(COT")$_2$] (**8**).

As can be seen from Table 3, the average Ln-C bond lengths vary between 2.785 Å in the lanthanum complex **2** to 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,[14,20] Pr (**3**), Nd,[27] Gd (**4**), Dy,[17] Er,[21] Tm (**6**), Lu (**8**)) and also the recently reported [Li(DME)$_3$][U(COT")$_2$][27] crystallize in the triclinic space group P-1 and are isostructural. The same can be said about the series of known [Li(THF)$_4$][Ln(COT")$_2$] complexes,[14,17,19]

New Journal of Chemistry Accepted Manuscript

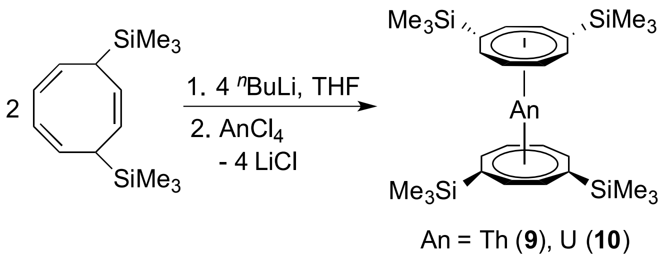
including the new derivatives $[Li(THF)_4][Ho(COT'')_2]$ (**5**) and *(b)* $[Li(THF)_4][Tm(COT'')_2]$ (**7**). The *Ctr*-Ln-*Ctr* angles (*Ctr* = ring centroid) are found to be in the very narrow range between 177.8° for $[Li(THF)_4][Tm(COT'')_2]$ (**7**) and 175.59° for $[Li(DME)_3][Ln(COT'')_2]$ (**2**). Thus there is onle little deviation from the ideal linear sandwich arrangement. Clearly the bulky cyclooctatetraenyl ligand COT" is ideally suited for studying homologous series of lanthanide and actinide sandwich complexes comprising the full range of ionic radii possible. Table 4 provides an overview of all anionic lanthanide sandwich complexes of the types $[Li(THF)_4][Ln(COT'')_2]$ and $[Li(DME)_3][Ln(COT'')_2]$ reported thus far in order to show which gaps have been filled by the present study.

Table 4 Overview of all known anionic lanthanide sandwich complexes of the type $[Li(THF)_4][Ln(COT'')_2]$ (denoted THF) and $[Li(DME)_3][Ln(COT'')_2]$ (denoted DME). Blue boxes: Compounds rescribed in this work.

Ln	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
THF	X[19]		X[19]	X[19]	X[14,19]	X[19]		X[17]		X[17]	X		X		
DME	X	X	X[14,20]	X				X		X[17]		X[21]	X		X

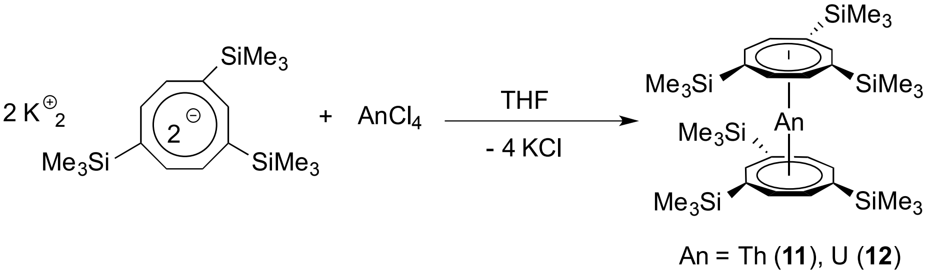
In a similar manner, the closely related neutral actinidocenes $An(COT'')_2$ (An = Th (**9**), U (**10**)) have also been prepared. As outlined in Scheme 4, these sandwich complexes were made in a straightforward manner by reaction of anhydrous $ThCl_4$ or UCl_4 with 2 equiv. of *in situ*-prepared Li_2COT''. Due to the high solubility of all the reactants in THF, the reactions were finished after 2 h stirring at r.t. In contrast, reactions of $AnCl_4$ with the unsubstituted K_2COT normally take days.[11,12] Bright yellow $Th(COT'')_2$ (**9**) and dark green (dichroitic red/green) $U(COT'')_2$ (**10**) were both isolated in high yields of ca. 80%. Purification could be achieved either by high-vacuum sublimation at 240 °C or by slow crystallization from the oily crude products. In this context it is interesting to note that Murugesu *et al.* very recently prepared compound **10** *via* a two-step synhesis where $U^{III}I_3(1,4\text{-dioxane})_{1.5}$ and $[Li(THF)_2]_2[Li_2(COT'')_2]$[28b] were first combined in THF to afford the anionic uranium(III) sandwich complex $[Li(DME)_3][U(COT'')_2]$ which was then oxidized to the uranium(IV) sandwich **10** using $FeCl_2$.[27]

New Journal of Chemistry Accepted Manuscript



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

For comparison, two neutral actinide sandwich complexes comprising the bulky 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl ligand (COT''') have also been prepared. These compounds have earlier been mentioned in two communications, but structural characterization through X-ray diffraction was lacking.[24] Both compounds were prepared according to the straightforward synthetic protocol illustrated in Scheme 5. In this case, the use of the potassium precursor K$_2$COT''' provided the products **11** and **12** in yields around 80% after crystallization from concentrated solutions in *n*-pentane. Like their tetrasubstituted congeners **9** and **10**, the 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.



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

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 Figures 3 and 4. As can bee 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 distorsion from the ideal linear arrangement with *Ctr*-M-*Ctr* angles of about 174°. As expected, evidence for actinide contraction is found

New Journal of Chemistry Accepted Manuscript

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).

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

	Th (**9**)	U (**10**)	Th (**11**)	U (**12**)
M-C	2.696- 2.745 (2.718)	2.642- 269.0 (2.663)	2.709-2.763 2.705-2.762 (2.735/2.732)	2.643-2.727 2.647-2.727 (2.679/2.681)
M-*Ctr*	1.987 1.999 (1.993)	1.921 / 1.913 (1.917)	2.012 2.010 (2.011)	1.942, 1.944 1.938, 1.945 (1.942)
Ctr-M-*Ctr*	172.9	173.0	174.3, 175.3	174.3, 174.9
Pl / *Pl*	7.1	7.4	6.3	5.7/6.0

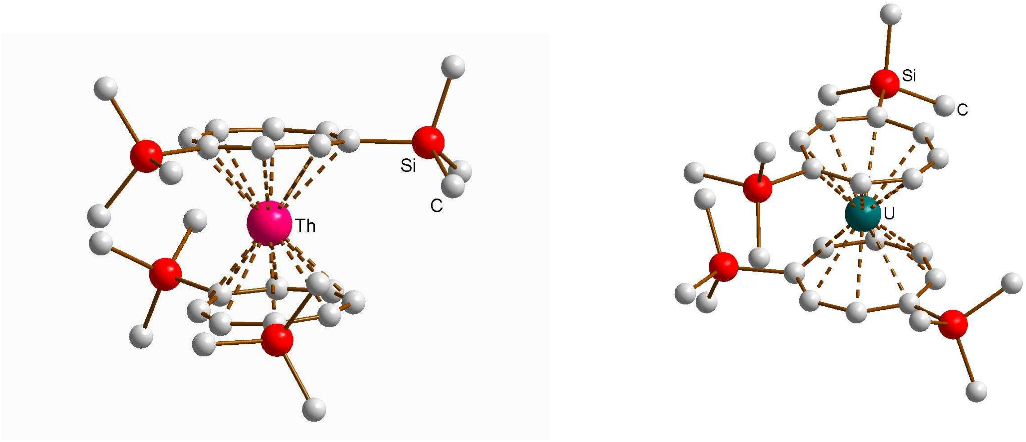


Figure 3 Molecular structures of Th(COT")$_2$ (**9**) and U(COT")$_2$ (**10**).

New Journal of Chemistry Accepted Manuscript

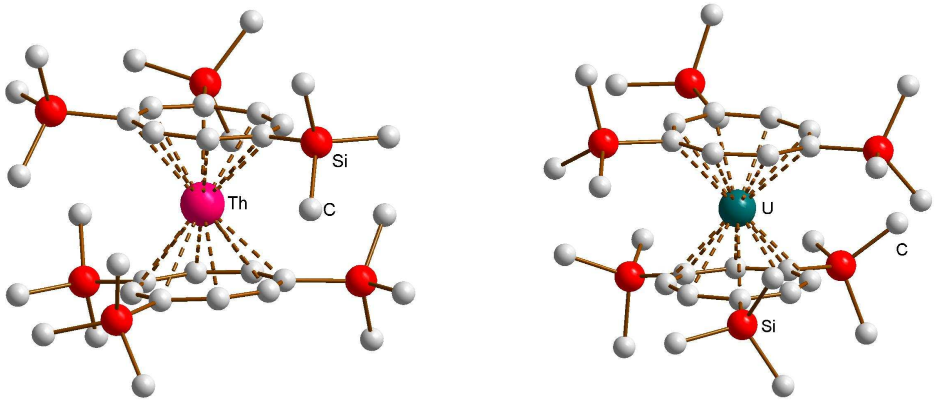


Figure 4 Molecular structures of Th(COT''')$_2$ (**11**) and U(COT''')$_2$ (**12**).

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[29] (Table 4). 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 ans 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 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, 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[29a] but with a significant distorsion caused by steric effects due to the trimethylsilyl substituents at the COT rings. A significantly stronger tilting of the two cyclooctatetraenyl rings has been

New Journal of Chemistry Accepted Manuscript

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]

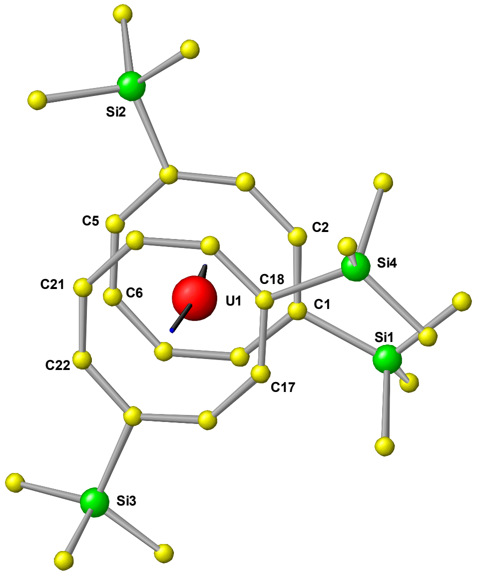


Figure 5 Top view of the molecular structure of U(COT")$_2$ (**10**).

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 actinidocenes. Frequencies arising from the COT" ligand increase slightly upon complexation as compared to K$_2$COT". However, the spectra are more complicated than those of the unsubstituted actinidocenes as the SiMe$_3$-substituents give rise to strong absorptions themselves and cause a distortion from the ideal D_{8h}-symmetry observed in the actinidocenes leading to a higher number of observed frequencies.[31] However, the general congruency of the IR and FIR spectra clearly show 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 $5f^2$-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. The absorptions at 592, 618, 635 nm are caused by strong charge transfer transitions typical for actinocene complexes, however being more intense in symmetry-distorted systems.[32] In the range from 800 to 2000 nm, the UV-vis spectrum does not show any significant differences between the solid state and the solution, indicating that the solid state structure is retained in solution and no adduct formation takes place. Accordingly, the absorptions at 980, 1322, 1486, 1710, 1755,

New Journal of Chemistry Accepted Manuscript

1793, 1865 nm are caused by *f-f* transitions which are characteristic for U(IV)-organometallics.[33] The *f-f* transitions are in this case of higher intensity than for the unsubstituted uranocene due to the observed distortion of the complex symmetry by the $SiMe_3$ substitutents which causes an increase of the intensity for the symmetry-forbidden *f-f* transitions. These are, however, between 10 to 100 times less intense than the charge transfer absorptions.

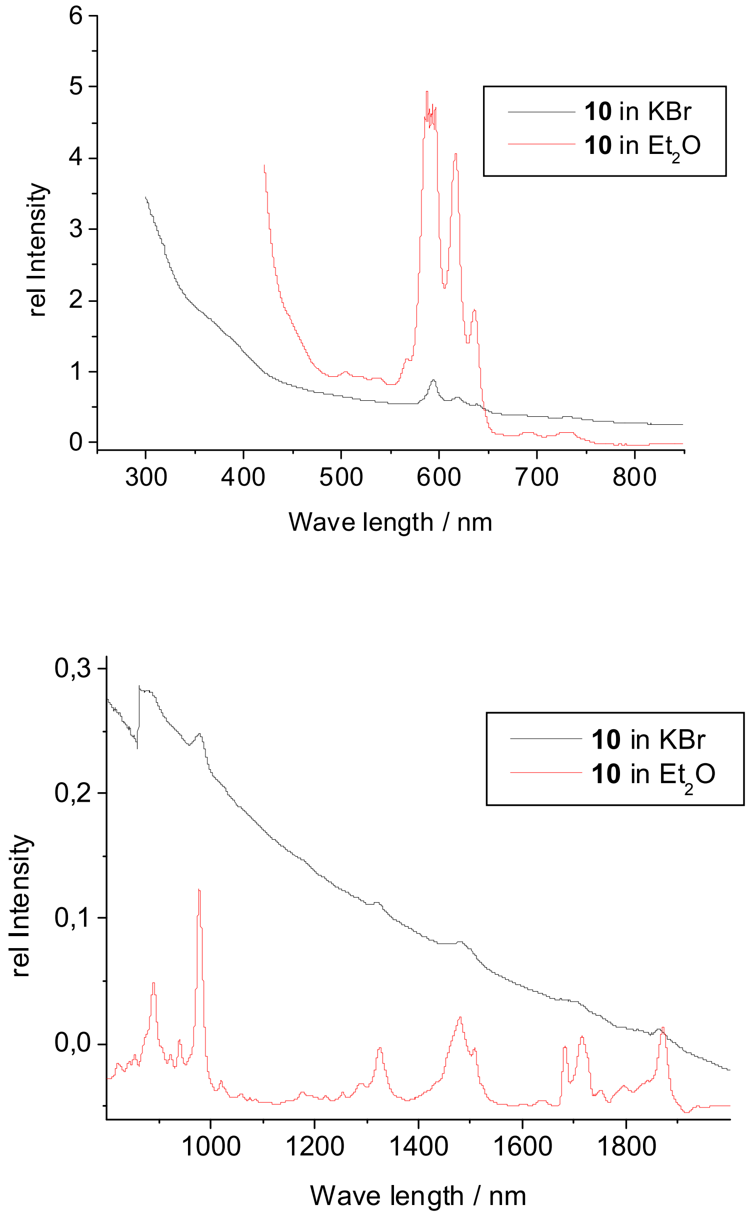


Figure 6 UV-vis spectra of U(COT")$_2$ (**10**).

New Journal of Chemistry Accepted Manuscript

The paramagnetism of **10** is also clearly seen in its NMR data (Figs. 7-9) where for all signals a typical downfield shift is observed.[7a,34] In good agreement with the solid state structure, the ^{1}H NMR spectrum of **10** (Fig. 7) shows four well-separated singlets at -9.99, -25.20, -39.63, and -45.62 ppm. The latter three each correspond to four ring protons, whereas the first resonance can be clearly assigned to the protons of the $SiMe_3$ substituents. In the two-dimensional HH-correlated spectrum the resonances at -39.63 and -45.62 ppm (*β*-position to the $SiMe_3$-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).

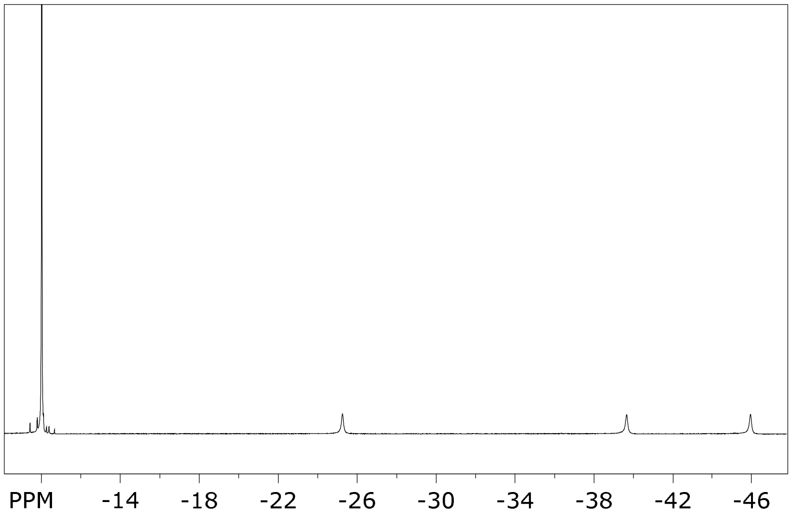


Figure 7 ^{1}H NMR spectrum of $U(COT'')_2$ (**10**).

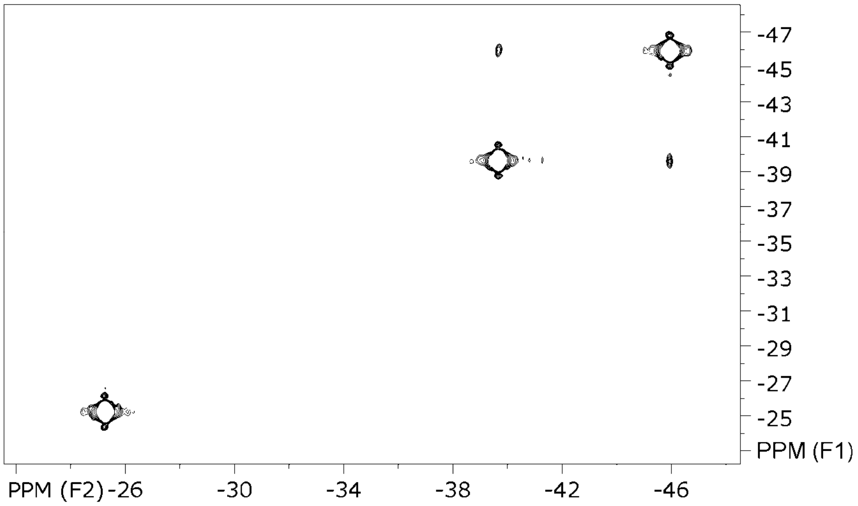


Figure 8 HH correlated NMR spectrum of $U(COT'')_2$ (**10**).

New Journal of Chemistry Accepted Manuscript

This assignment is in good agreement with published data where a strong influence of the paramagnetism on the chemical shifts in uranocene derivatives is described.[34] However, in this paper for the first time the ^{13}C chemical shifts of a uranocene complex are reported. The carbon resonance of the $SiMe_3$ groups was localized at -3.5 ppm. The proton resonance at -25.20 ppm exhibits a cross peak at 325.9 ppm in the ^{13}C 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.[35]

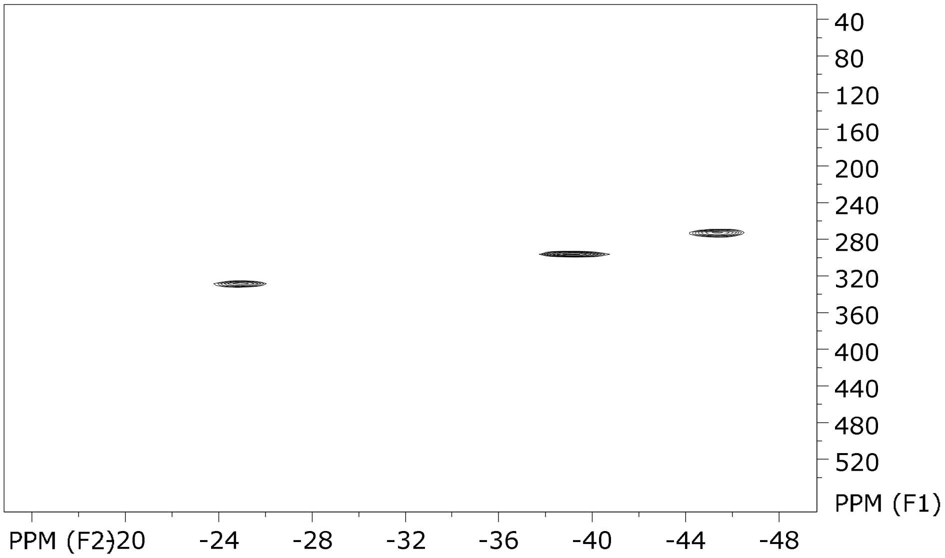


Figure 9 CH correlated NMR spectrum of $U(COT'')_2$ (**10**).

3. Conclusions

In summarizing the results reported here, 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 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 (Ln^{3+}/An^{4+}) 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), $[Li(THF)_4]$-$[Ln(COT'')_2]$ (**5**, **7**; Ln = Ho Tm), $An(COT'')_2$ (**9**, **10**; An = Th, U) and $An(COT''')_2$ (**11**, **12**; An = Th, U). In all cases the slight deviation from from the ideal sandwich structure is in the same range. Through this comparative study anionic sandwich complexes containing the $[Ln(COT'')_2]^-$ 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.

New Journal of Chemistry Accepted Manuscript

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 O_2, <1 ppm H_2O). THF, DME. toluene, and cyclopentane were dried over sodium/benzophenone and freshly distilled under 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 $LnCl_3$ (Ln = Ce, Nd),[36] $ThCl_4$,[37] UCl_4,[38] $C_8H_8(SiMe_3)_2$,[10] Li_2(COT''),[10] and K_2COT''' [24,25] were prepared according to published procedures. The NMR spectra were recorded in C_6D_6 or d_8-THF solutions on a Bruker DPX 600 (^{1}H: 600.1 MHz; ^{13}C: 150.9 MHz) or a Bruker-AVANCE-DMX400 (5 mm BB, ^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz) (Ln compounds), or a Bruker-AVANCE 250 (5 mm TBI, ^{1}H: 250.1 MHz; ^{13}C: 62.5 MHz) (An compounds). ^{1}H and ^{13}C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. IR (KBr) spectra were measured using a Perkin-Elmer FT-IR 2000 spectrometer. UV-Vis spectra were registered 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 923 apparatus. Metal analyses were performed via ICP AES.

4.2 Preparation of the anionic lanthanide sandwich complexes 1-8 (general synthetic protocols)

a) DME solvates [Li(DME)$_3$][Ln{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (Ln = Y (1), La (2), Pr (3), Gd (4), Tm (6), Lu (8)): Li_2(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) $C_8H_8(SiMe_3)_2$ 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)$_3$][Ln{$C_8H_6(SiMe_3)_2$}$_2$] crystallized upon standing at room temperature for a few days.

New Journal of Chemistry Accepted Manuscript

b) THF solvates [Li(THF)$_4$][Ln{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (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)$_4$][Ln{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] crystallized directly upon standing at room temperature for a few days.

[Li(DME)$_3$][Y{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (1): Yield: 3.57 g (69%), dec. > 90 °C. Elemental analysis calcd. for $C_{40}H_{78}LiO_6Si_4Y$ (M_r = 863.24 g·mol^{-1}): C, 55.66; H, 9.11. Found: C, 54.98; H, 8.88%. IR (KBr disc): ν = 3222m, 3092m, 3037m, 2962s, 2933s, 2531m, 2360m, 2224m, 2029m, 1959m, 1638vs, 1497m, 1445s, 1408s, 1384s, 1371s, 1309s, 1248vs, 1181s, 1155s, 1044m, 1027m, 985m, 934w, 837vs, 810m, 750m, 719m, 692w, 651w, 636w, 626w, 589vw, 555w, 505w, 480vw, 457vw cm^{-1}. ^{1}H NMR (400.1 MHz, d_8-THF, 24 °C): δ = 3.40 (s, 12H, DME), 3.26 (s, 18H, DME), 0.43 (s, 36H, Si(C*H*$_3$)$_3$), 6.09-6.04 (m, 8H, COT-*H*), 5.91-5.87 (m, 4H, COT-*H*) ppm. ^{13}C NMR (100.6 MHz, d_8-THF, 24 °C): δ = 99.4 (COT), 99.3 (COT), 97.3 (COT), 96.6 (COT), 72.7 (DME), 58.9 (DME), 1.6 (Si(CH$_3$)$_3$) ppm. ^{29}Si NMR (79.5 MHz, d_8-THF, 24 °C): δ = 0.7 ppm. MS (EI): *m/z* 586 (26%, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Y]), 514 (6, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Y – SiMe$_3$]), 337 (35, [{C$_8$H$_6$(SiMe$_3$)$_2$}Y]), 263 (14, [{C$_8$H$_6$(SiMe$_3$)$_2$}Y – SiMe$_3$]), 248 (42, [C$_8$H$_6$(SiMe$_3$)$_2$]), 207 (66, [C$_8$H$_6$(SiMe$_3$)$_2$ – 3Me]).

[Li(DME)$_3$][La{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (2): Yield: 3.34 g (61%), dec. 104 °C. Elemental analysis calcd. for $C_{40}H_{78}LaLiO_6Si_4$ (M_r = 913.25 g·mol^{-1}): C, 52.61; H, 8.61. Found: C, 52.70; H, 8.10%. IR (KBr disc): ν = 3436w, 3223w, 3090w, 2995m, 2954s, 2897m, 2830w, 2537vw, 2363vw, 2100vw, 1959vw, 1868vw, 1757vw, 1638w, 1599w, 1452w, 1405w, 1370w, 1312w, 1248s, 1210w, 1193w, 1181w, 1156w, 1124w, 1086m, 1065w, 1052m, 1028w, 981w, 932w, 910w, 837vs, 783vs, 750m, 716m, 690w, 681w, 651w, 636w, 550vw, 514vw, 504vw, 478vw, 459vw, 423vw cm^{-1}. ^{1}H NMR (400.1 MHz, d_8-toluene, 24 °C): δ = 2.31 (s, 18H, DME), 1.94 (s, 12H, DME), 0.67 (s, 36H, Si(C*H*$_3$)$_3$), 6.51-6.44 (m, 8H, COT-*H*), 6.40-6.35 (m, 4H, COT-*H*) ppm. ^{13}C NMR (100.6 MHz, d_8-toluene, 24 °C): δ = 103.6 (COT), 102.6 (COT), 101.3 (COT), 100.3 (COT), 69.3 (DME), 57.5 (DME), 1.1 (Si(CH$_3$)$_3$) ppm. ^{29}Si NMR (79.5 MHz, d_8-toluene, 24 °C): δ = 0.5 ppm. MS (EI): *m/z* 636 (1%, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$La]), 387 (38, [{C$_8$H$_6$(SiMe$_3$)$_2$}La]), 248 (28, [C$_8$H$_6$(SiMe$_3$)$_2$]), 207 (34, [C$_8$H$_6$(SiMe$_3$)$_2$] – 3Me).

[Li(DME)$_3$][Pr{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (3): Yield: 4.12 g (75%), dec. 98 °C. Elemental analysis calcd. for $C_{40}H_{78}LiO_6PrSi_4$ (M_r = 915.25 g·mol^{-1}): C, 52.49; H, 8.59. Found: C, 51.49; H,

New Journal of Chemistry Accepted Manuscript

8.31%. IR (KBr disc): ν = 3437m, 3222m, 3091m, 3036m, 2960s, 2933m, 2535w, 2224vw, 2029vw, 1972vw, 1959w, 1743vw, 1637s, 1447m, 1419m, 1383m, 1371m, 1343m, 1308s, 1245vs, 1181s, 1157vs, 1081m, 1050m, 985m, 933w, 909vw, 837s, 745m, 733w, 698w, 637w, 588vw, 555w, 504m, 467vw, 458vw, 451vw cm^{-1}. ^{1}H NMR (400.1 MHz, d_8-THF, 25 °C): δ = 3.63 (12H, DME), 3.31 (18H, DME), -6.17 (s, 27H, Si(C*H*$_3$)$_3$), -13.52, -9.54, -0.05 (br, s, COT-*H*) ppm. ^{13}C NMR (100.6 MHz, d_8-THF, 25 °C): δ = 229.5 (COT), 216.6 (COT), 204.9 (COT), 192.7 (COT), 72.8 (DME), 59.0 (DME), 0.6 (Si(CH$_3$)$_3$) ppm. ^{29}Si NMR (79.5 MHz, d_8-THF, 25 °C): δ = -46 ppm. MS (EI): *m/z* 637 (4%, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Pr]), 389 (100, [{C$_8$H$_6$(SiMe$_3$)$_2$}Pr]), 315 (10, [{C$_8$H$_6$(SiMe$_3$)$_2$}Pr – SiMe$_3$]), 248 (22, [C$_8$H$_6$(SiMe$_3$)$_2$]), 207 (26, [C$_8$H$_6$(SiMe$_3$)$_2$] – 3Me).

[Li(DME)$_3$][Gd{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (4): Yield: 4.08 g (73%), dec. 128 °C. Elemental analysis calcd. for C$_{40}$H$_{78}$GdLiO$_6$Si$_4$ (M_r = 931.59 g·mol^{-1}): C, 51.57; H, 8.44. Found: C, 50.83; H, 8.59%. IR (KBr disc): ν = 3788vw, 3546w, 3220w, 2997m, 2953s, 2897m, 2829m, 2540vw, 2101vw, 1959vw, 1871vw, 1800vw, 1753vw, 1637w, 1599w, 1543w, 1474w, 1451m, 1404w, 1369w, 1310w, 1248s, 1210w, 1192w, 1124m, 1086m, 1066m, 1053m, 1028w, 982w, 933m, 909w, 837vs, 782w, 769w, 750m, 717m, 680w, 651w, 636w, 548w, 521vw, 510w, 478vw, 459vw, 421vw cm^{-1}. NMR data could not be obtained for [Li(DME)$_3$][Gd{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] due to the paramagnetic character of the Gd^{3+}-ion. MS (EI): *m/z* 655 (6%, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Gd]), 580 (1, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Gd – SiMe$_3$]), 406 (14, [{C$_8$H$_6$(SiMe$_3$)$_2$}Gd]), 335 (9, [{C$_8$H$_6$(SiMe$_3$)$_2$}Gd – SiMe$_3$]), 248 (54, [C$_8$H$_6$(SiMe$_3$)$_2$]), 207 (32, [C$_8$H$_6$(SiMe$_3$)$_2$ – 3Me]).

[Li(THF)$_4$][Ho{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (5): Yield: 3.30 g (57%), dec. 113 °C. Elemental analysis calcd. for C$_{44}$H$_{80}$LiO$_4$Si$_4$Ho (M_r = 957.33 g·mol^{-1}): C, 55.20; H, 8.42. Found: C, 54.93; H, 8.29%. IR (KBr disc): ν = 3036w, 2953vs, 2896s, 2833m, 2088vw, 1932vw, 1876vw, 1834vw, 1779vw, 1667vw, 1590w, 1536w, 1487w, 1446m, 1403m, 1317w, 1247vs, 1214m, 1049s, 1038m, 982m, 939s, 910m, 894m, 839vs, 783m, 748s, 735vs, 686m, 651w, 636s, 573vw, 550m, 540w, 522vw, 512w, 488vw, 463vw, 423vw cm^{-1}. NMR data could not be obtained for [Li(THF)$_4$][Ho{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] due to the paramagnetic character of the Ho^{3+}-ion. MS (EI): *m/z* 662 (5%, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Ho]), 589 (5, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Ho – SiMe$_3$]), 412 (5, [C$_8$H$_6$(SiMe$_3$)$_2$Ho]), 340 (30, [C$_8$H$_6$(SiMe$_3$)$_2$Ho – SiMe$_3$]), 248 (40, [C$_8$H$_6$(SiMe$_3$)$_2$]), 206 (100, [C$_8$H$_6$(SiMe$_3$)$_2$ – 3Me]).

New Journal of Chemistry Accepted Manuscript

[Li(DME)$_3$][Tm{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (6): Yield: 3.79 g (67 %), dec. 125 °C. Elemental analysis calcd. for $C_{40}H_{78}LiO_6Si_4Tm$ (M_r = 943.27 g·mol^{-1}): C, 50.93; H, 8.33. Found: C, 50.50; H, 7.95%. IR (KBr disc): ν = 3469w, 3222w, 2994m, 2956s, 2898m, 2535vw, 1959vw, 1637m, 1450w, 1406w, 1385w, 1314w, 1248s, 1212w, 1181w, 1152w, 1125w, 1081w, 1052w, 1028w, 982w, 934w, 837vs 750m, 736w, 719m, 691w, 651w, 634w, 547vw, 519vw, 505vw, 479vw, 463vw cm^{-1}. NMR data could not be obtained for [Li(DME)$_3$][Tm{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] due to the paramagnetic character of the Tm^{3+}-ion.

[Li(THF)$_4$][Tm{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (7): Yield: 3.17 g (55%), dec. 133 °C. Elemental analysis calcd. for $C_{44}H_{80}LiO_4Si_4Tm$ (M_r = 961.33 g·mol^{-1}): C, 54.97; H, 8.39. Found: C, 54.15; H, 7.80%. IR (KBr disc): ν = 3469vw, 3030m, 2996m, 2952s, 2897m, 2830m, 2543vw, 2349vw, 2271vw, 2102vw, 1959vw, 1872vw, 1803vw, 1754vw, 1636w, 1599w, 1549w, 1475ww, 1451m, 1404w, 1369w, 1328w, 1311w, 1247s, 1214w, 1192w, 1158w, 1124m, 1087s, 1053m, 1028w, 983w, 934m, 911w, 836vs, 783w, 771w, 750m, 719s, 680w, 651w, 636m, 573vw, 547w, 518vw, 507w, 479vw, 457vw, 423vw cm^{-1}. NMR data could not be obtained for [Li(DME)$_3$][Tm{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] due to the paramagnetic character of the Tm^{3+}-ion. MS (EI): *m/z* 665 (8%, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Tm]), 593 (2, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Tm – SiMe$_3$]), 417 (22, [{C$_8$H$_6$(SiMe$_3$)$_2$}Tm]), 343 (3, [{C$_8$H$_6$(SiMe$_3$)$_2$}Tm – SiMe$_3$]), 248 (48, [C$_8$H$_6$(SiMe$_3$)$_2$]), 207 (66, [C$_8$H$_6$(SiMe$_3$)$_2$ – 3Me]).

[Li(DME)$_3$][Lu{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$] (8): Yield: 4.21 g (74%), dec. ca. 90 °C. Elemental analysis calcd. for $C_{40}H_{78}LiLuO_6Si_4$ (M_r = 949.31 g·mol^{-1}): C, 50.61; H, 8.28. Found: C, 49.47; H, 8.20%. IR (KBr disc): ν = 3437w, 3222w, 2994m, 2956s, 2897m, 2536vw, 2354vw, 2096vw, 1959vw, 1868vw, 1635w, 1599m, 1452w, 1406w, 1385w, 1317w, 1248s, 1206w, 1181w, 1113w, 1097w, 1065w, 1044w, 1028w, 983w, 940w, 837vs, 810m, 750m, 738w, 720m, 692w, 674w, 651w, 624w, 556vw, 503vw, 478vw, 459w, 437vw, 422vw cm^{-1}. ^{1}H NMR (400.1 MHz, d_8-THF, 25 °C): δ = 3.39 (s, 12H, DME), 3.25 (s, 18H, DME), 0.43 (s, 36H, Si(CH_3)$_3$), 6.06-6.03 (m, 8H, COT-*H*), 5.85-5.82 (m, 4H, COT-*H*) ppm. ^{13}C NMR (100.6 MHz, d_8- THF, 25 °C): δ = 98.1 (COT), 97.9 (COT), 95.9 (COT), 94.9 (COT), 72.4 (DME), 58.7 (DME), 1.4 (Si(CH$_3$)$_3$) ppm. ^{29}Si NMR (79.5 MHz, d_8-THF, 25 °C): δ = 0.8 ppm. MS (EI): *m/z* 672 (71%, [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Lu + H]), 423 (64, [{C$_8$H$_6$(SiMe$_3$)$_2$}Lu]), 248 (64, [C$_8$H$_6$(SiMe$_3$)$_2$]), 207 (34, [C$_8$H$_6$(SiMe$_3$)$_2$ – 3Me]).

New Journal of Chemistry Accepted Manuscript

4.3 Preparation of the actinide sandwich complexes An(COT'')$_2$ (An = Th (9), U (10)) (general synthetic protocol)

~200 mg of anhydrous AnCl$_4$ (An = Th, U; ~ 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 the 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 ~80% yield. From the waxy yellow thorium complex **9** (m.p. 135 °C) single-crystals were obtained by recrystallation 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[C$_8$H$_6$(SiMe$_3$)$_2$]$_2$ (9): Elemental analysis calcd. for $C_{28}H_{48}Si_4Th$ (M_r = 729.07 g·mol^{-1}): C, 46.13; H, 6.64; Th, 31.83. Found: Th, 32.0%. IR (KBr disc): ν = 3036w, 3002m, 2954m, 2895m, 1447w, 1403w, 1382w, 1370w, 1330w, 1302w, 1249s, 1119w, 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$_3$): δ = 6.86 (m, 12H, CH), 0.60 (br, 36H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ = 113.1 , 112.3, 110.0 (CH), 0.9 (CH$_3$) ppm.

U[C$_8$H$_6$(SiMe$_3$)$_2$]$_2$ (10): Elemental analysis calcd. for $C_{28}H_{48}Si_4U$ (M_r = 735.06 g·mol^{-1}): C, 45.75; H, 6.58; U, 32.38. Found: U, 31.9%. IR (KBr disc): ν = 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, 283w, 249m cm^{-1}. UV-vis (Et$_2$O, λ, nm (ε, cm·l·mol^{-1})): 360, 380, 503, 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$_3$): δ = -9.99 (36H, CH$_3$), -25.20 (4H, CH), -39.63 (4H, CH), -45.62 (4H, CH) ppm. ^{13}C NMR (CDCl$_3$): δ = 325.9 (CH), 293.8 (CH), 270.3 (CH), -3.5 (CH$_3$) ppm.

4.4 Preparation of the actinide sandwich complexes An(COT''')$_2$ (An = Th (11), U (12)

These two polysilylated actinidocenes **11** and **12** were preared by treatment of AnCl$_4$ (An = Th, U) with 2 equiv. of K$_2$(COT''') following the procedure reported by Edelmann and Kanellakopulos et al. (*cf.* Scheme 5).[24b] Bright yellow **11** and dichroitic red/green **12** were isolated in high yields around 80% after recrystallization from *n*-pentane.

New Journal of Chemistry Accepted Manuscript

4.5 Crystal structure determinations

The intensity data of the lanthanide sandwich complexes **1-8** were collected on a Stoe IPDS 2T diffractometer with MoKα radiation. The data were collected with the Stoe XAREA program using ω-scans.[39] 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. Single-crystal X-ray analyses of the actinide complexes **9-12** were performed on a Bruker Apex II Quazar diffractometer at given temperature collecting two or four spheres of data with an irradiation time of 10 to 40 s per frame applying a combination of ω– and φ–scans. Maximum θ-values were in the range of 28°. Completeness of data to $\theta \leq 25°$ was higher than 99%. For more information be referred to Table 2 and to the Supplementary Information. Integration of the data proceeded with SAINT,[41] the data were corrected for Lorentz- and polarisation effects, and an experimental absorption correction with SADABS[41] was performed. For searches relating to single-crystal X-ray diffraction data, the Cambridge Structural Database was used. The structures have been solved by direct methods and refined to a minimum R-value with SHELXL-2013[42] *via* full-matrix least-squares on F^2. In the case of compound **9**, a second type of crystals could be isolated with a different elementary cell showing a strong disorder. The data have been deposited at the CCDC with the CCDC Number 1049928 but will not be discussed here in detail as due to the disorder the overall standard deviations for all values are significantly higher.

Acknowledgements

Financial support by the Otto-von-Guericke-Universität Magdeburg is gratefully acknowledged. Special thanks are due to Ms. Desirée Schneider for preparing the ChemDraw Schemes.

References

1 Review: F. T. Edelmann, *Complexes of Scandium, Yttrium and Lanthanide Elements*, in *Comprehensive Organometallic Chemistry III*, R. H. Crabtree and D. M. P. Mingos, (Eds.), Elsevier, Oxford, 2006, 1.

2 C. Meermann, K. Ohno, K. W. Törnroos, K. Mashima and R. Anwander, *Eur. J. Inorg. Chem.*, 2009, 76, and references cited therein.

3 (*a*) F. Mares, K. O. Hodgson and A. Streitwieser, *J. Organomet. Chem.,* 1970, **24**, C68; (*b*) K. O. Hodgson, F. Mares, D. Starks and A. Streitwieser, *J. Am. Chem. Soc.*, 1973,

New Journal of Chemistry Accepted Manuscript

85, 8650; (*c*) S. A. Kinsley, A. Streitwieser and A. Zalkin, *Organometallics*, 1985, **4**, 52; (*d*) A. L. Wayda, *Organometallics*, 1983, **2**, 565; (e) J. Jin, Z. Jin, G. Wei, W. Chen and Y. Zhang, *Chin. J. Inorg. Chem.*, 1993, **9**, 326; (*f*) U. Kilimann, M. Schäfer, R. Herbst-Irmer and F. T. Edelmann, *J. Organomet. Chem.,* 1994, **469**, C15; (*g*) S. Anfang, G. Seybert, K. Harms, G. Geiseler, W. Massa and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1187; (*h*) G. W. Rabe, M. Zhang-Presse, J. A. Golen and A. L. Rheingold, *Acta Crystallogr., Sect. E*, 2003, **59**, m255.

4 (*a*) F. Mares, K. O. Hodgson and A. Streitwieser, *J. Organomet. Chem.*, 1971, **28**, C24; (*b*) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, 1972, **11**, 171; (c) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.* 1972, **11**, 3030; (d) A. L. Wayda, *Organometallics*, 1983, **2**, 565; (e) J. Xia, Z. Jin, G. Wei and W. Chen, *Jiegou Huaxue*, 1992, **11**, 113.

5 (*a*) J. D. Jamerson, A. P. Masino and J. Takats, *J. Organomet. Chem*., 1974, **65**, C33; (*b*) A. Westerhoff and H. J. De LiefdeMeijer, *J. Organomet. Chem.*, 1976, **116**, 319; (*c*) K. Wen, Z. Jin and W. Chen, *J. Chem. Soc., Chem. Commun*., 1991, 680.

6 A. Greco, S. Cesca and G. Bertolini, *J. Organomet. Chem*., 1976, **113**, 321.

7 (*a*) A. Streitwieser and S. A. Kinsley, *in*: T. J. Marks and I. L. Fragalà (Eds.), *Fundamental and Technological Aspects of Organo-f-Element Chemistry*, NATO ASI Series, D. Reidel, Boston, 1985, **155**, 77; (*b*) A. Streitwieser and T. R. Boussie, *Eur. J. Solid State Inorg. Chem*., 1991, **28**, 399; (*c*) F. T. Edelmann, *New. J. Chem*., 1995, **19**, 535; (*d*) F. T. Edelmann, *Angew. Chem. Int. Ed*., 1995, **34**, 2466; (*e*) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev*., 2002, **102**, 1851; (*f*) H.-D. Amberger, F. T. Edelmann, J. Gottfriedsen, R. Herbst-Irmer, S. Jank, U. Kilimann, M. Noltemeyer, H. Reddmann and M. Schäfer, *Inorg. Chem*., 2009, **48**, 760; (*g*) F. T. Edelmann, *New. J. Chem.*, 2011, **35**, 517.

8 K. Mashima and H. Takaya, *Tetrahedron Lett.,* 1989, **30**, 3697.

9 (*a*) U. Kilimann, M. Schäfer, R. Herbst-Irmer and F. T. Edelmann, *J. Organomet. Chem.*, 1994, **469**, C10; (*b*) H. Schumann, J. Winterfeld, H. Hemling, F. E. Hahn, P. Reich, K.-W. Brzezinka, F. T. Edelmann, U. Kilimann, M. Schäfer and R. Herbst-Irmer, *Chem. Ber.*, 1995, **128**, 395; (*c*) U. Reißmann, P. Poremba, M. Noltemeyer, H.-G. Schmidt and F. T. Edelmann, *Inorg. Chim. Acta.*, 2000, **303**, 156.

10 (*a*) J. M. Bellama and J. B. Davidson, *J. Organomet. Chem.*, 1975, **86**, 69; (b) N. C. Burton, F. G. N. Cloke, P. B. Hitchcock, H. C. de Lemos and A. A. Sameh, *J. Chem.*

New Journal of Chemistry Accepted Manuscript

Soc., Chem. Commun., 1989, 1462; (*c*) N. C. Burton, F. G. N. Cloke, S. C. P. Joseph, H. Karamallakis and A. A. Sameh, *J. Organomet. Chem.*, 1993, **462**, 39.

11 A. Streitwieser and U. Müller-Westerhoff, *J. Am. Chem. Soc.*, 1968, **90**, 7364.

12 Review: D. Seyferth, *Organometallics*, 2004, **23**, 3562.

13 (*a*) A. Hervé, N. Garin, P. Thuéry, M. Ephritikhine and J.-C. Berthet, *Chem. Commun.*, 2013, **49**, 6304; (*b*) J.-C. Berthet, P. Thuéry, N. Garin, J.-P. Dognon, T. Cantat and M. Ephritikhine, J. Am. Chem. Soc., 2013, 135, 10003.

14 A. Edelmann, V. Lorenz, C. G. Hrib, L. Hilfert, S. Blaurock and F. T. Edelmann, *Organometallics*, 2013, **32**, 1435.

15 V. Lorenz, A. Edelmann, S. Blaurock, F. Freise and F. T. Edelmann, *Organometallics*, 2007, **26**, 4708.

16 V. Lorenz, S. Blaurock, C. G. Hrib and F. T. Edelmann, *Organometallics*, 2010, **29**, 4787.

17 J. J. Le Roy, M. Jeletic, S. I. Gorelski, I. Korobkov, L. Ungur, L. F. Chibotaru and M. Murugesu, *J. Am. Chem. Soc.*, 2013, **135**, 3502.

18 J. J. Le Roy, L. Ungur, I. Korobkov, L. F. Chibotaru and M. Murugesu, *J. Am. Chem. Soc.*, 2014, **136**, 8003.

19 P. Poremba, U. Reißmann, M. Noltemeyer, H.-G. Schmidt, W. Brüser and F. T. Edelmann, *J. Organomet. Chem*., 1997, **544**, 1.

20 J. J. Le Roy, I. Korobkov, J. E. Kim, E. J. Schelter and M. Murugesu, *Dalton Trans*., 2014, **43**, 2737.

21 J. J. Le Roy, I. Korobkov and M. Murugesu, *Chem. Commun.*, 2014, **50**, 1602.

22 V. Lorenz, A. Edelmann, S. Blaurock, F. Freise and F. T. Edelmann, *Organometallics,* 2007, **26**, 6681.

23 M. Jeletic, P.-H. Lin, J. J. Le Roy, I. Korobkov, S. I. Gorelsky and M. Murugesu, *J. Am. Chem. Soc.*, 2011, **133**, 19286.

24 (a) U. Kilimann, R. Herbst-Irmer, D. Stalke and F. T. Edelmann, *Angew. Chem. Int. Ed.,* 1994, **33**, 1618; (b) C. Apostolidis, F. T. Edelmann, B. Kanellakopulos and U. Reißmann, *Z. Naturforsch.*, 1999, **54b**, 960.

25 A. Edelmann, S. Blaurock, V. Lorenz, L. Hilfert and F. T. Edelmann, *Angew. Chem. Angew. Chem. Int. Ed.*, 2007, **46**, 6732.

26 A. Edelmann, C. G. Hrib, S. Blaurock and F. T. Edelmann, *J. Organomet. Chem.,* 2010, **695**, 2732.

New Journal of Chemistry Accepted Manuscript

27 J. J. Le Roy, S. I. Gorelsky, I. Korobkov and M. Murugesu, *Organometallics*, 2015, **34**, DOI: 10.1021/om501214c.

28 (*a*) P. Poremba, H. G. Schmidt, M. Noltemeyer, and F. T. Edelmann, *Organometallics*, 1998, **17**, 986; (*b*) M. Jeletic, F. A. Perras, S. I. Gorelsky, J. L. Le Roy, I. Korobkov, D. L. Bryce and M. Murugesu, *Dalton Trans*., 2012, **41**, 8060.

29 (*a*) A. Avdeef, K. N.Raymond, K. O. Hodgson and A. Zalkin, *Inorg. Chem.*, 1972, **11**, 1083; (*b*) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, 1973, **12**, 458; (*c*) L. K. Templeton, D. H. Templeton and R. Walker, *Inorg. Chem.*, 1976, **15**, 3000; (*d*) A. Zalkin, D. H. Templeton, S. R. Berryhill and W. D. Luke, *Inorg. Chem.* 1979, **18**, 2287; (*e*) A. Zalkin, D. H. Templeton, W. D. Luke and A. Streitwieser Jr., *Organometallics*, 1982, **1**, 618; (*f*) A. Zalkin, D. H. Templeton, R. Kluttz and A. Streitwieser Jr., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1985, **41**, 327.

30 V. Lorenz, B. M. Schmiege, C. G. Hrib, J. W. Ziller, A. Edelmann, S. Blaurock, W. J. Evans and F. T. Edelmann, *J. Am. Chem. Soc.,* 2011, **133**, 1257.

31 (*a*) H. P. Fritz. *Adv. Organomet. Chem.*, 1964, **1**, 239; (*b*) L. Hocks, J. Goffart, G. Duyckaert and P. Teyssie, *Spectrochim. Acta.*, 1974, **30A**, 907; (*c*) V. T. Aleksanyan, I. A. Garbusova, T. M. Chernyshova, Z. V. Todres, M. R. Leonov and N. I. Gramateeva, *J. Organomet. Chem.*, 1981, **217**, 169.

32 (*a*) A. Streitwieser and U. Müller-Westerhoff, *J. Am. Chem. Soc.,* 1973, **95**, 8644; (*b*) R. Bohlander, Dissertation University of Karlsruhe, 1986; KFK-Bericht Nr. 4152, 1986; (*c*) N. Magnani, C. Apostolidis, A. Morgenstern, E. Colineau, J.-C. Griveau, H. Bolvin, O. Walter and R. Caciuffo, *Angew. Chem. Int. Ed.,* 2011, **50**, 1696.

33 C. R. Graves, A. E. Vaughn, E. J. Schelter, B. L. Scott, J. D. Thompson, D. E. Morris and J. L. Kiplinger, *Inorg. Chem*., 2008, **47**, 11879, and references cited therein.

34 (*a*) A. Streitwieser, Jr., R. Q. Kluttz, K. A. Smith and W. D. Luke, *Organometallics*, 1983, **2**, 1873; (*b*) W. Jahn, K. Yünlü, W. Oroschin, H.-D. Amberger and R. D. Fischer, *Inorg. Chim. Acta*, 1984, **95**, 85; (*c*) A. Streitwieser Jr., M. H. Lyttle, H.-K. Wang, T. Boussie, A. Weinländer and J. P. Solar, *J. Organomet. Chem.*, 1995, **501**, 245.

35 (*a*) A. W. Spiegl, *Doctoral Dissertation*, University of Erlangen-Nürnberg, 1978; (*b*) R.D. Fischer, *NMR-spectroscopy of Organo-f-Element and Pre-Lanthanoid Complexes: Some Current Trends*, in *Fundamental and Technological Aspects of Organo-f-Element Chemistry*, T. J. Marks and I. L. Fragala (Eds.), D. Reidel Publishing Company, 1985, 277-326.

New Journal of Chemistry Accepted Manuscript

36 J. H. Freeman and M. L. Smith, *J. Inorg. Nucl. Chem.,* 1958, **7**, 224.

37 D. C. Bradley, M. A. Saad and W. wardlaw, *J. Chem. Soc.,* 1954, 2002.

38 J. A. Hermann, J. F. Suttle and H. R. Hoekstra, *Inorg. Synth.*, 1957, **5**, 143.

39 Stoe, *XAREA*, Program for X-ray Crystal Data Collection, (XRED32 included in XAREA) Stoe, 2002.

40 (*a*) G. M. Sheldrick, *SHELXL-97* Program for Crystal Structure Refinement, Universität Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SHELXS-97* Program for Crystal Structure Solution, Universität Göttingen, Germany, 1997.

41 Bruker APEX, SAINT, SADABS, programs for X-ray Crystal Data Collection, integration and absorption correction, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.

42 G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.

New Journal of Chemistry Accepted Manuscript