



# New sandwich complexes of di- and trivalent ytterbium: Reduction of Yb(3+) by a bulky cyclooctatetraenyl dianion

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Dedicated to the memory of Professor Herbert Schumann (12.01.2010), a pioneer of organolanthanide chemistry and a friend.

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## ABSTRACT

The influence of bulky silyl-substituted cyclooctatetraenyl ligands on the formation and structure of ytterbium sandwich complexes has been investigated. Treatment of anhydrous YbCl<sub>3</sub> with equimolar amounts of [K(DME)]<sub>2</sub>(COT<sup>TBS</sup>) (**2**, COT<sup>TBS</sup> = [C<sub>8</sub>H<sub>6</sub>(SiMe<sub>2</sub><sup>t</sup>Bu)<sub>2</sub>-1,4]<sup>2-</sup>) and KCp\* (Cp\* = pentamethylcyclopentadienyl) in DME solution (DME = 1,2-dimethoxyethane) afforded a mixture of neutral Cp\*Yb(COT<sup>TBS</sup>) (**3**, purple crystals) and anionic [K(DME)<sub>4</sub>][Yb(COT<sup>TBS</sup>)<sub>2</sub>] (**4**, royal blue crystals) which could be separated by selective extraction. In contrast, the closely related reaction of YbCl<sub>3</sub> with equimolar amounts of K<sub>2</sub>(DME)<sub>2</sub>(COT<sup>'''</sup>) (**5**, COT<sup>'''</sup> = [C<sub>8</sub>H<sub>5</sub>(SiMe<sub>3</sub>)<sub>3</sub>-1,3,6]<sup>2-</sup>) and KCp\* resulted in spontaneous reduction of Yb<sup>3+</sup> to the divalent oxidation state and formation of dark blue-green (DME)<sub>2</sub>K(μ-COT<sup>'''</sup>)YbCp\* (**6**) as the sole reaction product. The compounds **3**, **4**, and **6** were structurally characterized by X-ray diffraction.

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## 1. Introduction

Cyclooctatetraenyl ligands (=COT) play an important role in organolanthanide chemistry because the large, flat COT dianions are ideally suited to form sandwich complexes of the rare earth metals [1–5]. Long known and well established are the anionic lanthanide(III) sandwich complexes M[Ln(COT)<sub>2</sub>] (M = alkaline metal) [6]. More recently, bulky organosilyl-substituted COT ligands such as the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (=COT<sup>''</sup>) have become increasingly popular [7]. Anionic sandwich complexes of the type [Li(THF)<sub>4</sub>][Ln(COT<sup>''</sup>)<sub>2</sub>] (Ln = Ce, Pr, Sm, Y) are formed upon treatment of anhydrous LnCl<sub>3</sub> with 2 equiv of Li<sub>2</sub>(COT<sup>''</sup>) [8,9]. The solid state structure of [Li(THF)<sub>4</sub>][Sm(COT<sup>''</sup>)<sub>2</sub>] was found to consist of separated ions and thus displayed no unexpected structural features [8], whereas two very different modifications have been found for Li(DME)Tb(COT<sup>''</sup>)<sub>2</sub>. This compound crystallizes either in a monomeric form or as a coordination polymer depending on the solvent used for crystallization (pentane vs. toluene) [9]. Reactions of anhydrous lanthanide trichlorides with Li<sub>2</sub>(COT<sup>''</sup>) have been shown to strongly depend on

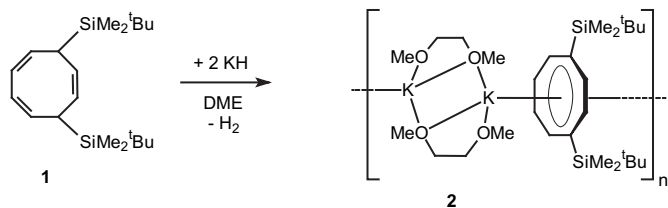
the reaction conditions and starting material ratios. Products isolated from such reactions include not only the anionic sandwich complexes [Ln(COT<sup>''</sup>)<sub>2</sub>]<sup>-</sup> [8,9] and the chloro-bridged dimers [(COT<sup>''</sup>)Ln(μ-Cl)THF]<sub>2</sub> [7a,b], but also unusual cluster-centered multidecker sandwich complexes [10] as well as the triple-deckers Ln<sub>2</sub>(COT<sup>''</sup>)<sub>3</sub> [2]. Besides the COT<sup>''</sup> ligand, other bulky cyclooctatetraenyl dianions such as 1,4-bis(triisopropylsilyl)cyclooctatetraenyl (=COT<sup>1,4-SiiPr3</sup>) [11], 1,4-bis(*t*-butyldimethylsilyl)cyclooctatetraenyl (=COT<sup>TBS</sup>) [12] and 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl (=COT<sup>'''</sup>) [13] have also been successfully employed in organolanthanide chemistry. Only with the use of the latter an unprecedented ytterbium(II) tetra-decker sandwich complex, Cp\*Yb(μ-COT<sup>'''</sup>)Yb(μ-COT<sup>'''</sup>)YbCp\*, has become available starting with ytterbium(II) diiodide [13b].

In an extension of this work we now report reactions of ytterbium trichloride with two different silyl-substituted cyclooctatetraenyl dianions where we found unexpected differences in reactivity as well as an unusual case of ligand-induced reduction of Yb(3+) to the divalent oxidation state.

## 2. Results and discussion

The bulky silyl-substituted cyclooctatetraenyl ligand [C<sub>8</sub>H<sub>6</sub>(SiMe<sub>2</sub><sup>t</sup>Bu)<sub>2</sub>-1,4]<sup>2-</sup> (=COT<sup>TBS</sup>) was first reported by Cloke et al. and

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Scheme 1.

successfully employed in the synthesis and characterization of the first sandwich complex of trivalent thorium [12]. The precursor 1,4-bis(*t*-butyldimethylsilyl)cycloocta-2,5,7-triene (**1**) is easily accessible in a one-pot reaction starting from cycloocta-1,5-diene. Following a published synthetic route for the COT<sup>'''</sup> derivative [13] we prepared the DME-solvated potassium salt of the (COT<sup>TBS</sup>)<sup>2-</sup> dianion as outlined in Scheme 1.

Unlike the previously reported lithium derivative Li<sub>2</sub>(COT<sup>TBS</sup>)·THF [12], the potassium precursor [K(DME)<sub>2</sub>](COT<sup>TBS</sup>) (**2**) is a white, crystalline solid which is easily obtained as a well-defined starting material which does not lose the coordinated DME upon drying under vacuum. According to its <sup>1</sup>H NMR data compound **2** contains one DME ligand per potassium ion, so that the structure (Scheme 1) can be assumed to be analogous to the previously reported COT<sup>'''</sup> derivative [13b].

In an attempt to prepare the neutral mixed-ligand sandwich complex Cp<sup>\*</sup>Yb(COT<sup>TBS</sup>) (**3**), anhydrous ytterbium trichloride was treated with equimolar amounts of KCP<sup>\*</sup> and **2** in DME solution, resulting in formation of a dark blue reaction mixture containing a white precipitate of KCl. *n*-Pentane extraction of the crude product obtained after removal of KCl and evaporation to dryness yielded a purple *n*-pentane-soluble fraction from which the desired neutral mixed-ligand sandwich complex Cp<sup>\*</sup>Yb(COT<sup>TBS</sup>) (**3**) could be isolated in the form of purple crystals in 31% yield. With its intense purple coloration compound **3** strongly resembles the previously reported unsubstituted congener Cp<sup>\*</sup>Yb(COT) [14]. Recrystallization of the *n*-pentane-insoluble residue from DME eventually produced a crop of royal-blue, needle-like crystals, which were shown to be the salt-like ytterbium(III) sandwich complex [K(DME)<sub>4</sub>][Yb(COT<sup>TBS</sup>)<sub>2</sub>] (**4**) (27% isolated yield). Due to their largely different solubilities, quantitative separation of these two reaction products was readily achieved in one step. Thus the overall reaction can be formulated as illustrated in Scheme 2.

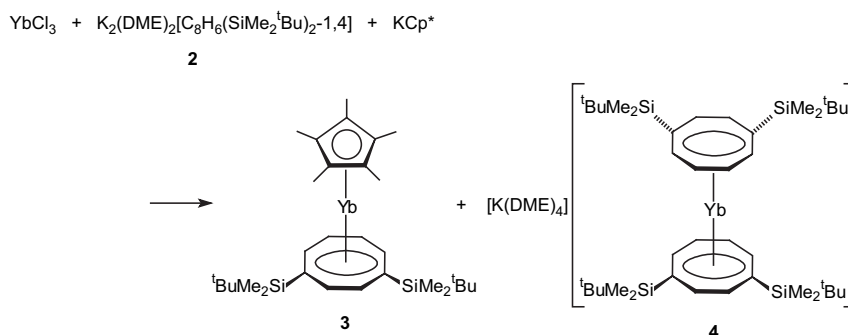
Both compounds **3** and **4** were fully characterized by spectroscopic and analytical methods. Despite the paramagnetic nature of the Yb<sup>3+</sup> ion, interpretable <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra could be obtained for both compounds. In the <sup>1</sup>H NMR spectrum of **3** the resonances of the COT ring protons are paramagnetically shifted

over a range of ca. 120 ppm. A notable spectroscopic detail is the appearance of two well-separated singlet resonances at δ –8.4 and –11.0 ppm for the SiMe<sub>2</sub> protons in the <sup>1</sup>H NMR spectrum of **3**, whereas the <sup>1</sup>H NMR spectrum of **4** displays only one singlet at δ –0.11 ppm. The reason for this difference became evident after elucidation of the crystal structures (*vide infra*). As expected, the <sup>29</sup>Si NMR spectrum of **3** displays only one signal (δ –9.3 ppm). The corresponding <sup>29</sup>Si NMR resonance for the anionic complex **4** was found at δ 1.3 ppm.

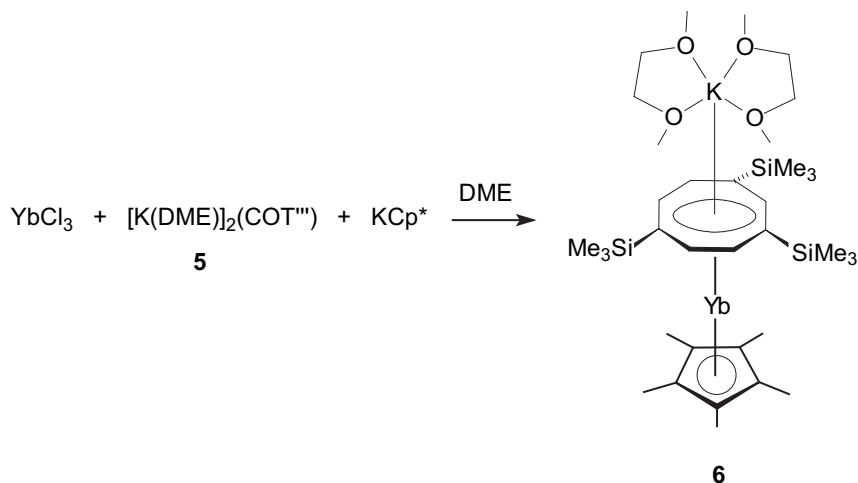
Much to our surprise, an analogous reaction of YbCl<sub>3</sub> with equimolar amounts of KCP<sup>\*</sup> and [K(DME)<sub>2</sub>](COT<sup>'''</sup>) (**5**) instead of **2** took an entirely different course. In this case, too, the precipitation of KCl was observed, and the color of the reaction mixture turned dark blue-green. In contrast to the reaction shown in Scheme 2, the residue after work-up contained no material that was soluble in *n*-pentane. Recrystallization from a small amount of DME (or directly from the concentrated reaction mixture) afforded well-formed, highly air-sensitive dark blue-green crystal blocks (47% yield), which were subsequently shown to be the heterobimetallic ytterbium(II) sandwich complex (DME)<sub>2</sub>K(μ-COT<sup>'''</sup>)YbCp<sup>\*</sup> (**6**). Thus the reaction leading to **6** as the only isolable ytterbium-containing product can be formulated as depicted in Scheme 3.

The very intense dark blue-green coloration of **6** already indicated that spontaneous reduction to the divalent oxidation state had taken place during the course of the reaction. The presence of ytterbium(2+) was verified by the observation of a <sup>171</sup>Yb NMR resonance at δ 579.4 ppm. This is in excellent agreement with the value reported for the outer ytterbium(2+) ions in the tetra-decker sandwich complex, Cp<sup>\*</sup>Yb(μ-COT<sup>'''</sup>)Yb(μ-COT<sup>'''</sup>)YbCp<sup>\*</sup>, which have an identical coordination environment. Here the <sup>171</sup>Yb resonance was observed at δ 595 ppm [13b]. The reduction of trivalent lanthanide precursors to the divalent state within the course of organolanthanide complex formation is rare, although not without precedent [15]. A prominent example from the early literature is the formation of Cp<sup>\*</sup><sub>2</sub>Eu(Et<sub>2</sub>O)(THF) upon treatment of EuCl<sub>3</sub> with 3 equiv of NaCp<sup>\*</sup> as reported by Zalkin et al. [15a]. Yet another example is the decomposition of the dimer [(MeH<sub>4</sub>C<sub>5</sub>)<sub>2</sub>Yb(μ-Me)]<sub>2</sub> to the Yb<sup>II</sup> metallocene in toluene or diethyl ether [15b] Spectacular cases of reduction of Yb(3+) and even Sm(3+) in the presence of a very bulky perphenylated cyclopentadienyl anion have recently been reported by Harder et al. [15c]. Apparently, the reduction reaction reported here is the first case involving a bulky substituted COT dianion as reducing agent. The reduction potential of the parent (COT)<sup>2-</sup> dianion has been reported to be in the range of –1.82 V [16a] to –1.86 V [16b]. Thus the (COT<sup>'''</sup>)<sup>2-</sup> dianion too should be a strong enough reducing agent to induce reduction of Yb(3+) (Yb<sup>3+</sup>/Yb<sup>2+</sup> E<sub>1/2</sub> = –1.15 V [16c]).

Single-crystal X-ray diffraction studies provided definitive structural data for the new ytterbium complexes **3**, **4**, and **6**. The



Scheme 2.



Scheme 3.

crystallographic data are summarized in Table 1. Views of the molecules as well as selected bond lengths and angles are given in Figs. 1–3.

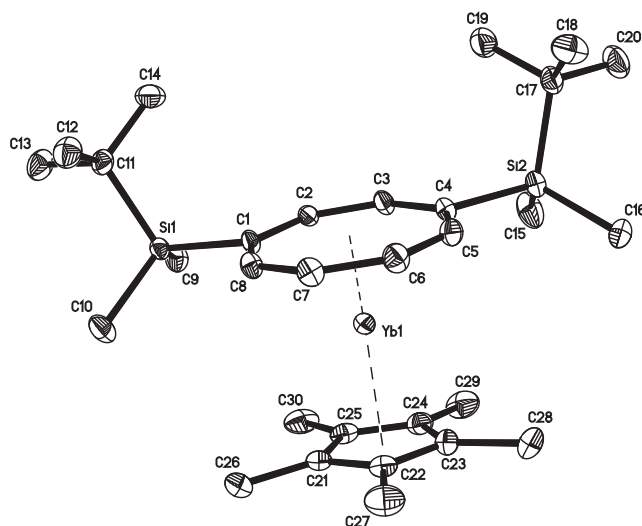
The neutral compound  $\text{Cp}^*\text{Yb}(\text{COT}^{\text{TBS}})$  (**3**) (Fig. 1) belongs to the fairly large group of mixed-ligand sandwich complexes of the type  $\text{CpLn}(\text{COT})$  with  $\eta^8$ -coordinated COT and  $\eta^5$ -cyclopentadienyl rings [17,18]. Not surprisingly, the two bulky substituted ring ligands in **3** leave no room for additional coordination of a solvent molecule. Several closely related pentamethylcyclopentadienyl derivatives,  $\text{Cp}^*\text{Ln}(\text{COT})$  ( $\text{Ln} = \text{Sm}, \text{Dy}, \text{Er}, \text{Yb}, \text{Lu}$ ) have already been structurally characterized by X-ray diffraction [14,17,18]. All Yb–C distances in **3** are virtually identical with those reported for  $\text{Cp}^*\text{Yb}(\text{COT})$  [14b]. The (ring centroid)–Yb–(ring centroid) angle in **3** is  $172.6^\circ$  as compared to  $171.5^\circ$  in  $\text{Cp}^*\text{Yb}(\text{COT})$ . It is almost identical with the value reported for  $\text{Cp}^*\text{Lu}(\text{COT})$  ( $172.9^\circ$  [18]). As mentioned above, the  $^1\text{H}$  NMR spectrum of **3** displays two well-separated resonances for the  $\text{SiMe}_2$  protons. It can be clearly seen in Fig. 1 that due to the specific 1,4-substitution pattern at the eight-membered ring the methyl groups at silicon are diastereotopic, giving rise to two peaks in the  $^1\text{H}$  NMR spectrum. A similar result was reported for the uranocene derivative  $\text{U}(\text{COT}^{\text{TBS}})_2$ . The  $^1\text{H}$  NMR spectrum of this compound exhibited  $\text{SiMe}_2$  proton resonances at  $\delta -16.7$  and  $-21.2$  ppm [12]. Fig. 1 also shows that the *t*-butyl groups at silicon are both pointing away from the central ytterbium in order to

minimize unfavorable steric repulsion by the  $\text{Cp}^*$  ligand on the opposite side of the molecule. The same phenomenon has been reported for the anionic thorium(III) complex  $(\text{DME})_2\text{K}[\text{Th}(\text{COT}^{\text{TBS}})_2]$  [12]

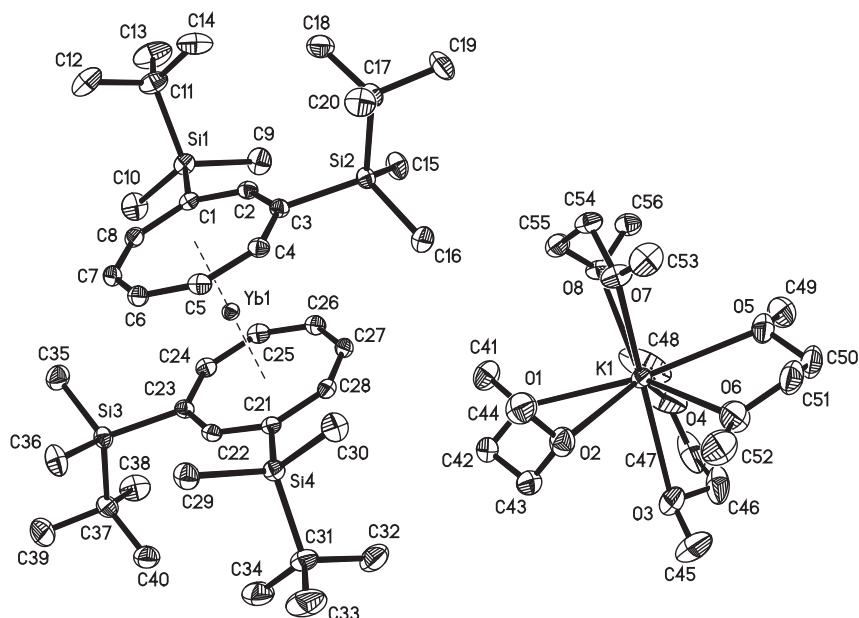
As depicted in Fig. 2, the blue product **4** is a salt consisting of a  $[\text{K}(\text{DME})_4]^+$  cation and a  $[\text{Yb}(\text{COT}^{\text{TBS}})_2]^-$  sandwich monoanion. Anionic sandwich complexes of the type  $[\text{Ln}(\text{COT})_2]^-$  are among the longest known lanthanide COT complexes [6,19], and ring-substituted derivatives containing various triorganosilyl-substituents are also well established [20]. Both  $(\text{COT}^{\text{TBS}})_2^{2-}$  rings in the anion are  $\eta^8$ -coordinated with Yb-distances being in the narrow range of  $2.5817(15)$ – $2.6444(14)$  Å. These values can be favorably compared to those in related Yb(COT) sandwich complexes [14]. Among the closest structurally characterized relatives are the samarium derivative  $[\text{Ph}_3\text{PNPPH}_3][\text{Sm}(\text{COT}'')_2]$  [20a],  $[\text{Li}(\text{diglyme})_2][\text{Ln}(\text{C}_8\text{H}_6\text{R}_2-1,4)_2]$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $\text{R} = o\text{-}N, N\text{-Me}_2\text{NC}_6\text{H}_4$ ,  $\text{SiMe}_2$ ) [20b] and the anionic trivalent thorium complex  $(\text{DME})_2\text{K}[\text{Th}(\text{COT}^{\text{TBS}})_2]$  [12]. In all cases the (ring centroid)–metal–(ring centroid) angles deviate only by a few degrees from linearity,

**Table 1**  
Crystallographic data for **3**, **4** and **6**.

	<b>3</b>	<b>4</b>	<b>6</b>
Empirical formula	$\text{C}_{30}\text{H}_{51}\text{Si}_2\text{Yb}$	$\text{C}_{56}\text{H}_{112}\text{KO}_8\text{Si}_4\text{Yb}$	$\text{C}_{35}\text{H}_{67}\text{KO}_4\text{Si}_3\text{Yb}$
<i>a</i> (Å)	20.5709(6)	16.6651(3)	12.670(3)
<i>b</i> (Å)	12.1006(5)	14.3679(2)	16.869(3)
<i>c</i> (Å)	12.3572(3)	28.1155(5)	20.810(4)
$\alpha$ (°)	90	90	90
$\beta$ (°)	99.179(2)	99.915(2)	100.09(3)
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	3036.57(17)	6631.50(19)	4379.0(15)
<i>Z</i>	4	4	4
Formula weight	640.93	1237.96	848.30
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
<i>T</i> (°C)	–143	–143	–143
$\lambda$ (Å)	0.71073	0.71073	0.71073
$D_{\text{calcd}}$ (g cm <sup>–3</sup> )	1.402	1.240	1.287
$\mu$ (mm <sup>–1</sup> )	3.174	1.590	2.343
<i>R</i> (Fo or Fo <sup>2</sup> )	0.0351	0.0251	0.0464
<i>R<sub>w</sub></i> (Fo or Fo <sup>2</sup> )	0.0867	0.0541	0.1202



**Fig. 1.** ORTEP view of the molecular structure of  $\text{Cp}^*\text{Yb}(\text{COT}^{\text{TBS}})$  (**3**) with thermal ellipsoids at the 30% probability level (H atoms are not shown for clarity). Selected bond lengths (Å) and angles (°): Yb(1)–COT(C1–C8) 2.462(3)–2.503(3), Yb(1)–Cp\*(C21–C25) 2.556(3)–2.574(3), Yb(1)–XCOT 1.646, Yb(1)–XCp\* 2.261, XCOT–Yb(1)–XCp\*  $172.6$  (X = ring centroids).



**Fig. 2.** ORTEP view of the structure of  $[\text{K}(\text{DME})_4][\text{Yb}(\text{COT}^{\text{TBS}})_2]$  (**4**) with thermal ellipsoids at the 30% probability level (H atoms are not shown for clarity). Selected bond lengths (Å) and angles ( $^\circ$ ): Yb(1)–COT(C1–C8) 2.5877(15)–2.6444(14), Yb(1)–COT(C21–C28) 2.5817(15)–2.6231(14), Yb(1)–XCOT(C1–C8) 1.849, Yb(1)–XCOT(C21–C28) 1.839, XCOT(C1–C8)–Yb(1)–XCOT(C21–C28) 179.7° (XCOT = COT ring centroid).

a situation which is typical for this type of COT sandwich complexes and presumably originates from intramolecular forces such as van der Waals attractions [21]. In the anion of **4**, the (ring centroid)–Yb–(ring centroid) angle is 179.7° (cf. 174.5° in

$(\text{DME})_2\text{K}[\text{Th}(\text{COT}^{\text{TBS}})_2]$  [12] and 177.2° in  $[\text{Ph}_3\text{PNPPh}_3][\text{Sm}(\text{COT}^{\text{H}})_2]$  [20a]). The four bulky  $\text{SiMe}_2^t\text{Bu}$ -substituents are arranged in an *anti*-conformation, and again they all point away from the metal, thereby alleviating unfavorable inter-ring steric interactions [12].

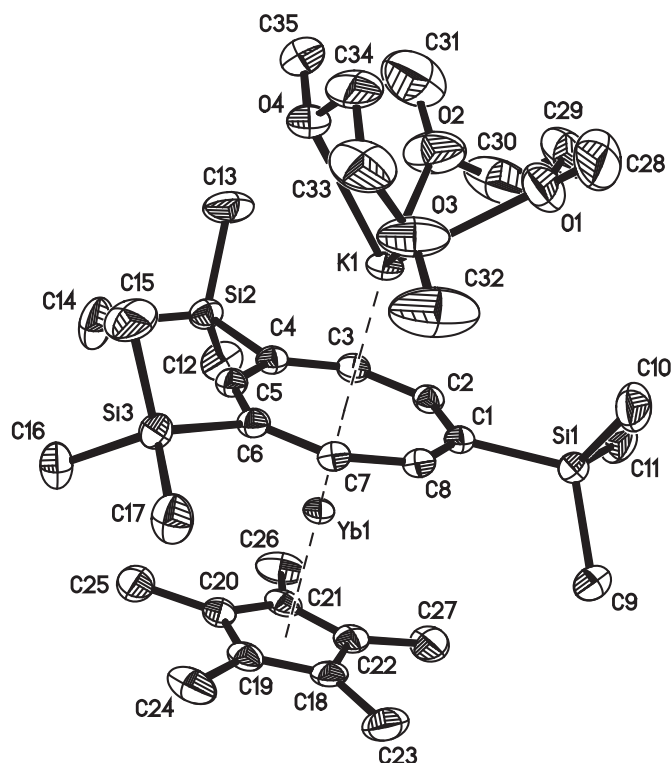
The molecular structure of  $(\text{DME})_2\text{K}(\mu\text{-COT}^{\text{H}})\text{YbCp}^*$  (**6**) is shown in Fig. 3. The compound represents a novel type of divalent lanthanide heterobimetallic sandwich complexes with an almost perfectly linear  $\text{Cp}^*\text{Yb}(\mu\text{-COT}^{\text{H}})\text{K}$  arrangement. The (ring centroid)–Yb–(ring centroid) angle in **6** is 178.9°. As in the heterobimetallic thorium(III) complex  $(\text{DME})_2\text{K}[\text{Th}(\text{COT}^{\text{TBS}})_2]$  [12] the coordination sphere around the potassium ion is complemented by two chelating DME ligands. The Yb–C bond lengths in **6** are in good agreement with those in related ytterbium(II) triple-decker sandwich complexes [11,22].

In summarizing the results reported here, we have prepared and structurally characterized the new ytterbium COT sandwich complexes  $\text{Cp}^*\text{Yb}(\text{COT}^{\text{TBS}})$  (**3**),  $[\text{K}(\text{DME})_4][\text{Yb}(\text{COT}^{\text{TBS}})_2]$  (**4**), and  $(\text{DME})_2\text{K}(\mu\text{-COT}^{\text{H}})\text{YbCp}^*$  (**6**). Particularly surprising was the finding that the use of two silyl-substituted COT ligands of comparable steric bulk led to formation of very different products in reactions with ytterbium trichloride. As was shown earlier for the tetra-decker sandwich  $\text{Cp}^*\text{Yb}(\mu\text{-COT}^{\text{H}})\text{Yb}(\mu\text{-COT}^{\text{H}})\text{YbCp}^*$  [13b] it appears once again that the trisubstituted  $\text{COT}^{\text{H}}$  ligand is particularly well suited for the construction of linear multidecker sandwich complexes of the lanthanide elements. Also quite remarkable is the observation of the first reduction of Yb(3+) to the divalent oxidation state induced by a bulky COT dianion.

### 3. Experimental section

#### 3.1. General procedures

The reactions were conducted in flame-dried glassware under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques. All solvents were distilled from sodium/benzophenone under nitrogen atmosphere prior to use. All glassware was oven-dried at 140 °C for at least 24 h, assembled while



**Fig. 3.** ORTEP view of the molecular structure of  $(\text{DME})_2\text{K}(\mu\text{-COT}^{\text{H}})\text{YbCp}^*$  (**6**) with thermal ellipsoids at the 30% probability level (H atoms are not shown for clarity). Selected bond lengths (Å) and angles ( $^\circ$ ): Yb(1)–COT(C1–C8) 2.601(4)–2.633(4), Yb(1)–Cp\*(C18–C22) 2.644(4)–2.689(4), Yb(1)–XCOT 1.834, Yb(1)–XCp\* 2.380, XCOT–Yb(1)–XCp\* 178.9° (X = ring centroids).



hot, and cooled under vacuum prior to use. The starting materials **1** [12], anhydrous YbCl<sub>3</sub> [23], and **5** [13b] were prepared according to the literature procedures. KCP\* was prepared by mixing a slight excess of Cp\*H with KH (Aldrich) in THF. NMR spectra were recorded in THF-*d*<sub>8</sub> solutions on a Bruker DPX 400 spectrometer at 25 °C. Chemical shifts were referenced to TMS. Microanalyses were performed using a Leco CHNS 923 apparatus. X-Ray intensity data for all compounds were collected on a Stoe IPDS 2 T diffractometer with MoK<sub>α</sub> radiation. The data were collected using the Stoe XAREA [25] program using ω-scans. Numeric absorption correction was applied for compound **6** using XRED32 [25]. The space group was determined with XRED32 [24] program. The structure was solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on *F*<sup>2</sup> using SHELXL-97 [25].

### 3.2. Preparation of the precursor [K(DME)]<sub>2</sub>(COT<sup>TBS</sup>) (**2**)

Potassium hydride (3.0 g, 75 mmol) was added to a stirred solution of **1** (11.4 g, 34 mmol) in DME (70 ml) and the mixture was stirred at reflux temperature for 24 h. After cooling to room temperature, unreacted KH was removed by filtration and the clear filtrate was evaporated to dryness. The residue was redissolved in 20 ml of DME. Addition of *n*-pentane (30 ml) and cooling to –20 °C afforded [K(DME)]<sub>2</sub>(COT<sup>TBS</sup>) (**2**) as a white, crystalline solid in 57% yield (11.5 g). Analysis (C<sub>28</sub>H<sub>56</sub>K<sub>2</sub>O<sub>4</sub>Si<sub>2</sub>, *M*<sub>w</sub> = 591.1 g/mol): C 56.21 (calcd. 56.89), H 9.05 (9.55) %. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400.1 MHz): δ = 6.23 (s br, 2H, COT), 6.12 (m, 2H, COT), 5.96 (m, 2H, COT), 3.40 (s, 8H, OCH<sub>2</sub>), 3.25 (s, 12H, OCH<sub>3</sub>), 0.91 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.31 (s, 12H, SiCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 100.6 MHz, 25 °C): δ = 99.2, 99.0, 96.2, 95.6, 93.3, 90.1, 86.3 (CCOT); 72.6 (OCH<sub>2</sub>), 58.8 (OCH<sub>3</sub>), 29.1 (s, C(CH<sub>3</sub>)<sub>3</sub>), 20.3 (C(CH<sub>3</sub>)<sub>3</sub>), –2.2 (SiCH<sub>3</sub>) ppm. <sup>29</sup>Si NMR (THF-*d*<sub>8</sub>, 79.5 MHz, 25 °C): δ = 3.6 ppm.

### 3.3. Synthesis of Cp\*Yb(COT<sup>TBS</sup>) (**3**) and [K(DME)<sub>4</sub>][Yb(COT<sup>TBS</sup>)<sub>2</sub>] (**4**)

A solution of 2.1 g (3.6 mmol) K<sub>2</sub>(DME)<sub>2</sub>[C<sub>8</sub>H<sub>6</sub>(SiMe<sub>2</sub><sup>t</sup>Bu)<sub>2</sub>-1,4] (**2**) in DME (30 ml) was slowly added to a stirred suspension of anhydrous YbCl<sub>3</sub> (1.0 g, 3.6 mmol) in the same solvent (30 ml), and stirring at room temperature was continued for 12 h. Addition of a solution of 0.6 g (3.6 mmol) KCP\* in DME (30 ml) caused the development of a dark blue color and formation of a white precipitate (KCl). After stirring for another 12 h, the precipitate was removed by filtration and the filtrate was evaporated to dryness. The purple residue was extracted with *n*-pentane (50 ml), resulting in formation of a purple solution, while a blue material remained undissolved. After filtration the clear, purple filtrate was concentrated *in vacuo* to a total volume of 15 ml. Crystallization at –20 °C for 3 d afforded 0.7 g (1.11 mmol, 31%) of **3** in the form of purple crystals. The blue residue remaining after the extraction with *n*-pentane was redissolved in DME (30 ml), filtered and concentrated to a total volume of ca. 10 ml. Cooling to –20 °C for 2 d afforded royal-blue, needle-like crystals of **4** in 27% yield (1.2 g, 0.96 mmol).

#### 3.3.1. Cp\*Yb(COT<sup>TBS</sup>) (**3**)

M.p. 242 °C. Analysis (C<sub>27</sub>H<sub>47</sub>Si<sub>3</sub>Yb, *M*<sub>w</sub> = 628.97 g/mol): C 55.88 (calcd. 56.31), H 7.60 (7.88) %. IR (KBr): ν<sub>max</sub> 2952vs, 2924vs, 2881s, 2852s, 2733w, 2706w, 1620wbr, 1471s, 1444w, 1408m, 1359m, 1329w, 1248vs, 1209m, 1181w, 1151w, 1046s, 1006m, 974m, 935s, 925m, 902m, 881w, 828vs, 803s, 787m, 765s, 748s, 671s, 585m, 561w cm<sup>-1</sup>. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400.1 MHz): δ = 50.1 (s, br, COT, 2H), 13.2 (s, br, COT, 2H), 5.9–5.3 (s, br, C<sub>5</sub>Me<sub>5</sub>), –0.9 (s, C(CH<sub>3</sub>)<sub>3</sub>–Si), –8.4 (s, CH<sub>3</sub>–Si), –11.0 (s, CH<sub>3</sub>–Si), –67.39 (s, br, COT, 2H) ppm. <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 100.6 MHz, 25 °C): δ = 142.7 (Ccot(SiMe<sub>2</sub><sup>t</sup>Bu)), 123–103 (Ccot) 108.2 (C<sub>5</sub>Me<sub>5</sub>), 27.2 (C(CH<sub>3</sub>)<sub>3</sub>), 33.1 (C(CH<sub>3</sub>)<sub>3</sub>), 18.06

(C<sub>5</sub>Me<sub>5</sub>), –14.56 (SiMe<sub>2</sub>) ppm. <sup>29</sup>Si NMR (THF-*d*<sub>8</sub>, 79.5 MHz, 25 °C): δ = –9.3 ppm.

#### 3.3.2. [K(DME)<sub>4</sub>][Yb(COT<sup>TBS</sup>)<sub>2</sub>] (**4**)

M.p. 305 °C (beginning dec.). Analysis (C<sub>56</sub>H<sub>112</sub>KO<sub>8</sub>Si<sub>4</sub>Yb, *M*<sub>w</sub> = 1237.96 g/mol): C 53.03 (calcd. 54.33), H 8.95 (9.12) %. IR (KBr): ν<sub>max</sub> 2954vs, 2927vs, 2885s, 2853s, 2730w, 2360w, 1916w, 1470s, 1408m, 1386m, 1360m, 1247vs, 1245w, 1082w, 1044m, 1030s, 1007w, 930w, 934m, 895w, 826vs, 807s, 786m, 762s, 736s, 666s, 581m, 555w, 505m, 459w cm<sup>-1</sup>. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400.1 MHz): δ = 6.18–5.25 (m, COT, 6 H), 0.65 (s, Si–C(CH<sub>3</sub>)<sub>3</sub>), –0.11 (s, Si–CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 100.6 MHz, 25 °C): δ = 146.0, 142.5, 136.5, 129.1 (Ccot); 44.0 (C(CH<sub>3</sub>)<sub>3</sub>), 17.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), –6.0 (s, Si(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>29</sup>Si NMR (THF-*d*<sub>8</sub>, 79.5 MHz, 25 °C): δ = 1.3 ppm.

### 3.4. Synthesis of (DME)<sub>2</sub>K(μ-COT<sup>'''</sup>)YbCp\* (**6**)

A 100 ml Schlenk flask was charged with anhydrous YbCl<sub>3</sub> (1.70 g, 6.0 mmol), KCP\* (1.05 g, 6.0 mmol) and 30 ml of DME. After stirring for 12 h at room temperature, a solution of K<sub>2</sub>(DME)<sub>2</sub>(COT<sup>'''</sup>) (**5**) in DME (30 ml) was added and stirring was continued for another 12 h. A white precipitate (KCl) was removed by filtration and the dark blue-green filtrate was concentrated *in vacuo* to a total volume of ca. 10 ml. Cooling to –20 °C afforded well-formed blue-green blocks in 47% yield (2.40 g). M.p. 363 °C (beginning dec.). Analysis (C<sub>35</sub>H<sub>65</sub>KO<sub>4</sub>Si<sub>3</sub>Yb, *M*<sub>w</sub> = 848.3 g/mol): C 49.3 (calcd. 49.5), H 7.4 (7.7) %. IR (KBr): ν<sub>max</sub> 2952s, 2898m, 2857m, 2734w, 2348w, 2927w, 1442w, 1400w, 1384w, 1310m, 1245vs, 1209w, 1181vw, 1153w, 1073m, 984m, 924w, 869m, 832vs, 765m, 747s, 681m, 636s, 567w, 513m cm<sup>-1</sup>. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400.1 MHz): δ = 6.2–6.5 (br m, 5H, COT<sup>'''</sup>), 1.6 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 0.4 (s br, 27H, CH<sub>3</sub>–Si) ppm. <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 100.6 MHz, 25 °C): δ = 109.9 (C<sub>5</sub>Me<sub>5</sub>); 99.7, 98.2, 96.6, 96.4, 94.1 (C COT<sup>'''</sup>); 10.6 (C<sub>5</sub>Me<sub>5</sub>); 2.1, –1.2 (CH<sub>3</sub>–Si, intensity ratio ca. 2:1) ppm. <sup>29</sup>Si NMR (THF-*d*<sub>8</sub>, 79.5 MHz, 25 °C): δ = –0.5, –1.1 (intensity ratio ca. 2:1) ppm. <sup>171</sup>Yb NMR (THF-*d*<sub>8</sub>, 70.0 MHz, 25 °C) δ = 579.4 ppm.

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### Appendix A. Supplementary material

CCDC 770762 (**3**), 770763 (**4**), and 770761 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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