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

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A R T I C L E   I N F O

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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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Cyclooctatetraenyl ligands
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1. Introduction

Cyclooctatetraenyl ligands (=COT) play an important role in organolanthanide chemistry because the large, flat COT diamions 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)2] (M = alkaline metal) [6]. More recently, bulky organosilyl-substituted COT ligands such as the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (=COTSiMe3) have become increasingly popular [7]. Anionic sandwich complexes of the type [Li(THF)4][Ln(COT)2] (Ln = Ce, Pr, Sm, Y) are formed upon treatment of anhydrous LnCl3 with 2 equiv of Li2(COT)2Cl [8,9]. The solid state structure of [Li(THF)4][Sm(COT)2]2 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)2Tb(COT)2 [7a,b]. The latter an unprecedented ytterbium(II) tetra-decker sandwich complex, Cp*Yb(µ-COT)4 (Cp*=pentamethylcy clopentadienyl) in DME solution (DME = 1,2-dimethoxyethane) afforded a mixture of neutral Cp*Yb(COT)6 (3, purple crystals) and anionic [K(DME)4]Yb(COT)2Cl2 (4, royal blue crystals) which could be separated by selective extraction. In contrast, the closely related reaction of YbCl3 with equimolar amounts of K2(DME)2(COT)00 has become available [8,9]. The solid state structure of [Li(THF)4][Sm(COT)2]2 (1), purple crystals) and anionic [K(DME)4]Yb(COT)2Cl2 (2), royal blue crystals) which could be separated by selective extraction. In contrast, the closely related reaction of YbCl3 with equimolar amounts of K2(DME)2(COT)00 has 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)4 (Cp*=pentamethylcyclopentadienyl) YbCp* (6) as the sole reaction product. The compounds 3, 4, and 6 were structurally characterized by X-ray diffraction.

The influence of bulky silyl-substituted cyclooctatetraenyl ligands on the formation and structure of ytterbium sandwich complexes has been investigated. Treatment of anhydrous YbCl3 with equimolar amounts of [(K(DME)2)2(COT)00, Yb(COT)2Cl2] (2, COTSiMe3 = [C8H6(SiMe2)2]2, 1,4-32 and KCP* (CP* = pentamethylcyclopentadienyl) in DME solution (DME = 1,2-dimethoxyethane) afforded a mixture of neutral Cp*Yb(COT)6 (3, purple crystals) and anionic [K(DME)4]Yb(COT)2Cl2 (4, royal blue crystals) which could be separated by selective extraction. In contrast, the closely related reaction of YbCl3 with equimolar amounts of K2(DME)2(COT)00 has 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)4 (Cp*=pentamethylcyclopentadienyl) YbCp* (6) as the sole reaction product. The compounds 3, 4, and 6 were structurally characterized by X-ray diffraction.

2. Results and discussion

The bulky silyl-substituted cyclooctatetraenyl ligand [C8H6(SiMe2)2]2-1,4-[COTSiMe3] was first reported by Cloke et al. and
YbCl$_3$ + K$_2$(DME)$_2$(SiMe$_2$Bu)$_2$ $\rightarrow$ 2KCP*  

**Scheme 1.**  

...over a range of ca. 120 ppm. A notable spectroscopic detail is the appearance of two well-separated singlet resonances at $\delta = 8.4$ and $-11.0$ ppm for the SiMe$_2$ protons in the $^1$H NMR spectrum of 3, whereas the $^1$H NMR spectrum of 4 displays only one singlet at $\delta = -0.11$ ppm. The reason for this difference became evident after elucidation of the crystal structures (*vide infra*). As expected, the $^{29}$Si NMR spectrum of 3 displays only one signal ($\delta = -9.3$ ppm). The corresponding $^{29}$Si NMR resonance for the anionic complex 4 was found at $\delta = 1.3$ ppm.

Much to our surprise, an analogous reaction of YbCl$_3$ with equimolar amounts of KCP* and [K(DME)$_2$(COT)$_2$] (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]$_2$K($\mu$-COT)$_2$YbCP* (6). Thus the reaction leading to 6 is 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 $^{171}$Yb NMR resonance at $\delta = 579.4$ ppm. This is in excellent agreement with the value reported for the outer ytterbium(2+) ions in the tetra-decker sandwich complex, Cp*Yb($\mu$-COT)$_2$Yb($\mu$-COT)$_2$YbCP*, which have an identical coordination environment. Here the $^{171}$Yb resonance was observed at $\delta = 595$ 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*Eu(Et$_2$O)(THF) upon treatment of EuCl$_3$ with 3 equiv of NaCP* as reported by Zalkin et al. [15a]. Yet another example is the decomposition of the dimer [(MeH$_4$C$_5$)$_2$Yb($\mu$-Me)$_2$] to the Yb$^{3+}$ metalloocene in toluene or diethyl ether [15b] Spectacular cases of reduction of Yb(3+) and even Sm(3+) in the presence of a very bulky perphénylated 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)$^{2-}$ dianion has been reported to be in the range of $-1.82$ V [16a] to $-1.86$ V [16b]. Thus the (COT)$_2$ dianion too should be a strong enough reducing agent to induce reduction of Yb(3+) ([Yb$^{3+}$/Yb$^{2+}$]$^{1/2} = -1.15$ V [16c]).

Single-crystal X-ray diffraction studies provided definitive structural data for the new ytterbium complexes 3, 4, and 6. The...
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 Cp'Yb(COT)3 (3) (Fig. 1) belongs to the fairly large group of mixed-ligand sandwich complexes of the type CpLn(COT) with η6-coordinated COT and η5-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, Cp'Ln(COT) (Ln = Sm, Dy, Er, Yb, 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 Cp'Yb(COT) [14b]. The (ring centroid)–Yb–(ring centroid) angle in 3 is 172.6° as compared to 171.5° in Cp'Yb(COT). It is almost identical with the value reported for Cp'Lu(COT) (172.9° [18]). As mentioned above, the 1H NMR spectrum of 3 displays two well-separated resonances for the SiMe3 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 1H NMR spectrum. A similar result was reported for the uranocene derivative U(COT)2. The 1H NMR spectrum of this compound exhibited SiMe3 proton resonances at δ = 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 Cp* ligand on the opposite side of the molecule. The same phenomenon has been reported for the anionic thorium(III) complex (DME)2K[Th(COT)3]2 [12].

As depicted in Fig. 2, the blue product 4 is a salt consisting of a [K(DME)]2+cation and a [Yb(COT)]−sandwich monoanion. Anionic sandwich complexes of the type [Ln(COT)]− are among the longest known lanthanide COT complexes [6,19], and ring-substituted derivatives containing various triorganosilyl-substituents are also well established [20]. Both (COT)2− rings in the anion are η6-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 [Ph2P(NPPh3)2][Sm(COT)3]2 [20a], [Li(diglyme)2][Ln(H2C=CH2)2](L n = Nd, Sm; R = o-, m-, or p-C6H4Me2NC6H4SiMe3) [20b] and the anionic trivalent thorium complex (DME)2K[Th(COT)3]2 [12]. In all cases the (ring centroid)–metal–(ring centroid) angles deviate only by a few degrees from linearity.

### Table 1

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<td>6631.50(19)</td>
<td>4379.0(15)</td>
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| Formula weight | 640.93 | 1237.96 | 848.30 |
| Space group    | P21/n  | P21/n  | P21/n  |
| T (°C)         | −143   | −143   | −143   |
| λ (Å)          | 0.71073 | 0.71073 | 0.71073 |
| Dab (g cm−3)   | 1.402  | 1.240  | 1.287  |
| μ (mm−1)       | 3.174  | 1.590  | 2.343  |
| R (Fo or Fc)   | 0.0351 | 0.0251 | 0.0464 |
| Rw (Fo or Fc)  | 0.0867 | 0.0541 | 0.1202 |

![Fig. 1. ORTEP view of the molecular structure of Cp'Yb(COT)3 (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)–XOT(C1) 1.646, Yb(1)–XCP* 2.261, XOT–Yb(1)–XCP* 172.6 (X = ring centroids).](image-url)
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 (DME)2K[Th(COT)2] [12] and 177.2° in [Ph3PNPPh3][Sm(COT)2] [20a]). The four bulky SiMe2Bu-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 (DME)2K(μ-COT)YbCp∗(6) is shown in Fig. 3. The compound represents a novel type of divalent lanthanide heterobimetallic sandwich complexes with an almost perfectly linear Cp∗Yb((μ-COT)K arrangement. The (ring centroid)--Yb--(ring centroid) angle in 6 is 178.9°. As in the heterobimetallic thorium(III) complex (DME)2K[Th(COT)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 Cp∗Yb(μ-COT) [3], [K(DME)2][Yb(COT)2] [4], and (DME)2K[μ-COT]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 tetradecamer sandwich Cp∗Yb(μ-COT)Yb(μ-COT)YbCp∗ [13b] it appears once again that the trisubstituted COT 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(III) 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
3.3. Synthesis of Cp

Stirring at room temperature was continued for 12 h. Addition of a precipitate (KCl). After stirring for another 12 h, the precipitate was filtered and concentrated to a total volume of ca. 10 ml. Cooling to 20 °C afforded [K(DME)4][Yb(COTTBS)2] (2) ppm.

3.3.2. [K(DME)4][Yb(COTTBS)2] (4)

M.p. 305 °C (beginning dec.). Analysis (C35H65KO4Si3Yb, Mw = 1237.96 g/mol): C 53.03 (calcd. 54.33), H 8.95 (9.12) %. IR (KBr): \( \nu_{\max } = 2952s, 2898m, 2857m, 2734w, 2348w, 2927w, 1442w, 1400w, 1384w, 1329w, 1245vs, 1209w, 1181vw, 1153w, 984m, 924w, 869m, 832v, 765m, 747s, 681m, 636s, 567w, 513m cm\(^{-1}\)). \( \delta = 6.25 – 6.52 \) (m, COT, 6 H), \( 0.65 \) (s, Si(CH3)3), \( 0.11 \) (s, Si(CH3)2), \( 2.91 \) (C(CH3)3). Afforded well-formed blue-green blocks in 47% yield (2.40 g). M.p. 363 °C (beginning dec.). Analysis (C93H162KO8Si4Yb, Mw = 848.3 g/mol): C 49.3 (calcd. 49.5), H 7.4 (7.7) %. IR (KBr): \( \nu_{\max } = 2952s, 2898s, 2857s, 2734s, 2348w, 2927w, 1442w, 1400w, 1384w, 1310m, 1245v, 1209w, 1181v, 1153w, 1073m, 984m, 924w, 869m, 832v, 765m, 747s, 681m, 636s, 567w, 513m cm\(^{-1}\)). \[ \delta = 6.2 – 6.5 \] (br (m, SiH), 27H, \( \delta = 109.9 \) (COT), 97.9, 98.2, 96.6, 96.4, 94.1 (COT)). A. Edelmann et al. / Journal of Organometallic Chemistry 695 (2010) 2732-2737.

3.3.3. Synthesis of CpYb(COT) (3) and [K(DME)4][Yb(COTTBS)2] (4)

A solution of 2.1 g (3.6 mmol) K2[DME]2[CpH3(SiMe2Bu)2] and 1.44 g (20 ml) DME (30 ml) was slowly added to a stirred suspension of anhydrous YbCl3 (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) KCl in DME (30 ml) caused the development of a dark blue color and 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 10 ml. Crystallization at 20 °C for 3 d afforded 0.7 g (1.11 mmol, 31%) of 2 ppm. 25Si NMR (THF-d8, 75.9 MHz, 25 °C): \( \delta = -9.3 \) ppm.

3.3.4. Synthesis of [DME]2[Yb(COTTBS)2] (6)

A 100 ml Schlenk flask was charged with anhydrous YbCl3 (1.70 g, 6.0 mmol), KCl (1.05 g, 6.0 mmol) and 30 ml of DME. After stirring for 12 at room temperature, a solution of [K(DME)4][Yb(COTTBS)2] (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 (C93H162KO8Si4Yb, Mw = 848.3 g/mol): C 49.3 (calcd. 49.5), H 7.4 (7.7) %. IR (KBr): \( \nu_{\max } = 2952s, 2898s, 2857s, 2734s, 2348w, 2927w, 1442w, 1400w, 1384w, 1310m, 1245v, 1209w, 1181v, 1153w, 1073m, 984m, 924w, 869m, 832v, 765m, 747s, 681m, 636s, 567w, 513m cm\(^{-1}\)). \( \delta = 6.2 – 6.5 \) (br (m, SiH), 27H, \( \delta = 109.9 \) (COT), 97.9, 98.2, 96.6, 96.4, 94.1 (COT)). A. Edelmann et al. / Journal of Organometallic Chemistry 695 (2010) 2732-2737.

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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.

References

(b) W.J. Evans, M.A. Johnston, M.A. Greci, J.W. Ziller, Organometallics 18 (1999) 1460–1464;