# Steric Effects in Lanthanide Sandwich Complexes Containing Bulky Cyclooctatetraenyl Ligands

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Ⓢ *Supporting Information*

ABSTRACT: This paper gives a full account of the complex reaction system $LnCl_3/(COT'')^{2-}$ (COT'' = 1,4-bis-(trimethylsilyl)cyclooctatetraenyl dianion). Four different series of organolanthanide complexes of this bulky COT ligand have been reported: (1) anionic sandwich complexes containing $[Ln(COT'')_2]^-$ anions, (2) dimeric chloro-bridged mono(COT'') complexes, (3) cluster-centered multidecker-sandwich complexes, and (4) linear triple-decker sandwich complexes. In order to get a more complete picture of the reaction system $LnCl_3/(COT'')^{2-}$ and to examine possible steric effects exerted by the COT'' ligand, four new rare-earth-metal COT'' complexes have been prepared: $[Li(DME)_3][Ce(COT'')_2]$ (1), $[Li(THF)_4][Nd(COT'')_2]$ (2), $[(COT'')Nd(\mu\text{-Cl})(THF)]_2$ (4), and $(COT'')Yb(^{DIPP}Form)(THF)$ (5; $^{DIPP}Form = [HC(NAr)_2]^-$, Ar = 2,6-diisopropylphenyl). For comparison, the COT^{TBS} derivative $[Li(DME)_3][Ce(COT^{TBS})_2]$ (3; COT^{TBS} = 1,4-bis(*tert*-butyldimethylsilyl)cyclooctatetraenyl dianion) has also been synthesized. It was found that the steric effect of either COT'' or COT^{TBS} on the molecular structures of the anionic sandwich complexes 1−3 with coplanar ring ligands is rather small. In $(COT'')Yb(^{DIPP}Form)(THF)$ (5), the combination of COT'' with a sterically demanding formamidinate ligand in the coordination sphere of Yb^{3+} still leaves room for THF coordination. For example, in 4, the bulky COT'' leads to coordination of only one THF per Ln in comparison to the parent chloro-bridged dimers $[(COT)Ln(\mu\text{-Cl})(THF)_2]_2$. However, in the dimeric chloro-bridged mono(COT'') complexes the presence of COT'' reduces the number of coordinated THF molecules. Quite surprisingly, an attempt to prepare the holmium analogue of the known linear triple-decker sandwich complex $(COT'')Nd(\mu\text{-}\eta^8:\eta^8\text{-COT}'')Nd(COT'')$ led to formation of the isomerized triple-decker $(COT'')Ho[\mu\text{-}\eta^8:\eta^8\text{-}C_8H_6(SiMe_3)_2\text{-}1,5]Ho(COT'')$ (6), as a result of steric pressure-induced silyl group migration. All new complexes 1−6 have been structurally characterized by X-ray diffraction.
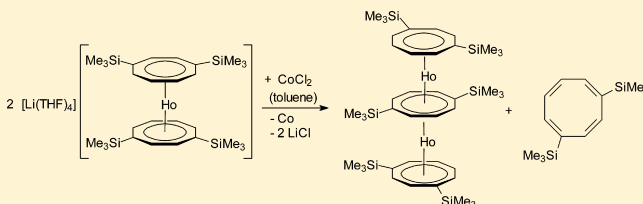
INTRODUCTION

Second only to the countless cyclopentadienyl complexes, the cyclooctatetraenyl ligand ($C_8H_8^{2-}$, commonly abbreviated as COT) has played a preeminent role in organolanthanide chemistry for more than four decades.[1] Early work in this area was mainly focused on complexes bearing unsubstituted COT ligands.[2] Scheme 1 illustrates prototypical complexes of this type which can be considered milestones in the development of organolanthanide chemistry involving COT ligands. These include the anionic sandwich complexes $K[Ln(COT)_2]$ (**A**),[3] the dimeric mono(cyclooctatetraenyl)lanthanide chlorides $[(COT)Ln(\mu\text{-Cl})(THF)_2]_2$ (**B**),[4] the mixed-sandwich complexes $(COT)LnCp$ (**C**),[5] and the so-called cerocene, $Ce\text{-}(COT)_2$ (**D**).[6] The chemistry of these and related compounds has been compiled in several review articles.[2,7]

The use of the unsubstituted COT ligand is associated with several drawbacks. Not only is cyclooctatetraene very expensive[4h] but also the most important series of precursors in this chemistry, the chloro-functional mono(COT) complexes $[(COT)Ln(\mu\text{-Cl})(THF)_2]_2$ (**B**),[4] lack good solubility even in THF. As a consequence, alternative and more soluble 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 developed. However, even their use as precursors in organo-lanthanide chemistry remains limited.[2]
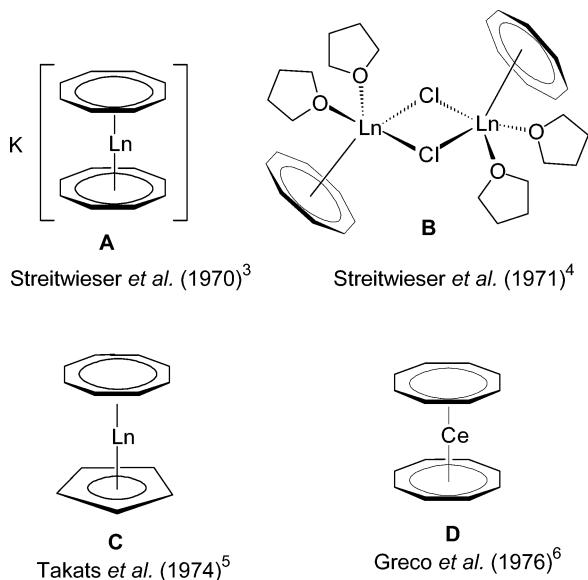
More recently, lanthanide COT chemistry received fundamental new impulses through the use of bulky silyl-substituted cyclooctatetraenyl ligands. The initial idea originated from the pioneering work of Cloke et al., who first employed the 1,4-bis(trimethylsilyl)cyclooctatetraenyl dianion (=COT'')[10] in organolanthanide chemistry.[10b,c] Since then, various other silylated cyclooctatetraenyl ligands have been developed (Scheme 2) which constitute a highly useful library of bulky eight-membered-ring ligands to study steric effects in lanthanide sandwich complexes.[10−16] The use of these bulky COT ligands not only improves the solubility of the products but also can be expected to lead to unprecedented reactivity of these compounds. Among the most notable steric effects are the stabilization of a linear ytterbium(II) quadruple-decker sandwich complex by COT''' ligands and the unprecedented

Scheme 1. Prototypical COT Lanthanide Complexes

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 2. Known Silyl-Substituted Cyclooctatetraenyl Ligands

(COT″)[10,11]

(COT^TBS)[12]

(COT^SiiPr3)[13]

(COT^ArN)[4i,14]
Ar = -C₆H₄NMe₂-o

Ar = -$C_6H_4NMe_2$-o

(COT^BIG)[15]

(COT‴)[16]
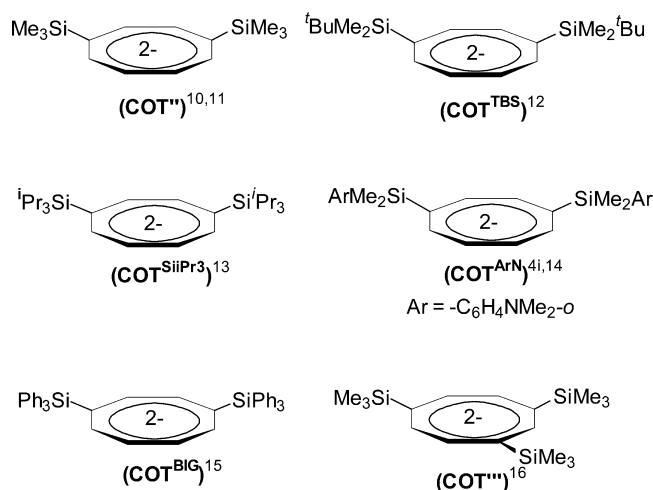
bending of lanthanide sandwich complexes bearing COT^BIG ligands.[15]

The general synthesis of the 1,4-disubstituted ligands shown in Scheme 2 is quite simple and straightforward. It involves metalation of the cheap starting material cycloocta-1,5-diene with *n*-butyllithium followed by addition of a triorganosilyl chloride or triflate to the Li₂COT intermediate.[10−15] Repeated metalation/silylation is required to synthesize the very bulky COT‴ dianion.[16]

■ SHORT OVERVIEW OF LANTHANIDE COT″ COMPLEXES

The largest body of research in this field is centered around the longest known and most easily available ligand, COT″.[10,11] Typically, rare-earth-metal complexes bearing COT″ ligands are prepared by treatment of anhydrous lanthanide trichlorides, LnCl₃, with Li₂COT″ in suitable solvents such as THF (=tetrahydrofuran) or DME (=1,2-dimethoxyethane). The dilithium reagent Li₂COT″ is 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. This way most of the previously reported lanthanide COT″ complexes have been synthesized. However, it is also possible to isolate crystalline adducts of Li₂COT″: e.g. [Li(TMEDA)]₂(COT″) (TMEDA = *N,N,N′,N′*-tetramethyl-ethylenediamine)[10c] and [Li(DME)]₂(COT″).[11e] The latter has been structurally characterized and shown to be an inverse sandwich complex with the two lithium atoms coordinated to the bridging 1,4-bis(trimethylsilyl)cyclooctatetraene dianion ring in an η³-allyl-like fashion.[11e]

The first group 3 and rare-earth-metal COT″ complexes were reported by Cloke et al. in 1989.[10b] This early work already demonstrated that the bulky COT″ exerts steric effects on the resulting complexes, leading in some cases to unprecedented molecular structures not observed in parent COT chemistry. A typical example is the dimeric scandium complex (μ-THF)[(COT″)Sc(μ-Cl)]₂, which was obtained from a reaction of ScCl₃(THF)₃ and Li₂COT″ and was shown to contain a novel semibridging THF ligand.[10b] During the following years it became more and more clear that the reaction system LnCl₃/Li₂COT″ is far more complicated than originally anticipated and that very different reaction products can be formed, depending on the stoichiometries of the starting materials and the reaction conditions. By now, four different types of compounds are known to originate from the combination of the COT″ dianion with lanthanide ions:

1. Anionic Sandwich Complexes Containing [Ln-(COT″)₂]⁻ Ions.[11a,h,17] Anionic sandwich complexes of the type [Li(THF)₄][Ln(COT″)₂] (Scheme 3; **A**, Ln = Y, Ce, Pr,

Scheme 3. Known Complexes Comprising [Ln(COT″)₂]⁻ Anions

Ln = Y, Ce, Pr, Sm[11a]

A

Ln = Tb (L = none),[11h] Dy (L = THF)[17]

B
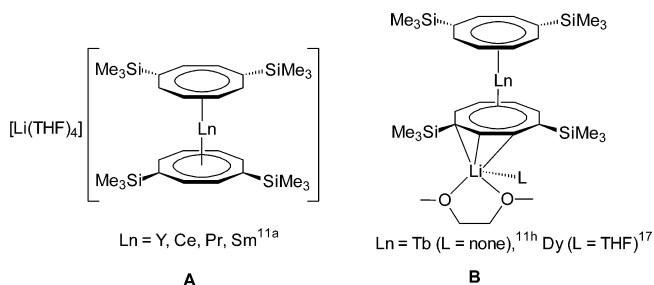
Sm) were first reported in 1997. They are formed upon treatment of anhydrous LnCl₃ with 2 equiv of Li₂(COT″) in THF solution. The solid-state structure of [Li(THF)₄][Sm-(COT″)₂] was found to consist of separated ions and thus displayed no unexpected structural features.[11a] The same reactions carried out in DME solution led to DME-solvated lithium salts of the anionic [Ln(COT″)₂]⁻ sandwich complexes, but these compounds were not further investigated in the course of the earlier study.[11a] Here the influence of the ionic radius of the respective lanthanide element becomes evident. While the large Ce³⁺ ion afforded [Li(DME)₃][Ce-(COT″)₂], monosolvated Li(DME)Tb(COT″)₂ was formed with the "middle lanthanide element" terbium (Scheme 3; **B**). In this case not only the monomeric form shown in Scheme 3 but also a polymeric modification has been structurally characterized. The crystal structure of this modification ([Li(DME)Tb(COT″)₂]ₙ) consists of polymeric, one-dimensional zigzag chains, in which [Tb(COT″)₂]⁻ anions are alternatingly bridged by [Li(DME)]⁺ units. The COT″ rings are η⁸ coordinated to terbium, while the coordination to the

bridging Li atoms is μ-η^2:η^2.[11h] Most recently, the exciting discovery was made that the analogous dysprosium compound Li(DME)(THF)Dy(COT″)$_2$ (Scheme 3; **B**) behaves as a single-ion magnet and demonstrates unusual relaxation modes. The observed relaxation pathways were found to strongly depend on the applied static direct current fields. This first example of an organometallic lanthanide sandwich single-ion magnet underlines once again the potential importance of rare-earth-metal COT complexes.[17]

2. Dimeric Chloro-Bridged Mono(COT″) Complexes.[10b] Only two compounds of this type have been reported by Cloke et al.[10b] The scandium and yttrium complexes depicted in Scheme 4 were prepared by treatment of either

Scheme 4. Known Chloro-Bridged Mono(COT″) Dimers
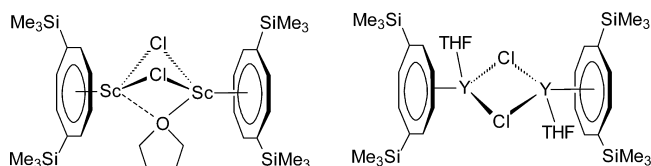
ScCl$_3$(THF)$_3$ or YCl$_3$(THF)$_3$ with Li$_2$COT″ in THF in a 1:1 molar ratio. Here, for the first time, the steric effect of the bulky COT″ ligand on the molecular structures of the products became evident. All previously reported dimeric mono-(cyclooctatetraenyl)lanthanide chlorides [(COT)Ln(μ-Cl)-(THF)$_2$]$_2$ (Scheme 1; **B**)[4] contained two THF ligands attached to each lanthanide ion. In contrast, the combination of COT″ with yttrium leaves room for only two THF ligands in the dimeric molecule. With the small Sc^{3+} ion a chloro-bridged dimer is formed which contains only one THF ligand in an unusual semibridging bonding situation.[10b]

3. Cluster-Centered Multiple-Decker Sandwich Complexes.[11g] In one instance, the reaction of anhydrous PrCl$_3$ with Li$_2$(COT″) in THF solution afforded the unprecedented cluster-centered Pr/Li multiple-decker sandwich complex of the composition [Pr(COT″)]$_2$[Pr$_2$(COT″)$_2$]$_2$Li$_2$(THF)$_2$Cl$_8$ (Scheme 5). Originally, the reaction was intended to yield the triple-decker sandwich complex Pr$_2$(COT″)$_3$ (vide infra). Surprisingly, the structurally characterized cluster complex

Scheme 5. Cluster-Centered Pr/Li Multiple-Decker Sandwich Complex [Pr(COT″)]$_2$[Pr$_2$(COT″)$_2$]$_2$Li$_2$(THF)$_2$Cl$_8$
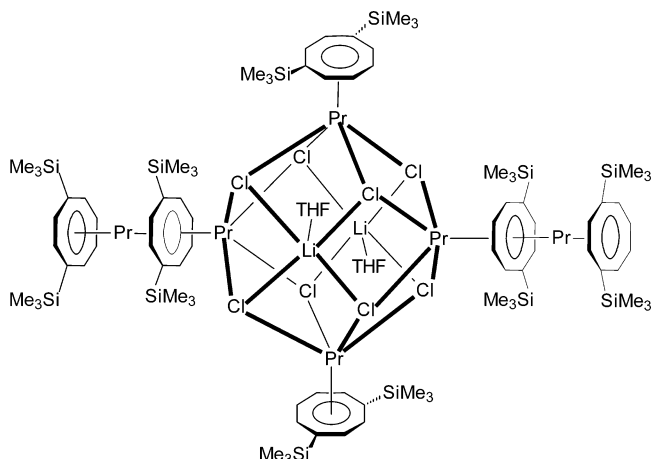
[Pr(COT″)]$_2$[Pr$_2$(COT″)$_2$]$_2$Li$_2$(THF)$_2$Cl$_8$ was reproducibly isolated in high yields (>80%), clearly establishing this novel species as the major product of the reaction.[11g] Initial experiments indicated that the cluster formation is not restricted to Pr. Similar reactions of other anhydrous lanthanide trichlorides (LnCl$_3$, Ln = Ce, Er, Tb) with Li$_2$(COT″) according to Scheme 5 in THF in a molar ratio of 3:2, followed by recrystallization from toluene, afforded brightly colored products (Ce, green; Tb, Er, yellow-orange). In all three cases elemental analyses and IR spectra were in good agreement with the formation of analogous cluster molecules, but all attempts to grow X-ray-quality crystals of the Ce, Tb, and Er derivatives failed, as they crystallized from THF or toluene in the form of extremely thin needles with a cottonlike appearance. These were found to be virtually insoluble in pentane and *n*-hexane, whereas in DME solution the cluster was irreversibly disrupted, presumably with formation of DME solvates of the anionic sandwich complexes Li[Ln-(COT″)$_2$].[11a,h,17] Similarly to the Pr cluster, mass spectra of these species showed the molecular ions of the neutral triple-decker sandwich complexes Ln$_2$(COT″)$_3$ (vide infra) with high intensity. However, this should not be seen as positive proof of the clusters being intermediates in the synthesis of the triple-decker sandwiches in solution. In any case these findings clearly indicated that the system LnCl$_3$/Li$_2$(COT″) is much more diverse than originally anticipated.

4. Linear Triple-Decker Sandwich Complexes..[11d,i] In 1997, we discovered that reactions between anhydrous lanthanide trichlorides, LnCl$_3$ (Ln = Ce, Nd, Sm), with Li$_2$COT″ in the exact molar ratio of 2:3 in THF solution afforded brightly colored complexes, which analyzed well for the desired triple deckers (Scheme 6).[11d]

Scheme 6. Proposed Formation of Lanthanide Triple-Decker Complexes Ln$_2$(COT″)$_3$

$$2\ LnCl_3 + 3\ Li_2COT'' \xrightarrow[-\ 3\ LiCl]{THF}$$

Ln = Ce, Nd, Sm
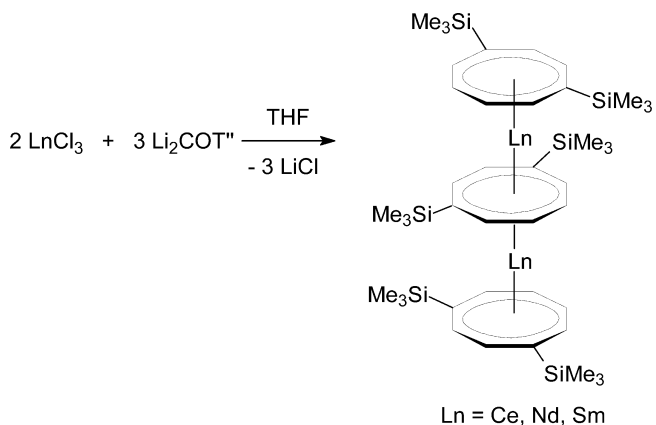
Mass spectra of all three products showed the molecular ions of the unsolvated triple deckers with the correct isotopic patterns. Also in accordance with the triple-decker structure was the appearance of only two ^{29}Si NMR signals for the trimethylsilyl groups (inner and outer rings). Despite numerous attempts, however, all these products failed to give X-ray-quality single crystals, so that the details of the bonding in these compounds remained unknown.[11d] Only very recently a breakthrough was made leading to the first structural authentication of a linear, homoleptic lanthanide triple-decker sandwich complex. This was made possible through a novel access to the triple-decker molecule Nd$_2$(COT″)$_3$. Treatment

of $[Li(THF)_4][Nd(COT'')_2]$[11a] with anhydrous cobalt(II) chloride (molar ratio ca. 2:1) in toluene suspension produced a dark green solution accompanied by formation of a black precipitate of metallic Co (admixed with LiCl). Crystallization of the toluene-soluble material from cyclopentane afforded dark green needlelike crystals, which were identified as the pure triple-decker sandwich complex $Nd_2(COT'')_3$. Its formation (72% yield) in this unexpected redox process is illustrated in Scheme 7. In the course of the reaction, one of the dianionic COT'' ligands in $[Li(THF)_4][Nd(COT'')_2]$ is oxidized to 1,4-bis(trimethylsilyl)cyclooctatetraene.[11i]

Scheme 7. Synthesis of the Linear Nd Triple-Decker Sandwich Complex $Nd_2(COT'')_3$
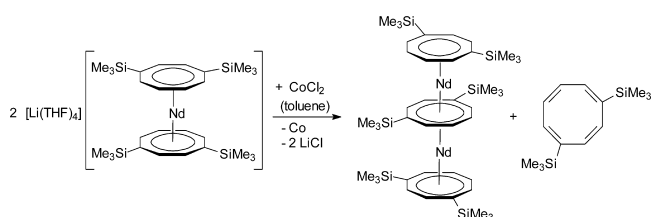
This short overview may illustrate how diverse the reaction system $LnCl_3/Li_2COT''$ really is. In this contribution we try to round out the picture by adding some new facets to this part of organolanthanide chemistry. Moreover, we intend to outline the possible steric effects exerted by the bulky COT'' ligand when it is attached to rare-earth-metal ions.

■ RESULTS AND DISCUSSION

Thus far, steric effects in anionic lanthanide sandwich complexes coordinated by two COT ligands have only been observed in a cerium(III) complex containing the superbulky ligand COT^{BIG} (cf. Scheme 1). It was found that in the complex $[Li(DME)_2][Ce(COT^{BIG})_2]$ the anion is significantly bent (tilt angle between the eight-membered rings: 15.1°).[16] In contrast, no notable deviation from coplanarity of the COT rings was found for the structurally characterized complexes $[Li(THF)_4]$-$[Sm(COT'')_2]$,[11a] $Li(DME)Tb(COT'')_2$,[11h] $[Li(DME)Tb-(COT'')_2]_n$,[11h] $Li(DME)(THF)Dy(COT'')_2$,[17] and $[K-(DME)_4][Yb(COT^{TBS})_2]$.[12b] In order to further elucidate possible structural effects and to get a more complete picture, three anionic sandwich complexes of this type with early lanthanide metals, shown in Scheme 8, have been structurally investigated by X-ray diffraction.

All three complexes, $[Li(DME)_3][Ce(COT'')_2]$ (**1**), $[Li-(THF)_4][Nd(COT'')_2]$ (**2**), and $[Li(DME)_3][Ce(COT^{TBS})_2]$ (**3**), were prepared following the established protocol by treatment of anhydrous lanthanide trichlorides with 2 equiv of the dilithium COT reagent in either DME or THF.[11,12] Cerium(III) complexes **1** and **3** both form bright green,

exceedingly air-sensitive crystals. It should be noted that the $[Ce(COT'')_2]^-$ anion has previously been generated in situ and used as an intermediate in the synthesis of the purple tetrasilylated cerocene derivative $Ce(COT'')_2$.[16a] The Nd derivative **2** forms dark green, air-sensitive crystals. The lithium salt **3** additionally contains 1 equiv of DME of crystallization in the unit cell. In general, DME appears to be the solvent of choice for crystallizing the anionic sandwich complexes. The DME solvates **1** and **3** easily form very large (edge dimensions up to ca. 0.5 cm), bright green single crystals which apparently do not lose DME even under vacuum or upon prolonged standing in the drybox. In contrast, crystals of **2** become opaque when stored in the drybox, indicating an easier loss of solvent. All complexes were structurally characterized through X-ray crystallography (Table 1, Figures 1−3).

The crystal structure analyses revealed that the compounds **1**−**3** all comprise separated ion pairs in the solid state, composed of either octahedrally coordinated $[Li(DME)_3]^+$ (**1**, **3**) or tetrahedrally coordinated $[Li(THF)_4]^+$ (**2**) cations and the respective sandwich anion $[Ln(COT'')_2]^-$ (Ln = Ce (**1**), Nd (**2**)) or $[Ce(COT^{TBS})_2]^-$ (**3**). As expected, the planar eight-membered COT rings are η^8 coordinated to the lanthanide ions. In the two cerium(III) derivatives the Ce−C bond lengths fall in the narrow ranges of 2.748(3)−2.772(3) Å (**1**) and 2.734(2)−2.802(2) Å (**3**). These data already indicated that the two bulky COT'' and COT^{TBS} ligands exert virtually the same low steric effects, as the differences in Ce−C bond lengths are negligible. Figure 3 nicely illustrates how the four *tert*-butyl groups are all pointing away from the cerium center. This makes it plausible to assume that, despite the presence of two *tert*-butyl groups at silicon in COT^{TBS}, there is little or no difference in the steric bulk between the two cyclooctatetraenyl dianions $(COT'')^{2-}$ and $(COT^{TBS})^{2-}$. A very similar behavior of a disubstituted COT ligand has been reported earlier by Roesky et al. for the anionic lanthanide sandwich complexes $[Li(diglyme)_2][Ln(COT^{ArN})_2]^-$ (Ln = Nd, Sm; for COT^{ArN} see Scheme 2).[14a] A crystal structure determination of the neodymium derivative revealed that the *N,N*-dimethylaniline substituents at silicon are all turned away from the neodymium center. Despite the possibility of intra- or intermolecular coordination of the *N,N*-dimethylaniline moieties the COT^{ArN} ligand does not differ significantly from COT'' in its steric effects.[14a] This is further underlined by the fact that in all anionic lanthanide sandwich complexes comprising COT'', COT^{TBS}, or COT^{ArN} ligands the two COT rings are always in a nearly parallel arrangement. Typical tilt angles are in the range from 5.8° in **1** through 3.59° in $Li(DME)(THF)Dy(COT'')_2$[17] to 2.2° in **2**. A very significant deviation from the coplanar coordination mode of the COT rings in anionic lanthanide sandwiches was recently reported for the trivalent cerium complex $[Li(DME)_2][Ce(COT^{BIG})_2]$.[15] For this compound an astonishingly high tilt angle of 15.1° has been determined, clearly a result of steric hindrance between opposing phenyl rings of the $SiPh_3$ substituents.

Surprisingly, the number of well-characterized mono(COT'') lanthanide halides is limited to the two scandium and yttrium derivatives described in the early work of Cloke et al.[10b] In the course of the present study we developed a simple one-pot synthesis leading to a new member of this series, the dimeric mono(COT'') neodymium chloride complex $[(COT'')Nd(\mu\text{-}Cl)(THF)]_2$ (**4**). The compound was prepared in 69% yield by treatment of anhydrous neodymium trichloride with in situ prepared Li_2COT'' in a 1:1 molar ratio in THF solution

Scheme 8. Anionic COT'' Sandwich Complexes 1−3

1: Ln = Ce, $[Li(solv)_n] = [Li(DME)_3]$
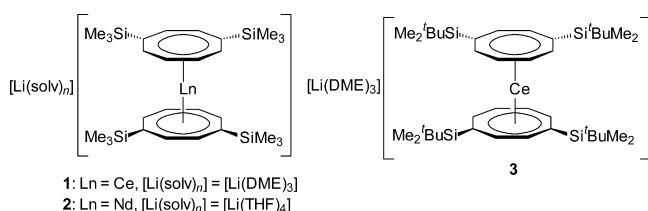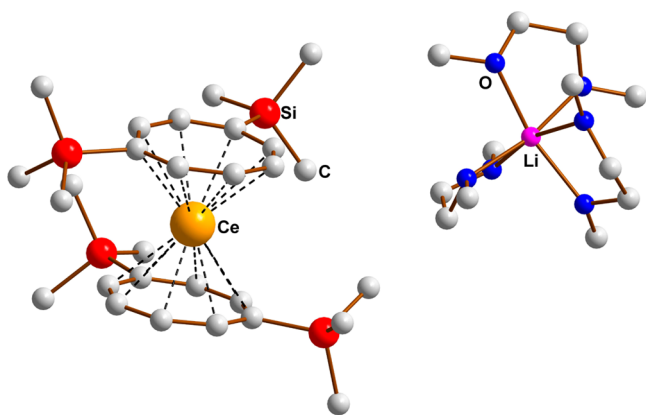**2**: Ln = Nd, $[Li(solv)_n] = [Li(THF)_4]$

Table 1. Crystallographic Data for 1−6

|	1	2	3	4	5	6
empirical formula	$C_{40}H_{78}CeLiO_6Si_4$	$C_{44}H_{80}LiNdO_4Si_4$	$C_{56}H_{112}CeLiO_8Si_4$	$C_{50}H_{80}Cl_2Nd_2O_2Si_4$	$C_{57}H_{83}N_2OSi_2Yb$	$C_{42}H_{72}Ho_2Si_6$
a (Å)	11.616(2)	11.3988(2)	18.051(4)	12.462(3)	12.529(3)	11.800(2)
b (Å)	12.321(3)	11.7195(2)	19.402(4)	10.798(2)	32.137(6)	13.130(3)
c (Å)	18.436(4)	19.5981(4)	21.261(4)	21.049(4)	14.071(3)	15.747(3)
α (deg)	98.92(3)	87.119(2)	90	90	90	87.29(3)
β (deg)	102.40(3)	81.867(2)	114.30(3)	102.05(3)	105.77(3)	81.26(3)
γ (deg)	98.87(3)	78.888(2)	90	90	90	86.64(3)
V (Å³)	2497.3(9)	2542.44(8)	6787(2)	2770.0(10)	5452.2(19)	2405.4(8)
Z	2	2	4	4	4	2
formula wt	914.46	936.62	1172.88	1184.88	1041.47	1075.40
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
T (°C)	−93	−120	−100	−100	−140	−140
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calcd} (g cm⁻³)	1.216	1.223	1.148	1.421	1.269	1.485
μ (mm⁻¹)	1.045	1.151	0.785	2.071	1.797	3.441
$R(F_o$ or $F_o^2)$	0.0325	0.0292	0.0310	0.0349	0.0541	0.0583
$R_w(F_o$ or $F_o^2)$	0.0783	0.0644	0.0672	0.0970	0.1273	0.1011

Figure 1. ORTEP drawing of the molecular structure of $[Li(DME)_3]$-$[Ce(COT'')_2]$ (**1**). Selected bond lengths (Å) and angles (deg): Ce−$C_{COT''}$, 2.748(3)−2.772(3); Li−O, 2.058(5)−2.223(5); Ce−$X_{COT''}$, 2.055, 2.055; $X_{COT''}$−Ce−$X_{COT''}$, 176; $X_{COT''}$−$X_{COT''}$ tilt angle, 3.8 ($X_{COT''}$ = ring center). H atoms have been omitted for clarity.

(Scheme 9). The air-sensitive green compound was fully characterized by spectroscopic methods (IR; MS; ^1H, ^{13}C, and ^{29}Si NMR) and elemental analysis. The ^1H and ^{13}C NMR spectra both showed the presence of one coordinated THF
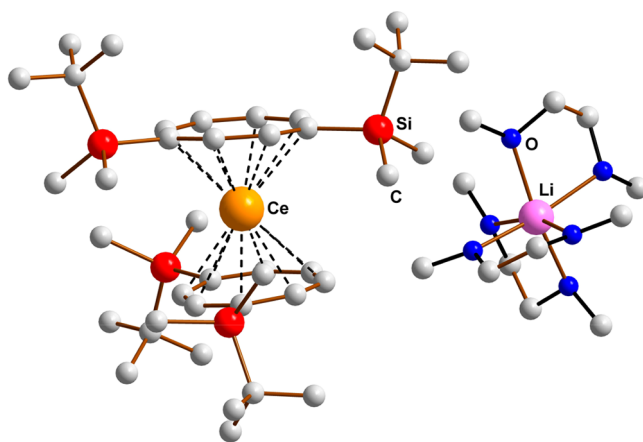

Figure 3. Molecular structure of $[Li(DME)_3][Ce(COT^{TBS})_2]$·DME (**3**). Selected bond lengths (Å) and angles (deg): Ce−$C_{COT''}$, 2.734(2)−2.802(2); Li−O, 2.109(5)−2.177(5); Ce−$X_{COT''}$, 2.043, 2.066; $X_{COT''}$−Ce−$X_{COT''}$, 174.3; $X_{COT''}$−$X_{COT''}$ tilt angle, 5.8 ($X_{COT''}$ = ring center). H atoms and the DME of crystallization have been omitted for clarity.

molecule per neodymium. The ^{29}Si NMR spectrum displayed only one singlet at δ −46.4 ppm for the SiMe₃ substituents,
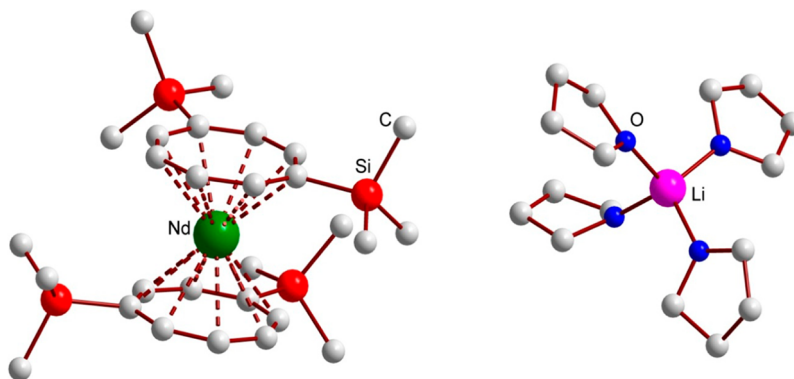

Figure 2. Molecular structure of $[Li(THF)_4][Nd(COT'')_2]$ (**2**). Selected bond lengths (Å) and angles (deg): Nd−$C_{COT''}$, 2.693(2)−2.725(2); Li−O, 1.914(4)−1.927(4); Nd−$X_{COT''}$, 1.993, 1.996; $X_{COT''}$−Nd−$X_{COT''}$, 177.5; $X_{COT''}$−$X_{COT''}$ tilt angle, 2.2 ($X_{COT''}$ = ring center). H atoms have been omitted for clarity.

Scheme 9. Synthesis of the Dimeric Mono(COT″) Neodymium Complex 4
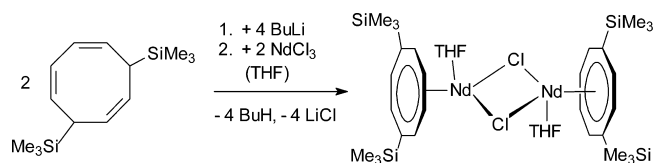
indicative of a centrosymmetric dimeric structure in which the trimethylsilyl groups are chemically equivalent.

The presence of a centrosymmetric dimer was confirmed by the X-ray structural analysis of **4** (Table 1, Figure 4). Deep green X-ray-quality single crystals of a ditoluene solvate were obtained by recrystallization from toluene.
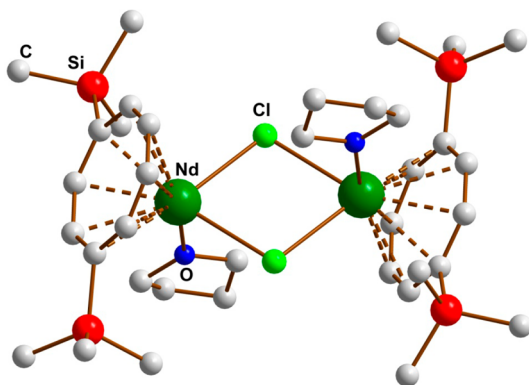

Figure 4. Molecular structure of $[(COT'')Nd(\mu\text{-}Cl)(THF)]_2 \cdot 2\text{-}(toluene)$ (**4**). Selected bond lengths (Å) and angles (deg): Nd−$C_{COT''}$, 2.628(4)−2.664(4); Nd−Cl, 2.8288(1); Nd−Cl#1, 2.8463(12); Nd−O, 2.503(3); Nd−$X_{COT''}$, 1.896, 1.896; Cl−Nd−Cl#1, 76.68(4); Nd−Cl−Nd#1, 103.32(4) ($X_{COT''}$ = ring center; (#1) −x + 1, −y + 1, −z + 1). H atoms and the toluene of crystallization have been omitted for clarity.

The most notable structural feature of **4** is the presence of only one coordinated THF molecule per neodymium. Despite the significantly larger neodymium ions in **4** (ionic radius of Nd^{3+} 0.99 Å)[18] the coordination environment around the rare-earth-metal centers is identical with that in the previously reported yttrium dimer $[(COT'')Y(\mu\text{-}Cl)(THF)]_2$[10b] (ionic radius of Y^{3+} 0.900 Å). This is in contrast to the case for all structurally characterized mono(COT) lanthanide halide dimers comprising the unsubstituted COT ligand, including $[(COT)Ln(\mu\text{-}Cl)(THF)_2]_2$ (Scheme 1, **B**; Ln = Ce, Pr, Nd, Sm)[4] and $[(COT)La(\mu\text{-}I)(THF)_2]_2$[2] which all have two THF ligands attached to each of the lanthanide centers. Clearly, in this group of organolanthanide complexes, the bulky COT″ does have a measurable steric influence, as it reduces the degree of THF solvation. Apart from this significant result, the molecular structure of **4** displays no unusual structural features. The Nd−C bond lengths in **4** range from 2.628(4) to 2.664(4) Å (average 2.649(4) Å) and are well within the range typical for Nd(COT) complexes reported previously.[1,2,14] The central four-membered $Nd(\mu\text{-}Cl)_2Nd$ unit forms a planar rectangle with a large angle (103.32(4)°) at chlorine and a much smaller angle (76.68(4)°) at Nd. The Nd−Cl distances are 2.8288(10) and 2.8463(12) Å. At 2.503(3) Å the Nd−O(THF) bond length is in the normal range (cf. Nd−O 2.509(4)−2.580(4) Å in $(COT)NdI(THF)_3$).[2]

Mono(cyclooctatetraenyl)lanthanide complexes containing additional amidinate ligands have been reported many years ago by Schumann and Edelmann et al.[19] A series of complexes of the general formula $(COT)Ln[p\text{-}RC_6H_4C(NSiMe_3)_2]\text{-}(THF)$ (Ln = Y, Ce, Pr, Nd, Sm; R = H, OMe, CF_3) have been prepared and structurally characterized. The formation of mono(THF) solvates was observed throughout the series, independent of the ionic radius of the rare-earth metal used.[19] More recently, the same basic structure was found for the mono(COT″) samarium amidinate complex $(COT'')Sm\text{-}(^{DIPP}Form)(THF)$ $(^{DIPP}Form = [HC(NAr)_2]^-$, Ar = 2,6-diisopropylphenyl).[20] Despite the presence of two significantly more bulky ligands, i.e. COT″ and $^{DIPP}Form$,[21] no unsolvated material could be isolated. In the present work we investigated the crystal structure of the ytterbium analogue $(COT'')Yb\text{-}(^{DIPP}Form)(THF)$ (**5**) in order to get a more complete picture. Compound **5** was prepared according to the published procedure by treatment of anhydrous ytterbium trichloride with a 1:1 mixture of in situ prepared $Li(^{Dipp}Form)$[21] and $Li_2(COT'')$ in THF, as shown in Scheme 10.[20] The molecular structure of **5** is depicted in Figure 5.

Scheme 10. Synthesis of $(COT'')Yb(^{DIPP}Form)(THF)$ (5)
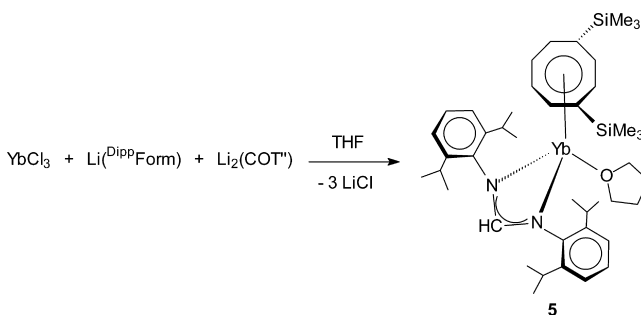
Surprisingly, despite the presence of two very bulky ligands, COT″ and $^{Dipp}Form$, in combination with the small Yb^{3+} ion (ionic radius 0.868 Å versus 0.958 Å for Sm^{3+})[18] the molecule still contains one coordinated THF ligand. Thus, the overall coordination geometry around Yb can be best described as a three-legged piano stool with the COT″ ligand being η^8
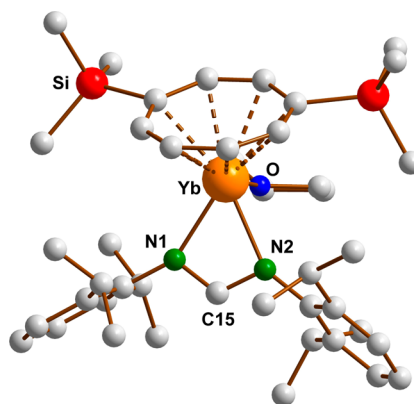
**Figure 5.** Molecular structure of $(COT'')Yb(^{DIPP}Form)(THF)$ (**5**). Selected bond lengths (Å) and angles (deg): Yb−$C_{COT''}$, 2.748(3)−2.772(3); Yb−N1, 2.341(4), Yb−N2, 2.372(4); Yb−O, 2.340(4); C15−N1, 1.333(6); C15−N2, 1.324(6); Yb−$X_{COT''}$, 1.768; N−Yb−N, 57.70(14); N−C−N, 117.8(5); $X_{COT''}$−$X_{COT''}$ tilt angle, 3.8 ($X_{COT''}$ = ring center). H atoms have been omitted for clarity.

coordinated and the (^{Dipp}Form)$^-$ anion acting as a N,N′-chelating ligand. Typical for amidinate- and guanidinate-type chelating ligands is the very small bite angle, which in the case of **5** is 57.70(14)°. The Yb−C(COT″) distances, ranging from 2.748(3) to 2.772(3) Å, are significantly elongated in comparison to previously reported Yb−C(COT) bond lengths (e.g., Yb−C 2.462(3)−2.503(3) Å in Cp*Yb(COT^{TBS}),[12b] 2.5877(15)−2.6444(14) Å in [K(DME)$_4$][Yb(COT^{TBS})$_2$],[12b] and 2.550(3) Å (av) in Cp*Yb(COT″)[22]). This is certainly a strong indication for steric congestion around the central Yb^{3+} ion caused by this particular ligand set. However, an unsolvated complex of the type (COT)Ln(amidinate) remains elusive.

Certainly the most remarkable steric effects of bulky COT ligands on the structures of organo-rare-earth-metal complexes were seen in some unique triple- and quadruple-decker sandwich complexes.[7g] In the divalent ytterbium quadruple-decker sandwich molecule Cp*Yb(μ-COT‴)Yb(μ-COT‴)-YbCp* the COT‴ rings as middle decks effectively prevent bending of the quadruple-decker structure.[15] Previously reported triple-decker complexes of divalent lanthanides (Sm, Eu, Yb) were always found to be strongly bent at the metal sites. Typical structurally characterized examples include e.g. the bent triple deckers (μ-η^8:η^8-COT)[(C$_5$Me$_4$R)Ln]$_2$ (Ln = Sm, Eu, Yb; R = Me, Et) (Scheme 11) reported by Evans et al.[23]

**Scheme 11. Bent Triple-Decker Structures of Divalent Lanthanides[23]**

R = Me, Et
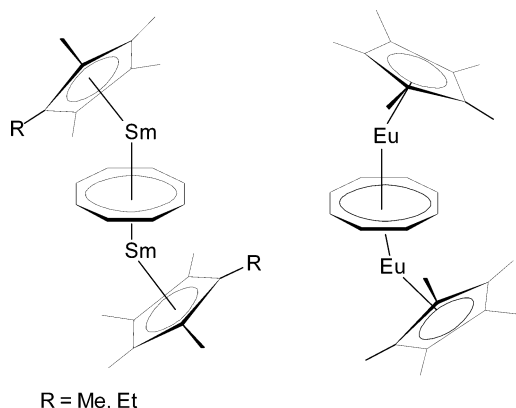
As illustrated in Scheme 7, the synthesis of the first structurally characterized linear homoleptic lanthanide triple-decker complex, Nd$_2$(COT″)$_3$, was made possible through the use of the bulky COT″ ligand. Here the steric benefits of this bis(silylated) COT ring become immediately evident. Most of

the parent triple deckers Ln$_2$(COT)$_3$ either have unknown structures[6,24] or tend to add THF to give bent arrangements.[25] The only exception is Ce$_2$(COT)$_3$, for which the linear triple-decker structure was established by EXAFS.[24] The dinuclear neodymium complex Nd$_2$(COT″)$_3$ is soluble in organic solvents and can be recrystallized from toluene to give well-formed, dark green crystals that allowed structural characterization through X-ray crystallography. In the course of the present study we became interested in expanding the scope of the CoCl$_2$-based synthetic protocol shown in Scheme 7 to other lanthanide elements. An initial experiment with the smaller holmium(3+) ion produced a very surprising result. As illustrated in Scheme 12, the anionic sandwich precursor [Li(THF)$_4$][Ho(COT″)$_2$] (prepared in situ) could also be converted to a triple decker using anhydrous cobalt(II) chloride (molar ratio 2:1) in toluene suspension. Once again, the reaction was accompanied by formation of metallic Co and LiCl as well as the soluble oxidation product 1,4-bis(trimethylsilyl)-cyclooctatetraene. Orange crystals could be isolated in fairly good yield (62%) after extraction with cyclopentane followed by crystallization from the same solvent. An elemental analysis was in good agreement with the formation of the desired triple decker Ho$_2$(COT″)$_3$ (**6**). However, due to the strongly paramagnetic nature of the Ho^{3+} ion, no meaningful NMR data could be gathered for the product. A mass spectrum showed mostly nonassignable fragments and no molecular ion. Thus, in this case structural characterization through X-ray diffraction was particularly important.

An X-ray crystal structure determination of the bright orange Ho$_2$(COT″)$_3$ (**6**) revealed a highly unusual structural feature (Figure 6). However, one has to look twice to see the fundamental difference between the reaction products shown in Schemes 7 and 11. Despite the use of pure [Li(THF)$_4$][Ho-(COT″)$_2$] starting material, the holmium triple-decker contains the hitherto unknown *1,5-bis(trimethylsilyl)cyclooctatetraenyl* dianion as the middle deck! The presence of this isomer as an impurity in any of the starting materials used to prepare [Li(THF)$_4$][Ho(COT″)$_2$] can be ruled out, since the purity was checked at every stage and the product Ho$_2$(COT″)$_3$ was isolated in over 60% yield. The formation of (COT″)Ho[μ-C$_8$H$_6$(SiMe$_3$)$_2$-1,5]Ho(COT″), as it should be more appropriately formulated, can only be explained by a sterically induced silyl group migration. Going from the large Nd^{3+} ion to the smaller Ho^{3+} obviously causes too much steric hindrance between opposing SiMe$_3$ groups, which can be diminished by formation of the less constrained isomer containing the new [C$_8$H$_6$(SiMe$_3$)$_2$-1,5]$^{2-}$ dianion as bridging ligand. A comparable case of sterically induced silyl group migration has recently been reported for the formation of the neutral "superbulky"

Scheme 12. Synthesis of the Triple-Decker Sandwich Complex (COT″)Ho[μ-η^8:η^8-C$_8$H$_6$(SiMe$_3$)$_2$-1,5]Ho(COT″) (6)
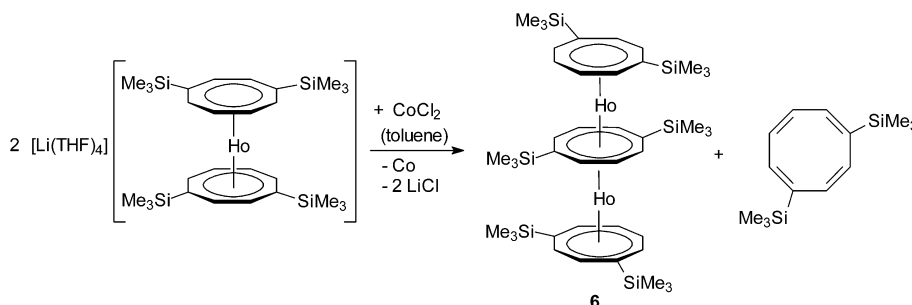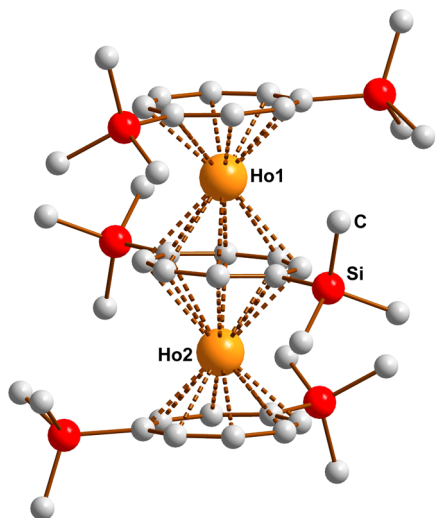
Figure 6. Molecular structure of $(COT'')Ho[\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_6(SiMe_3)_2\text{-}1,5]Ho(COT'')$ (**6**). Selected bond lengths (Å) and angles (deg) are as follows ($X_{COT''}$ = ring center). Molecule 1: $Ho-C_{COT''(inner)}$, 2.703(9)−2.881(8); $Ho-C_{COT''(outer)}$, 2.510(8)−2.570(7); $Ho-X_{COT''(inner)}$, 2.064; $Ho-X_{COT''(outer)}$, 1.747; $X_{COT''(outer)}-Ho-X_{COT''(inner)}$, 177.1; $X_{COT''(outer)}-Ho-X_{COT''(inner)}$ tilt angle, 3.4. Molecule 2: $Ho-C_{COT''(inner)}$, 2.716(9)−2.803(8); $Ho-C_{COT''(outer)}$, 2.519(11)−2.580(9); $Ho-X_{COT''(inner)}$, 2.048; $Ho-X_{COT''(outer)}$, 1.751; $X_{COT''(outer)}-Ho-X_{COT''(inner)}$, 175.3; $X_{COT''(outer)}-Ho-X_{COT''(inner)}$ tilt angle, 4.7. H atoms have been omitted for clarity.

cerocene $Ce(COT^{BIG(1,3)})_2$ by Ag[I] oxidation of the anionic cerium(III) precursor $[Li(DME)_2][Ce(COT^{BIG})_2]$.[15] While the substitution pattern in the latter is 1,4, the resulting neutral cerocene molecule contains the novel 1,3-isomer of the COT^{BIG} ligand. Obviously steric pressure becomes too severe upon oxidation to the neutral species so that $SiPh_3$ group migration is induced for relief. The result of this unprecedented rearrangement is the sterically more relaxed and highly symmetrical molecular structure of $Ce(COT^{BIG(1,3)})_2$.[15] The unexpected synthesis of **6** provides the first example of such sterically induced silyl group migration involving the COT″ ring ligand. By formation of the hitherto unknown 1,5-bis(trimethylsilyl)cyclooctatetraenyl ligand as the middle deck the resulting molecule can also adopt a highly symmetrical and sterically more relaxed structure which is much better adjusted to the smaller ionic radius of trivalent holmium as compared to Nd^{3+}. The triple decker **6** is centrosymmetric, with the central holmium forming the center of inversion. The crystal structure of **6** comprises two independent molecules which differ only slightly in their structural parameters: e.g., the tilt angles between two eight-membered rings are 3.4° in one molecule and 4.7° in the other. Like its Nd congener, the holmium derivative **6** features a near-linear arrangement of the COT″ ring with $X_{COT''(outer)}-Ho-X_{COT''(inner)}$ = 177.1° (molecule 1) and 175.3° (molecule 2) ($X_{COT''}$ = ring center). These values are virtually identical with those found for $Nd_2(COT'')_3$ (175.6, 176.1, and 177.9°).[11i] The Ho−C distances in **6** are in the expected range and can be favorably compared to the Dy−C distances in $Li(DME)(THF)Dy(COT'')_2$.[17] As in the Nd triple decker, the Ho−C bond lengths to the bridging COT″ ring are ca. 0.2 Å longer (range 2.703(9)−2.881(8) Å for both independent molecules) than the Ho−C distances to the outer COT″ ligands (range 2.510(8)−2.580(9) Å for both independent molecules).

CONCLUSIONS

In summarizing the work reported here, the chemistry of organolanthanide complexes comprising bulky COT ligands has been expanded by six new structurally characterized sandwich and half-sandwich complexes. The present study also tries to put the results obtained with the complex reaction system $LnCl_3/(COT'')^{2-}$ (COT″ = 1,4-bis(trimethylsilyl)-cyclooctatetraenyl dianion) into a broader context. It is shown that the steric effects of bulky COT ligands imposed on the structures of anionic lanthanide(III) sandwich complexes, such as $[Li(DME)_3][Ce(COT'')_2]$ (**1**), $[Li(THF)_4][Nd(COT'')_2]$ (**2**), and $[Li(DME)_3][Ce(COT^{TBS})_2]$ (**3**), are quite small, with the only exception being the "superbulky" ligand COT^{BIG}. In dimeric mono(COT) lanthanide halides, use of the sterically demanding COT″ ligand leads to a lower degree of solvation even for the early lanthanides, as exemplified by $[(COT'')Nd(\mu\text{-}Cl)(THF)]_2$ (**4**). In $(COT'')Yb(^{DIPP}Form)(THF)$ (**5**), the combination of COT″ with a sterically demanding formamidinate ligand in the coordination sphere of Yb^{3+} still leaves room for THF coordination. Much to our surprise, an attempt to prepare the holmium analogue of the known linear triple-decker sandwich complex $(COT'')Nd(\mu\text{-}\eta^8{:}\eta^8\text{-}COT'')Nd(COT'')$ led to formation of the isomerized triple decker $(COT'')Ho[\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_6(SiMe_3)_2\text{-}1,5]Ho(COT'')$ (**6**) as a result of steric pressure induced silyl group migration. Here the steric influence of the bulky COT″ ring ligand becomes most evident. This exciting result clearly shows that significantly more work is required in order to gain a better understanding of such lanthanide triple-decker sandwich complexes containing bulky COT ligands.

EXPERIMENTAL SECTION

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 a nitrogen atmosphere prior to use. All glassware was oven-dried at 120 °C for at least 24 h, assembled while hot, and cooled under high vacuum prior to use. The starting materials, anhydrous $LnCl_3$ (Ln = Ce, Nd),[26] $C_8H_8(SiMe_3)_2$,[10] $Li_2(COT'')$,[10] $Li_2(COT^{TBS})$·THF,[12] and anhydrous $CoCl_2$,[27] and compound **5**[20] were prepared according to published procedures. The NMR spectra were recorded in C_6D_6 or THF-d_8 solutions on a Bruker DPX 600 (^1H, 600.1 MHz; ^{13}C, 150.9 MHz) or a Bruker AVANCE-DMX400 instrument (5 mm BB; ^1H, 400.1 MHz; ^{13}C, 100.6 MHz), ^1H 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. Mass spectra (EI, 70 eV) were run on a MAT 95 apparatus. Microanalyses of the compounds were performed using a Leco CHNS 923 apparatus.

Synthesis of $[Li(DME)_3][Ce(COT'')_2]$ (1). Anhydrous $CeCl_3$ (4.6 g, 18.6 mmol) was added to a stirred THF (100 mL) solution of in situ prepared $Li_2(COT'')$ (from 74.4 mmol (=46.5 mL) of 1.6 M n-butyllithium solution in n-hexane and 37 mmol (=9.3 g) of $C_8H_8(SiMe_3)_2$) at room temperature. The reaction mixture was stirred for 48 h, the precipitated LiCl was removed by filtration through a thin layer of Celite filter aid, and the clear, green filtrate was evaporated in vacuo to give a green oil, which solidified upon trituration with 40 mL of n-pentane. Recrystallization from DME (50 mL) at −20 °C afforded $[Li(DME)_3][Ce(COT'')_2]$ (**1**) in the form of exceedingly air sensitive, bright green crystals (10.5 g, 71%) which were suitable for X-ray crystallography. Anal. Calcd for $C_{40}H_{78}CeLiO_6Si_4$ (M_r = 914.46): C, 52.54; H, 8.60. Found: C, 53.44; H, 8.09. The low carbon value might be traced back to the

extreme air sensitivity of **1**, which makes the compound difficult to handle. IR (KBr disk): ν 3024 w, 2949 s, 2894 m, 1450 m, 1243 s, 1078 s, 1051 s, 832 vs, 717 s cm^{-1}. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 6.5−5.7 (br m, 12H, COT-H), 3.20 (br s, 12H, DME-CH_2), 3.18 (br s, 18H, DME-CH_3), 2.74 (br s, 18H, SiCH_3) ppm. ^{13}C NMR (100.6 MHz, THF-d_8, 25 °C): δ 102.4, 101.2, 100.9, 98.8 (br, COT), 72.4 (br s, DME-CH$_2$), 58.9 (br s, DME-CH$_3$), 5.3 (s, SiCH$_3$) ppm. ^{29}Si NMR (79.5 MHz, THF-d_8, 25 °C): δ −16.0 ppm.

Synthesis of [Li(THF)$_4$][Nd(COT″)$_2$] (2). Anhydrous NdCl$_3$ (1.5 g 6.0 mmol) was added to a stirred THF (150 mL) solution of in situ prepared Li$_2$(COT″) (from 24.0 mmol (=15.0 mL) of 1.6 M *n*-butyllithium solution in *n*-hexane and 12.0 mmol (=3.0 g) of C$_8$H$_6$(SiMe$_3$)$_2$) at room temperature. The reaction mixture was stirred for 24 h, and the solvents were evaporated under vacuum. The solid residue was extracted with 150 mL of toluene. The toluene was removed and replaced by a few milliliters of THF to form a brownish green oil. Then *n*-pentane was added and [Li(THF)$_4$][Nd(COT″)$_2$] precipitated at room temperature as green crystals (5.0 g, 89%), which were suitable for X-ray crystallography. Anal. Calcd for C$_{44}$H$_{80}$LiNdO$_4$Si$_4$ (M_r = 936.62): C, 56.42; H, 8.61. Found: C, 55.94; H, 8.29. IR (KBr disk): ν 2953 s, 2833 m, 1608 w, 1494 w, 1474 w, 1448 w, 1401 w, 1246 s, 1212 w, 1049 s, 980 w, 934 m, 908 w, 832 vs, 783 w, 741 s, 686 m, 636 m, 553 w, 510 w cm^{-1}. ^{1}H NMR (600 MHz, THF-d_8, 25 °C): δ 3.57 (s, 16H, THF), 1.72 (s, 16H, THF), −0.14 (s, 36H, Si(CH_3)$_3$), −7.41 (br s, 4H, COT-H), −8.67 (br s, 4H, COT-H), −10.44 (br s, 4H, COT-H) ppm. ^{13}C NMR (150.9 MHz, THF-d_8, 25 °C): δ 138.0 (br s, COT), 132.7 (br s, COT), 131.5 (br s, COT), 120.3 (br s, COT), 68.2 (THF), 26.3 (THF), 7.0 (s, SiCH$_3$) ppm. ^{29}Si NMR (79.5 MHz, THF-d_8, 25 °C): δ −52.0 ppm. Mass spectrum (EI): *m/z* 1032 (50%) [{C$_8$H$_6$(SiMe$_3$)$_2$}$_3$Nd$_2$], 961 (10%) [{C$_8$H$_6$(SiMe$_3$)$_2$}$_3$Nd$_2$ − Si(CH$_3$)$_3$], 784 (8%) [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Nd$_2$], 567 (10%), 392 (100%) [{C$_8$H$_6$(SiMe$_3$)$_2$}$_2$Nd], 318 (30%).

Synthesis of [Li(DME)$_3$][Ce(COT^{TBS})$_2$]·DME (3). Anhydrous CeCl$_3$ (3.9 g, 16 mmol) and Li$_2$(COT^{TBS})·THF (11.3 g, 34 mmol) were combined in 80 mL of DME. The reaction mixture was stirred for 24 h at room temperature to give a dark green solution with the concomitant formation of a fine white precipitate (LiCl). After filtration through a thin layer of Celite filter aid, the clear green filtrate was concentrated in vacuo to a total volume of ca. 50 mL. Crystallization at room temperature for 1 week afforded [Li(DME)$_3$]-[Ce(COT^{TBS})$_2$] in the form of exceedingly air-sensitive bright green crystals (5.3 g, 31%), which were suitable for X-ray crystallography. Anal. Calcd for C$_{56}$H$_{112}$CeLiO$_8$Si$_4$ (M_r = 1172.88): C, 57.35; H, 9.62. Found: C, 57.11; H, 10.02. IR (KBr disk): ν 3025 m, 2954 vs, 2881 vs, 1648 w, 1540 w, 1490 w, 1471 s, 1444 s, 1408 w, 1385 m, 1357 m, 1245 vs, 1212 m, 1193 m, 1124 s, 1079 s, 1047 s, 1007 m, 978 m, 931 s, 900 w, 867 m, 827 vs, 806 vs, 781 m, 724 s, 667 s, 584 m, 555 mw, 515 m cm^{-1}. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 5.6−4.0 (br m, 12H, COT-H), 3.42 (br s, 12H, DME-CH_2), 3.26 (br s, 18H, DME-CH_3), 0.9 (br s, 24H, SiCH_3), −0.05 (br s, 36H, ^{t}Bu) ppm. ^{13}C NMR (100.6 MHz, THF-d_8, 25 °C): δ 72.6 (br s, DME-CH$_2$), 58.8 (br s, DME-CH$_3$), 27.6, 21.9 (^{t}Bu), −0.2 (s, SiCH$_3$) ppm. Signals assignable to the COT ring carbon atoms could not be clearly distinguished from the baseline. ^{29}Si NMR (79.5 MHz, THF-d_8, 25 °C): δ −8.8 ppm.

Synthesis of [(COT″)Nd(μ-Cl)THF]$_2$·2(toluene) (4). Anhydrous NdCl$_3$ (12.0 mmol, 3.0 g) was added to a stirred THF (150 mL) solution of in situ prepared Li$_2$(COT″) (from 24.0 mmol (=15.0 mL) of 1.6 M *n*-butyllithium solution in hexane and 12.0 mmol (=3.0 g) of C$_8$H$_6$(SiMe$_3$)$_2$) at room temperature. The reaction mixture was stirred for 24 h, and the solvents were evaporated under vacuum. The solid residue was extracted with 150 mL of toluene. A 100 mL portion of the toluene was evaporated under vacuum. [{C$_8$H$_6$(SiMe$_3$)$_2$}Nd(μ-Cl)THF]$_2$·2(toluene) precipitated at room temperature as green crystals (4.9 g, 69%), which were suitable for X-ray crystallography. Anal. Calcd for C$_{50}$H$_{80}$Cl$_2$Nd$_2$O$_2$Si$_4$ (M_r = 1184.88): C, 50.68; H, 6.81; Cl, 5.98. Found: C, 50.26; H, 6.54; Cl, 5.43. IR (KBr disk): ν 2948 s, 2893 m, 1624 w, 1588 w, 1552 w, 1488 w, 1444 w, 1401 w, 1313 w, 1247 s, 1207 w, 1183 w, 1048 s, 975 m, 932 m, 901 w, 846 s, 843 vs, 839 vs, 831 s, 822 vs, 780 m, 747 s, 727 s, 680 m, 635 m, 555 w, 507 w

cm^{-1}. Mass spectrum (EI): *m/z* 746 (6%), 674 (6%), 580 (20%), 524 (20%), 498 (70%) [C$_8$H$_6$(SiMe$_3$)$_2$NdCl(THF)], 423 (70%), 414 (70%), 351 (40%), 335 (100%). ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 25 °C): δ 7.11 (toluene), 7.04 (toluene), 7.01 (toluene), 6.25 (br d, COT-H), 6.56 (br s, COT-H), 3.11 (THF), 1.11 (THF), 2.11 (toluene), 0.67 (br s, SiCH_3), −7.31 (br s, COT-H), −9.01 (br s, COT-H) ppm. The intensities of the signals do not exactly fit the numbers of hydrogen atoms, due to the paramagnetic properties of the Nd^{3+} ion. ^{13}C NMR (150.9 MHz, C$_6$D$_6$, 25 °C): δ 137.8, 129.3, 128.5, 125.7 (toluene), 93.9 (br s, COT), 93.5 (br s, COT), 92.6 (br s, COT), 89.9 (br s, COT), 89.7 (br s, COT), 85.8 (br s, COT), 68.6 (THF), 25.3 (THF), 21.4 (toluene), −1.43 (br s, SiCH$_3$) ppm. ^{29}Si NMR (79.5 MHz, C$_6$D$_6$, 25 °C): δ −46.4 ppm.

Synthesis of (COT″)Ho[μ-η^8:η^8-C$_8$H$_6$(SiMe$_3$)$_2$-1,5]Ho(COT″) (6). Anhydrous HoCl$_3$ (0.57 g, 2.1 mmol) was added to a stirred THF (50 mL) solution of in situ prepared Li$_2$COT″ (from 8.4 mmol (=5.3 mL) of 1.6 M *n*-butyllithium solution in *n*-hexane and 4.2 mmol (=1.05 g) of C$_8$H$_6$(SiMe$_3$)$_2$) at room temperature. The reaction mixture was stirred for 24 h, and the solvents were evaporated under vacuum. The solid residue was taken up in 100 mL of toluene, and anhydrous CoCl$_2$ (1.0 mmol, 0.13 g) was added to the solution at room temperature. The reaction mixture was stirred for 24 h and refluxed for an additional 2 h, causing the formation of a black precipitate. After filtration the solvent was evaporated under vacuum. The solid residue was extracted with 100 mL of cyclopentane. A ca. 90 mL portion of the cyclopentane was evaporated under vacuum. (COT″)Ho[μ-η^8:η^8-C$_8$H$_6$(SiMe$_3$)$_2$-1,5]Ho(COT″) (6) crystallized upon standing at a temperature of about 3 °C as orange prisms (0.7 g, 62%), which were suitable for X-ray crystallography. Anal. Calcd for C$_{42}$H$_{72}$Ho$_2$Si$_6$ (M_r = 1075.40): C, 46.91; H, 6.75. Found: C, 46.57; H, 7.03. IR (KBr disk): ν 3037 vw, 2953 s, 2896 m, 2087 vw, 1931 vw, 1876 vw, 1834 vw, 1779 vw, 1667 vw, 1590 w, 1536 vw, 1488 vw, 1446 w, 1403 m, 1318 vw, 1247 vs, 1215 m, 1048 s, 1038 m, 982 m, 939 s, 910 m, 894 m, 839 vs, 783 m, 748 s, 735 vs, 686 m, 651 w, 637 m, 550 w, 540 vw, 522 vw, 512 vw, 488 w cm^{-1}. Mass spectrum (EI): *m/z* 994 (2%), 745 (5%), 672 (3%), 497 (12%), 423 (10%), 398 (3%) [Ho(COT″) − CH$_3$], 352 (5%), 335 (5%), 261 (10%), 249 (30%) [COT″], 206 (100%) [COT″ − 3CH$_3$].

X-ray Crystallographic Studies. The intensity data of **1−6** were collected on a Stoe IPDS 2T diffractometer with Mo Kα radiation. The data were collected with the Stoe XAREA[28] program using ω scans. The space groups were determined with the XRED32[28] program. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on F^2 using SHELXL-97.[29] Data collection parameters are given in Table 1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, tables, and figures giving the X-ray structural data for **1−6** as well as NMR data for compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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