

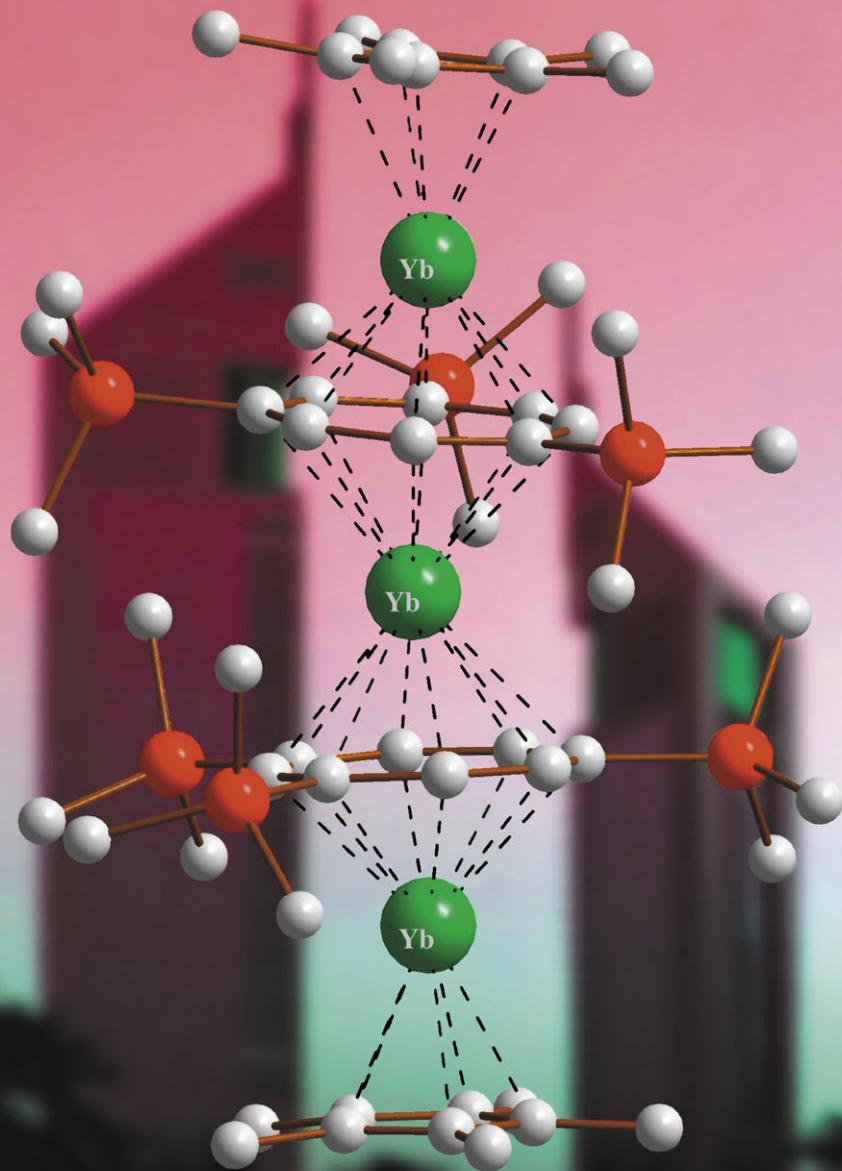
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Multiple-decker sandwich complexes of f-elements†

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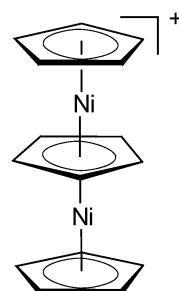
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Extended sandwich structures (triple-deckers, tetra-deckers etc.) containing d-transition metals are well established for more than 30 years. In contrast, similar complexes containing lanthanide or actinide elements are still rare. In recent years, however, significant progress has been made in this area. This has mainly been achieved with the use of sterically demanding π -ligands such as pentamethylcyclopentadienyl (=Cp*) or silyl-substituted cyclooctatetraenyl dianions like $[C_8H_5(SiMe_3)_3]^{1,3,6}^{2-}$ (=COT²⁻). Suitable combinations of such ligands in the coordination sphere of f-elements allowed the synthesis and structural characterization of bent and linear triple-decker sandwich complexes as well as the first tetra-deckers and novel cluster-centered multidecker sandwich complexes. This NJC Perspective article gives an overview on recent achievements in this field and looks forward to future developments.

Introduction

The discovery of the very first transition metal triple-decker sandwich complex dates back to the year 1972, when Werner and Salzer reported the tris(cyclopentadienyl)dinickel cation (Scheme 1).^{1,2} This was followed by vigorous research activities which resulted in the isolation and structural characterization of a large variety of transition metal triple-decker and



Scheme 1 The tris(cyclopentadienyl)dinickel cation.^{1,2}

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† Dedicated to Professor Ulrich Behrens on the occasion of his 65th birthday.



Frank T. Edelmann

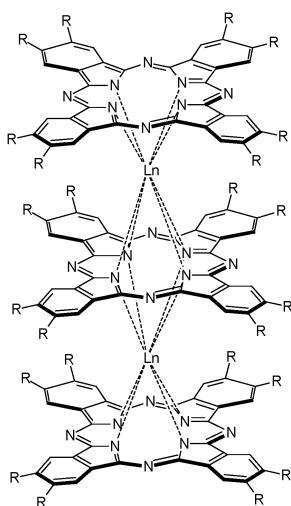
Frank T. Edelmann was born in Hamburg, Germany, in 1954. He studied chemistry at the University of Hamburg, where he obtained his diploma degree in 1979 and PhD in 1983 under the guidance of Prof. Ulrich Behrens. After 2 years of postdoctoral research with Josef Takats (University of Alberta), John W. Gilje (University of Hawaii) and Tristram Chivers (University of Calgary) he finished his habilitation at the University of Göttingen in 1991 in the group of Herbert W. Roesky. In 1995 he was appointed Full Professor of Inorganic Chemistry at the Otto-von-Guericke-University in Magdeburg. His main research interests are in organolanthanide and -actinide chemistry, silicon chemistry (silsesquioxanes and metallasilsesquioxanes), and fluorine chemistry. His work is documented in over 300 scientific papers, 2 books and several patents. In 2008 he was awarded the "Terrae Rarae 2008 Award" for his "eminent work in coordination chemistry of the rare earth elements".

multiple-decker complexes. Especially boron-containing five-membered heterocycles were soon found to be highly suitable building-blocks for the construction of such extended sandwich structures.^{3,4} Various other ring ligands can also act as bridging units in multiple-decker sandwiches, including arenes,⁵ anionic phospholyl ligands,⁶ boroles,⁷ and boratabenzenes,⁸ as well as purely inorganic ring systems like boranes,⁹ carboranes,¹⁰ P₅ and P₆,^{11,12} As₅,^{12a,13} and Sb₅.¹⁴ Triple-decker sandwich complexes have also been reported for certain main-group elements.¹⁵

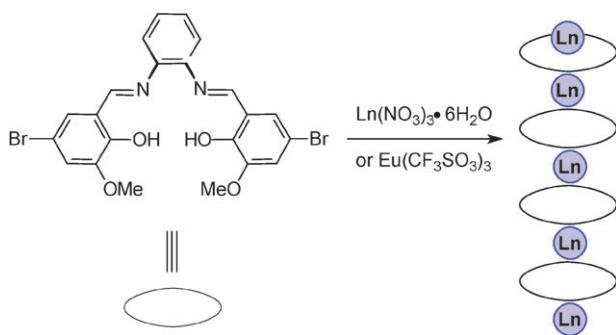
In contrast, studies on related organometallic triple-decker and multiple-decker sandwich complexes containing f-elements (lanthanides or actinides) remain scarce, although the first compounds for which a triple-decker structure was postulated were reported in the 1970's.^{16,17} These early studies already showed that the 10 π -aromatic cyclooctatetraenyl dianion, C₈H₈²⁻ (=COT²⁻), is apparently best suited for constructing larger sandwich structures for f-elements. The first compound of this type, Ce₂(COT)₃, was described in 1976 by Cesca *et al.*¹⁶ This compound was prepared in a rather unexpected manner *via* reduction of the cerium(IV) alkoxide Ce(O*i*Pr)₄(PrOH) by AlEt₃ in the presence of cyclooctatetraene. Other materials presumed to be Ln₂(COT)₃ (Ln = La, Ce, Nd, Er) were obtained as the initial products from co-condensation reactions of rare-earth metal vapors with cyclooctatetraene at -196 °C.¹⁷ However, during the course of the early studies, none of these initial unsolvated products could be authenticated by X-ray structural analyses. The past ten years

have witnessed some exciting new developments in this field which were mainly achieved with the use of bulky, substituted COT ligands instead of the parent $C_8H_8^{2-}$ -dianion. This article intends to present an overview on the recent advantages in this fascinating area of organometallic triple-decker, tetra-decker, and multiple-decker sandwich complexes containing lanthanide and actinide elements. Not included in this review are triple-decker and related sandwich complexes of the lanthanides and actinides which do not comprise metal–carbon bonds. Most prominent examples are the long-known and well established lanthanide triple-decker sandwiches containing tetrapyrrolato-type ligands (*e.g.* phthalocyanines and porphyrins), which were first reported by Buchler *et al.*¹⁸ This fascinating class of lanthanide coordination compounds have been comprehensively covered in several excellent review articles.¹⁹ Scheme 2 shows a typical example for such lanthanide triple-decker structures comprising phthalocyanine ligation.²⁰

In addition, unusual lanthanide triple-, tetra-, and penta-decker sandwiches have been assembled with the use of a variety of “salen” style Schiff-base ligands.²¹ Scheme 3 illustrates the self-assembly of pentanuclear lanthanide tetra-decker sandwich complexes of this type.^{21b} However, these species, too, do not contain Ln–C bonds and are thus excluded from the present review article.



Scheme 2 Lanthanide triple-decker sandwich with phthalocyanine ligands.



Scheme 3 Self-assembly of pentanuclear lanthanide tetra-decker sandwich complexes with “salen” type Schiff-base ligands.^{21b}

Lanthanide complexes

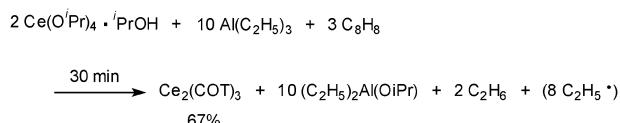
Lanthanide(3+) complexes

(a) **Triple-decker sandwiches.** As noted in the Introduction, the very first homoleptic lanthanide triple-decker sandwich complex was reported in 1976. A reaction of the cerium(IV) alkoxide $Ce(O^{\prime}Pr)_4 \cdot ^{\prime}PrOH$ with $AlEt_3$ in the presence of cyclooctatetraene afforded a green product analyzing for $Ce_2(COT)_3$ (Scheme 4). A major disadvantage of this synthetic route is that it requires large quantities of expensive cyclooctatetraene both as reagent and solvent.¹⁶

The high sensitivity towards oxygen and moisture combined with its very low solubility in organic solvents and its micro-crystalline nature prevented all attempts to characterize this material through 1H NMR spectroscopy or single-crystal X-ray diffraction. Only very recently, $Ce_2(COT)_3$ has been reinvestigated by Andersen *et al.* using EPR and EXAFS methods, with the latter being consistent with a triple-decker sandwich structure.²² In this paper, new synthetic methods for the preparation of cerocene, $Ce(COT)_2$, and $Ce_2(COT)_3$ in high yield and purity were also reported. It was found that heating of dark red $Ce(COT)_2$ to 300 °C under dynamic vacuum over a period of 15 minutes resulted in nearly quantitative (94%) conversion to light green $Ce_2(COT)_3$ (Scheme 5). Thus the clean thermal decomposition of cerocene provides an excellent synthesis of the dicerium triple-decker sandwich compound. The latter could be converted back to cerocene upon prolonged heating with an excess of C_8H_8 in C_6D_6 at 65 °C.²²

Lanthanide triple-decker sandwiches of the type $Ln_2(COT)_3$ ($Ln = La, Ce, Nd, Er$) were also reported in 1978 to be the initial products formed by co-condensation of lanthanide metal atoms and C_8H_8 at –196 °C.¹⁷ Only the reaction with Yb atoms afforded the known divalent compound $Yb(COT)$.²³ With La, Ce, and Er, gold-colored substances were formed, while with Nd the product was bright green. However, the unsolvated triple-deckers could not be isolated and characterized as such but were Soxhlet-extracted with THF to afford the solvated binuclear species $[Ln(COT)(THF)_2][Ln(COT)_2]$. The Nd derivative was structurally characterized by X-ray diffraction. As shown in Scheme 6, the presumably linear original triple-decker sandwich is severely distorted upon addition of THF, resulting in a formally ionic binuclear structure. A cationic $[Nd(COT)(THF)_2]^+$ moiety is connected to the anionic $[Nd(COT)_2]^-$ sandwich part *via* an allyl-like $Nd-\eta^3-COT$ interaction.¹⁷

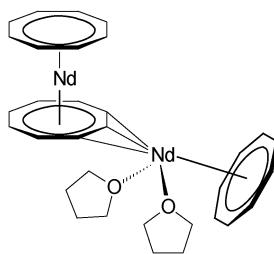
It should be emphasized at this stage, however, that despite these important early achievements none of the parent $Ln_2(COT)_3$ triple-decker sandwich complexes have thus far



Scheme 4 Original synthesis of $Ce_2(COT)_3$.¹⁶



Scheme 5 Improved synthesis of $Ce_2(COT)_3$.²²



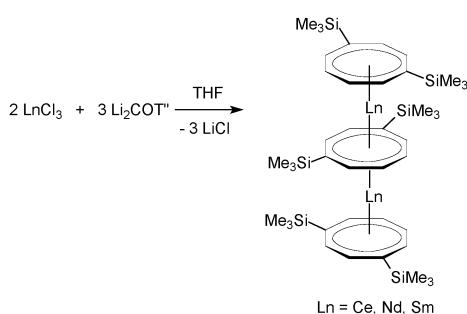
Scheme 6 Schematic representation of $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$.¹⁷

been structurally authenticated by X-ray diffraction. The structural characterization of an unsubstituted $\text{Ln}_2(\text{COT})_3$ triple-decker remains one of the major challenges in this area.

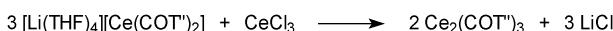
Major advances in the chemistry of trivalent lanthanide triple-decker complexes have been made only very recently through the use of bulky silyl-substituted COT^{2-} dianions. Particularly useful in this respect is the bis(trimethylsilyl) derivative $[\text{C}_8\text{H}_6(\text{SiMe}_3)_2-1,4]^{2-}$ ($= \text{COT}''$), which was introduced into organolanthanide chemistry by Cloke *et al.*²⁴ When we started working in this area in 1997, we reasoned that the bis(silylated) COT'' ligand might lead to more soluble lanthanide triple-decker sandwich complexes.²⁴ In fact, reactions between anhydrous lanthanide trichlorides, LnCl_3 ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Sm}$), with $\text{Li}_2\text{COT}''$ in the exact molar ratio of 2 : 3 in THF solution afforded brightly colored complexes, which analyzed well for the desired triple-deckers (Scheme 7).²⁵

Apparently these new binuclear complexes showed a surprisingly high tendency of formation. It was found that the cerium complex $\text{Ce}_2(\text{COT}'')_3$ was also accessible by a ligand redistribution reaction between the anionic sandwich complex $[\text{Li}(\text{THF})_4][\text{Ce}(\text{COT}'')_2]$ ²⁶ and anhydrous cerium trichloride in THF solution (Scheme 8, 65% yield).²⁵

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 impact of this early study was severely diminished by the lack of unambiguous structural proof.²⁵ Further investigation of the systems $\text{LnCl}_3/\text{Li}_2(\text{COT}'')$ revealed that the outcome of these reactions strongly depends



Scheme 7 Synthesis of lanthanide triple-decker complexes $\text{Ln}_2(\text{COT}'')_3$.²⁵



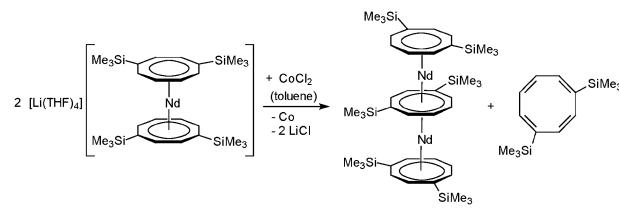
Scheme 8 Alternative synthesis of $\text{Ce}_2(\text{COT}'')_3$.²⁵

on subtle changes *e.g.* of the reaction conditions and the starting material ratios. Besides the triple-decker sandwiches,²⁵ products isolated from such reactions also include the anionic sandwich complexes $[\text{Ln}(\text{COT}'')_2]^-$ ²⁶ and the chloro-bridged dimers $[(\text{COT}'')\text{Ln}(\mu\text{-Cl})(\text{THF})_2]$ ²⁴ as well as unusual cluster-centered multiple-decker sandwich complexes (*vide infra*).²⁷ This might be the reason why no single-crystalline samples of any $\text{Ln}_2(\text{COT}'')_3$ species could be isolated from metathetical reactions between LnCl_3 and $\text{Li}_2(\text{COT}'')$.²⁵

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 by the discovery of a rather unexpected and novel access to the triple-decker molecules $\text{Ln}_2(\text{COT}'')$. Treatment of $[\text{Li}(\text{THF})_4][\text{Nd}(\text{COT}'')_2]$ ²⁶ 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). It should be noted that the reaction was initially carried out with the intention to make a heterobimetallic Nd/Co tetra-decker sandwich complex. However, crystallization of the toluene-soluble material from cyclopentane afforded dark green, needle-like crystals, which were identified as the pure triple-decker sandwich complex $\text{Nd}_2(\text{COT}'')_3$. Its formation (72% yield) in this unexpected redox process is illustrated in Scheme 9. In the course of the reaction, one of the dianionic COT'' ligands in $[\text{Li}(\text{THF})_4][\text{Nd}(\text{COT}'')_2]$ is oxidized to 1,4-bis(trimethylsilyl)-cyclooctatetraene (admixed with its 1,6-isomer), which was isolated from the concentrated mother liquid and identified unambiguously by comparison with the NMR data of an authentic specimen.^{24b} Apparently two important factors contribute to the success of this novel synthetic route. One is certainly the enhanced solubility of the product imparted by the use of the bulky, silyl-substituted COT'' ligands.²⁴ The other is the heterogeneous reaction in a non-polar solvent (toluene) which prevents the formation of solvated species like the binuclear complexes $[\text{Ln}(\text{COT})(\text{THF})_2][\text{Ln}(\text{COT})_2]$ formed upon contact of the unsubstituted triple-deckers $\text{Ln}_2(\text{COT})_3$ with THF.¹⁷

A mass spectrum of $\text{Nd}_2(\text{COT}'')_3$ showed the molecular ion of the triple-decker at m/z 1032 with 100% relative intensity. Dark green X-ray quality crystals were obtained by crystallization from cyclopentane. An X-ray diffraction analysis of $\text{Nd}_2(\text{COT}'')_3$ clearly established the presence of the first homoleptic, linear triple-decker sandwich complex of an f-element (Fig. 1).²⁸

All three COT'' rings are η^8 -coordinated to neodymium, with the central ring acting as $\mu\text{-}\eta^8\text{:}\eta^8$ -bridging ligand. The most notable structural feature of $\text{Nd}_2(\text{COT}'')_3$, however, is the near-linear arrangement of the COT'' rings with



Scheme 9 Synthesis of $\text{Nd}_2(\text{COT}'')_3$.²⁸

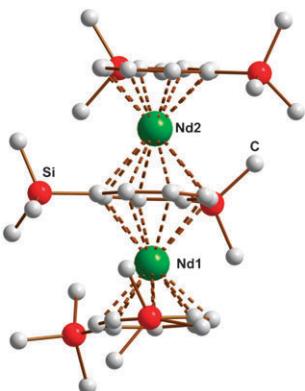
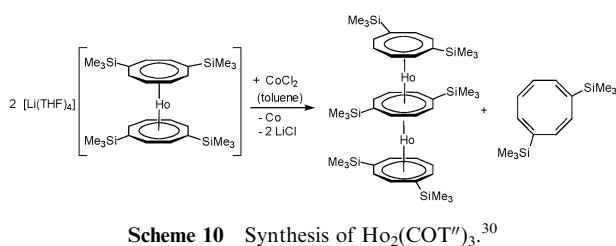


Fig. 1 The molecular structure of $\text{Nd}_2(\text{COT}'')_3$.²⁸

(ring centroid)–Nd–(ring centroid) angles of 176.1° (Nd1) and 175.6° (Nd2), respectively, and a Nd–(ring centroid)–Nd angle of 177.9° . In contrast, all other triple-decker compounds containing lanthanide elements comprise bent configurations (*vide infra*). It was recently pointed out by Cloke *et al.* that lanthanide triple-decker sandwich complexes would provide excellent molecular models for $\text{Ln}(\text{COT})$ sandwich nanowires.²⁹ In this sense the Nd complex $\text{Nd}_2(\text{COT}'')_3$ represents the first true molecular model for such organo lanthanide-based nanowires.

After having established a novel high-yield synthetic route to $\text{Nd}_2(\text{COT}'')_3$ involving oxidation of the anionic sandwich complex $[\text{Li}(\text{THF})_4][\text{Nd}(\text{COT}'')_2]$ with CoCl_2 , an important question was if this method could be employed to prepare other $\text{Ln}_2(\text{COT}'')_3$ derivatives. An initial experiment with the smaller holmium(3+) ion produced yet another very surprising result.³⁰ As illustrated in Scheme 10, $[\text{Li}(\text{THF})_4][\text{Ho}(\text{COT}'')_2]$ ²⁶ could also be converted to the 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. However, one has to look twice to see the major difference between the reactions shown in Scheme 9 and 10.

An X-ray crystal structure determination of bright orange $\text{Ho}_2(\text{COT}'')_3$ revealed a highly unusual structural feature.³⁰ Despite the use of pure $[\text{Li}(\text{THF})_4][\text{Ho}(\text{COT}'')_2]$ as starting material, the holmium triple-decker contains the hitherto unknown 1,5-bis(trimethylsilyl)cyclooctatetraenyl dianion as middle-deck (Fig. 2)! The presence of this isomer as an impurity in any of the starting materials used to prepare $[\text{Li}(\text{THF})_4][\text{Ho}(\text{COT}'')_2]$ can be ruled out, since the purity was checked at every stage and the product $\text{Ho}_2(\text{COT}'')_3$ was isolated in *ca.* 40% yield. The formation of $(\text{COT}'')\text{Ho}[\mu\text{-C}_8\text{H}_6(\text{SiMe}_3)_2\text{-1,5}]\text{Ho}(\text{COT}'')$, as it should be



Scheme 10 Synthesis of $\text{Ho}_2(\text{COT}'')_3$.³⁰

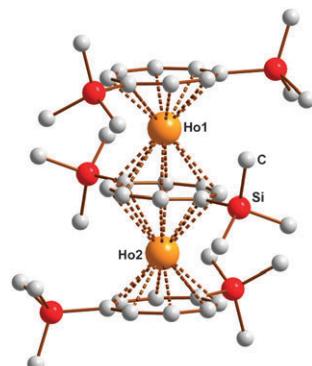
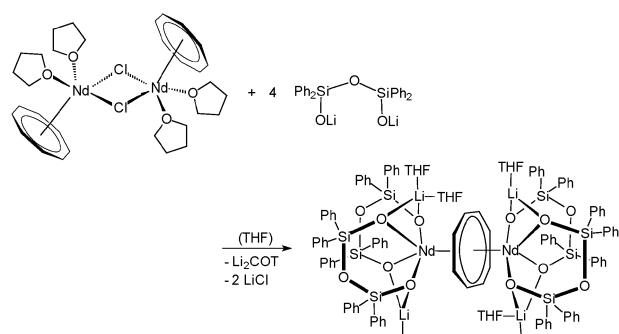


Fig. 2 The molecular structure of $(\text{COT}'')\text{Ho}[\mu\text{-C}_8\text{H}_6(\text{SiMe}_3)_2\text{-1,5}]\text{Ho}(\text{COT}'')$.³⁰

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 $[\text{C}_8\text{H}_6(\text{SiMe}_3)_2\text{-1,5}]^{2-}$ dianion as bridging ligand. These exciting initial results clearly show that significant more work is required in order to gain a better understanding of such lanthanide triple-decker sandwich complexes containing bulky COT ligands.

Most recently we reported the synthesis and structural characterization of an unprecedented organic/inorganic lanthanide triple-decker sandwich complex. The compound was unexpectedly obtained when the dimeric mono-COT precursor $[(\text{COT})\text{Nd}(\text{THF})_2(\mu\text{-Cl})_2]$ was treated with dilithium tetraphenyldisiloxanediolate, $(\text{LiOSiPh}_2)_2\text{O}$, in a molar ratio of 1 : 4 (Scheme 11).³¹

A single-crystal X-ray diffraction study revealed the presence of an unprecedented organic/inorganic lanthanide triple-decker sandwich-complex, $(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})[\text{Nd}\{\text{Ph}_2\text{SiO}\}_2\text{O}_2\{\text{Li}(\text{THF})_2\}\{\text{Li}(\text{THF})\}]_2$, in which two twelve-membered $\text{Si}_4\text{O}_6\text{Li}_2$ inorganic ring systems form the outer decks and the two Nd atoms are symmetrically bridged by a $\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}$ ligand (Fig. 3). The outer decks of the triple-decker sandwich structure are formed by $\text{Si}_4\text{O}_6\text{Li}_2$ inorganic ring systems, each of them being composed of two lithium tetraphenyldisiloxanediolate units. These Si–O-based inorganic ring ligands are well established to effectively shield one side of even the largest lanthanide ions.³²



Scheme 11 Synthesis of $(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})[\text{Nd}\{\text{Ph}_2\text{SiO}\}_2\text{O}_2\{\text{Li}(\text{THF})_2\}\{\text{Li}(\text{THF})\}]_2$.³¹

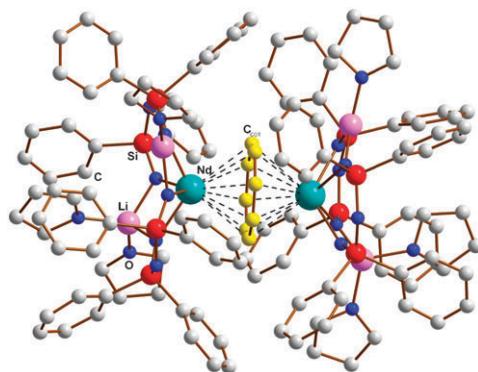


Fig. 3 The molecular structure ($\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}$) $[\text{Nd}\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}\{\text{Li}(\text{THF})\}]_2$.³¹

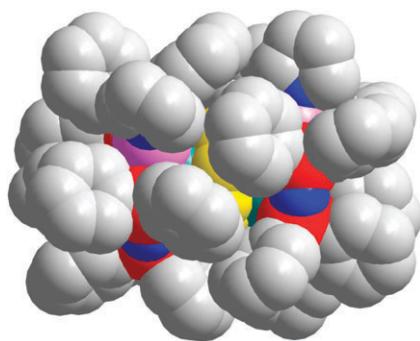


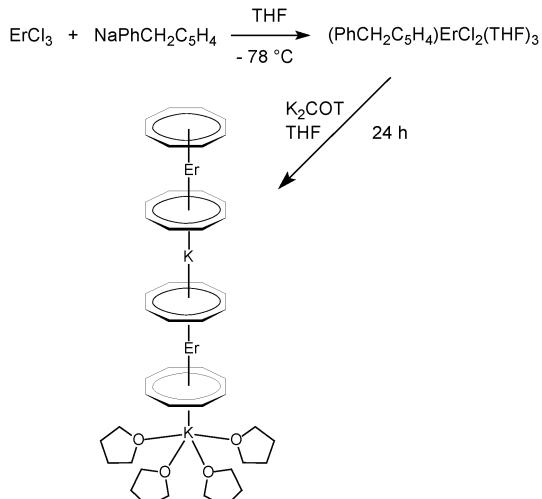
Fig. 4 Space-filling view of the molecular structure of ($\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}$) $[\text{Nd}\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}\{\text{Li}(\text{THF})\}]_2$.³¹

The high steric congestion in ($\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}$) $[\text{Nd}\{(\text{Ph}_2\text{SiO})_2\text{O}\}_2\{\text{Li}(\text{THF})_2\}\{\text{Li}(\text{THF})\}]_2$ becomes evident from the space-filling view of the molecular structure depicted in Fig. 4. This view also gives a good impression of how phenyl groups of the opposite disiloxanediolate interlock, thereby encapsulating the central $\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}$ ligand like “a golden ring in a silicate box”.³¹

(b) Tetra- and multiple-decker sandwiches. The first tetra-decker sandwich structure containing trivalent lanthanide ions was reported in 1991 by Chen *et al.*³³ The linear K_2Er_2 tetra-decker complex $(\text{THF})_4\text{K}_2\text{Er}_2(\text{COT})_4$ was obtained in an unexpected manner by treatment of (benzylcyclopentadienyl)-erbium dichloride with K_2COT in a 1 : 1 molar ratio in THF (Scheme 12).

An analogous complex was also obtained with ytterbium, while the early and late lanthanides failed to give related mixed-metal tetra-decker sandwiches. Although this is not an all-lanthanide sandwich molecule, this interesting early report already provided a clear indication that especially COT ligands are well suited for the construction of higher sandwich aggregates in combination with lanthanide ions.³¹

Until now, the erbium complex $(\text{THF})_4\text{K}_2\text{Er}_2(\text{COT})_4$ remains the only well-defined organometallic tetra-decker sandwich complex containing trivalent lanthanide ions. As mentioned earlier, the reaction systems $\text{LnCl}_3/\text{Li}_2(\text{COT}')$ are quite complex, giving rise to different mono- and di-nuclear products. In two cases, higher aggregates could be isolated and structurally characterized. In one instance, the reaction of

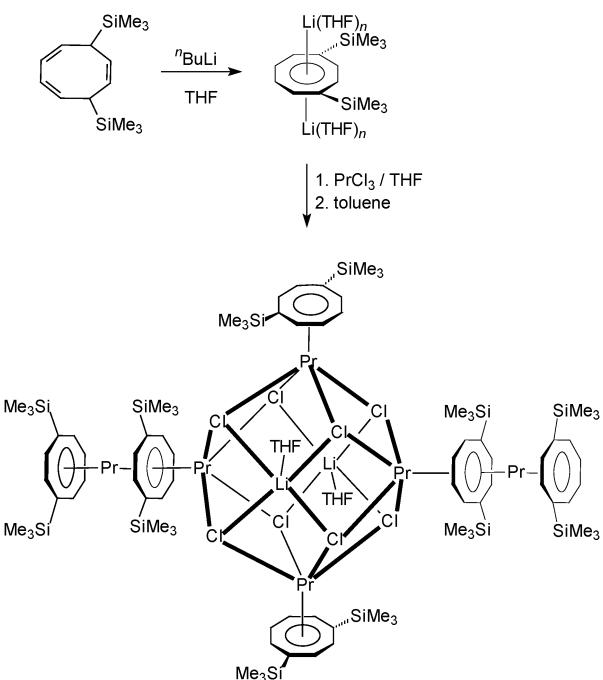


Scheme 12 Formation of $(\text{THF})_4\text{K}_2\text{Er}_2(\text{COT})_4$.³¹

anhydrous PrCl_3 with $\text{Li}_2(\text{COT}')$ in THF solution afforded an unprecedented cluster-centered Pr/Li multidecker sandwich complex of the composition $[\text{Pr}(\text{COT}')]_2[\text{Pr}_2(\text{COT}')]_2\text{Li}_2(\text{THF})_2\text{Cl}_8$ (Scheme 13).²⁷

In this unique cluster molecule a central cube of eight Cl atoms is capped by two $[\text{Pr}(\text{COT}')]^+$ half-sandwich and two $[\text{Pr}_2(\text{COT}')]^-$ sandwich units as well as two $[\text{Li}(\text{THF})]^+$ moieties (Fig. 5).²⁷

A closely related reaction between $\text{TbCl}_3(\text{THF})_3$ and $\text{Li}_2(\text{COT}')$ in a molar ratio of 1 : 2 afforded the formally anionic sandwich complex $\text{Li}(\text{DME})\text{Tb}(\text{COT}')]_2$, which was found to be monomeric when crystallized from *n*-pentane. In contrast, crystallization from toluene afforded a polymeric modification. The crystal structure of this modification, $[\text{Li}(\text{DME})\text{Tb}(\text{COT}')]_n$, consists of polymeric, one-dimensional



Scheme 13 Synthesis of $[\text{Pr}(\text{COT}')]_2[\text{Pr}_2(\text{COT}')]_2\text{Li}_2(\text{THF})_2\text{Cl}_8$.²⁷

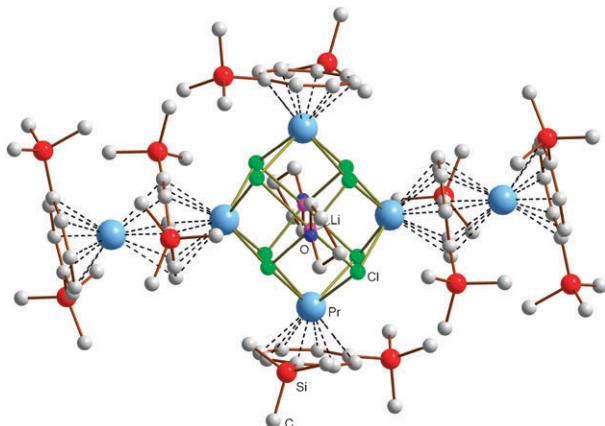


Fig. 5 The molecular structure of $[Pr(COT'')]_2[Pr_2(COT'')_2]_2Li_2(THF)_2Cl_8$.²⁷

zig-zag chains, in which $[Tb(COT'')]^-$ anions are alternatingly bridged by $[Li(DME)]^+$ units. The COT'' rings are η^8 -coordinated to terbium, while the coordination to the bridging Li atoms can be best described as $\mu\text{-}\eta^2\text{:}\eta^2$ -bridging (Fig. 6).³⁴

This leads us to an exciting class of lanthanide multiple-decker sandwich complexes which have been extensively investigated in recent years in the context of molecular spintronics. Molecular spintronics is an exciting new and emergent sub-area of spintronics that benefits from achievements in molecular electronics and molecular magnetism.³⁵ During the past few years, molecular spintronics using single molecules has attracted enormous attention both experimentally and theoretically since it holds promise for the next generation of electronic devices with enhanced functionality and improved performance, especially in high-density information storage and quantum computing.³⁶ In this context, various one-dimensional organometallic sandwich molecular wires (SMW's) are studied for their anticipated unique electronic and magnetic properties. Among the promising examples are lanthanide-based multiple-decker sandwich complexes of the type $Ln_n(COT)_{n+1}$ ($COT = \eta^8\text{-cyclooctatetraenyl}$) (Fig. 7), which can be synthesized *via* a combination of laser vaporization and molecular beam methods.³⁷ In a typical study, a molecular beam of europium–cyclooctatetraene sandwich nanowires $Eu_n(COT)_m$ was produced by a laser vaporization synthesis method. The formation mechanism of the nanowires was quantitatively revealed by photoelectron and photoionization spectroscopies of the Eu–COT species, together with supporting theoretical calculations. From these results, it was confirmed

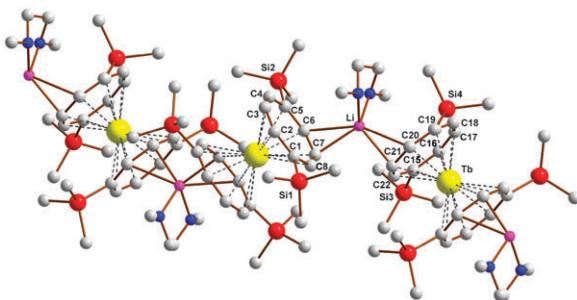


Fig. 6 The supramolecular structure of $[Li(DME)Tb(COT'')]_n$.³²

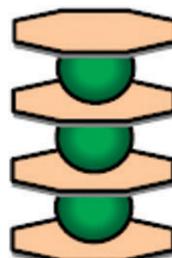


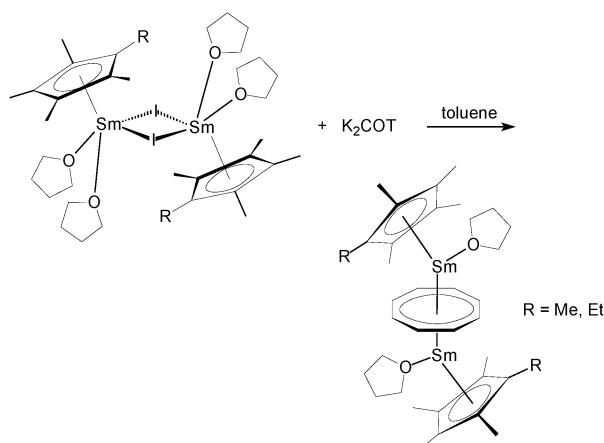
Fig. 7 Schematic representation of $Ln_3(COT)_{n+1}$ ($n = 3$).^{35g}

that growth processes extending the length of Eu–COT nanowires involve a series of elementary reactions in which efficient charge transfer occurs at the terminal reaction sites. This way nanowires up to 8 nm in length ($Ln = Eu$, $n = 18$) have been obtained.^{37e} A major obstacle making these oligomers difficult to manipulate and to investigate is their low solubility. This is why well-defined organolanthanide triple- and multiple-decker sandwich complexes can be expected to play an ever-increasing role as molecular models for the $Ln(COT)$ sandwich nanowires.²⁹

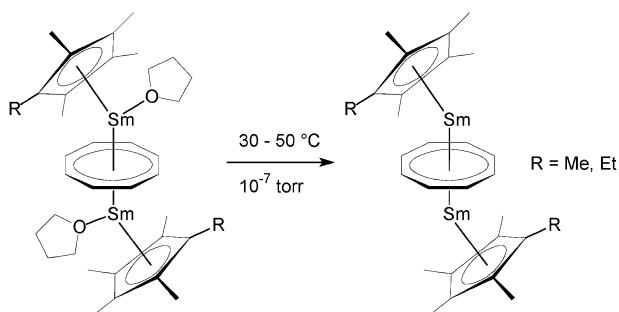
In the gas-phase, Na-atom adducts have also been produced for the organometallic lanthanide complexes $Ln_n(COT)_{n+1}$ ($Ln = Eu, Ho$) by a combination of two-laser vaporization and a molecular beam methods. The number of attached Na atoms was explained by the charge distributions of the complexes, where Eu and Ho exist as Eu^{2+} and Ho^{3+} , respectively, and the C_8H_8 molecules as COT^{2-} , accepting two excess electrons.^{37g}

Lanthanide(2+) complexes

Perhaps the most thoroughly investigated group of lanthanide triple-decker sandwich complexes are those containing divalent lanthanide ions. This interesting class of compounds was mainly explored by Evans *et al.*³⁸ and Cloke *et al.*²⁹ A prominent structural feature is their bent configuration. For example, a series of bimetallic triple-decked organometallic sandwich complexes involving Sm(II) were prepared according to Scheme 14 by treatment of $[(C_5Me_4R)Sm(\mu\text{-I})(THF)_2]_2$ with one equivalent of K_2COT in toluene to form $[(C_5Me_4R)Sm(THF)]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$ ($R = Me, Et$).^{38a}



Scheme 14 Synthesis of $[(C_5Me_4R)Sm(THF)]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$ ($R = Me, Et$).^{38a}



Scheme 15 Synthesis of $[(C_5Me_4R)Sm]_2(\mu-\eta^8:\eta^8\text{-COT})$ ($R = \text{Me, Et}$).^{38a}

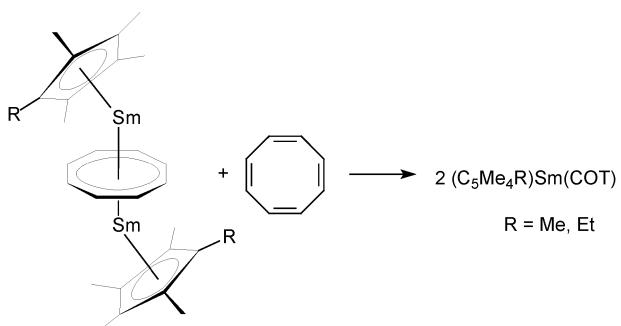
The diglyme ($[\text{MeOCH}_2\text{CH}_2]_2\text{O}$) adduct $\{[(C_5\text{Me}_5)\text{Sm}](\text{diglyme})_2(\mu-\eta^8:\eta^8\text{-COT})\}(\text{THF})_2$ crystallized from THF with a bridging $C_8\text{H}_8^{2-}$ dianion sandwiched between two $[(C_5\text{Me}_5)\text{Sm}(\text{diglyme})]^+$ cations with a ($C_5\text{Me}_5$ ring centroid)–Sm–($C_8\text{H}_8$ ring centroid) angle of 137.6° .^{38a}

The compounds $[(C_5\text{Me}_4\text{R})\text{Sm}(\text{THF})]_2(\mu-\eta^8:\eta^8\text{-COT})$ ($R = \text{Me, Et}$) can be desolvated at $30 - 50^\circ\text{C}$ under high vacuum over several hours to yield $[(C_5\text{Me}_4\text{R})\text{Sm}]_2(\mu-\eta^8:\eta^8\text{-COT})$ (Scheme 15, $R = \text{Me, Et}$).^{38a}

Of course it was of interest to determine if these materials had triple-decked metallocene structures with three parallel rings, since previously characterized bis(cyclooctatetraenyl) lanthanide and actinide complexes such as uranocene, $\text{U}(\text{COT})_2$, and $[\text{Ce}(\text{COT})_2]^-$ have parallel rings whereas $(C_5\text{Me}_5)_2\text{Sm}$ is bent. The $C_5\text{Me}_5$ derivative was found to crystallize from toluene with a structure that retains the bent geometry of the solvated precursor with 149.3° and 148.9° ($C_5\text{Me}_5$ ring centroid)–Sm–($C_8\text{H}_8$ ring centroid) angles. The compound with $R = \text{Et}$ crystallized from toluene with a similar bent triple-decked metallocene structure with 157.6° ($C_5\text{Me}_5$ ring centroid)–Sm–($C_8\text{H}_8$ ring centroid) angles.³⁸ Initial reactivity studies showed that the solvated complexes $[(C_5\text{Me}_4\text{R})\text{Sm}(\text{THF})]_2(\mu-\eta^8:\eta^8\text{-COT})$ ($R = \text{Me, Et}$) each do two-electron reductions of cyclooctatetraene to form $(C_5\text{Me}_4\text{R})\text{Sm}(\text{COT})(\text{THF})$ (Scheme 16).^{38a}

The unsolvated complexes react similarly with cyclooctatetraene to form unsolvated $(C_5\text{Me}_4\text{R})\text{Sm}(\text{COT})$ (Scheme 17, $R = \text{Me, Et}$).^{38a}

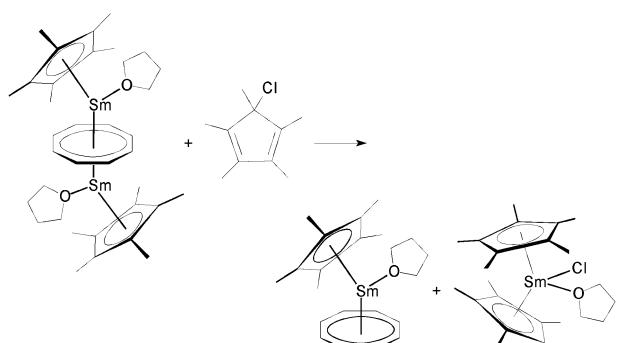
Finally, a two-electron reduction of $C_5\text{Me}_5\text{Cl}$ by $[(C_5\text{Me}_5)\text{Sm}](\text{THF})_2(\mu-\eta^8:\eta^8\text{-COT})$ generated $(C_5\text{Me}_5)\text{Sm}(\text{COT})(\text{THF})$ and $(C_5\text{Me}_5)_2\text{SmCl}(\text{THF})$, a product in which $C_5\text{Me}_5\text{Cl}$ had been added to a single $(C_5\text{Me}_5)\text{Sm}(\text{THF})$ unit in



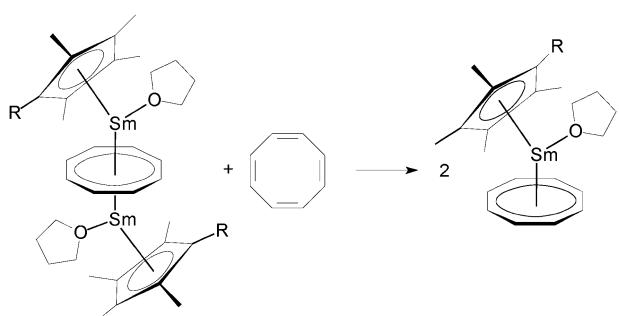
Scheme 17 Formation of $(C_5\text{Me}_4\text{R})\text{Sm}(\text{COT})$ ($R = \text{Me, Et}$).^{38a}

$[(C_5\text{Me}_5)\text{Sm}(\text{THF})]_2(\mu-\eta^8:\eta^8\text{-COT})$. This reaction is illustrated in Scheme 18.^{38a}

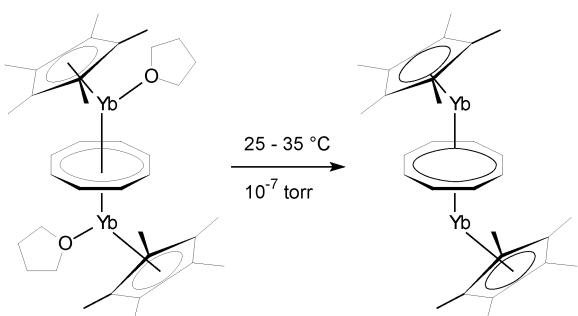
In an extension of this work, Evans *et al.* also reported the synthesis, structure, and reactivity of the analogous unsolvated bent triple-deckers of divalent europium and ytterbium.^{38b} In particular, the europium and ytterbium complexes of formula $[(C_5\text{Me}_5)\text{Ln}]_2(\mu-\eta^8:\eta^8\text{-COT})$ have been synthesized and structurally characterized to determine the dependence of the (ring centroid)–metal–(ring centroid) angles on the size and electron configuration of the metal. $\text{YbI}_2(\text{THF})_2$ reacts with KC_5Me_5 and $\text{K}_2\text{C}_8\text{H}_8$ in THF to form $[(C_5\text{Me}_5)\text{Yb}(\text{THF})]_2(\mu-\eta^8:\eta^8\text{-COT})$ in 80% yield (Scheme 19). This compound could be readily desolvated at 30°C and 10^{-7} Torr to afford $[(C_5\text{Me}_5)\text{Yb}]_2(\mu-\eta^8:\eta^8\text{-COT})$ in 80% yield. The unsolvated species was crystallized from toluene and found to consist of two divalent $[(C_5\text{Me}_5)\text{Yb}]^+$



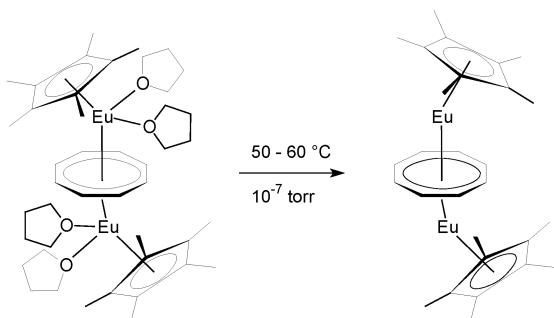
Scheme 18 Reaction of $[(C_5\text{Me}_5)\text{Sm}(\text{THF})]_2(\mu-\eta^8:\eta^8\text{-COT})$ with $C_5\text{Me}_5\text{Cl}$.^{38a}



Scheme 16 Formation of $(C_5\text{Me}_4\text{R})\text{Sm}(\text{COT})(\text{THF})$ ($R = \text{Me, Et}$).^{38a}



Scheme 19 Synthesis of $[(C_5\text{Me}_5)\text{Yb}]_2(\mu-\eta^8:\eta^8\text{-COT})$.^{38b}



Scheme 20 Synthesis of $[(C_5Me_5)Eu]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$.^{38b}

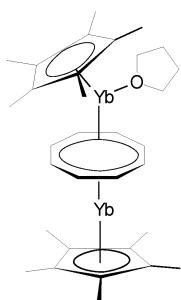
moieties bridged by a C₈H₈²⁻ unit with 159° and 161° (C₅Me₅ ring centroid)–Yb–(C₈H₈ ring centroid) angles.^{38b}

In a similar manner, $[(C_5Me_5)Eu(\text{THF})_2]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$ could be desolvated at 55 °C and 10⁻⁷ Torr to afford $[(C_5Me_5)Eu]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$ (Scheme 20) in 90% yield. The europium triple-decker has 149.3° and 148.9° (C₅Me₅ centroid)–Eu–(C₈H₈ centroid) angles.^{38b}

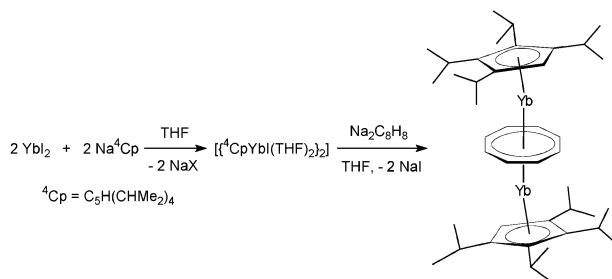
The THF-free complex $[(C_5Me_5)Yb]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$ was found to react with cyclooctatetraene to form (C₅Me₅)Yb(C₈H₈) (cf. Scheme 17).^{38b} A partially solvated triple-decker sandwich complex of divalent ytterbium, $[(C_5Me_5)Yb(\text{THF})_2](\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})[(C_5Me_5)Yb]$ (Scheme 21), was fortuitously obtained from a reaction of one equivalent of AlEt₃ with $[(C_5Me_5)Yb(\text{THF})_2](\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$ in efforts to determine if a $[(C_5Me_5)Yb(\text{THF})_2](\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})[(C_5Me_5)Yb(\text{THF})\cdot\text{AlEt}_3]$ complex would form. The two (C₅Me₅ ring centroid)–Yb–(C₈H₈ ring centroid) angles in this complex are significantly different: 145.5° on the solvated side and 170.9° on the unsolvated side.^{38c}

In summarizing this work by Evans *et al.*, it was shown that the triple-decked mixed ligand metallocenes, $[(C_5Me_5)Ln]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$, were synthetically accessible for Ln = Eu and Yb as well as for Sm and constituted a new series of unsolvated sterically unsaturated organolanthanide complexes. The complexes are bent regardless of the 4f⁶, 4f⁷, and 4f¹⁴ electron configurations, and the amount of bending depends on the radius of the metal as was noted earlier for the (C₅Me₅)₂Ln metallocenes. The reduction of cyclooctatetraene by $[(C_5Me_5)Yb]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$ indicated that the Yb derivative has a substantial reduction chemistry like that of $[(C_5Me_5)Sm]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$.^{38c}

Variations in these divalent lanthanide triple-deckers have been made both at the cyclopentadienyl sides and the bridging



Scheme 21 Schematic representation of $[(C_5Me_5)Yb(\text{THF})_2](\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})[(C_5Me_5)Yb]$.^{38c}



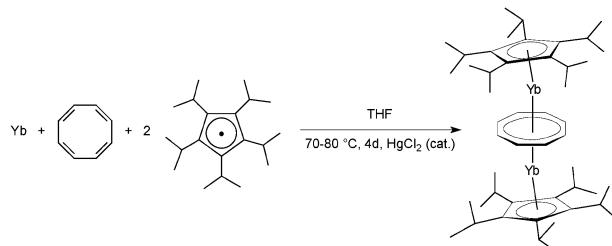
Scheme 22 Synthesis of $[{}^4\text{Cp}Yb]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$.³⁹

ligands. For example, Sitzmann *et al.* reported two synthetic routes leading to analogous ytterbium complexes containing very bulky poly(isopropyl)-substituted cyclopentadienyl ligands. Due to the high steric demand of the cyclopentadienyl outer decks these compounds were directly obtained as unsolvated materials. Scheme 22 illustrates the preparation of the blue-red tetraisopropylcyclopentadienyl (=⁴Cp) derivative.³⁹

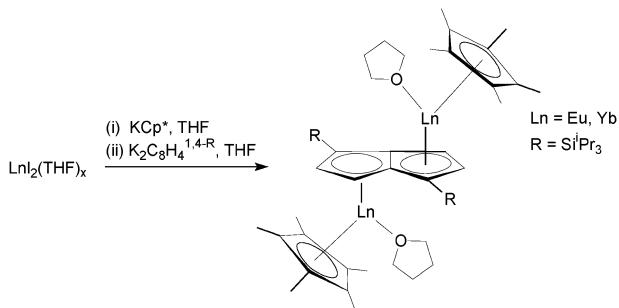
The corresponding pentaisopropylcyclopentadienyl (=⁵Cp) derivatives was made *via* an alternative route starting with the stable pentaisopropylcyclopentadienyl radical. Ytterbium metal, pentaisopropylcyclopentadienyl radical, and cyclooctatetraene were found to react smoothly in THF at 70–80 °C to yield $[{}^5\text{Cp}Yb]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$ as blue-purple powder in moderate yield (57%) (Scheme 23). It is very soluble in THF, moderately soluble in aromatic hydrocarbons, and sparingly soluble in aliphatic solvents. Unfortunately no structural data are available for these two interesting ytterbium(2+) triple-deckers.³⁹

A recent study by Cloke *et al.* dealt with the use of silylated pentalene and COT bridging ligands in such divalent lanthanide triple-decker complexes. The new pentalene antimonometallic compounds $[(C_5Me_5)Ln(\text{THF})_2](\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_8H_4^{1,4\text{-Si}^{\prime}\text{Pr}_3})$ were prepared for Ln = Eu, Yb from the one-pot reaction of LnI₂(THF)_x and KC₅Me₅ and the subsequent addition of one-half equivalent of K₂(C₈H₄^{1,4-Si[′]Pr₃) in THF (Scheme 24). The crystalline products were found to have surprisingly low solubilities in pentane and toluene and even in strongly coordinating solvents such as THF and DME. Attempts to desolvate the THF adducts *in vacuo* at temperatures up to 180 °C at 10⁻⁶ Torr were unsuccessful. However, the compounds were found to be stable under these conditions.²⁹ This was quite surprising, given that the less hindered system $[(C_5Me_5)Sm(\text{THF})_2](\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$ may be readily desolvated at significantly lower temperatures (30–50 °C at 10⁻⁶ Torr).^{38a}}

Once again a notable structural feature of the divalent lanthanide triple-deckers is the bent configuration of the



Scheme 23 Synthesis of $[{}^5\text{Cp}Yb]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT})$.³⁹

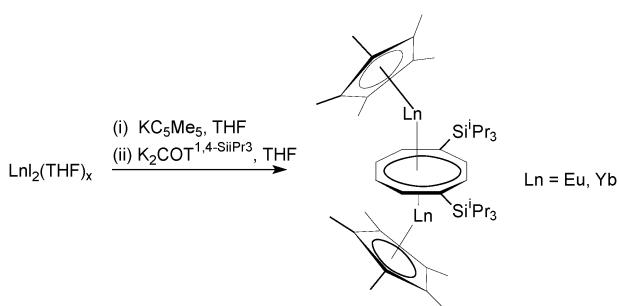


Scheme 24 Synthesis of $[(\text{C}_5\text{Me}_5)\text{Ln}(\text{THF})]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_8\text{H}_4^{1,4\text{-Si}^i\text{Pr}_3})$ ($\text{Ln} = \text{Eu}, \text{Yb}$).²⁹

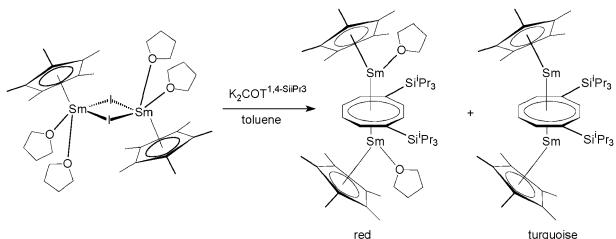
C_5Me_5 rings with respect to the pentalene rings. The pentalene ligand coordinates in an approximate $\eta^5\text{:}\eta^5$ mode, with the metal centers slipped toward the wingtip carbons.²⁹

The related series of $\text{COT}^{1,4\text{-Si}^i\text{Pr}_3}$ -bridged triple-deckers $[(\text{C}_5\text{Me}_5)\text{Ln}]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}^{1,4\text{-Si}^i\text{Pr}_3})$ ($\text{Ln} = \text{Eu}, x = 0; \text{Ln} = \text{Yb}, x = 0; \text{Ln} = \text{Sm}, x = 1$) were synthesized similarly as illustrated in Scheme 25. Unlike the pentalene compounds (*cf.* Scheme 24) these COT species are readily soluble in hydrocarbons (Eu, Yb) or ethers (Eu, Sm, Yb). The smaller Eu and Yb directly give rise to base-free compounds and show higher levels of solubility than the THF adduct with $\text{Ln} = \text{Sm}$.²⁹

Here, too, it was not possible to desolvate the THF adduct of the samarium derivative. However, it was found that the base-free adduct could be prepared by an alternative synthetic route, *via* the reaction of $[(\text{C}_5\text{Me}_5)\text{Sm}(\mu\text{-I})(\text{THF})_2]_2$ with $\text{K}_2(\text{COT}^{1,4\text{-Si}^i\text{Pr}_3})$ in toluene with heating (Scheme 26). This initially yielded a turquoise-blue solution, from which the toluene-soluble base-free product $[(\text{C}_5\text{Me}_5)\text{Sm}]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}^{1,4\text{-Si}^i\text{Pr}_3})$ could be isolated directly. The remaining red solid could be subsequently extracted using THF or Et_2O and identified as the THF adduct $[(\text{C}_5\text{Me}_5)\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}^{1,4\text{-Si}^i\text{Pr}_3})$. It was pointed out that is very unusual to obtain a mixture of base-free and THF-bound complexes in the same reaction pot for the electropositive f-elements. A further oddity is the large difference in solubilities of these species, which, while making their separation possible, appears counterintuitive. The methyl groups on the C_5Me_5 ligand and the trialkylsilyl groups confer a high degree of solubility to the base-free species, while the coordination of a THF molecule to each Sm center appears to counteract solubility, for reasons unknown.²⁹



Scheme 25 Synthesis of $[(\text{C}_5\text{Me}_5)\text{Ln}]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}^{1,4\text{-Si}^i\text{Pr}_3})$ ($\text{Ln} = \text{Eu}, \text{Yb}$).²⁹

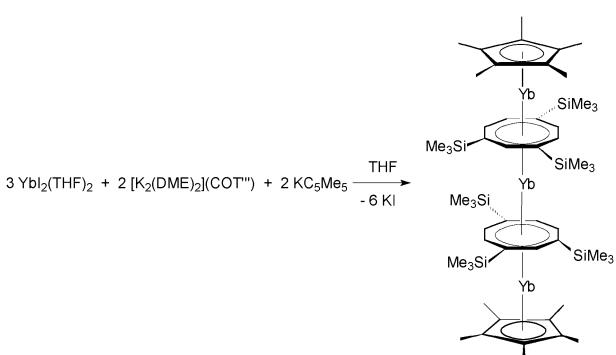


Scheme 26 Synthesis of $[(\text{C}_5\text{Me}_5)\text{Sm}]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}^{1,4\text{-Si}^i\text{Pr}_3})$ and $[(\text{C}_5\text{Me}_5)\text{Sm}(\text{THF})]_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}^{1,4\text{-Si}^i\text{Pr}_3})$.²⁹

The typical bent triple-decker configuration was also found for the $(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT}^{1,4\text{-Si}^i\text{Pr}_3})$ -bridged complexes, regardless of the presence of coordinated solvent.²⁹

The first and thus far only tetra-decker sandwich of an f-element was prepared in our laboratory in 2007. The unprecedented ytterbium(II) tetra-decker complex $(\text{C}_5\text{Me}_5)\text{Yb}(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT'''})\text{Yb}(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT'''})\text{Yb}(\text{C}_5\text{Me}_5)$ ($\text{COT}''' = \text{C}_8\text{H}_5(\text{SiMe}_3)_3\text{-1,6}$) was synthesized according to Scheme 27 (forest-green crystals, 64% yield) and fully characterized by X-ray diffraction and spectroscopic methods, including ^{171}Yb NMR spectroscopy.⁴⁰

An X-ray study (Fig. 8) clearly established the presence of the first neutral tetra-decker sandwich complex of an f-element in which a central $[\text{Yb}(\text{COT}''')_2]^{2-}$ unit is extended on both



Scheme 27 Synthesis of $(\text{C}_5\text{Me}_5)\text{Yb}(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT'''})\text{Yb}(\text{C}_5\text{Me}_5)$.⁴⁰

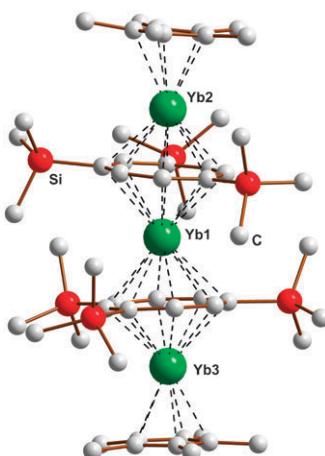


Fig. 8 The molecular structure $(\text{C}_5\text{Me}_5)\text{Yb}(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT'''})\text{Yb}(\mu\text{-}\eta^8\text{:}\eta^8\text{-COT'''})$.²⁹

sides by a $[(C_5Me_5)Yb]^{+}$ fragment. For the first time this molecule also offered the unique opportunity to directly observe two chemically non-equivalent ^{171}Yb nuclei in a single compound. The ^{171}Yb NMR spectrum of the tetra-decker sandwich complex in a THF- d_8 solution displayed two signals at δ 595 and 364 ppm in an intensity ratio of approximately 2 : 1, thereby allowing a clear assignment to the two different ^{171}Yb nuclei.⁴⁰

Apparently, the use of the very bulky COT''' ligand is the reason for the near-linear arrangement of the rings in the ytterbium tetra-decker sandwich. In contrast, all other related triple-deckers comprise significantly bent structures. It was noted by Cloke *et al.*, that although several theories have been proposed to explain this anomalous structural preference (a bent ring configuration), there is no currently accepted explanation for the phenomenon.²⁹ Table 1 lists the tilt angles for the lanthanide triple- and tetra-decker sandwich complexes which have been structurally characterized thus far.

Low-valent scandium complexes

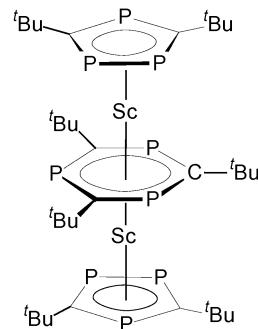
There are a few reports in the literature dealing with triple- and multiple-decker complexes of scandium in very low formal oxidation states (Sc^{1+} and Sc^0). The very first example of a formal scandium(i) complex, reported in 1996 by Cloke *et al.*, was an unusual triple-decker incorporating the novel 1,3,5-triphosphabenzene ring as middle-deck. Co-condensation of electron beam-vaporized scandium with an excess of the phosphaalkyne ' $BuC\equiv P$ ' at 77 K afforded the forest-green complex $[(\eta^5-P_3C_2'Bu_2)Sc]_2(\mu-\eta^6:\eta^6-P_3C_3'Bu_3)$ (Scheme 28) in 5–10% yield (based on scandium) after workup.⁴¹

The molecular structure of $[(\eta^5-P_3C_2'Bu_2)Sc]_2(\mu-\eta^6:\eta^6-P_3C_3'Bu_3)$ was determined by X-ray crystallography. The central 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene ring in the triple decker structure lies on a crystallographic mirror plane and is planar with no significant variation in ring P–C bond lengths, indicative of binding as a $\mu-\eta^6:\eta^6$ -aromatic ligand.⁴¹

In a similar manner as for the Ln-COT nanowires (*vide supra*), multiple-decker sandwich complexes have also been prepared with neutral benzene as bridging ligand.^{37d,h} For example, a molecular beam of multilayer metal–benzene

Table 1 Ring tilt angles for lanthanide triple- and tetra-decker complexes

Compound	Angle (°)	Ref.
$[(C_5Me_5)Eu(THF)]_2(\mu-C_8H_4^{1,4-Si^4Pr_3})$	132	29
$[(C_5Me_5)Yb(THF)]_2(\mu-C_8H_4^{1,4-Si^4Pr_3})$	133	29
$\{[(C_5Me_5)Sm(\text{diglyme})]_2(\mu\text{-COT})\}(\text{THF})_2$	138	38a
$[(C_5Me_5)Eu(THF)]_2(\mu-\eta^8:\eta^8\text{-COT})$	139	38b
$[(C_5Me_5)Sm(THF)]_2(\mu\text{-COT}^{1,4-Si^4Pr_3})$	140, 142	29
$[(C_5Me_5)Eu]_2(\mu\text{-COT})$	148	38b
$[(C_5Me_5)Sm]_2(\mu\text{-COT})$	149	38a
$[(C_5Me_5)Eu]_2(\mu\text{-COT}^{1,4-Si^4Pr_3})$	153	29
$[(C_5Me_5)Sm]_2(\mu\text{-COT}^{1,4-Si^4Pr_3})$	153	29
$[(C_5Me_5)Yb]_2(\mu\text{-COT})$	160	38b
$[(C_5Me_5)Yb]_2(\mu\text{-COT}^{1,4-Si^4Pr_3})$	161	29
$[(C_5Me_5)Yb(THF)]_2(\mu-\eta^8:\eta^8\text{-COT})[(C_5Me_5)Yb]$	171, 146	38c
$(COT'')Ho[\mu-C_8H_6(SiMe_3)_2-1,5]Ho(COT'')$	175, 177	30
$Nd_2(COT'')_3$	176	28
$(C_5Me_5)Yb(\mu-\eta^8,\eta^8\text{-COT}'')-$ $Yb(\mu-\eta^8,\eta^8\text{-COT}'')Yb(C_5Me_5)$	177, 179	40
	—	—

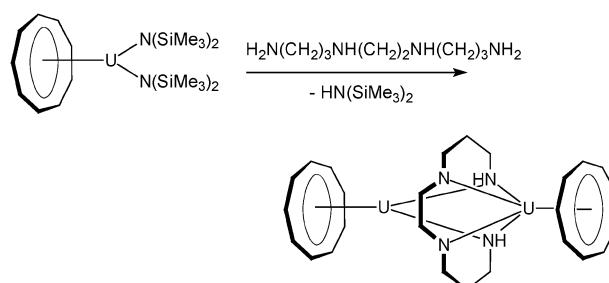


Scheme 28 Schematic representation of $[(\eta^5-P_3C_2'Bu_2)Sc]_2(\mu-\eta^6:\eta^6-P_3C_3'Bu_3)$.⁴¹

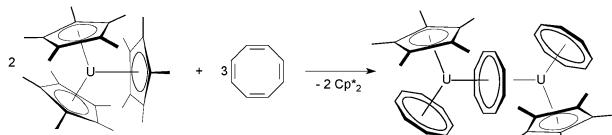
organometallic clusters $Sc_n(C_6H_6)_m$ was produced by a laser vaporization synthesis method, and their magnetic deflections were measured. Multidecker sandwich clusters of scandium atoms and benzene $Sc_n(C_6H_6)_{n+1}$ ($n = 1, 2$) possess magnetic moments that increase monotonously with n . The magnetic moments $Sc_n(C_6H_6)_{n+1}$ are smaller than that of their spin-only values as a result of intracluster spin relaxation, an effect that depends on the orbital angular momenta and bonding characters of the orbitals containing electron spin. The mechanism of ferromagnetic spin ordering in $Sc_2(C_6H_6)_3$ was discussed qualitatively in terms of molecular orbital analysis. These sandwich species represent a new class of one-dimensional molecular magnets in which the scandium atoms are formally zerovalent.^{37d,h}

Actinide complexes

In contrast to the exciting progress in the chemistry of lanthanide triple- and multiple-deckers, there are only scattered reports dealing with triple-decker-like structures of uranium, and linear triple- or multiple-decker sandwiches are completely unknown in organoactinide chemistry. A triple-decker-like dinuclear compound with a bridging tetra-amide ligand was reported by Ephritikhine *et al.*⁴² The compound was prepared by the transamination reaction of $(COT)U[N(SiMe_3)_2]_2$ and tetrazadodecane, $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, according to Scheme 29. In the product, two $(COT)U$ units are linked by a tetra-amide ligand in a $\mu-\eta^4:\eta^4$ fashion. The X-ray crystal structure revealed the shortest U–U distance (3.3057(9) Å) ever observed in a molecular compound at the time of publication.⁴²



Scheme 29 Formation of $[(COT)U]_2(\mu-\eta^4:\eta^4\text{-HN(CH}_2\text{)}_3\text{N(CH}_2\text{)}_2\text{N-(CH}_2\text{)}_3\text{NH})$.⁴²



Scheme 30 Synthesis of $[(\text{COT})(\text{C}_5\text{Me}_5)\text{U}]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-COT})$.^{43a}

A dinuclear uranium COT complex showing some resemblance with the divalent lanthanide bent triple-decker sandwiches, $[(\text{COT})(\text{C}_5\text{Me}_5)\text{U}]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-COT})$, was reported by Evans *et al.* This compound is accessible *via* two different routes. It was first made by the reaction of $(\text{C}_5\text{Me}_5)_3\text{U}$ with cyclooctatetraene in a 1 : 1 stoichiometry as illustrated in Scheme 30 (75% yield).^{43a}

The compound is stable in THF and can also be obtained using the THF adduct $(\text{COT})(\text{C}_5\text{Me}_5)\text{U}(\text{THF})$ instead of $(\text{C}_5\text{Me}_5)_3\text{U}$. Another alternative synthesis involves treatment of $(\text{C}_5\text{H}_5)_2\text{UH}(\text{DMPE})$ ($\text{DMPE} = 1,2\text{-bis(dimethylphosphino)ethane}$) (88%). This can be considered an improved synthesis of $[(\text{COT})(\text{C}_5\text{Me}_5)\text{U}]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-COT})$, since reaction times are shorter and the synthesis does not require the preparation of $(\text{C}_5\text{Me}_5)_3\text{U}$.^{43b} The product contains two mixed ligand bent metallocene units, $[(\text{COT})(\text{C}_5\text{Me}_5)\text{U}]^+$, coordinated to a bridging $\text{C}_8\text{H}_8^{2-}$ moiety. This bridging $\text{C}_8\text{H}_8^{2-}$ moiety is nonplanar and is bound in an unusual $\eta^3\text{:}\eta^3$ -fashion in which one atom is common to both *pseudo*-allyl moieties.^{43a}

Future outlook

The chemistry of f-element multiple-decker sandwich complexes is still in its infancy, although significant and exciting progress has been made in recent years. In the case of the COT derivatives, this progress has been made possible through the use of sterically demanding silyl-substituted cyclooctatetraenyl ligands. However, there is plenty of room for very interesting future investigations in this field. One of the big open questions concerns the factors which govern the configuration of organolanthanide triple-decker complexes. What are the reasons for the pronounced tendency towards bent configurations in the case of divalent lanthanide triple-deckers? How can these configurations be influenced in a more systematic manner by a proper choice of ligand combinations? Little is known about the reactivity of such triple- or tetra-decker sandwich complexes. Can reactions be designed in the course of which the triple- or tetra-decker is retained? Are stable cationic derivatives of these extended sandwich structures accessible? Will it be possible to prepare lanthanide triple-decker sandwich complexes with “non-classical” Ln^{2+} ions (*e.g.* Tm^{2+})? Are heterobimetallic lanthanide triple- and tetra-decker sandwich complexes accessible? Finally, the COT-based lanthanide nanowires should inspire new thoughts in material science because it is hoped that the regular arrangement of metal ions can introduce useful properties such as electroconductivity and magnetism. As for now, the claimed existence of such nanowires is mainly based on mass spectrometry data, but structural proof is lacking. Future work in this area will show if the promises which these materials hold for practical applications in the next generation

of electronic devices with enhanced functionality and improved performance, especially in high-density information storage and quantum computing, can be fulfilled.

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