Lanthanide Sandwich Complexes

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$[(C_5Me_5)Yb(\mu\text{-}\eta^8,\eta^8\text{-cot}''')Yb(\mu\text{-}\eta^8,\eta^8\text{-cot}''')Yb(C_5Me_5)]$—A Unique Tetradecker Sandwich Complex of a Divalent Lanthanide**

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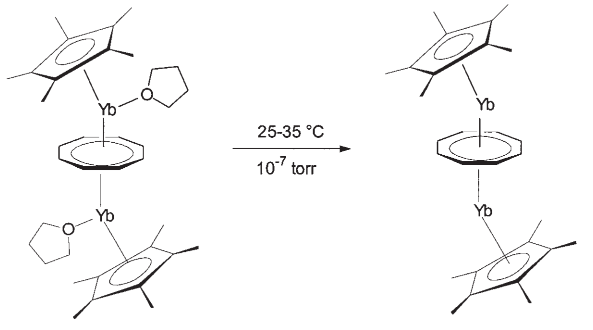
Dedicated to Professor William J. Evans on the occasion of his 60th birthday

Since its discovery in 1984 the unsolvated divalent lanthanide metallocene $[(C_5Me_5)_2Sm]$ continues to hold great fascination.[1] It has been the subject of theoretical studies aiming to rationalize why the C_5Me_5 ligands in $[(C_5Me_5)_2Ln]$ (Ln = Sm, Eu, Yb) adopt a bent geometry instead of the sterically more favorable structure with parallel rings.[2] Evidence was found for both valence and metal-core electron participation in the bending process.[3] Moreover, $[(C_5Me_5)_2Ln]$ complexes display an exceptionally high and unique reactivity towards a large variety of reagents.[4] Among the most prominent examples are the formation of $[(\mu\text{-}N_2)\{Sm(C_5Me_5)_2\}_2]$, the first dinitrogen complex of an f element,[5] the trimerization of carbon monoxide,[6] and the preparation of heterobimetallic $[(C_5Me_5)_2Ln{-}Al(C_5Me_5)]$.[7]

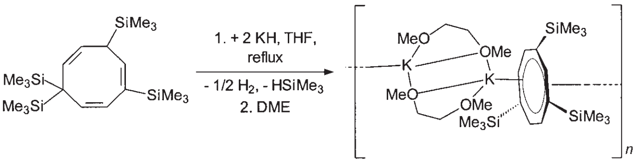
More recently, Evans et al. discovered a novel class of unsolvated triple-decker bent metallocenes of divalent lanthanides.[8] The compounds $[(\mu\text{-}\eta^8,\eta^8\text{-cot})\{Ln(C_5Me_5)\}_2]$ (Ln = Sm, Eu, Yb; cot = cyclooctatetraenyl) were prepared according to Scheme 1 by desolvation of the corresponding THF solvates. Structural studies revealed that these triple-decker sandwich complexes are also bent, regardless of the $4f^6$, $4f^7$, and $4f^{14}$ electron configurations, and that the amount of bending depends on the radius of the metal center, as was noted earlier for the $[(C_5Me_5)_2Ln]$ metallocenes.[2,3]

The first tetradecker sandwich complexes of transition metals (Fe, Co, Mn) were reported almost thirty years ago by Siebert et al.[9] In contrast, linear triple- or tetradecker sandwich complexes containing two or three lanthanide centers sandwiched between polyhapto ring ligands have not yet been isolated, although there is solid evidence that the large, flat cot ligands are capable of forming such complexes with f elements.[10–13]



Scheme 1. Preparation of the bent triple-decker sandwich complex $[(\mu\text{-}\eta^8,\eta^8\text{-cot})\{Yb(C_5Me_5)_2\}_2]$ through desolvation of the corresponding THF adduct.[8]

We set out our investigation in this area by reasoning that the use of very bulky cot ligands might discourage the bending process and favor the formation of linear triple-decker sandwich structures. One of the most sterically encumbered cot ligands currently available is the 1,3,6-tris(trimethylsilyl)-cyclooctatetraenyl dianion (cot‴).[14,15] The dipotassium salt of this ligand is accessible through a deprotonation/desilylation reaction of 1,3,6,6-tetrakis(trimethylsilyl)cyclooctatriene with potassium hydride in refluxing THF.[14] The deprotonation/desilylation of 1,3,6,6-tetrakis(trimethylsilyl)cyclooctatriene with two equivalents of KH as reported in the literature affords the THF adduct $[K_2(thf)_3](cot''')$, which partially loses THF upon drying under vacuum and is thus difficult to isolate in a well-defined state. We found that the corresponding DME adduct $[K_2(dme)_2](cot''')$ (**1**, Scheme 2; off-white, needle-like crystals) is much better suited as a cot‴ transfer reagent, as it is perfectly stable with respect to loss of coordinated solvent even under vacuum. Analytical and spectroscopic data of **1** confirmed the K/dme ratio of 1:1.[16] In the solid state, the potassium salt **1** forms a one-dimensional supramolecular arrangement of alternating $[cot''']^{2-}$ ions and $[K_2(dme)_2]^{2+}$ units. In the latter, each of the two



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Scheme 2. Preparation of **1** from 1,3,6,6-tetrakis(trimethylsilyl)cyclooctatriene.

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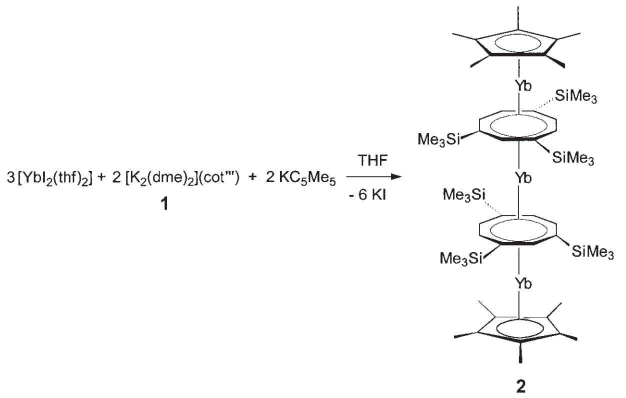
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DME molecules acts both as a chelating and bridging ligand. To our knowledge, such an arrangement has not been observed before, although various DME-solvated potassium salts have been structurally characterized in the past. In those, the cationic moieties range from $[K(dme)]^+$ ions associated with the anionic complexes through coordination to heteroatoms to separated $[K(dme)_4]^+$ cations.[17]

With the cot‴ precursor **1** in hand, we attempted a synthesis of the triple-decker complex $[(C_5Me_5)Yb(\mu\text{-}\eta^8,\eta^8\text{-}cot''')Yb(C_5Me_5)]$ by the reaction of $[YbI_2(thf)_2]$ with KC_5Me_5 and **1** (molar ratio 2:2:1) in THF. From the resulting intensely green reaction mixture a small amount of forest-green crystals suitable for X-ray diffraction could be isolated by repeated crystallizations from *n*-pentane. Much to our surprise, the single-crystal X-ray study revealed the presence of the unprecedented ytterbium(II) tetradecker complex $[(C_5Me_5)Yb(\mu\text{-}\eta^8,\eta^8\text{-}cot''')Yb(\mu\text{-}\eta^8,\eta^8\text{-}cot''')Yb(C_5Me_5)]$ (**2**). Once we knew the composition, the tetradecker sandwich could be isolated in much higher yields (ca. 64 %) by adjusting the stoichiometry of the reactants to the correct ratio of 3:2:2 (Scheme 3).



Scheme 3. Synthesis of the ytterbium(II) tetradecker complex **2**.

Figure 1 depicts the molecular structure of **2**.[18] The X-ray study clearly established the presence of the first neutral tetradecker sandwich complex of an f element in which a central $[Yb(cot''')_2]^{2-}$ unit is extended on both sides by a $[Yb(C_5Me_5)]^+$ fragment. It also confirmed our initial assumption that the use of bulky cot ligands as central decks would inhibit the bending of the resulting multiple-decker sandwich complex. With a $X_{cot'''}$-Yb-$X_{cot'''}$ angle of 173.8° and X_{Cp*}-Yb-$X_{cot'''}$ angles of 176.6° and 178.5° ($Cp^* = C_5Me_5$), the geometry of **2** is very close to a linear tetradecker arrangement. The observed small deviations from linearity can be traced back to repulsive interactions between the methyl groups of the ring substituents. All analytical and spectroscopic data of **2** are also consistent with the tetradecker structure.[16] Especially informative is the mass spectrum of **2**, which shows the molecular ion of the tetradecker sandwich with 10 % relative intensity. Peaks at *m*/*z* 801 (100 %) and 629 (65 %) can be assigned to the fragments $[M-\{cot'''YbCp^*\}^+]$ and $[M-\{cot'''Yb_2Cp^*\}^+]$.

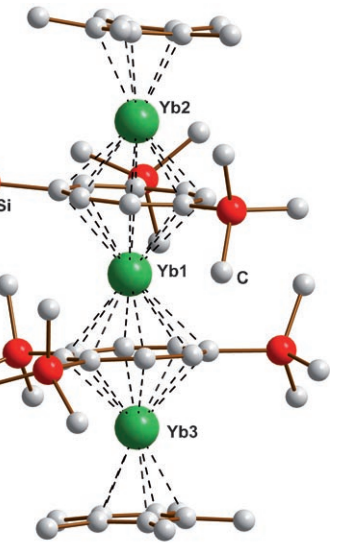


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: $C_{cot'''}$-Yb1 2.61(1)–2.83(1), Yb2-$C_{cot'''}$ 2.64(1)–2.73(1), Yb3-$C_{cot'''}$ 2.61(1)–2.68(1), C_{Cp*}-Yb 2.61(1)–2.65(1), Yb1-$X_{cot'''}$ 2.040(4)–2.060(4), Yb2-$X_{cot'''}$ 1.911(4), Yb3-$X_{cot'''}$ 1.895(4), Yb2-X_{Cp*} 2.352(6), Yb3-X_{Cp*} 2.342(5); $X_{cot'''}$-Yb1-$X_{cot'''}$ 173.8(4), $X_{cot'''}$-Yb2-X_{Cp*} 176.6(9), $X_{cot'''}$-Yb3-X_{Cp*} 178.5(6) (X = ring center).

High-resolution ^{171}Yb NMR spectroscopy was introduced into organo-f-element chemistry by Lappert and co-workers in 1989[19] and has since been demonstrated to be a versatile tool for characterizing divalent organoytterbium complexes.[20] ^{171}Yb NMR chemical shifts in the range from about $\delta = -30$ ppm to about $\delta = 1060$ ppm have been reported in the literature.[20,21] All three ytterbium ions in **2** are divalent. Thus, for the first time, this molecule offers the unique opportunity to directly observe two chemically non-equivalent ^{171}Yb nuclei in a single compound. Indeed, the ^{171}Yb NMR spectrum of **2** in a $[D_8]$THF solution displayed two signals at $\delta = 595$ and 364 ppm in an intensity ratio of approximately 2:1, thereby allowing a clear assignment to the two different ^{171}Yb nuclei. The latter value, assigned to the central ytterbium atom, can be favorably compared to that reported for $[(cot'')Yb^{II}\{PhN{=}C(Me)C(Me){=}NPh\}(thf)]$ at $\delta = 224$ ppm (cot″ = 1,4-bis(trimethylsilyl)cyclooctatetraenyl).[22] However, for $[(C_5Me_5)_2Yb]$ derivatives large variations in chemical shifts have been reported, thus making a meaningful comparison difficult.[21] When discussing ^{171}Yb NMR spectra, it should also be taken into account that relativistic effects on ^{171}Yb NMR chemical shifts are significant, and these effects are not yet well-understood for organoytterbium(II) species.[21,23]

The study reported here demonstrates that well-defined, unprecedented multidecker sandwich complexes of f elements can be made available given the right choice of ligand sets. Current efforts are directed to extending this chemistry to other divalent lanthanides (Sm, Eu, Tm) and alkaline-earth metals.

Experimental Section

2: THF (40 mL) was added to a mixture of $[\mathrm{YbI_2(thf)_2}]$ (0.90 g, 1.58 mmol) and $\mathrm{KC_5Me_5}$ (0.18 g, 1.05 mmol) to give a yellow suspension. A solution of **1** (0.61 g, 1.05 mmol) in THF (20 mL) was added with vigorous stirring, resulting in a rapid color change to bright green with concomitant formation of a white precipitate (KI). After 24 h the precipitate was separated by filtration, and the intensely green filtrate was reduced in volume to dryness to afford a green oil, which slowly crystallized upon standing at room temperature. Recrystallization from *n*-pentane (ca. 30 mL) afforded 0.48 g (64%) of **2** as forest-green crystals. Correct elemental analysis for $\mathrm{C_{54}H_{94}Si_6Yb_3}$, calcd: C 45.33, H 6.62; Found: C 44.17, H 7.01. $M_r =$ 1430.95 $\mathrm{g\,mol^{-1}}$. ^{1}H NMR ($[\mathrm{D_8}]$THF, 400.1 MHz, 25 °C): $\delta = 5.8$–6.2 (br m, 10 H, cot′′′), 1.4 (br s, 30 H, $\mathrm{C_5Me_5}$), 0.2 ppm (br s, 54 H, $\mathrm{CH_3}$-Si); ^{13}C NMR ($[\mathrm{D_8}]$THF, 100.6 MHz, 25 °C): $\delta = 108.7$ ($C_5\mathrm{Me_5}$), 100.2, 99.1, 96.8, 94.9, 91.9 ($\mathrm{C_{cot'''}}$), 10.8 ($\mathrm{C_5}Me_5$), 1.6 ppm ($\mathrm{CH_3}$-Si); ^{29}Si NMR ($[\mathrm{D_8}]$THF, 79.5 MHz, 25 °C): $\delta = 0.99$, 0.40, 0.02 ppm; ^{171}Yb NMR ($[\mathrm{D_8}]$THF, 70.0 MHz, 25 °C): $\delta = 595$, 364 ppm (2:1); MS (EI, 70 eV): *m*/*z* (%) 1430 (10) $[M^+]$, 936 (30) $[M-\{\mathrm{cot'''Yb}\}^+]$, 801 (100) $[M-\{\mathrm{cot'''YbCp^*}\}^+]$, 665 (38)$[M-\{\mathrm{cot'''YbCp^*_2}\}^+]$, 629 (65) $[M-\{\mathrm{cot'''Yb_2Cp^*}\}^+]$, 579 (38); IR (KBr disk): $\tilde{\nu} = 2954$ (s), 2900 (m), 2857 (m), 1575 (vw), 1509 (vw), 1444 (w), 1405 (w), 1249 (s), 1210 (w), 1181 (vw), 1064 (s), 1044 (s), 977 (w), 925 (vw), 862 (vs), 836 (vs) 779 (m), 750 (m), 687 (w), 638 (m), 560 (vw), 505 $\mathrm{cm^{-1}}$ (vw).

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[15] Denoted in analogy to Cp′′′, which is 1,2,4-tris(trimethylsilyl)cyclopentadienyl.

[16] Experimental details including the synthetic procedures and spectroscopic data can be found in the Supporting Information.

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