Fluorenyl and *ansa*-Dimethylsilyl*bis*(fluorenyl) Derivatives of Divalent Ytterbium and Samarium − Synthesis and Structure of the First Mixed-Ligand Ln^{II} Classic Sandwich Complex $(C_{13}H_9)(C_5Me_5)Yb(DME)$

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Novel fluorenyl complexes of divalent ytterbium $(C_{13}H_9)_2Yb(L)_n$ [L = THF, *n* = 2 (**1**); L = DME, *n* = 1 (**2**)] have been prepared by reaction of $YbI_2(THF)_2$ with 2 equiv. of $C_{13}H_9K$ as well as by reaction of $(C_{10}H_8)Yb(THF)_2$ with fluorene in THF. Oxidation of **1** by *t*BuN=CHCH=N*t*Bu (DAD) resulted in the formation of $(C_{13}H_9)_2Yb(DAD)$ (**3**). The reaction of $\{YbI(DME)_2]_2(\mu\text{-}C_{10}H_8)\}$ (**4**) with fluorene did not give $(C_{13}H_9)YbI(DME)$ (**5**), but the redistribution products $YbI_2(DME)$ and **2**. The first mixed-ligand sandwich complex of a divalent lanthanide metal $(C_{13}H_9)(C_5Me_5)Yb(DME)$ (**6**) was prepared in a one-pot reaction of **4** with C_5Me_5H and $C_{13}H_9K$ in DME. *ansa*-$Me_2Si(C_{13}H_8)_2Yb(THF)$ (**7**) and *ansa*-$Me_2Si(C_{13}H_8)_2Sm(THF)_4$ (**8**) were obtained by treatment of the appropriate Ln^{II} iodides with *ansa*-$Me_2Si(C_{13}H_9)_2K_2$ in THF. The molecular structures of **1** and **6** were determined by single-crystal X-ray diffraction.

Introduction

The increased attention given to the fluorenyl ligand and the extensive work in synthesis and investigation of its d-metal block complexes has been observed during the last decade. This was mainly provoked by the discovery of the high efficiency of fluorenylzirconium complexes in the stereospecific propylene polymerization.[1,2] The remarkable activity of fluorenyl-derived group-4 metallocene complexes in α-olefin polymerization was explained by the characteristics of the ligand, namely by the easy η^5-η^3-η^1 interconversion of the five-membered ring−metal bonding mode (ring slippage), providing a free site for a substrate in the metal center's coordination sphere.

The complexes with η^5- bonded aromatic carbocyclic (mainly cyclopentadienyl) ligands form the most explored class of organolanthanide compounds.[3,4] These ancillaries have proved themselves to be a suitable coordination environment of the lanthanide metal atom providing the unique reactivity of the derived hydrido and hydrocarbyl complexes in various reactions involving unsaturated substrates.[5−18] Some cyclopentadienyl derivatives of divalent lanthanides also show catalytic activity in α-olefin polymerization.[19−22]

To date the fluorenyl ligand has not been significantly involved in organolanthanide chemistry. The lanthanide fluorenyl complexes $(C_{13}H_9)_2Ce$[23] and $(C_{13}H_9)_2LnCl_2$-$Li(THF)_2$ (Ln = La, Nd, Sm, Ho, Lu)[24,25] were described twenty years ago and are poorly characterized, but were classified by the authors as complexes with metal−ligand σ-bonds on the basis of spectroscopic data. The only fluorenyl derivative of a divalent lanthanide, $(C_{13}H_9)_2Sm(THF)_2$, was reported and structurally characterized by Evans.[26] X-ray diffraction has shown the coordination of the fluorenyl ligands in this complex to be partially distorted from η^5 towards η^3. Dramatic influence of ligation of the central atom on the fluorenyl ligand bonding mode has been found for (cyclopentadienyl)(*ansa*-fluorenyl)yttrocene complexes.[27] In *ansa*-$Me_2Si(\eta^3\text{-}C_{13}H_9)(\eta^5\text{-}Cp')YCl_2Li(OEt_2)_2$ an X-ray diffraction study revealed η^3-coordination of the central fluorenyl ring, while in the related amido derivative *ansa*-$Me_2Si(\eta^3\text{-}C_{13}H_9)(\eta^5\text{-}Cp')YN(SiMe_3)_2$, the fluorenyl ligand bonding is just partially tilted towards η^3-, but basically approaches an η^5-arrangement.

Being sterically demanding, the fluorenyl ligand is an attractive and easily available ancillary which is able to stabilize the Ln^{+2} oxidation state. This also proves that there is a well-defined environment around the metal center that allows control of reaction stereochemistry in its coordination sphere. In this paper we present the synthesis and structure investigations of novel (fluorenyl)Yb^{II} and -Sm^{II} sandwich complexes.

Results and Discussion

Two different approaches were used to synthesize the bis(fluorenyl) complex of divalent ytterbium: (i) the metathetic reaction of $YbI_2(THF)_2$ with 2 equiv. of $C_{13}H_9K$ in THF, which resulted in the formation of $(C_{13}H_9)_2Yb(THF)_2$ (**1**) in 72% yield, and (ii) by protolytic substitution of the naphthalene ligand in $(C_{10}H_8)Yb(THF)_2$[28] (**3**) by fluorene which also afforded **1** in reasonable yields. Although in the

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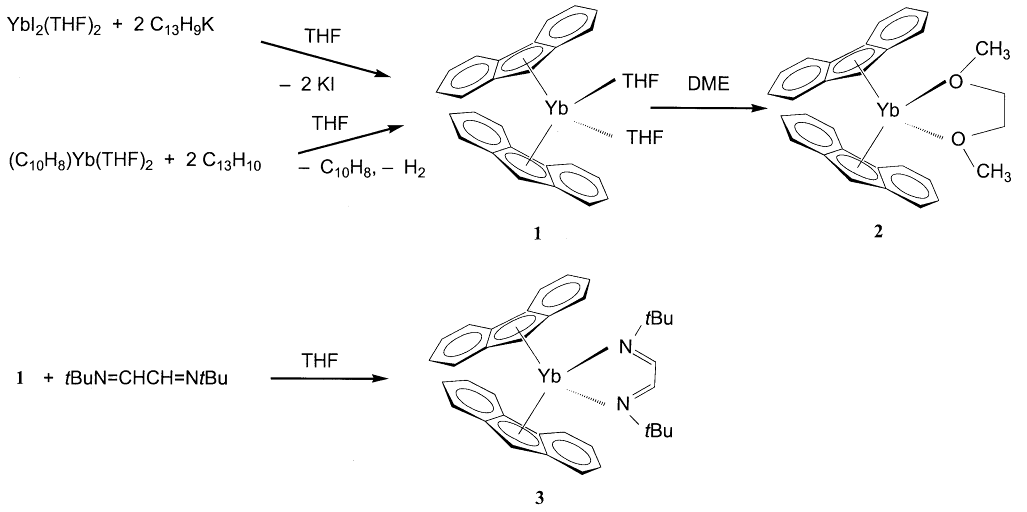


Scheme 1

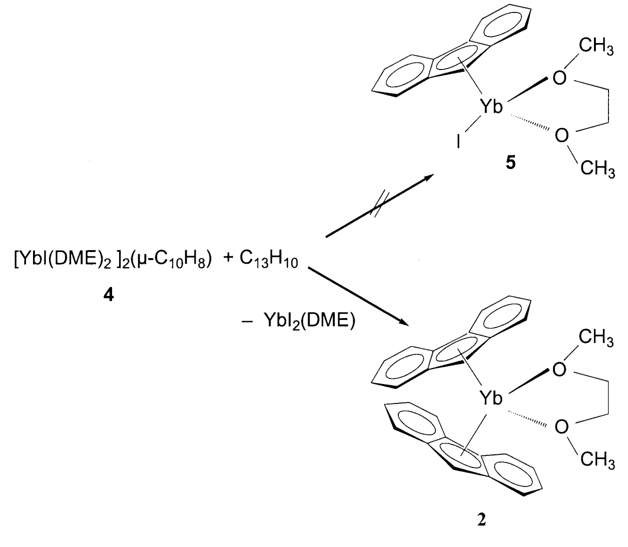
latter method the yield is somewhat lower, this allows the avoidance of the tedious procedure of KI separation (Scheme 1).

Bis(fluorenyl)bis(tetrahydrofuran)ytterbium(II) (**1**) is isolated after recrystallization from hot toluene/THF mixtures (30:1) in the form of ruby-red crystals, extremely sensitive towards moisture and air. It is soluble in THF, DME, and pyridine, moderately soluble in toluene and insoluble in aliphatic hydrocarbons. Recrystallization from DME produces $(C_{13}H_9)_2Yb(DME)$ (**2**) as deep yellow crystals, which show a slightly lower solubility in the solvents mentioned above compared to **1**. Both complexes **1** and **2** are diamagnetic corresponding to the Yb^{2+} oxidation state;[29] they were characterized by means of ^1H and ^{13}C NMR and IR spectroscopy as well as by elemental analysis, and an X-ray structural analysis was also performed on **1**.

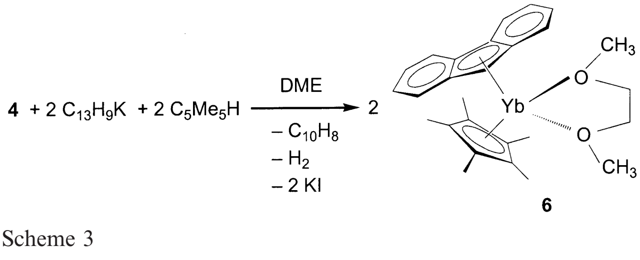
Compound **1** can easily be oxidized by tBuN=CHCH=NtBu (DAD) in THF solution forming the corresponding (diazabutadiene)Yb^{III} derivative **3** as deep green crystals after recrystallization from hexane with nearly quantitative yield. It is very soluble in THF and toluene and moderately soluble in hexane. The magnetic moment of **3** (4.8 BM, 293 K) corresponds well to the values normally observed for complexes of trivalent ytterbium. For **3** as for other diazabutadiene derivatives of Yb^{III} [30,31] no signals of DAD radical anions were observed by ESR spectroscopy.

Heteroleptic sandwich complexes bearing different carbocyclic ligands are of essential practical interest since selection of ligands could be a useful tool for fine-tuning steric and electronic properties of the metal atom's environment. It is known from the literature,[4] that lanthanide mixed-ligand systems are predisposed to ligand redistribution, which favours the formation of homoleptic derivatives. To date, mixed ligand Ln^{II} classic sandwich complexes having two different π-donor carbocyclic ligands, are unknown. Heteroleptic Ln^{II} derivatives, in general, still remain rare. Recently, Evans described the synthesis and X-ray structure of $[Cp^*Yb(THF)]_2(\mu\text{-}\eta^8{:}\eta^8\text{-}C_8H_8)$, a binuclear (cyclooctatetraenyl)(pentamethylcyclopentadienyl) triple-decker complex.[32] Some (aryloxy)(cyclopentadienyl),[33,34] linked (η^6-carboranyl)(cyclopentadienyl),[35] linked (alkoxy)(cyclopentadienyl),[36–38] and (cyclopentadienyl)(pyrazolylborato) derivatives[39] have also been reported.

Our first attempts to obtain a starting material for heteroleptic fluorenyllanthanide complexes failed. Splitting of the naphthalene-bridged dinuclear complex $[(DME)_2(I)Yb(\mu\text{-}C_{10}H_8)Yb(I)(DME)_2]$ (**4**) by fluorene in DME did not yield the expected heteroleptic dimethoxyethane complex of fluorenylytterbium(II)iodide (**5**); the dis-



Scheme 2



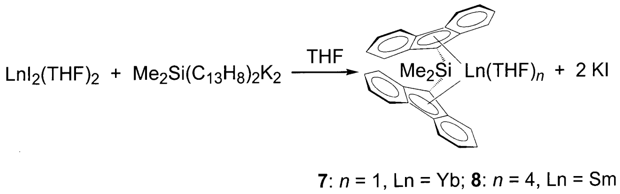
Scheme 3

mutation products $YbI_2(DME)_2$ and **2** could be isolated instead (Scheme 2). The second experiment, the consecutive "one-pot" treatment of **4** with C_5Me_5H and $C_{13}H_9K$ in DME was successful. Ligand redistribution was avoided and $(C_{13}H_9)(C_5Me_5)Yb(DME)$ (**6**) crystallized in 46% yield as diamagnetic deep-green crystals from toluene (Scheme 3).

Compound **6** is stable at room temperature in the solid state as well as in benzene, toluene and DME, but not in THF. Thus, the ^1H NMR spectrum of **6** in $[D_6]$benzene shows a singlet signal at $\delta = 2.06$ due to the CH_3 protons of the pentamethylcyclopentadienyl ligand and a set of signals typical for the fluorenide anion[40,41] in the aromatic region. The proton signals of the CH_3O groups of the DME ligand appear as a broad multiplet, significantly high-field shifted, while the signals for the CH_2 protons keep their normal position. The high-field shift of the methyl proton signals of DME can be attributed either to the influence of coordination to the Yb^{II} ion or to the influence of the ring current of the coordinated fluorenyl ligand. In contrast, the ^1H NMR spectrum of **6**, on dissolving the compound in $[D_8]$THF, immediately shows two singlet signals for the Cp* protons at $\delta = 1.82$ and 1.87 (with the ratio 3:8 which does not change within 100 h) and a complex set of signals in the region between $\delta = 6.12$ and 7.93 for the protons of the fluorenyl ligand. The reason for this may be a dismutation reaction forming partly the symmetric products $(C_{13}H_9)_2Yb(THF)_2$ (**1**) and $(C_5Me_5)_2Yb(THF)_2$ in THF solution. This could be shown in the case of other lanthanoidocene derivatives, which undergo a facile transfer of η^5-bonded cyclopentadienyl ligands.[42−44] Neither **1** nor $Cp^*{}_2Yb(THF)_2$ could be isolated from the reaction mixture in a pure state.

With respect to catalytic activity, the *ansa*-bis(cyclopentadienyl) and *ansa*-bis(indenyl) framework provides a considerable opening of the metal coordination sphere in lanthanidocene complexes which facilitates the substrates access to the metal centers, improving its electronic properties as well as the configuration of its frontier orbitals.[7,45−47] The *ansa*-bis(fluorenyl) ancillary ligation is supposed to combine advantages of design of the metal atom environment peculiar to the *ansa* system and flexibility of coordination of the fluorenyl ligand. Therefore *ansa*-bis(fluorenyl) derivatives of Sm^{II} and Yb^{II} should be promising catalysts for olefin polymerization.

The *ansa*-bis(fluorenyl)lanthanide(II) complexes $Me_2Si(C_{13}H_8)_2Yb(THF)$ (**7**) and $Me_2Si(C_{13}H_8)_2Sm(THF)_4$ (**8**) were obtained in more than 70% yield as red and brown solids from the reaction of $YbI_2(THF)_2$ and $SmI_2(THF)_2$, respectively, with $Me_2Si(C_{13}H_8)_2K_2$ in THF (Scheme 4). Both complexes are only slightly soluble in THF and DME. All attempts to obtain single crystals useable for X-ray structure investigations, failed. They could be characterized by ^1H, ^{13}C NMR, IR spectroscopy, and elemental analysis. The IR spectrum of **7** only shows bands for coordinated THF molecules (860 and 1020 cm^{-1}), whereas that of **8** presents bands in the range of coordinated (860 and 1040 cm^{-1}) and noncoordinated THF (910 and 1070 cm^{-1}).



Scheme 4

Molecular Structure of 1 and 6

Compound **1** crystallizes with two crystallographically independent molecules in the asymmetric unit (Figure 1). **1** was found to be an eight-coordinate complex having a bent sandwich structure with bond angles of $(C_{13}H_9)_{Cent}-Yb-(C_{13}H_9)_{Cent} = 125.58(11)$ and

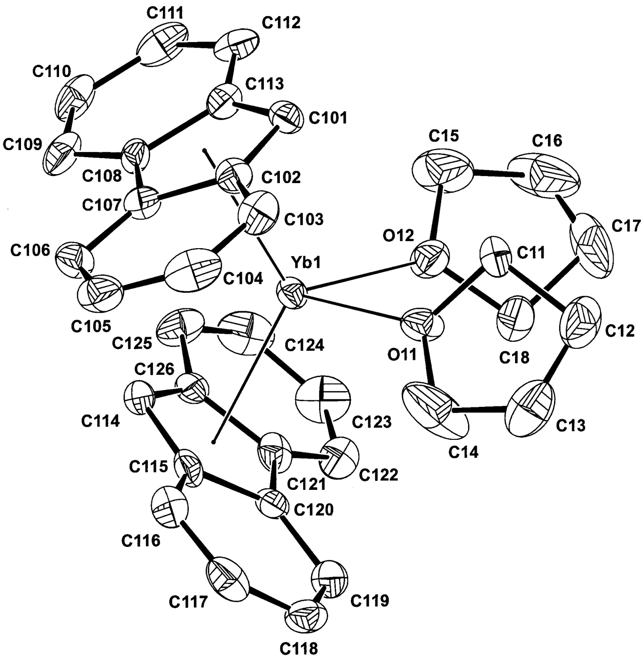


Figure 1. ORTEP[48] drawing and numbering scheme of the molecular structure of **1** with thermal ellipsoids drawn at the 50% probability level; only one of the two crystallographically independent molecules is shown; hydrogen atoms are omitted; selected bond lengths [Å] and angles [°] [Cg(1) and Cg(2) are defined by the ring atoms C(101), C(102), C(107), C(108), C(113) and C(114), C(115), C(120), C(121), C(126); Cg(3) and Cg(4) were defined by the ring atoms C(201), C(202), C(207), C(208), C(213) and C(214), C(215), C(220), C(221), C(226)]: Yb(1)−Cg(1) 2.503(3) [Yb(2)−Cg(3) 2.513(3)], Yb(1)−Cg(2) 2.512(4) [Yb(2)−Cg(4) 2.518(3)], Yb(1)−O(11) 2.389(5) [Yb(2)−O(21) 2.403(5)], Yb(1)−O(12) 2.398(5) [Yb(2)−O(22) 2.409(5)], Yb(1)−C(101) 2.663(7) [Yb(2)−C(201) 2.672(7)], Yb(1)−C(102) 2.756(7) [Yb(2)−C(202) 2.732(7)], Yb(1)−C(107) 2.852(7) [Yb(2)−C(207) 2.857(7)], Yb(1)−C(108) 2.867(6) [Yb(2)−C(208) 2.898(7)], Yb(1)−C(113) 2.774(7) [Yb(2)−C(213) 2.798(7)], Yb(1)−C(114) 2.626(7) [Yb(2)−C(214) 2.622(6)], Yb(1)−C(115) 2.780(7) [Yb(2)−C(215) 2.786(7)], Yb(1)−C(120) 2.952(7) [Yb(2)−C(220) 2.951(7)], Yb(1)−C(121) 2.893(7) [Yb(2)−C(221) 2.908(7)], Yb(1)−C(126) 2.696(7) [Yb(2)−C(226) 2.702(7)]; Cg(1)−Yb(1)−Cg(2) 125.58(11) [Cg(3)−Yb(2)−Cg(4) 124.87(10)], Cg(1)−Yb(1)−O(11) 104.63(15) [Cg(3)−Yb(2)−O(21) 106.21(15)], Cg(1)−Yb(1)−O(12) 118.14(15) [Cg(3)−Yb(2)−O(22) 116.44(15)], Cg(2)−Yb(1)−O(11) 115.40(15) [Cg(4)−Yb(2)−O(21) 114.32(15)], Cg(2)−Yb(1)−O(12) 105.25(2) [Cg(4)−Yb(2)−O(22) 106.22(15)], O(11)−Yb(1)−O(12) 78.37(18) [O(21)−Yb(2)−O(22) 80.14(18)]; ring slippage [Å]: Cg(1) 0.233, Cg(2) 0.384, Cg(3) 0.253, Cg(4) 0.392

124.87(10)°, respectively. The distances $(C_{13}H_9)_{Cent}$−Yb are 2.503(3), 2.513(3), 2.512(4), and 2.518(3) Å for both molecules, however substantial scattering in $Yb-C_{Flu}$ bond lengths is observed for both ligands. Analysis of the bond situation reveals shorter distances between the ytterbium ion and three carbon atoms [C(113)−C(101)−C(102), C(115)−C(114)−C(126) and C(213)−C(201)−C(202), C(215)−C(214)−C(226)], while two Yb−C distances [C(107)−C(108), C(120)−C(121) and C(207)−C(208), C(220)−C(221)] are somewhat longer compared to the average value (2.78 Å). The deviation of the Yb−C distances in the range of 0.25 Å for one five-membered ring and 0.38 Å for the second one suggests a partial tilting of the fluorenyl ligand toward η^3-fashion as it has already been observed for $(C_{13}H_9)_2Sm(THF)_2$[26] and $Me_2Si(\eta^3-C_{13}H_9)(\eta^5-Cp')YN(SiMe_3)_2$.[27] It should be mentioned that in the case of the samarium analogue a significant deviation of the Sm−C distances occurs only in one of the fluorenyl ligands, while in **1** for both of them. This interesting structural feature obviously arises from the smaller radius of the Yb^{2+} ion and a consequent steric hindrance and repulsion of the bulky fluorenyl ligands.

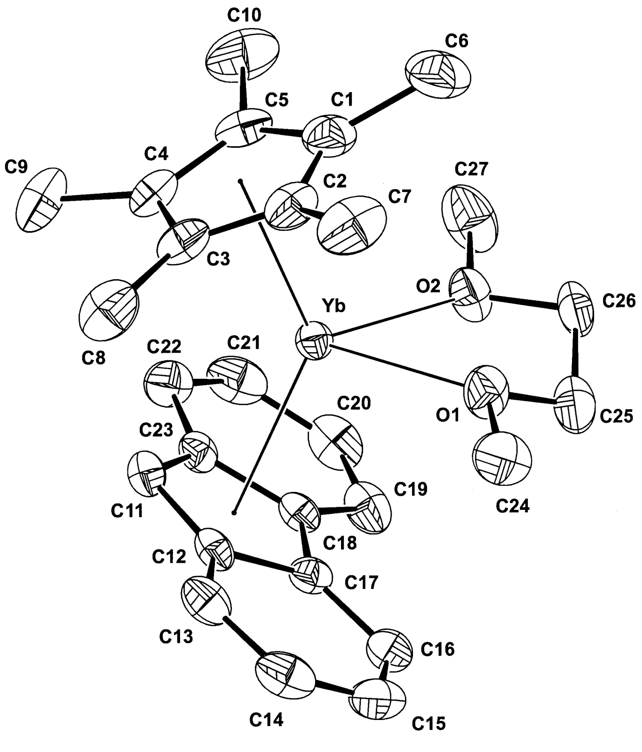


Figure 2. ORTEP[48] drawing and numbering scheme of the molecular structure of **6** with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted; selected bond lengths [Å] and angles [°] [Cg(1) and Cg(2) were defined by the ring atoms C(1)−C(5) and C(11), C(12), C(17), C(18), C(23)]: Yb−Cg(1) 2.392(2), Yb−Cg(2) 2.505(2), Yb−O(1) 2.415(4), Yb−O(2) 2.440(3), Yb−C(1) 2.673(5), Yb−C(2) 2.663(5), Yb−C(3) 2.671(5), Yb−C(4) 2.695(5), Yb−C(5) 2.698(5), Yb−C(11) 2.661(4), Yb−C(12) 2.782(5), Yb−C(17) 2.915(5), Yb−C(18) 2.857(5), Yb−C(23) 2.710(4); Cg(1)−Yb−O(2) 112.73(10), Cg(2)−Yb−O(1) 107.23(9), Cg(1)−Yb−Cg(2) 134.86(8), Cg(1)−Yb−O(1) 110.07(10), Cg(2)−Yb−O(2) 104.14(9), O(1)−Yb−O(2) 68.05(12); ring slippage [Å]: Cg(1) 0.059, Cg(2) 0.286

The single-crystal X-ray structure determination of **6** shows a bent sandwich complex of divalent ytterbium with coordination number 8 (Figure 2). The $Yb-Cp^*_{Cent}$ bond length is 2.392(2) Å, and $Yb-(C_{13}H_9)_{Cent}$ = 2.505(2) Å, which is close to the value obtained for **1**. The difference of five bond lengths between the ytterbium ion and the carbon atoms of the central five-membered ring of the fluorenyl ligand (0.254 Å) indicates a partial distortion toward an η^3 coordination, while the Cp* ligand is η^5-bonded. The bond angle $Cp^*_{Cent}-Yb-(C_{13}H_9)_{Cent}$ [134.86(8)°] is significantly larger than the angle $(C_{13}H_9)_{Cent}-Yb-(C_{13}H_9)_{Cent}$ in **1** [125.58(11)/124.87(10)°] and is consistent with the higher steric demand of the Cp* ligand vs. $C_{13}H_9$.

Experimental Section

General Remarks: All experiments were performed in evacuated tubes, using standard Schlenk techniques with rigorous exclusion of traces of moisture and air. THF, DME, diethyl ether, toluene, and hexane were purified by distillation from sodium/benzophenone ketyl and were condensed under vacuum prior to use. Fluorene and pentamethylcyclopentadiene were commercially available and used as received. $YbI_2(THF)_2$,[3] $(C_{10}H_8)Yb(THF)_2$,[28] $(\mu-C_{10}H_8)[YbI(DME)_2]_2$ (**4**),[49] and $Me_2Si(C_{13}H_9)_2$[50] were prepared according to literature procedures. − IR spectra were recorded as Nujol mulls with a Specord M80 spectrophotometer, NMR spectra with a Bruker DPX200 spectrometer in [D$_6$]benzene or [D$_8$]THF at 298 K, chemical shifts for ^1H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to TMS. − Magnetic susceptibility measurements were carried out according to the published procedure.[51]

$(C_{13}H_9)_2Yb(THF)_2$ (1). − a) To a solution of $C_{13}H_9K$ (2.21 g, 10.84 mmol) in THF (40 mL), $YbI_2(THF)_2$ (3.09 g, 5.42 mmol) was added slowly at 0 °C under rigorous stirring. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. After filtration, THF was removed under vacuum and the resulting crude product was recrystallized from THF/toluene (1:30) to yield 2.52 g (72%) of **1**. − IR (Nujol): $\tilde{\nu}$ = 3020 (m), 1590 (m), 1320 (m), 1200 (m), 1090 (w), 1030 (s), 990 (w), 925 (w), 825 (m), 750 (s), 720 (s), 700 (s) cm^{-1}. − ^1H NMR (200 MHz, [D$_8$]THF): δ = 5.63 (s, 2 H, aryl-C^9), 6.76 [t, ^3J(H,H) = 14.4 Hz, 4 H, aryl-H^7], 7.04 [t, ^3J(H,H) = 14.6 Hz, 4 H, aryl-H^6], 7.44 [d, ^3J(H,H) = 8 Hz, 4 H, aryl-H^8], 7.93 [^3J(H,H) = 8 Hz, 4 H, aryl-H^5]. − ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 113.8, 118.3, 119.8, 120.5, 122.3, 126.5, 133.7. − $C_{34}H_{34}O_2Yb$ (647.7): calcd. C 63.05, H 5.29, Yb 26.72; found C 62.76, H 4.87, Yb 26.92. − **b)** To a suspension of $(C_{10}H_8)Yb(THF)_2$ (2.13 g, 4.78 mmol) in THF (30 mL) was added fluorene (1.58 g, 9.56 mmol). The reaction mixture was heated to 60 °C for 8 h, filtered and THF was removed under vacuum. Recrystallization of the crude product from THF/toluene (1:30) yielded 2.06 g (64%) of **1**.

$(C_{13}H_9)_2Yb(DME)$ (2). − a) Compound **2** was obtained by recrystallization of **1** from DME as fine yellow crystals. − IR (Nujol): $\tilde{\nu}$ = 3020 (m), 1590 (m), 1320 (m), 1200 (m), 1090 (m), 1050 (s), 990 (w), 925 (w), 750 (s), 720 (s), 700 (s) cm^{-1}. − ^1H NMR (200 MHz, [D$_8$]THF): δ = 3.24 (s, 6 H, CH$_3$), 3.48 (s, 4 H, CH$_2$), 5.70 (s, 2 H, aryl-C^9), 6.72 [t, ^3J(H,H) = 14 Hz, 4 H, aryl-H^7], 7.00 [t, ^3J(H,H) = 14.2 Hz, 4 H, aryl-H^6], 7.50 [d, ^3J(H,H) = 8.8 Hz, 4 H, aryl-H^8], 8.00 [d, ^3J(H,H) = 8.2 Hz, 4 H, aryl-H^5]. − ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 36.8, 83.0, 113.9, 118.2, 120.0, 120.4, 122.3, 126.5, 133.5. − $C_{30}H_{28}O_2Yb$ (594.1): calcd. C 60.59, H 4.71, Yb 29.28; found C 60.33, H 4.29, Yb 29.18. − **b)** To a suspension of [Yb-I(DME)$_2$]$_2$(μ-$C_{10}H_8$) (**4**) (2.11 g, 1.94 mmol) in DME (30 mL) was added a solution of fluorene (0.64 g, 3.88 mmol) in DME (10 mL) at room temperature and stirred for 12 h. The resulting yellowish-brown solution was separated from a precipitate of off-white crystals of YbI_2(DME) (0.82 g, 82%) by filtration, concentrated and cooled to 0 °C. Evaporation of DME yielded 0.64 g (56%) of **2**. IR and ^{1}H NMR spectra are identical to the spectra of **2** formed in the reaction pathway a).

($C_{13}H_9$)$_2$Yb(*t*BuN=CHCH=N*t*Bu) (3): To a solution of **1** (0.87 g, 1.34 mmol) in THF (15 mL), was added a solution of *t*BuN=CHCH=N*t*Bu (0.23 g, 1.36 mmol) in THF (2 mL) at room temperature. The red solution was stirred for 2 h, THF was removed in vacuo and the resulting greenish-brown solid was recrystallized from hexane yielding 0.88 g (98%) of deep-green crystals of **3**. − IR (Nujol): ṽ = 3160 (m), 2710 (w), 2280 (m), 1620 (m), 1300 (m), 1260 (s), 1200 (s), 995 (m), 900 (m), 790 (s), 720 (s) cm^{-1}. − $C_{36}H_{38}N_2Yb$ (672.2): calcd. C 64.26, H 5.70, Yb 25.87; found C 63.99, H 5.63, Yb 25.29.

($C_{13}H_9$)(C_5Me_5)Yb(DME) (6): To a suspension of **4** (2.70 g, 2.48 mmol) in DME (35 mL), was added a solution of C_5Me_5H (0.77 g, 4.96 mmol) in DME (5 mL) at room temperature. The reaction mixture was stirred at 60 °C for 18 h, $C_{13}H_9K$ (1.01 g, 4.96 mmol) in DME (10 mL) was added and the resulting suspension was stirred overnight at room temperature. The green solution was filtered, DME was removed in vacuo and the resulting solid was extracted with toluene. Recrystallization from toluene yielded 1.28 g (46%) of yellow crystals of **6**. − IR (Nujol): ṽ = 3050 (m), 1590 (m), 1320 (s), 1210 (s), 1110 (m), 1090 (s), 1050 (m), 890 (s), 750 (s), 720 (s), 700 (s) cm^{-1}. − ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 2.06 (s, 15 H, CH_3), 2.16 (m, 6 H, OCH_3), 3.49 [s(br), 4 H, CH_2O], 6.66 (s, 1 H, aryl-H), 6.94 [t, ^3J(H,H) = 14.6 Hz, 2 H, aryl-H], 7.65 [t, ^3J(H,H) = 14.6 Hz, 2 H, aryl-H], 7.86 [d, ^3J(H,H) = 8 Hz, 2 H, aryl-H], 7.97 [d, ^3J(H,H) = 7.8 Hz, 2 H, aryl-H]. − ^{13}C NMR (50.3 MHz, [D$_6$]benzene): δ = 11.1, 36.7, 82.9, 112.1, 114.1, 118.5, 120.0, 120.6, 122.9, 125.1, 126.8. − $C_{27}H_{34}O_2Yb$ (563.6): calcd. C 57.54, H 6.08, Yb 30.70; found C 57.14, H 5.77, Yb 30.58.

[$Me_2Si(C_{13}H_8)_2$]K_2: To a solution of $Me_2Si(C_{13}H_9)_2$ (1.20 g, 3.10 mmol) in THF (30 mL) was slowly added a solution of $C_{10}H_8K$, obtained from K (0.24 g, 6.20 mmol) and $C_{10}H_8$ (0.80 g, 6.25 mmol) in THF (30 mL) at room temperature while stirring. The reaction mixture was stirred for another 8 h and the solvent was removed in vacuo. The resulting residue was extracted with hexane (3 × 30 mL) to remove $C_{10}H_8$ and was dried in vacuo (80 °C, 3 h) to give 1.32 g (92%) of [$Me_2Si(C_{13}H_8)_2$]K_2 as a dark red solid. − IR (Nujol): ṽ = 3050 (m), 1550 (w), 1320 (m), 1290 (m), 1275 (m), 1240 (m), 1150 (m), 1130 (w), 1080 (w), 1005 (m), 990 (w), 970 (w), 875 (m), 830 (w), 820 (m), 805 (s), 755 (s), 740 (s), 715 (s), 690 (m), 630 (w) cm^{-1}. − ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 6.5−8.2 (m, 16 H, Ar), 0.03 (s, 6 H, CH_3). − ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 1.6, 116.5, 119.7, 124.9, 126.5, 127.9, 129.0, 142.0. − $C_{28}H_{22}K_2Si$ (464.1): calcd. C 72.40, H 4.78, K 16.79; found C 69.90, H 4.95, K 16.70.

$Me_2Si(C_{13}H_8)_2$Yb(THF) (7): To a solution of [$Me_2Si(C_{13}H_8)_2$]K_2 (1.43 g, 3.09 mmol) in THF (30 mL) was slowly added a solution of $YbI_2(THF)_2$ (1.76 g, 3.09 mmol) in THF (10 mL) at room temperature, and the reaction mixture was stirred for 20 h. The solution was concentrated in vacuo. Slow diffusion of toluene into the resulting solution produced red diamagnetic crystals of **7** (1.46 g, 75%). − IR (Nujol): ṽ = 3050 (m), 1600 (w), 1570 (w), 1330 (m), 1290 (m), 1275 (m), 1245 (m), 1200 (m), 1155 (m), 1130 (w), 1020 (m), 980 (w), 960 (s), 860 (m), 840 (m), 830 (m), 810 (s), 760 (s), 745 (s), 720 (s) cm^{-1}. − ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 6.7−8.1 (m, 16 H, Ar), 0.034 (s, 6 H, CH_3). − ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 1.7, 116.5, 119.7, 124.7, 126.5, 127.9, 128.7, 142.0. − $C_{32}H_{30}OSiYb$ (631.7): calcd. C 60.84, H 4.79, Yb 27.39; found C 59.96, H 5.03, Yb 27.20.

$Me_2Si(C_{13}H_8)_2Sm(THF)_4$ (8): To a solution of [$Me_2Si(C_{13}H_8)_2$]K_2 (2.38 g, 5.14 mmol) in THF (20 mL), was added a solution of $SmI_2(THF)_2$ (2.82 g, 5.14 mmol) in THF (30 mL) under rigorous stirring at room temperature and the reaction mixture was stirred for 20 h. The solution was concentrated in vacuo and filtered from the precipitated KI. Slow diffusion of toluene into the resulting solution produced brown crystals of **8** (3.61 g, 85%). μ_{eff} = 3.6 BM (298 K). − IR (Nujol): ṽ = 3050 (m), 1600 (m), 1570 (m), 1330 (s), 1290 (s), 1280 (s), 1240 (m), 1200 (m), 1155 (m), 1120 (m), 1070 (s), 1040 (s), 965 (m), 910 (m), 860 (m), 840 (m), 830 (m), 820 (m), 800 (m), 760 (s), 735 (s), 730 (s) cm^{-1}. − $C_{44}H_{54}O_4SiSm$ (825.4): calcd. C 64.03, H 6.59, Sm 18.22; found C 63.87, H 6.23, Sm 18.22.

X-ray Structure Determination of 1 and 6: Crystals suitable for single-crystal X-ray diffraction were obtained from toluene. The crystal and structure refinement data are listed in Table 1. Data were collected with a Siemens SMART CCD diffractometer (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å) with area detector by use of ω scans at 173 K. The structures were solved by direct methods using SHELXS-97[52] and refined on F^2 using all reflections with SHELXL-97.[53] All non-hydrogen atoms were

Table 1. Crystal data and structure refinement for **1** and **6**

	1	**6**
Empirical formula	$C_{34}H_{34}O_2Yb$	$C_{27}H_{34}O_2Yb$
M_r [g·mol^{-1}]	647.65	563.58
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
Unit cell dimensions		
a [Å]	10.8261(1)	17.2533(2)
b [Å]	13.2109(2)	15.4878(2)
c [Å]	19.5494(2)	18.1545(1)
α [°]	84.106(1)	90
β [°]	77.256(1)	90
γ [°]	89.855(1)	90
V [Å^3]	2712.13(6)	4851.17(9)
Z	4	8
$\rho_{calcd.}$ [g/cm^3]	1.586	1.543
μ(Mo-K_α) [mm^{-1}]	3.477	3.875
F(000)	1296	2256
Crystal dimensions [mm]	0.36×0.10×0.10	0.48×0.34×0.16
θ [°]	1.07 → 27.50	2.09 → 27.50
Index ranges		
h	−13 → 14	−22 → 18
k	−9 → 17	−20 → 19
l	−25 → 24	−23 → 23
Reflections collected	20830	34936
Independent reflections	12317 [*R*(int) = 0.0607]	5559 [*R*(int) = 0.0793]
Reflections with $I > 2\sigma(I)$	7031	3970
Max./min. transmission	0.7744/0.5613	0.6392/0.3417
Goodness-of-fit on F^2	0.916	1.052
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0472, wR_2 = 0.0784	R_1 = 0.0392, wR_2 = 0.0700
R indices (all data)	R_1 = 0.1073, wR_2 = 0.0987	R_1 = 0.0705, wR_2 = 0.0804
Larg. diff. peak/hole [e/Å^3]	1.095/−1.389	1.097/−0.888

refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2.The idealized methyl groups were allowed to rotate about their X−C bond. SADABS[54] was used to perform area-detector scaling and absorption corrections. The maximum and minimum transmission factors are summarized in Table 1. The PLATON[55] program was used for the geometric analysis of the structures. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-162390 (**1**) and -162391 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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