A new bifunctional ligand: $C_5Me_4SiMe_2OSiMe_2O^{2-}$. Synthesis, properties and crystal structure of the first Yb(II) half-sandwich complex with a heterobidentate cyclopentadienyl ligand, $[\{(\eta^5\text{-}C_5Me_4)SiMe_2OSiMe_2(\eta^1\text{-}O)\}Yb(thf)]_2$

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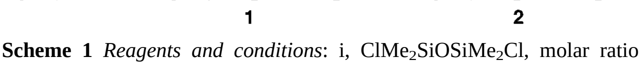
The synthesis and crystal structure of the Yb(II) half-sandwich complex $[\{(\eta^5\text{-}C_5Me_4)SiMe_2OSiMe_2(\eta^1\text{-}O)\}Yb(thf)]_2$ containing the new linked tetramethylcyclopentadienyl-silanolate ligand $C_5Me_4SiMe_2OSiMe_2O^{2-}$ are reported.

Lanthanide compounds coordinated by bidentate cyclopentadienyl ligands with different coordination mode capacities are of essential fundamental interest from the point of view of their structure, stability and chemical properties.Various cyclopentadienyl ligands bearing in the side chain a Lewis base group such as an ether,[1,2c] amine,[1c,2] or phosphine[3] have been successfully employed in organolanthanide chemistry and derived complexes have attracted considerable interest in recent years. Examples of substituted cyclopentadienyl ligands with a pendant functional group able to form σ Ln–X (X = oxygen,[4] nitrogen[5]) bonds and to realize constrained geometry complexes are not numerous and are limited mainly to the trivalent Sc, Y and Lu derivatives of the linked cyclopentadienyl-amido class.[5a–e] To the best of our knowledge, half-sandwich *divalent* lanthanide analogues have not yet been reported.

Complexes with heterobifunctional cyclopentadienyl ligands are very intriguing and promising because of their use as effective and stereoselective catalysts in various reactions. The complex $[\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}(PMe_3)Sc(\mu_2\text{-}H)]_2$ has been shown to exhibit catalytic activity in α-olefin polymerization[5b] while the 'ate'-complexes $Li[Ln\{(\eta^5\text{-}C_5R_4)SiMe_2(\eta^1\text{-}NCH_2CH_2X)\}_2]$ (Ln = Y, Lu; $C_5R_4 = C_5Me_4$, $C_5H_3Bu^t$; X = OMe, NMe_2) readily initiate ring-opening polymerization of ε-caprolactones.[5d]

The present research was aimed towards the preparation of a new functionalized cyclopentadienyl ligand with a pendant hydroxy group suitable for coordination to a divalent lanthanide ion and to the synthesis of the corresponding Yb(II) derivative. Related ligands with pendant O or N functional groups are of great importance in organotransition metal chemistry.[6] Up to now, linked cyclopentadienyl-silanol ligands have not been described. 1,1,3,3-Tetramethyl-3-tetramethylcyclopentadienyl-disiloxane-1-ol was synthesized in two steps (Scheme 1).

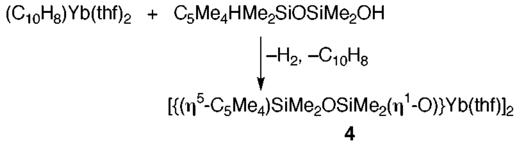


$$C_5Me_4HLi \xrightarrow{\text{i}} \underset{\mathbf{1}}{C_5Me_4HMe_2SiOSiMe_2Cl} \xrightarrow{\text{ii}} \underset{\mathbf{2}}{C_5Me_4HMe_2SiOSiMe_2OH}$$

Scheme 1 *Reagents and conditions*: i, $ClMe_2SiOSiMe_2Cl$, molar ratio $C_5Me_4HLi:ClMe_2SiOSiMe_2Cl$ = 1:5, thf, 18 h room temp.; ii, H_2O, py, thf, 4 h, room temp.

In the first step (Scheme 1, step i)† a five-fold excess of $ClMe_2SiOSiMe_2Cl$ was used to avoid possible formation of $C_5Me_4HMe_2SiOSiMe_2C_5Me_4H$. Hydrolysis of **1** was carried out in thf in the presence of pyridine and afforded **2** in 68% yield, which was purified by flash chromatography on silica gel. Compound **2**‡ gave a satisfactory microanalysis and ^1H NMR spectrum. An HPLC analysis confirmed its purity.

For the synthesis of the targeted ytterbium(II) complex the reaction of protolytic substitution of naphthalene in highly reactive $(C_{10}H_8)Yb(thf)_2$ **3**[7] by the new ligand was used. Similar reactions have been previously shown to be a convenient synthetic route to various Yb(II) and Yb(III) derivatives.[8] Interaction of $(C_{10}H_8)Yb(thf)_2$ with $C_5Me_4HSiMe_2OSiMe_2OH$ readily occurs in thf at room temperature, affording H_2, $C_{10}H_8$ and $[\{(\eta^5\text{-}C_5Me_4)SiMe_2OSiMe_2(\eta^1\text{-}O)\}Yb(thf)]_2$ **4** (Scheme 2) which was obtained as ruby red crystals after recrystallization from thf–hexane in 57% yield.§ Surprisingly no oxidation with formation of Yb^{3+} species takes place during the course of the reaction despite the presence of siloxide functional groups.



$$(C_{10}H_8)Yb(thf)_2 + C_5Me_4HMe_2SiOSiMe_2OH \xrightarrow{-H_2,\ -C_{10}H_8} \underset{\mathbf{4}}{[\{(\eta^5\text{-}C_5Me_4)SiMe_2OSiMe_2(\eta^1\text{-}O)\}Yb(thf)]_2}$$

Scheme 2

Compound **4** is highly sensitive to oxygen and moisture, soluble in thf and DME, sparingly soluble in toluene and diethyl ether and insoluble in aliphatic hydrocarbons. Magnetic measurement and NMR studies have shown **4** to be diamagnetic, corresponding to the Yb^{2+} oxidation state. Compound **4** has been characterized by microanalysis, IR and ^1H NMR spectroscopy as well as by an X-ray diffraction study (Fig. 1).¶ The dimeric complex possesses inversion symmetry imposing the central four membered ring Yb–O2–Yba–O2a to be planar. The endocyclic ytterbium oxygen distances are slightly different [Yb–O2 227.4(2), Yb–O2a 231.9(2) pm] and somewhat shorter than the exocyclic one [Yb–O3 238.1(1) pm]. The tetra-

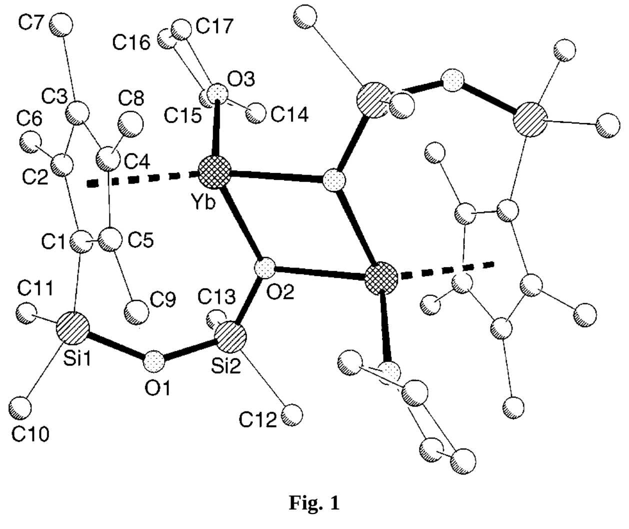


Fig. 1

methylcyclopentadienyl ligand is essentially planar with an ytterbium–centroid distance of 241 pm. The thf molecule displays an envelope conformation with O3 52.5 pm out of the plane defined by C14, C15, C16 and C17. The mean deviation from this best plane is 5.2 pm. The silicon oxygen bond lengths vary from 161.2(2) pm (Si2–O2, the ytterbium briding oxygen) to 164.7(2) pm (Si1–O1).

In an initial reactivity study it was found that **4** does not catalyze propylene polymerization at 20 °C and atmospheric pressure.

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Notes and references

† *Synthesis* of **1**: to the solution of 5.04 g (24.85 mmol) of $ClSiMe_2OSiMe_2Cl$ in 20 ml of thf solid C_5Me_4HLi (0.637 g, 4.97 mmol) was added under stirring at −30 °C. The reaction mixture was stirred for 2 h, warmed to room temp. and left overnight. The volatiles were removed under reduced pressure (20 mm Hg), the residue was washed with hexane and the extract was filtered to separate the product from LiCl. Hexane was evaporated under reduced pressure and the resulting yellow oil was distilled under vacuum (106–108 °C/4 mm Hg) yielding 1.26 g (88%) of **1**. Anal. Calc. for $C_{13}H_{25}ClOSi_2$: C, 54.07; H, 8.65; Cl, 12.27. Found: C, 54.36; H, 8.18; Cl, 12.73%. ^1H NMR ($CDCl_3$): δ 0.04–0.08 (m, 12H, $SiMe_2$), 1.94 (s, 6H, C_5Me_4H), 2.00 (s, 6H, C_5Me_4H), 2.98 (m, 1H, C_5Me_4H).

‡ *Synthesis* of **2**: to a solution of **1** (1.26 g, 4.36 mmol) and 0.35 ml (0.345 g, 4.36 mmol) of pyridine(py) in 15 ml of thf, 0.078 ml (4.36 mmol) of H_2O were added dropwise at 0 °C and the reaction mixture warmed to room temp. and stirred for 4 h. A white precipitate was separated by filtration; thf was evaporated in vacuum and the resulting pale-yellow oil purified by flash chromatography on silica gel 60 (cyclohexane–ethylacetate, 20 : 1) yielding 0.79 g (68%) of **2**. Anal. Calc. for $C_{13}H_{26}O_2Si_2$: C, 57.76; H, 9.61; Si, 20.78. Found: C, 57.30; H, 9.57; Si, 20.34%. ^1H NMR ($CDCl_3$): δ 0.04–0.08 (m, 12H, $SiMe_2$), 1.90 (br s, 1H, OH), 1.92 (s, 6H, $C_5\mathit{Me}_4H$), 2.00 (s, 6H, $C_5\mathit{Me}_4H$), 2.98 (m, 1H, $C_5Me_4\mathit{H}$).

§ *Synthesis* of **4**: to a suspension of 0.62 g (1.39 mmol) of **3** in 25 ml of thf a solution of 0.38 g (1.40 mmol) of **2** in 10 ml of thf was added slowly under vigorous stirring. The reaction mixture turned reddish-brown, the residue of **3** slowly dissolved and H_2 evolved. After 16 h the solution was filtered, thf was evaporated under vacuum and the resulting brown residue was heated (1 h, 50 °C) to separate by sublimation the naphthalene by-product (0.16 g, 93%). The resulting brown solid was recrystallized from thf–hexane to afford 0.41 g (57%) of **4** as ruby red crystals. Anal. Calc. for $C_{17}H_{32}O_3Si_2Yb$: C, 39.77; H, 6.23; Yb, 33.69. Found: C, 39.55; H, 6.11; Yb, 33.98%. IR (Nujol, KBr, cm^{-1}): 460, 610, 680, 740, 800, 830, 890, 950, 1025, 1035, 1050, 1075, 1150, 1260, 1325. ^1H NMR (d^8-thf): δ 0.04 (s, 6H, $SiMe_2$), 0.21 (s, 6H, $SiMe_2$), 1.84 (s, 6H, C_5Me_4), 1.93 (s, 6H, C_5Me_4).

¶ *Crystal data*: the measurement on **4** was performed at −100 °C using a Siemens SMART CCD system with Mo-Kα X-radiation (λ = 0.71073 Å) and a graphite monochromator. A selected crystal of **4** was coated with mineral oil, mounted on a glass fibre and transferred to the cold nitrogen stream (Siemens LT-2 attachment). A full hemisphere of the reciprocal space was scanned by ω in three sets of frames of 0.3°. As an absorption correction the SADABS routine was applied.

4: $C_{34}H_{64}O_6Si_4Yb_2$, M = 1027.29, orthorhombic, space group *Pbca*, a = 14.6684(10), b = 16.4898(2), c = 17.3574(2) Å, U = 4198.39(8) Å^3, Z = 4, D_c = 1.625 Mg m^{-3}, F(000) = 2048, μ(Mo-Kα) = 4.579 mm^{-1}, max/min transmission 1.00/0.69, ruby red prism 0.56 × 0.52 × 0.32 mm. A total of 26491 reflections were collected, over a range $2.2 < \theta < 28.3°$, of which 5197 were independent (R_{int} = 0.023). The structure was solved by direct methods.[9] Refinement was by full-matrix least squares on F^2 and converged to $R1$ = 0.0194 (conventional) and $wR2$ = 0.0461 (all data), with goodness of fit = 1.091, 216 parameters, weighting scheme $[\sigma^2(F_o^2) + 0.0181P)^2 + 4.3441P]$, where $P = (F_o^2 + 2F_c^2)/3$. CCDC 182/1430.

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