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Synthesis and Structural Characterization of Novel Ytterbium(III) Complexes with both a μ-Oxo Group and Bridged Indenyl Ligands, and Ytterbium(II) Complexes with Bridged Indenyl Ligands

Lin Cheng,[a] Yan Feng,[a] Shaowu Wang,*[a,b] Wei Luo,[a] Wei Yao,[a] Zeyan Yu,[a] Xiaobing Xi,[a] and Zixiang Huang[c]

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The reactivity of the ytterbium(III) amide $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(thf)_3$ with different bridged indene compounds in the presence of external donor ligands was studied. Reaction of $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(thf)_3$ with the corresponding 1,2-bis(indenyl)ethane $[(CH_2)_2(C_9H_7)_2]$ or $Me_2Si(C_9H_7)_2$, followed by the addition of excess thf, produced a novel tetranuclear ytterbium complex $[\{\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2\}Yb(\mu\text{-}Cl)(\mu_3\text{-}O)Yb(Cl)N(SiMe_3)_2Li(thf)_4]_2$ (**1**) or a novel dinuclear ytterbium complex $[\eta^5{:}\eta^5\text{-}(CH_3)_2Si(C_9H_6)_2Yb]_2(\mu\text{-}Cl)(\mu\text{-}O)Li(thf)_2$ (**2**), respectively. Treatment of $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(thf)_3$ with $(CH_2)_2(C_9H_6SiMe_3)_2$ (**3**) or $Me_2Si(C_9H_7)_2$ under different conditions produced ytterbium(II) complexes $[\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_5SiMe_3)_2]Yb(thf)_2\cdot(C_6H_{14})_{0.5}$ (**4**) and $[\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_5SiMe_3)_2]Yb\cdot dme$ (**5**) or $[\eta^5{:}\eta^5\text{-}(CH_3)_2Si(C_9H_6)_2]Yb\cdot tmeda$ (**6**), respectively. Interaction of the ytterbium(III) amide $[\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2]YbN(SiMe_3)_2$ with excess tmeda afforded the ytterbium(II) complex $[\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2]Yb\cdot tmeda$ (**7**). All the compounds were fully characterized by spectroscopic methods and elemental analyses. Complexes **1**, **2**, and **4** were additionally characterized by single-crystal X-ray diffraction analyses. The solvents and temperature effects on the reaction are discussed.

Introduction

Lanthanide complexes have received continuous interest because of their potential applications as catalysts in a wide range of olefin transformations such as olefin polymerization,[1] hydroamination/cyclization,[2] hydrophosphanation,[3] and hydrosilylation of a variety of unsaturated compounds, for example, functionalized alkenes, -alkynes, -allenes, and -dienes.[4] The lanthanide complexes with a Ln–N bond are among the lanthanide complexes that show diverse reactivity toward the Tishchenko reaction,[5] ring-opening polymerization of ε-caprolactone and δ-valerolactone,[6] olefin polymerization,[1,7] hydroamination/cyclization,[2] hydrosilylation,[4a,4b] dimerization of terminal alkyne,[8a] as well as toward the Cannizzaro-type disproportionation of aromatic aldehydes to amides and alcohols.[8b]

It has been documented that lanthanide complexes with pentamethylcyclopentadienyl,[9] Schiff base,[10] dipyrrolide,[11] triamidoamine,[12] carborane,[13] and porphyrinogen[14] ligands can react with thf or oxygen-containing compounds such as epoxides to give the μ-oxo-containing or enolate complexes. It was also reported that the alkyl lanthanide complexes can thermally decompose to give the enolate complexes in the presence of thf/LiCl.[15] However, the synthesis and characterization of lanthanide complexes with either indenyl ligands or the μ-oxo-containing group has been far less studied.

We have reported that the treatment of functionalized indene compounds having internal donor-substituted groups such as the *N*,*N*-dimethylaminoethyl group[16] and the methoxyethyl[17] group with $[(Me_3Si)_2N]_3Ln^{III}(\mu\text{-}Cl)Li(thf)_3$ (Ln = Yb, Eu) affords organolanthanide(II) complexes. The treatment of the indenes $C_9H_6\text{-}1\text{-}R\text{-}3\text{-}CH_2SiMe_2NC_4H_8$ (R = H, CH_3) with $[(Me_3Si)_2N]_3Eu^{III}(\mu\text{-}Cl)Li(thf)_3$ were also studied, and novel tetranuclear triple-decker and monomeric europium(II) complexes were isolated and characterized.[18a] A novel ytterbium(II) complex in which the indenyl ligand is bonded to the metal through the benzo ring with an η^4-hapticity was isolated and characterized by treatment of the *N*-piperidinylethyl-functionalized indene compound with the ytterbium(III) amide $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$.[18b] The above study indicated that the electronic and steric effects of the ligands have an influence on the homolytic reaction of the Ln–N (Ln = Yb, Eu) bond. In this paper, we report on the reactivity of the ytterbium(III) amide with bridged indene com-

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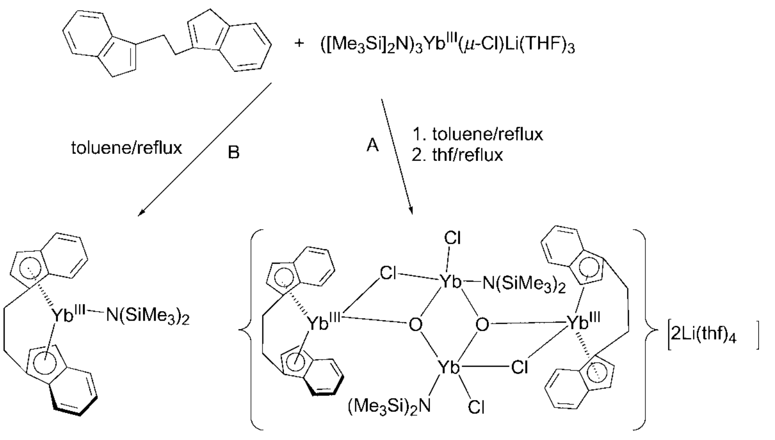
[a] Anhui Key Laboratory of Functional Molecular Solids, Institute of Organic Chemistry, College of Chemistry and Materials Science, Anhui Normal University,
Wuhu, Anhui 241000, China
Fax: +86-553-3883517
E-mail: swwang@mail.ahnu.edu.cn
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry,
Shanghai 200032, China
[c] Fujian Institute of Research on the Structure of Matters, Chinese Academy of Sciences,
Fuzhou 350002, China



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Scheme 1.

pounds in the presence of external donor ligands such as thf, dme, and tmeda, with the isolation and characterization of a series of novel ytterbium(III) and ytterbium(II) complexes. The effect of the donor ligands and the temperature on the reactivity of the Yb–N bond is also discussed.

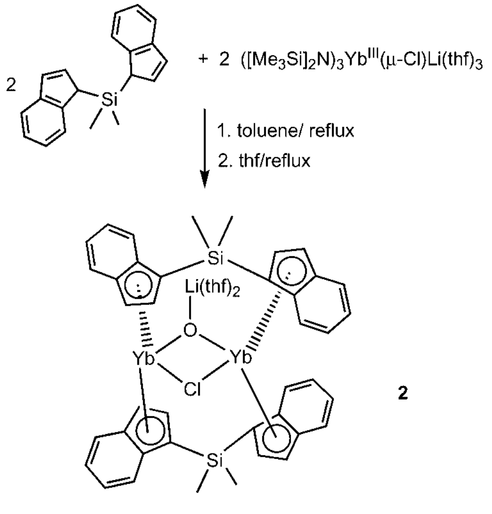
Results and Discussion

Synthesis and Characterization of Ytterbium(III) and Ytterbium(II) Complexes

Treatment of 1,2-bis(indenyl)ethane with 1 equiv. $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ in refluxing toluene overnight, followed by the addition of excess thf afforded, after workup, a novel tetranuclear ytterbium(III) complex $[\{\eta^5\text{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2\}Yb(\mu\text{-}Cl)(\mu_3\text{-}O)Yb(Cl)N(SiMe_3)_2\text{-}Li(thf)_4]_2$ (**1**) as red crystals (Scheme 1, path A). This result is different from that of our previous studies, which showed that the treatment of indene compounds having internal donor substituents with lanthanide(III) amides $[(Me_3Si)_2N]_3\text{-}Ln^{III}(\mu\text{-}Cl)Li(THF)_3$ (Ln = Yb, Eu) produce the lanthanide(II) complexes through a tandem silylamine elimination and homolysis of the Ln–N bond.[16–18] This result is also different from that obtained from the direct treatment of 1,2-bis(indenyl)ethane with 1 equiv. $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ in refluxing toluene, the indenyl ytterbium(III) amide complex $[\eta^5\text{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2]YbN(SiMe_3)_2$ (Scheme 1, path B).[16a] The color change from yellow to dark blue and the isolation of indenyl ytterbium(III) amide $[\eta^5\text{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2]YbN(SiMe_3)_2$ from the dark blue solution suggests that the formation of complex **1** may occur via the indenyl ytterbium(III) amide as intermediate.

X-ray analysis reveals that complex **1** is a centrosymmetric structure and contains a discrete dianion $[\{\eta^5\text{:}\eta^5\text{-}(CH_2)_2\text{-}(C_9H_6)_2\}Yb(\mu\text{-}Cl)(\mu_3\text{-}O)Yb(Cl)N(SiMe_3)_2]_2^{2-}$, with two μ_3-O atoms, and the cations $Li(thf)_4^+$. The presence of the oxygen atoms in **1** likely arises from cleavage of thf, a process that is well documented in lanthanide chemistry.[9–15] In order to extend the scope of the reaction, the reaction of $Me_2Si(C_9H_7)_2$ with $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ was studied.

Treatment of $Me_2Si(C_9H_7)_2$ with $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ in toluene, followed by the addition of excess thf and by heating the mixture at reflux for 6 h produced an ytterbium(III) complex $[\eta^5\text{:}\eta^5\text{-}(CH_3)_2Si(C_9H_6)_2Yb]_2(\mu\text{-}Cl)(\mu\text{-}O)Li(thf)_2$ (**2**) (Scheme 2).



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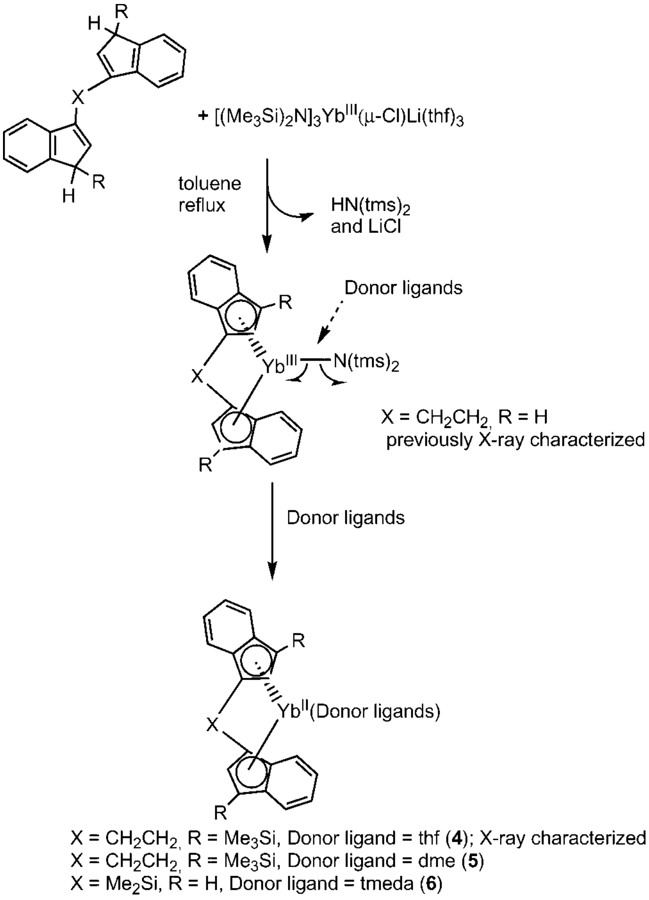
Scheme 2.

Complexes **1** and **2** are soluble in thf and pyridine, but they are insoluble in toluene and hexane. They were fully characterized by spectroscopic methods and elemental analyses, and their structures were determined by single-crystal X-ray analyses. ^1H NMR analyses of the complexes gave no information because of the lack of locking signals, which probably results from the strong paramagnetic property of the complexes. This suggests that the oxidation state of the central ytterbium metal atom may be +3, which was confirmed by X-ray structural analyses. The formation of complexes **1** and **2** is somewhat different from the thermal decomposition of alkyl lanthanide complexes to form the enolate complexes in the presence of thf/LiCl.[15]

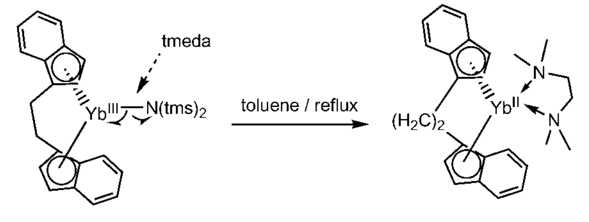
When $(CH_2)_2(C_9H_6SiMe_3)_2$ (**3**) and 1 equiv. ytterbium(III) amide $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ were treated in refluxing thf and not in toluene, with the addition of excess thf, an ytterbium(II) complex [η^5:η^5-$(CH_2)_2(C_9H_5SiMe_3)_2$]Yb(thf)$_2$·$(C_6H_{14})_{0.5}$ (**4**) (Scheme 3) was isolated and characterized on the basis of elemental, spectroscopic, and single-crystal X-ray analyses. The solvated *n*-C_6H_{14} and coordinated thf can be evaporated under vacuum, as suggested by the elemental analyses data. The formation of the ytterbium(II) complex **4** suggests that the reaction involves a one-electron reductive elimination process, which is different from process for the formation of complexes **1** and **2** and indicates the temperature or solvent effects on the reaction that result from the difference in the boiling points of the refluxing toluene and thf. The experiments to prove the hypothesis that the formation of complexes **1** and **2** occurs via an ytterbium(II) intermediate, which then reacts with thf to give the μ-oxo complexes that results from the abstraction of the oxygen atom of the thf ring, by heating complex **4** in toluene at reflux were unsuccessful. This is because of the formation of an insoluble solid, which is difficult to purify by recrystallization or other techniques. Formation of complex **4** indicates that interaction of the Yb–N bond with an external donor ligand may provide a new method for the preparation of organolanthanide(II) complexes. Thus, the interactions of the Yb–N bond with other external donor ligands such as dme and tmeda were studied.



Scheme 3.

Reaction of [$(Me_3Si)_2N]_3Yb^{III}$(μ-Cl)Li(thf)$_3$ with $(CH_2)_2(C_9H_6SiMe_3)_2$ (**3**) in refluxing dme for 24 h produced, after workup, an ytterbium(II) complex [η^5:η^5-$(CH_2)_2(C_9H_5SiMe_3)_2$]Yb·dme (**5**) (Scheme 3). The reaction of [$(Me_3Si)_2N]_3Yb^{III}$(μ-Cl)Li(thf)$_3$ and $(CH_2)_2(C_9H_6SiMe_3)_2$ (**3**) in toluene at first, followed by the addition of excess dme also produced complex **5**, on the basis of elemental and spectroscopic analyses. Treatment of $Me_2Si(C_9H_7)_2$ with [$(Me_3Si)_2N]_3Yb^{III}$(μ-Cl)Li(thf)$_3$ in refluxing toluene for 6 h, followed by the addition of excess tmeda, produced, after workup, an ytterbium(II) complex [η^5:η^5-$(CH_3)_2Si(C_9H_6)_2$]Yb·tmeda (**6**) (Scheme 3). The μ-oxo-containing complex has not been isolated in the above reactions. ^{1}H NMR analyses showed that the ratio of the indenyl ligand and the dme or tmeda ligands is 1:1. The diamagnetic property of the complexes suggests that the oxidation state of the central metal is +2. These complexes are extremely air- and moisture sensitive and they are soluble in thf and dme.

The fact that reaction of the ytterbium(III) amide [η^5:η^5-$(CH_2)_2(C_9H_6)_2$]YbN(SiMe$_3$)$_2$ with tmeda produced the ytterbium(II) complex [η^5:η^5-$(CH_2)_2(C_9H_6)_2$]Yb·tmeda (**7**) (Scheme 4) suggests that the formation of **4**–**6** may involve indenyl ytterbium(III) amide as an intermediate. Moreover, homolysis of the Yb–N bond has not been observed either by heating the indenyl ytterbium(III) amide [η^5:η^5-$(CH_2)_2(C_9H_6)_2$]YbN(SiMe$_3$)$_2$ at reflux in toluene for 3 d, by heating the ytterbium(III) amide [$(Me_3Si)_2N]_3Yb^{III}$(μ-Cl)Li(thf)$_3$ at reflux in toluene, or by sublimation of the amide [$(Me_3Si)_2N]_3Yb^{III}$(μ-Cl)Li(thf)$_3$ in vacuo.



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Scheme 4.

The above results suggest that a one-electron reductive elimination process occurs after the formation of the indenyl ytterbium(III) amides [η^5:η^5-(X)$(C_9H_5R)_2$]Yb^{III}N(SiMe$_3$)$_2$ (X = bridging group CH_2CH_2 or Me_2Si; R = H or Me_3Si) resulting from the reactions of the indene compounds with the ytterbium(III) amide [$(Me_3Si)_2N]_3Yb^{III}$(μ-Cl)Li(thf)$_3$. Reactions of external donor ligands such as thf, dme, or tmeda with the resulting indenyl ytterbium(III) amides [η^5:η^5-(X)$(C_9H_5R)_2$]Yb^{III}N(SiMe$_3$)$_2$ produce the ytterbium(II) complexes. The above results also indicate that this method for the preparation of organoytterbium(II) complexes by interaction of the Yb–N bond with external donor ligands at moderately high temperatures can be suitable for different cases.

On the basis of these results, the pathway for the formation of ytterbium(II) complexes **4**–**6** is proposed as follows: the reactions of the bridged indene compounds (X)-$(C_9H_6R)_2$ (X = bridging group CH_2CH_2 or Me_2Si; R = H or Me_3Si) with the ytterbium(III) amide $[(Me_3Si)_2N]_3$-$Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ produces the indenyl ytterbium(III) amide $[\eta^5{:}\eta^5\text{-}(X)(C_9H_5R)_2]Yb^{III}N(SiMe_3)_2$, which then reacts with external donor ligands to give the ytterbium(II) complex $[\eta^5{:}\eta^5\text{-}(X)(C_9H_5R)_2]Yb^{II}(D)$ (D = thf, dme, or tmeda) by coordination of the donor ligands to the central metal, leading to the homolysis of the Yb–N bond that resulted in the reduction of ytterbium(III) to ytterbium(II) (Scheme 3). Thus, the method for the preparation of the ytterbium(II) complexes through homolysis of the Yb–N bond by treatment of internally substituted indene compounds with $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ may be extended to the reaction of ytterbium complexes having the Yb–N bond with suitable external donor ligands at moderately high temperatures such that the reduction of ytterbium(III) to ytterbium(II) may proceed relatively easily.[16–18] However, the formation pathway of complexes **1** and **2** remains to be further examined.

Molecular structure

The structures of complexes **1** (Figures 1 and 2), **2** (Figure 3), and **4** (Figure 4) were determined by single-crystal X-ray analyses, which reveals that both **1** and **2** are oxygen-containing complexes and that the central ytterbium atoms are in the +3 oxidation state.

The key structural feature of complex **1** (Figures 1 and 2) is that the four ytterbium atoms Yb(1), Yb(1A), Yb(2), Yb(2A), the two oxygen atoms O and O(OA), and two chlorine atoms Cl(2), Cl(2A) are coplanar with a mean deviation of 0.0588 Å on the basis of a least-squares calculation. It represents the first example of a tetranuclear ytterbium complex containing both μ-oxo groups and bridged indenyl ligands in the molecular structure.[19] The Yb–O distances of 2.126(8), 2.107(9), and 2.200(9) Å (Table 1) in **1** are also notable – these distances are longer than the Sm–O distance in $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$[9] {2.094(1) Å} but are comparable to that in $\{[Cy(C_4H_3N)_2]Sm\}_4(\mu\text{-}O)$[11] {2.1844(4) Å}. The Yb–O distances in **1** are shorter than the average Sm–O(μ_4-O) distance of 2.346(1) Å in $[\{[\eta^5\text{-}Me_2Si(C_5Me_4)\text{-}(C_2B_{10}H_{11})]Sm\}_2(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_4Li(OEt_2)_2Li(thf)_2Sm(\mu_4\text{-}O)]_2$[13b] and the average Sm–O distance of 2.211(8) Å found in $[\{\eta^5\text{-}(Me_3Si)_2C_2B_4H_4\}Sm]_3[\{\eta^5\text{-}(Me_3Si)_2C_2B_4H_4\}Li]_3(\mu_3\text{-}OMe)][\mu_3\text{-}Li(thf)]_3(\mu_3\text{-}O)$.[13a] The differences in the bond lengths may arise because of the different ionic radii of the lanthanide metals and the O atom and because of the steric effects in the complex.

The structural feature of the oxygen-containing dinuclear complex **2** (Figure 3) is that the silylene-bridged indenyl ligand adopts a bridging coordination, instead of the normal chelating coordination found in organometallic compounds with ligands that contain a silylene-bridge and two cyclopentadienyl or two tetramethylcyclopentadienyl groups.[20] The bridging coordination phenomenon is similar to those found in lanthanide complexes with silylene-bridged fluorenyl cyclopentadienyl ligands.[21]

The Yb(2)–O–Yb(1) angle of 109.7(2)° (Table 1) in **2** is smaller than the Yb(1)–O–Yb(2) angle of 113.4(4)° and the Yb(2A)–O–Yb(1) angle of 144.6(5)° in **1**, but larger than the Yb(2A)–O–Yb(2) angle of 101.9(3)° in **1**. The Yb(1)–Cl–Yb(2) angle of 80.40(7)° in **2** is also smaller than the Yb(1)–Cl(2)–Yb(2) angle of 84.98(11)° in **1**. Both the Yb(1)–Cl(2)–Yb(2) angle of 84.98(11)° in **1** and the Yb(1)–Cl–Yb(2) angle of 80.40(7)° in **2** is smaller than the Yb(1)–Cl(3)–Yb(1a) angle of 104.54(8)° in the dimeric ytterbium(III) chloride $[\{\eta^5{:}\eta^1{:}\sigma\text{-}Me_2Si(C_9H_5CH_2CH_2NMe_2)\text{-}(C_2B_{10}H_{10})\}Yb(\mu\text{-}Cl)]_2$.[22] The Yb–O distances of 2.070(5) Å and 2.063(5) Å in **2** are comparable to the Sm–O distance of 2.094(1) Å in $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$ if the difference in ionic radii is taken into account.[23] The Yb–Cl distances of 2.603(3) Å and 2.632(2) Å in **2** are longer than the Yb(1)–Cl(2) distance of 2.572(4) Å and the Yb(2)–Cl(1) bond length of 2.532(4) Å in **1**, but shorter than the Yb(2)–Cl(2) bond length of 2.778(4) Å in **1**. The average Yb–C distance (C_5 ring) of 2.657(10) Å in **2** is shorter than that in **1** [2.691(17) Å]. These differences are probably due to the differences in the ionic radii and due to steric effects.

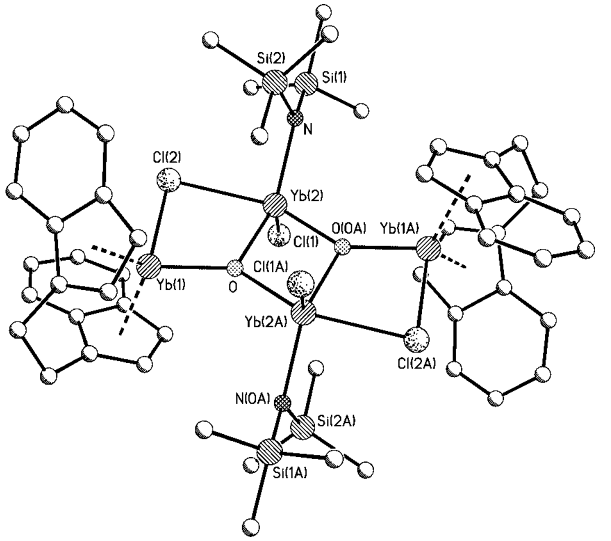

Figure 1. Molecular structure of the dianion $[\{\eta^5{:}\eta^5\text{-}(CH_2)_2\text{-}(C_9H_6)_2\}Yb(\mu\text{-}Cl)(\mu_3\text{-}O)Yb(Cl)N(SiMe_3)_2]_2{}^{2-}$ in **1**.

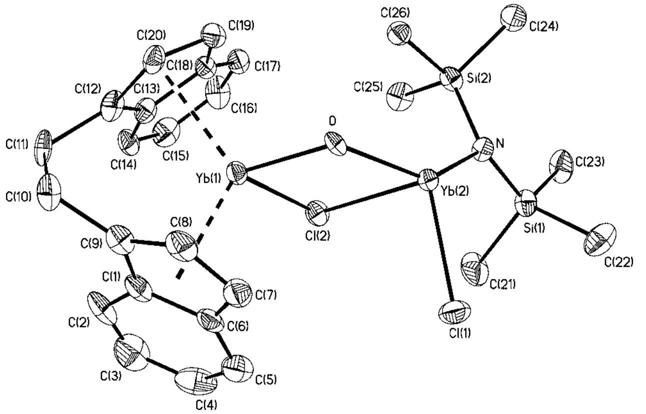

Figure 2. Structure of one symmetrical unit of the dianion in **1**. The atoms are labelled.

Table 1. Selected bond lengths [Å] and bond angles [°] in **1**, **2**, and **4**.

1		**2**		**4**	
Yb(1)–O	2.126(8)	Yb(1)–O	2.070(5)	Yb–O(1)	2.381(6)
Yb(2)–O	2.200(9)	Yb(2)–O	2.063(5)	Yb–O(2)	2.381(5)
Yb(1)–Cl(2)	2.572(4)	Yb(1)–Cl	2.603(3)	Yb–C(4)	2.811(7)
Yb(2)–Cl(2)	2.778(4)	Yb(2)–Cl	2.632(2)	Yb–C(5)	2.849(6)
Yb(2)–Cl(1)	2.532(4)	Yb(1)–C(11)	2.649(8)	Yb–C(10)	2.812(7)
Yb(2)–O(OA)	2.107(9)	Yb(1)–C(12)	2.602(8)	Yb–C(11)	2.749(7)
Yb(2)–N	2.226(11)	Yb(1)–C(13)	2.650(9)	Yb–C(12)	2.735(8)
Yb(1)–C(1)	2.804(15)	Yb(1)–C(14)	2.727(10)	Yb–C(15)	2.719(7)
Yb(1)–C(6)	2.769(16)	Yb(1)–C(15)	2.697(8)	Yb–C(16)	2.800(7)
Yb(1)–C(7)	2.602(17)	Yb(1)–C(31)	2.651(8)	Yb–C(21)	2.852(7)
Yb(1)–C(8)	2.570(15)	Yb(1)–C(32)	2.618(8)	Yb–C(22)	2.799(9)
Yb(1)–C(9)	2.677(15)	Yb(1)–C(33)	2.655(10)	Yb–C(23)	2.714(7)
Yb(1)–C(12)	2.694(14)	Yb(1)–C(34)	2.665(10)	Yb–C(av.)	2.784(9)
Yb(1)–C(13)	2.766(14)	Yb(1)–C(35)	2.685(9)	O(2)–Yb–O(1)	91.1(2)
Yb(1)–C(18)	2.777(13)	Yb(2)–C(22)	2.643(8)		
Yb(1)–C(19)	2.651(16)	Yb(2)–C(23)	2.648(9)		
Yb(1)–C(20)	2.598(16)	Yb(2)–C(24)	2.647(9)		
Yb–C(av.)	2.691(17)	Yb(2)–C(25)	2.667(9)		
O(OA)–Yb(2)-O	78.1(3)	Yb(2)–C(26)	2.671(8)		
O–Yb(2)–Cl(2)	77.5(2)	Yb(2)–C(42)	2.610(9)		
O–Yb(1)–Cl(2)	83.6(3)	Yb(2)–C(43)	2.619(9)		
Yb(1)–O–Yb(2)	113.4(4)	Yb(2)–C(44)	2.649(10)		
Yb(2A)–O–Yb(1)	144.6(5)	Yb(2)–C(45)	2.727(9)		
Yb(2A)–O–Yb(2)	101.9(3)	Yb(2)–C(46)	2.667(9)		
N–Yb(2)–Cl(2)	89.9(3)	Yb–C(av.)	2.657(10)		
N–Yb(2)–Cl(1)	108.0(3)	Li–O	1.830(18)		
O–Yb(2)–N	140.5(4)	Li–O(1)	1.97(2)		
N–Yb(2)–Cl(1)	108.0(3)	Li–O(2)	1.98(2)		
O(OA)–Yb(2)–N	106.7(4)	O–Yb(1)–Cl	85.27(15)		
Yb(1)–Cl(2)–Yb(2)	84.98(11)	O–Yb(2)–Cl	84.65(15)		
		Yb(1)–Cl–Yb(2)	80.40(7)		
		Yb(2)–O–Yb(1)	109.7(2)		

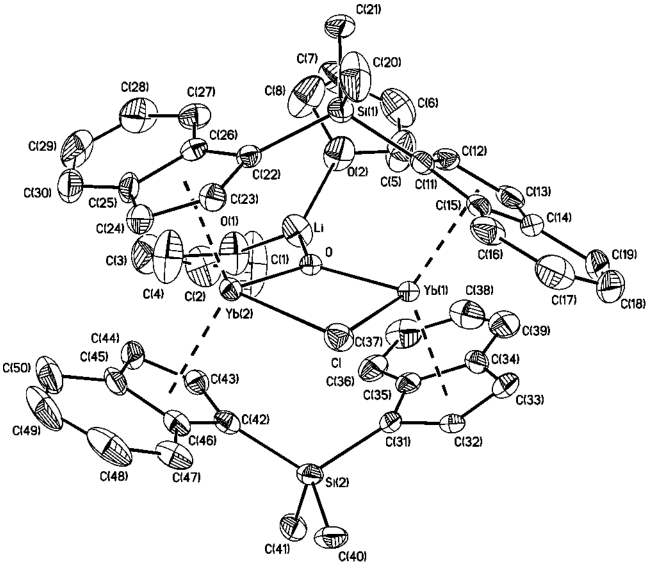

Figure 3. Molecular structure of $[\eta^5{:}\eta^5\text{-}(CH_3)_2Si(C_9H_6)_2Yb]_2(\mu\text{-}Cl)(\mu\text{-}O)Li(thf)_2$ (**2**).

X-ray analyses confirmed that the central ytterbium atom of complex **4** (Figure 4) is in the +2 oxidation state. The central ytterbium atom is coordinated by two indenyl ligands in an η^5 mode and by two oxygen atoms of the thf molecules in distorted tetrahedral geometry. The Yb–C distances range from 2.714(7) to 2.852(7) Å (Table 1), with an average length of 2.784(9) Å, which is slightly longer than those in $(\eta^5{:}\eta^1\text{-}MeOCH_2CH_2C_9H_5SiMe_3)_2Yb$[17] {2.741(14) Å} and in $(\eta^5{:}\eta^1\text{-}Me_2NCH_2CH_2C_9H_5SiMe_3)_2Yb$ {2.778(14) Å}.[16a] The average Yb–O distance of 2.381(6) Å in **4** is slightly shorter than that in $(\eta^5{:}\eta^1\text{-}MeOCH_2CH_2C_9H_5SiMe_3)_2Yb$[17] {of 2.462(9) Å}, but the O(2)–Yb–O(1) angle of 91.1(2)° in **4** is larger than those in $(\eta^5{:}\eta^1\text{-}MeOCH_2CH_2C_9H_5SiMe_3)_2Yb$[17] {84.5(3)° and 86.3(3)°}, which indicates the influence of steric effects on the coordination geometry of the complex.

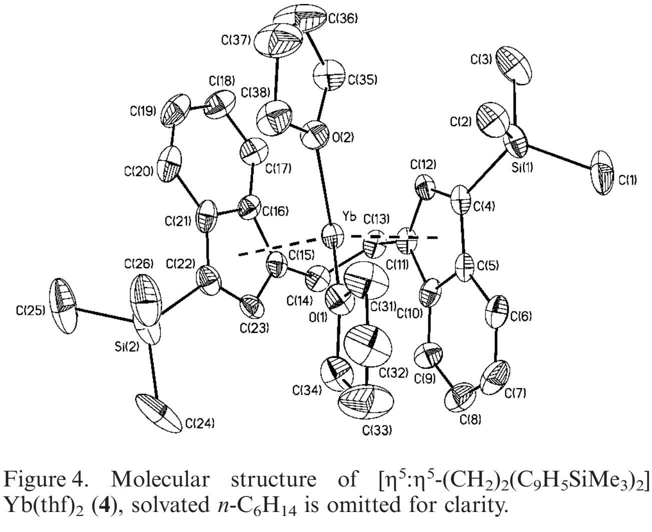

Figure 4. Molecular structure of $[\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_5SiMe_3)_2]Yb(thf)_2$ (**4**), solvated *n*-C_6H_{14} is omitted for clarity.

Conclusions

In summary, the reaction of the ytterbium(III) amide $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(thf)_3$ with various bridged indene compounds in the presence of external donor ligands was studied for the first time. In contrast to the result that the indenyl ytterbium(III) amide $[\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2]$-$YbN(SiMe_3)_2$ was isolated by direct treatment of the bridged indene compound $(CH_2)_2(C_9H_7)_2$ with the ytterbium(III) amide $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(thf)_3$ in refluxing toluene, the ytterbium(II) complexes were isolated and characterized by direct treatment of indenyl ytterbium(III) amide with external donor ligands such as tmeda or treatment of the bridged indene compounds with the ytterbium(III) amide $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(thf)_3$ at moderately high temperatures in the presence of excess external donor ligands such as dme or tmeda. This work also demonstrates that when thf was used as the external donor ligand, the reaction products were complicated depending on the reaction temperatures and the indenyl ligands; when the reaction was carried out in the refluxing toluene in the presence of excess thf, a novel tetranuclear or dinuclear ytterbium(III) complex containing μ-oxo group(s) was isolated, and when the reaction was performed in refluxing thf, and not in toluene with the addition of excess thf, an ytterbium(II) complex was isolated. Thus, this work indicates that reactions of lanthanide(III) complexes having the Ln–N bond with suitable external donor ligands at moderately high temperatures may provide a new method for the preparation of organolanthanide(II) complexes.

Experimental Section

General Remarks: All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a Schlenk line. All solvents were refluxed and distilled from either finely divided $LiAlH_4$ or sodium benzophenone ketyl under argon prior to use unless otherwise noted. $CDCl_3$ was dried with activated by 4-Å molecular sieves. $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$,[16a] $(CH_2)_2(C_9H_7)_2$,[24] and $[\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2]YbN(SiMe_3)_2$[16a] were prepared according to the reported procedures. Elemental analyses data were obtained with a Perkin–Elmer 2400 Series II elemental analyzer. IR spectra were recorded with a Perkin–Elmer 983(G) spectrometer (CsI crystal plate, Nujol and Fluorolube mulls. Melting points were determined in sealed capillaries without correction. ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded with a Bruker Avance-300 NMR spectrometer in $[D_5]$pyridine for lanthanide complexes and in $CDCl_3$ for organic compounds, and chemical shifts for ^1H and ^{13}C NMR spectra were reported with reference to internal solvent resonances.

$[\{\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2\}Yb(\mu\text{-}Cl)(\mu_3\text{-}O)Yb(Cl)N(SiMe_3)_2Li(thf)_4]_2$ (1): To a toluene solution (50.0 mL) of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ (2.208 g, 2.42 mmol) was added $(CH_2)_2(C_9H_7)$ (0.624 g, 2.42 mmol). The reaction mixture was heated at reflux overnight, and the color of the solution changed to dark blue. An ytterbium(III) amide complex with the formula $[\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_6)_2]YbN(SiMe_3)_2$ (determined by X-ray data) was isolated from this solution. To the reaction mixture was added thf (2.0 mL, 24.66 mmol, excess). The reaction mixture was then heated at reflux for 2 d. The color of the mixture gradually changed from dark blue to dark purple. The solvents were pumped off under vacuum. The residue was washed with *n*-hexane (10.0 mL) and was then extracted with thf (2 × 10.0 mL). The extract was combined and concentrated to about 10.0 mL. Dark red crystals were obtained by cooling the concentrated solution at –10 °C for several days (1.49 g, 44%). M.p. 243–245 °C (dec.). NMR analyses were not informative because of the lack of locking signals, which results from the paramagnetic property of the complex. IR (Nujol and Fluorolube mulls): $\tilde{\nu}$ = 2952 (s), 2851 (s), 2725 (s), 1693 (w), 1606 (w), 1461 (s), 1377 (s), 1305 (w), 1260 (m), 1094 (m), 1019 (m), 933 (w), 805 (m), 768 (m), 720 (m), 393 (w) cm^{-1}. $C_{84}H_{132}Cl_4Li_2N_2O_{10}Si_4Yb_4$ (2290.12): calcd. C 44.06, H 5.81, N 1.22; found C 44.32, H 5.74, N 1.10.

$[\eta^5{:}\eta^5\text{-}(CH_3)_2Si(C_9H_6)_2Yb]_2(\mu\text{-}Cl)(\mu\text{-}O)Li(thf)_2$ (2): To a toluene solution (30.0 mL) of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ (1.10 g, 1.20 mmol) was slowly added a toluene solution (10.0 mL) of $(CH_3)_2Si(C_9H_7)_2$ (0.35 g, 1.20 mmol). The reaction mixture was stirred and heated at reflux for 6 h. To the reaction mixture was added thf (1.0 mL, 12.33 mmol, excess). The reaction mixture was heated at reflux for another 24 h. The color of the mixture gradually changed to dark red. The solvent was pumped off under vacuum, leaving a dark red solid. The solid was washed with *n*-hexane (10.0 mL), and the residue was extracted with toluene (2 × 10.0 mL). The extract was combined and concentrated to about 15.0 mL. Dark red crystals were obtained by cooling the solution at 0 °C for several days (0.75 g, 56%). M.p. 180–182 °C. NMR analyses were not informative because of the lack of locking signals, which probably results from the paramagnetic property of the complex. IR (Nujol and Fluorolube mulls): $\tilde{\nu}$ = 2930 (s), 2958 (s), 1461 (m), 1383 (m), 1251 (w), 1143 (w), 1025 (w), 959 (w), 810 (w), 715 (w) cm^{-1}. $C_{48}H_{52}ClLiO_3Si_2Yb_2{\cdot}C_7H_8$ (1213.70): calcd. C 54.42, H 4.98; found C 53.91, H 5.25.

$(CH_2)_2(C_9H_6SiMe_3)_2$ (3): To a diethyl ether solution of $(CH_2)_2(C_9H_7)_2$ (6.0 g, 23.3 mmol) was slowly added a 1.59 M *n*-hexane solution of *n*BuLi (29.3 mL, 46.6 mmol) at 0 °C. The reaction temperature was gradually raised to room temperature, and the reaction mixture was stirred at room temperature overnight. The reaction mixture was cooled to 0 °C. To the reaction mixture was added Me_3SiCl (15.0 mL, 119.0 mmol, excess) in one portion. The mixture was then stirred at room temperature overnight. The precipitate was filtered off, and the solvent and excess Me_3SiCl was evaporated under reduced pressure to leave a yellow solid, which was then washed with *n*-hexane to give a pale yellow solid (7.4 g, 65%). M.p. 143–145 °C. ^1H NMR ($CDCl_3$): δ = 7.10–7.50 (m, 8 H), 6.36 (m, 2 H), 3.36 (m, 2 H, C_9H_6), 2.96 (m, 4 H, CH_2CH_2), –0.09 [s, 18 H, $Si(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 146.0, 144.4, 141.6, 130.1, 124.6, 123.7, 122.9, 119.0, 44.6 (C_9H_6), 27.2 (CH_2CH_2), –2.3 [$Si(CH_3)_3$] ppm. IR (Nujol and Fluorolube mulls): $\tilde{\nu}$ = 2923 (s), 2854 (s), 1714 (m), 1604 (m), 1461 (s), 1377 (m), 1345 (m), 1259 (m), 1248 (m), 1034 (m), 937 (w), 877 (m), 763 (m), 737 (w), 699 (w), 615 (w), 368 (w) cm^{-1}. $C_{26}H_{34}Si_2$ (402.66): calcd. C 77.54, H 8.51; found C 77.32, H 8.81.

$[\eta^5{:}\eta^5\text{-}(CH_2)_2(C_9H_5SiMe_3)_2]Yb(thf)_2{\cdot}(C_6H_{14})_{0.5}$ (4): To a thf solution (30.0 mL) of $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-}Cl)Li(thf)_3$ (1.290 g, 1.41 mmol) was added a thf solution (10.0 mL) of $(CH_2)_2(C_9H_6SiMe_3)_2$ (0.570 g, 1.41 mmol). After the reaction mixture was heated at reflux for 24 h, the solvent was evaporated under vacuum, leaving a red solid. The residue was extracted with *n*-hexane (2 × 10.0 mL), and the extract was combined and concentrated to about 10.0 mL. Red crystals were obtained by cooling the concentrated solution at –10 °C for several days (0.46 g, 46%). M.p. 154–

157 °C. ^{1}H NMR ([D$_5$]pyridine): δ = 8.63–8.46 (m, 8 H), 7.16 (s, 2 H, C_9H_5), 4.78 (m, 8 H, OC_4H_8), 2.73 (m, 8 H, OC_4H_8), 2.22 (m, 2 H), 1.88 (m, 2 H, CH_2CH_2), 1.10 [s, 18 H, Si(CH_3)$_3$] ppm. ^{13}C NMR ([D$_5$]py): δ = 147.7, 145.8, 142.8, 137.1, 136.5, 125.1, 124.4, 121.1, 68.94, 26.9, 4.2, 3.7, 3.3, –1.2, –1.8 ppm. IR (Nujol and Fluorolube mulls): $\tilde{\nu}$ = 2949 (m), 2600 (m), 1249 (m), 1160 (w), 1031 (m), 931 (w), 878 (m), 839 (s), 763 (m), 722 (m), 617 (w), 239 (w) cm^{-1}. $C_{26}H_{32}Si_2Yb$ (**4** – 2thf – 1/2C_6H_{14}) (573.69): calcd. C 54.45, H 5.62; found C 54.54, H 6.07.

Heating **4** in toluene at reflux led to an insoluble solid, which could not be purified by recrystallization and other methods.

[η^5:η^5-$(CH_2)_2(C_9H_5SiMe_3)_2$]Yb·dme (5): To a dme solution (30.0 mL) of [$(Me_3Si)_2N]_3Yb^{III}(\mu$-Cl)Li(thf)$_3$ (1.414 g, 1.55 mmol) was added a dme solution (10.0 mL) of $(CH_2)_2(C_9H_6SiMe_3)_2$ (0.624 g, 1.55 mmol). After the reaction mixture was heated at reflux for 24 h, the solvent was pumped off, leaving a red solid. The solid was washed with *n*-hexane (8.0 mL). The solid was extracted with toluene (2 × 10.0 mL), and the extract was combined and concentrated to about 10.0 mL. The red crystalline solid was obtained by cooling the concentrated solution at –10 °C for several days (0.57 g, 55%). M.p. 165–168 °C. ^{1}H NMR ([D$_5$]pyridine): δ = 7.30–6.43 (m, 10 H, C_9H_5), 3.46 (m, 4 H), 3.23 (m, 4 H, $CH_3OCH_2CH_2OCH_3$), 2.71 (s, 6 H, $CH_3OCH_2CH_2OCH_3$), –0.10 [s, 18 H, Si(CH_3)$_3$] ppm. IR (Nujol and Fluorolube mulls): $\tilde{\nu}$ = 2925 (s), 2855 (s), 1602 (m), 1460 (s), 1377 (m), 1260 (m), 1249 (m), 1104 (m), 1029 (m), 931 (m), 878 (m), 839 (s), 763 (m), 722 (m), 696 (m), 617 (m), 393 (w) cm^{-1}. $C_{30}H_{42}O_2Si_2Yb$ (663.83): calcd. C 54.28, H 6.38; found C 54.10, H 6.38.

Heating the reaction mixture of [$(Me_3Si)_2N]_3Yb^{III}(\mu$-Cl)Li(thf)$_3$ and $(CH_2)_2(C_9H_6SiMe_3)_2$ in toluene at reflux for 6 h followed by the addition of excess dme also produced complex **5**. The complex was characterized by elemental and spectroscopic analyses.

[η^5:η^5-$(CH_3)_2Si(C_9H_6)_2$]Yb·tmeda (6): To a toluene solution (30.0 mL) of [$(Me_3Si)_2N]_3Yb^{III}(\mu$-Cl)Li(thf)$_3$ (1.10 g, 1.20 mmol) was slowly added a toluene solution (10.0 mL) of $(CH_3)_2Si(C_9H_7)_2$ (0.35 g, 1.20 mmol). The reaction mixture was stirred at room temperature for 6 h. To the reaction mixture was added tmeda [$(CH_3)_2NCH_2CH_2N(CH_3)_2$] (1.0 mL, 6.62 mmol, excess). The reaction mixture was then heated at reflux for 24 h. The color of the solution changed to purple. The solvent was pumped off under vacuum, and the solid residue was washed with *n*-hexane (10.0 mL). The solid was extracted with toluene (2 × 10.0 mL), and the extract was combined and concentrated to about 15.0 mL. The purple crystalline solid was obtained by cooling the solution at 0 °C for several days (0.47 g, 68%). M.p. 98–100 °C. ^{1}H NMR ([D$_5$]pyridine): δ = 7.63–7.56 (m, 8 H), 7.26–7.19 (m, 4 H, C_9H_6), 2.19 (m, 4 H), 2.13 [s, 12 H, $(CH_3)_2NCH_2CH_2N(CH_3)_2$], 0.71–1.04 [m, 6 H, Si(CH_3)$_2$] ppm. $C_{26}H_{34}N_2SiYb$ (547.66): calcd. C 54.25, H 5.95, N 4.86; found C 54.23, H 6.20, N 4.83.

[η^5:η^5-$(CH_2)_2(C_9H_6)_2$]Yb·tmeda (7): To a toluene solution (15 mL) of [η^5:η^5-$(CH_2)_2(C_9H_6)_2$]YbN(SiMe$_3$)$_2$ (0.347 g, 0.059 mmol) was added a tmeda (1.20 mL, 7.95 mmol, excess). The mixture was heated at reflux for 24 h. The color of the mixture completely changed from dark blue to red. The solvent was evaporated under vacuum, and the resulting solid was washed with *n*-hexane and extracted with diethyl ether (2 × 10.0 mL). The extract was combined and was then evaporated to dryness to afford **7** as a red solid (0.13 g, 43%). M.p. 183–185 °C. ^{1}H NMR ([D$_5$]pyridine): δ = 7.36–7.21 (m, 8 H), 7.16–7.07 (m, 4 H, C_9H_6), 2.24 (m, 2 H), 1.89 (m, 2 H, CH_2CH_2), 2.20 (m, 4 H), 2.15 [s, 12 H, $(CH_3)_2NCH_2CH_2N(CH_3)_2$] ppm. $C_{28}H_{32}N_2Yb$ (569.61): calcd. C 57.27, H 5.87, N 5.13; found C 56.92, H 6.02, N 5.04.

Crystal Structure Analyses of 1, 2 and 4: Suitable crystals of complexes **1**, **2** and **4** were mounted in sealed capillaries. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), temperature 293(2) K, the ϕ and ω scan technique; SADABS effects and empirical absorption were applied to the data for correction. All structures were solved by direct methods (SHELXTL-97),[24] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-square calculations based on F^2 (SHELXTL-97). The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model

Table 2. Crystal Data for **1**, **2** and **4**.

	1	2	4
Empirical formula	$C_{84}H_{132}N_2Cl_4Li_2O_{10}Si_4Yb_4$	$C_{48}H_{52}ClLiO_3Si_2Yb_2$	$C_{37}H_{54}O_2Si_2Yb$
Formula weight	2290.12	1121.55	760.02
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$Fdd2$
a [Å]	14.3978(4)	11.3899(2)	33.0471(6)
b [Å]	14.4560(3)	19.5632(3)	35.7088(2)
c [Å]	14.7510(3)	20.0532(3)	14.9298(3)
α [°]	110.2180(10)	90	90
β [°]	107.8010(10)	94.1760(10)	90
γ [°]	96.8200(10)	90	90
V [Å^3]	2655.16(11)	4456.45(12)	17618.2(5)
T [K]	293(2)	293(2)	293(2)
$D_{\text{calcd.}}$ [g cm^{-3}]	1.432	1.672	1.146
Z	1	4	16
$F(000)$	1140	2208	6240
No. Reflections collected	13686	14956	22293
No. Unique Reflections	9193 (R_{int} = 0.054)	7766 (R_{int} = 0.035)	5786 (R_{int} = 0.040)
No. of Parameters	541	514	376
λ [Å] Mo-K_α	0.71073	0.71073	0.71073
μ [mm^{-1}]	3.682	4.325	2.202
θ range [°]	1.89 to 25.06	1.46 to 25.04	2.37 to 25.06
Goodness of fit	1.154	1.162	1.080
R [$I > 2\sigma(I)$]	0.078	0.048	0.034
wR_2	0.155	0.081	0.078

with varied thermal parameters. All the non-hydrogen atoms were refined anisotropically. The residual electron densities were of no chemical significance. Crystal data and details of the data collection and structure refinements are given in Table 1, and selected bond lengths and angles are compiled in Table 2.

CCDC-262319 for **1**, CCDC-262320 for **2**, CCDC-262321 for **4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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[1] a) Z. Hou, Y. Luo, X. Li, *J. Organomet. Chem.* **2006**, *691*, 3114–3121; b) H. Yasuda, *J. Organomet. Chem.* **2002**, *647*, 128; c) Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1; d) Y. Nakayama, H. Yasuda, *J. Organomet. Chem.* **2004**, *689*, 4489; and references cited therein.

[2] a) H. Kim, T. Livinghouse, J. H. Shim, S. G. Lee, P. H. Lee, *Adv. Synth. Catal.* **2006**, *348*, 701–704; b) D. V. Gribkov, K. C. Hultzsch, F. Hampel, *J. Am. Chem. Soc.* **2006**, *128*, 3748–3759; c) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673–686; d) K. C. Hultzsch, F. Hampel, T. Wagner, *Organometallics* **2004**, *23*, 2601–2612; e) F. Lauterwasser, P. G. Hayes, S. Brase, W. E. Piers, L. L. Schafer, *Organometallics* **2004**, *23*, 2234–2237; f) J.-S. Ryu, T. J. Marks, F. E. McDonald, *J. Org. Chem.* **2004**, *69*, 1038–1052; g) S. Hong, A. M. Kawaoka, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 15878–15892; h) S. Hong, S. Tian, M. V. Metz, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 14768–14783; i) Y. K. Kim, T. Livinghouse, Y. Horino, *J. Am. Chem. Soc.* **2003**, *125*, 9560–9561; j) S. Hong, T. J. Marks, *J. Am. Chem. Soc.* **2002**, *124*, 7886–7887; k) G. A. Molander, E. D. Dowdy, S. K. Pack, *J. Org. Chem.* **2001**, *66*, 4344–4347; l) J. Collin, J.-C. Daran, E. Schulz, A. Trifonov, *Chem. Commun.* **2003**, 3048–3049; m) Y. K. Kim, T. Livinghouse, *Angew. Chem. Int. Ed.* **2002**, *41*, 3645–3647; n) Y. K. Kim, T. Livinghouse, J. E. Bercaw, *Tetrahedron Lett.* **2001**, *42*, 2933; o) D. V. Gribkov, K. C. Hultzsch, F. Hampel, *Eur. J. Chem.* **2003**, *9*, 4796–4810; p) D. Riegert, J. Collin, A. Meddour, E. Schulz, A. Trifonov, *J. Org. Chem.* **2006**, *71*, 2514–2517; q) K. C. Hultzsch, *Adv. Synth. Catal.* **2005**, *347*, 367–391.

[3] a) A. M. Kawaoka, M. R. Douglass, T. J. Marks, *Organometallics* **2003**, *22*, 4630–4632; b) K. Takaki, G. Koshoji, K. Komeyama, M. Takeda, T. Shishido, A. Kitani, K. Takehira, *J. Org. Chem.* **2003**, *68*, 6554–6565; c) M. R. Douglass, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2001**, *123*, 10221–10238; d) M. R. Douglass, T. J. Marks, *J. Am. Chem. Soc.* **2000**, *122*, 1824–1825; e) K. Komeyama, T. Kawabata, K. Takehira, K. Takaki, *J. Org. Chem.* **2005**, *70*, 7260–7266.

[4] a) Y. Horino, T. Livinghouse, *Organometallics* **2004**, *23*, 12–14; b) D. V. Gribkov, F. Hampel, K. C. Hultzsch, *Eur. J. Inorg. Chem.* **2004**, 4091–4101; c) A. A. Trifonov, T. P. Spaniol, J. Okuda, *Organometallics* **2001**, *20*, 4869–4874; d) Z. Hou, Y. Zhang, O. Tardif, Y. Wakatsuki, *J. Am. Chem. Soc.* **2001**, *123*, 9216–9217; e) A. Z. Voskoboynikov, A. K. Shestakova, I. P. Beletskaya, *Organometallics* **2001**, *20*, 2794–2801.

[5] a) H. Berberich, P. W. Roesky, *Angew. Chem. Int. Ed.* **1998**, *37*, 1569; b) M. R. Bürgstein, H. Berberich, P. W. Roesky, *Chem. Eur. J.* **2001**, *7*, 3078.

[6] a) K. C. Hultsch, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4845; b) E. Martin, P. Dubois, R. Jerome, *Macromolecules* **2000**, *33*, 1530.

[7] a) M. A. Giardello, Y. Yamamoto, L. Brard, T. J. Marks, *J. Am. Chem. Soc.* **1995**, *117*, 3276; b) C. Qian, G. Zuo, Y. F. Chen, J. Sun, *Organometallics* **2001**, *20*, 3106; c) C. Boisson, F. Barbotin, R. Spitz, *Macromol. Chem. Phys.* **1999**, *200*, 1163; d) C. Qian, W. L. Nie, J. Sun, *Organometallics* **2000**, *19*, 4134; e) S. Zhou, S. Wang, G. Yang, X. Liu, E. Sheng, K. Zhang, L. Cheng, Z. Huang, *Polyhedron* **2003**, *22*, 1019–1024.

[8] a) K. Komeyama, T. Kawabata, K. Takehira, K. Takaki, *J. Org. Chem.* **2005**, *70*, 7260–7266; b) L. Zhang, S. Wang, S. Zhou, G. Yang, E. Sheng, *J. Org. Chem.* **2006**, *71*, 3149–3153.

[9] W. J. Evans, J. W. Grate, I. Bloom, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1985**, *107*, 405–409.

[10] T. Dubé, S. Gambarotta, G. P. A. Yap, *Organometallics* **1998**, *17*, 3967–3973.

[11] a) T. Dubé, S. Gambarotta, G. P. A. Yap, *Angew. Chem. Int. Ed.* **1999**, *38*, 1432–1435; b) T. Dubé, S. Conoci, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 1182–1185.

[12] H. C. Aspinall, M. R. Tillotson, *Inorg. Chem.* **1996**, *35*, 2163–2164.

[13] a) N. S. Hosmane, Y. Wang, A. R. Oki, H. Zhang, J. A. Maguire, *Organometallics* **1996**, *15*, 626; b) G. Zi, Q. Yang, T. C. W. Mak, Z. Xie, *Organometallics* **2001**, *20*, 2359–2366.

[14] J. Jubb, S. Gambarotta, R. Duchateau, J. H. Teuben, *J. Chem. Soc., Chem. Commun.* **1994**, 2461–2462.

[15] W. J. Evans, R. Dominguez, T. P. Hanusa, *Organometallics* **1986**, *5*, 1291–1296.

[16] a) E. Sheng, S. Wang, G. Yang, S. Zhou, L. Cheng, K. Zhang, Z. Huang, *Organometallics* **2003**, *22*, 684–692; b) E. Sheng, S. Zhou, S. Wang, G. Yang, Y. Wu, Y. Feng, L. Mao, Z. Huang, *Eur. J. Inorg. Chem.* **2004**, 2923–2932.

[17] K. Zhang, W. Zhang, S. Wang, E. Sheng, G. Yang, M. Xie, S. Zhou, Y. Feng, L. Mao, Z. Huang, *Dalton Trans.* **2004**, 1029–1037.

[18] a) S. Wang, S. Zhou, E. Sheng, M. Xie, K. Zhang, L. Cheng, Y. Feng, L. Mao, Z. Huang, *Organometallics* **2003**, *22*, 3546–3552; b) S. Wang, X. Tang, A. Vega, J. Saillard, E. Sheng, G. Yang, S. Zhou, Z. Huang, *Organometallics* **2006**, *25*, 2399–2401.

[19] For recent reviews, see: a) H. Schumann, J. A. Messe-Markscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865; b) F. T. Edelmann, in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, New York, **1995**, vol. 4, p. 11; c) H. C. Aspinall, *Chem. Rev.* **2002**, *102*, 1807–1850; d) F. T. Edelmann, D. M. M. Freckmann, H. Schumann, *Chem. Rev.* **2002**, *102*, 1851–1896; e) S. Arndt, J. Okuda, *Chem. Rev.* **2002**, *102*, 1953–1976; f) M. N. Bochkarev, *Chem. Rev.* **2002**, *102*, 2089–2118; g) W. J. Evans, B. L. Davis, *Chem. Rev.* **2002**, *102*, 2119–2136.

[20] a) W. Abriel, J. Heck, *J. Organomet. Chem.* **1986**, *302*, 363; b) G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann, T. J. Mark, *J. Am. Chem. Soc.* **1985**, *107*, 8103; c) C. M. Fendrick, E. A. Mintz, L. D. Schertz, T. J. Marks, V. W. Day, *Organometallics* **1984**, *3*, 819.

[21] C. Qian, W. Nie, J. Sun, *Organometallics* **2000**, *19*, 4134–4140.

[22] S. Wang, H.-W. Li, Z. Xie, *Organometallics* **2004**, *23*, 3780–3787.

[23] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

[24] G. M. Sheldrick, *SHELXTL*, version 5.10, Bruker Analytical X-ray Systems, Inc., Madison, WI, **1997**.

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