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β-SiH agostic bonding in sterically crowded lanthanidocene silylamide complexes

Michael G. Klimpel, Hans W. Görlitzer, Maxim Tafipolsky, Michael Spiegler, Wolfgang Scherer, Reiner Anwander *

Anorganisch-Chemisches Institut, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

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Abstract

The synthesis as well as the spectroscopic and structural characterization of mononuclear metallocene complexes of the trivalent rare earth elements yttrium and lanthanum is described. Lanthanidocene silylamide complexes were obtained ate-complex free and in high yields according to a silylamine elimination reaction from complexes $Ln[N(SiHMe_2)_2]_3(THF)_2$ (Ln = Y, La) and highly substituted cyclopentadiene derivatives $(CH_3)_5C_5H$, $(CH_3)_4C_5H_2$ and $(C_6H_5)_4C_5H_2$. Deprotonation of tetraphenylcyclopentadiene was accomplished only for the lanthanum derivative indicating steric constraints due to the size of the metal cation. IR and ^{1}H-NMR spectroscopy reveal the presence of asymmetrically bonded silylamide ligands featuring a strong agostic interaction between the electron-deficient metal centers and the SiH moiety of the bis(dimethylsilyl)amide ligand: SiH stretching vibrations as low as 1827 cm^{-1} are indicative of a distinct weakening of the SiH bonding. X-ray structure analyses of complexes $[(CH_3)_4C_5H]_2YN(SiHMe_2)_2$, $[(CH_3)_5C_5]_2YN(SiHMe_2)_2$ and $[(C_6H_5)_4C_5H]_2LaN(SiHMe_2)_2$ show that the structural features of the agostically bonded bis(dimethylsilyl)amide moiety depend on the steric crowding of the ancillary cyclopentadienyl ligand: Y···Si and Y···H contacts as close as 3.0506(7) and 2.40(3) Å, respectively, are detected, forcing Ln–N–Si angles as low as 99.7(1)°.

Keywords: Yttrium; Lanthanum; Metallocenes; Silylamide route; β-SiH monoagostic interactions; Pentamethylcyclopentadienyl; Tetramethylcyclopentadienyl; Tetraphenylcyclopentadienyl

1. Introduction

Work by Yasuda et al. revealed that achiral lanthanidocene complexes of type 'Cp^*_2LnR' ($Cp^* = (CH_3)_5C_5$]; R = H, Me) constitute highly efficient precatalyst systems for the stereospecific polymerization of acrylates [1]. In addition, lanthanidocene hydride, alkyl, and amide derivatives were successfully used in a variety of olefin transformation reactions including ethylene polymerization, oligomerization, hydrogenation, hydroamination, hydrosilylation, hydroboration, and hydrophosphination [2,3]. Such highly reactive rare earth metallocene species are routinely synthesized via successive (multiple-step), often low-yield salt metathesis reactions [4,5]. Transmetallation [6], reductive metallation [7] and desilylation reactions [8] have been reported as alternative preparation procedures, however, in this context attracted less attention [9]. More recently, the scope of alkane and amine elimination reactions, originally examined for systems such as $Ln(C_6F_5)_2$ [10], Ln/NH_3(liquid) [11], and $Ln[N(SiMe_3)_2]_3$ [12] was effectively increased by more versatile precursor compounds such as $Ln(CH_2SiMe_3)_3(THF)_2$ [13] and $Ln[N(SiHMe_2)_2]_3(THF)_x$ (**1**, $x = 1, 2$) [14] giving broad access to constrained geometry [15] and *ansa*-lanthanidocene complexes [16]. According to $Ln[N(SiHMe_2)_2]_3(THF)_x$-based silylamine elimination reactions [17] we were able to synthesize and structurally characterize the first Brintzinger-type C_2-symmetric *ansa*-metallocene complexes of the rare earth elements [16]. Here, we report on the feasibility and intrinsic limitations of this 'extended silylamide route' for the synthesis of non-linked rare earth metallocene complexes by considering various tetra- and penta-substituted cyclopentadiene derivatives. A full

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* Corresponding author. Fax: +49-89-289-13473.
E-mail address: reiner.anwander@ch.tum.de (R. Anwander).

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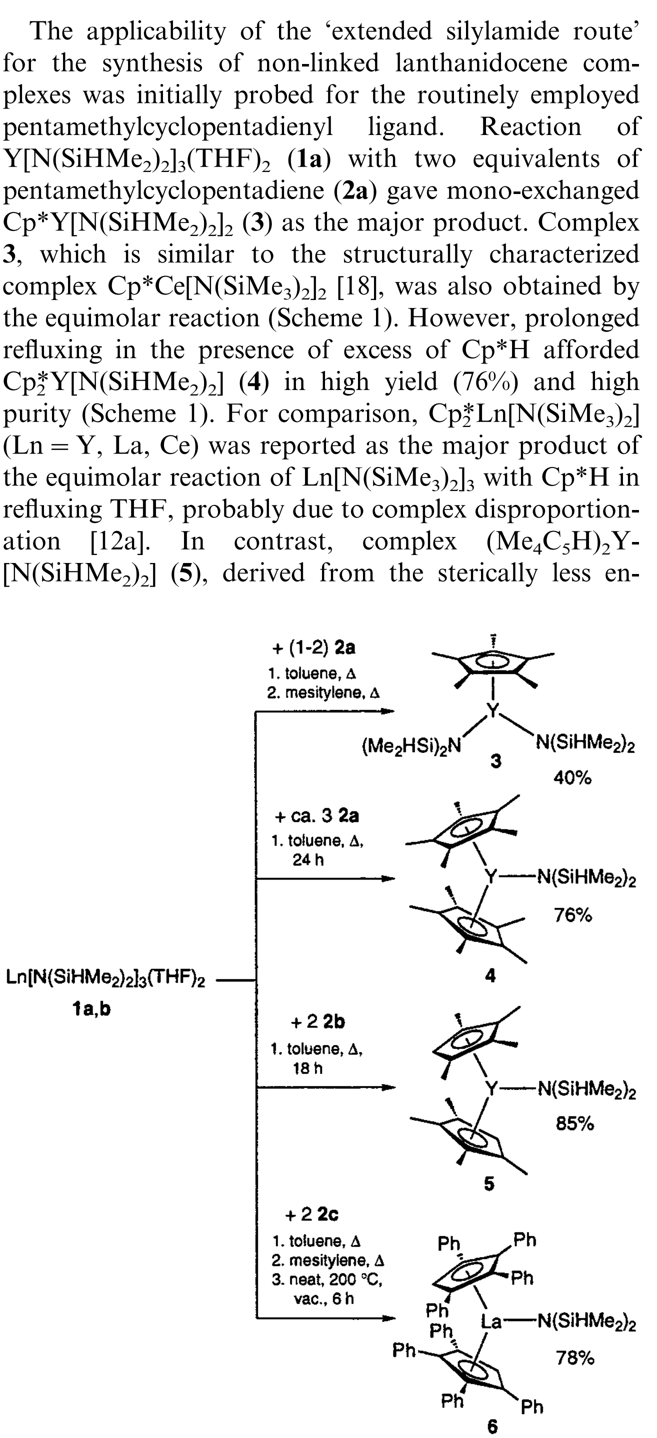
account of the synthesis as well as spectroscopic and structural features of these complexes is presented.

2. Results and discussion

2.1. Synthesis of non-linked lanthanidocene amide complexes

The applicability of the 'extended silylamide route' for the synthesis of non-linked lanthanidocene complexes was initially probed for the routinely employed pentamethylcyclopentadienyl ligand. Reaction of $Y[N(SiHMe_2)_2]_3(THF)_2$ (**1a**) with two equivalents of pentamethylcyclopentadiene (**2a**) gave mono-exchanged $Cp^*Y[N(SiHMe_2)_2]_2$ (**3**) as the major product. Complex **3**, which is similar to the structurally characterized complex $Cp^*Ce[N(SiMe_3)_2]_2$ [18], was also obtained by the equimolar reaction (Scheme 1). However, prolonged refluxing in the presence of excess of Cp*H afforded $Cp^*_2Y[N(SiHMe_2)_2]$ (**4**) in high yield (76%) and high purity (Scheme 1). For comparison, $Cp^*_2Ln[N(SiMe_3)_2]$ (Ln = Y, La, Ce) was reported as the major product of the equimolar reaction of $Ln[N(SiMe_3)_2]_3$ with Cp*H in refluxing THF, probably due to complex disproportionation [12a]. In contrast, complex $(Me_4C_5H)_2Y$-$[N(SiHMe_2)_2]$ (**5**), derived from the sterically less encumbered tetramethylcyclopentadiene (**1b**), could be obtained readily from a stoichiometric reaction under less drastic reaction conditions (85% yield, Scheme 1). In order to ultimately challenge the steric limitations of our 'extended silylamide route', tetraphenylcyclopentadiene (**1c**) was employed as a sterically even bulkier ligand than Cp*H (**2a**). While an yttrocene derivative did not form via $Y[N(SiHMe_2)_2]_3(THF)_2$ (**1a**) even under extremely vigorous conditions (neat, 200 °C under vacuum), the larger lanthanide center La(III) is able to accomodate two tetraphenylcyclopentadienyl ligands. Complex $(Ph_4C_5H)_2La[N(SiHMe_2)_2]$ (**6**) formed in 78% yield after refluxing in mesitylene over a period of 24 h and subsequent treatment of the residue at 200 °C/10^{-3} torr for 6 h (Scheme 1). Apparently, steric discrimination by the metal cation radii, which is commonly observed in organolanthanide chemistry, seems to be an important issue also in this case.

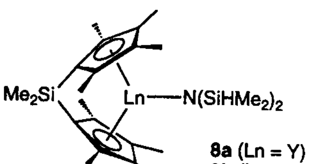


Scheme 1. Synthesis of lanthanidocene amide complexes according to the extended silylamide route.

A salt metathesis reaction was applied for the synthesis of metallocene complexes **4** and **5** in order to compare the effect of the synthetic procedure on product yield. Accordingly, $YCl_3(THF)_{3.5}$ was subsequently reacted with the alkali metal salts of **2a** (Na) and **2b** (K), respectively, as well as with $KN(SiHMe_2)_2$, in THF. Application of a one-pot reaction avoiding the isolation of the initially formed yttrocene choride complexes **7a** and **7b** afforded the lanthanidocene silylamide complexes in acceptable, although lower yields (**4**, 62%; **5**, 78%). Elemental analyses of complexes **3**, **4**, **5** and **6** are consistent with complete THF displacement at the metal center. Complexes **3**, **4** and **5** are readily soluble in hexane, while compound **6** dissolves in toluene.

*2.2. Spectroscopic characterization of lanthanidocene silylamide complexes **4**, **5** and **6***

The IR spectra of all of the isolated rare earth metallocene bis(dimethylsilyl)amide complexes were recorded as Nujol mulls. Interestingly, they show two well-separated bands for the Si–H stretching vibration (Table 1). While the higher energy band is in good agreement with that of the synthetic precursors **1a** (2072 cm^{-1}) and **1b** (2051 cm^{-1}) [14], a drastic shift of about 200 cm^{-1} to lower wavenumbers is observed for the second ν(Si–H) vibration suggesting a significant Si–H bond-weakening which typically hints to Y···H–Si agostic interactions [19–21]. Apparently, both the mono (**3**) and bis(silylamide) complexes (**4**–**6**) examined here display a β-SiH monoagostic interaction. This is in



8a (Ln = Y)
8b (Ln = La)

(1)

Table 1
Selected IR and ^{1}H-NMR spectroscopic data for bis(dimethylsilyl)amide complexes

Compound	IR [a] $\nu_{(SiH)}$ (cm^{-1})	IR [a] $\nu_{(SiH,\ agostic)}$ (cm^{-1})	^{1}H-NMR [b] $\delta_{(SiH)}$ (ppm)
$[(CH_3)_5C_5]Y[N(SiHMe_2)_2]_2$ (**3**)	2066	1833	4.49 (ψ-oct)
$[(CH_3)_5C_5]_2YN(SiHMe_2)_2$ (**4**)	2057	1827	4.07 (ψ-oct)
$[(CH_3)_4C_5H]_2YN(SiHMe_2)_2$ (**5**)	2043	1823	3.94 (ψ-oct)
$[Me_2Si(C_5Me_4)_2]Y[N(SiHMe_2)_2]$ (**8a**) [c]	–	1789	4.00 (ψ-oct)
$[(C_6H_5)_4C_5H]_2LaN(SiHMe_2)_2$ (**6**)	2068	1841	4.58
$[Me_2Si(C_5Me_4)_2]La[N(SiHMe_2)_2]$ (**8b**) [c]	–	1845	4.18(m)
$Y[N(SiHMe_2)_2]_3(THF)_3$ (**1a**)	2072	1939	4.99
$La[N(SiHMe_2)_2]_3(THF)_3$ (**1b**)	2051	1970	5.02

[a] IR spectra were recorded as Nujol mulls.

[b] NMR spectra were recorded at 25 °C as C_6D_6 solutions.

[c] Ref. [16], only one SiH vibration detected.

contrast to the diagostic interactions observed previously for *ansa*-bridged lanthanidocene silylamide complexes, e.g., $[Me_2Si(C_5Me_4)_2]Y[N(SiHMe_2)_2]$ (**8a**) (Formula 1) [16].

A ^{1}H-NMR spectroscopic study was performed in order to get more detailed information about the extent of SiH bonding in such non-linked lanthanidocene complexes. The presence of agostic SiH moieties is evidenced by a significant upfield shift of the SiH proton signal. However, only one signal is observed in solution at ambient temperature. A strong dependence of the SiH signal on the number and nature of the ancillary ligands was detected. Due to the decreased steric crowding caused by the tetramethylcyclopentadienyl ligand, complex **5** experiences an overall stronger agostic interaction than complex **4** ($\Delta\delta_{(SiH)} = 0.13$ ppm, Table 1). The agostic shifts are comparable to that detected for a diagostically fused silylamide moiety in $[Me_2Si(C_5Me_4)_2]Y[N(SiHMe_2)_2]$ (**8a**) ($\delta_{(SiH)} = 4.00$). Although significant, the SiH high-field shift in complex $(Ph_4C_5H)_2La[N(SiHMe_2)_2]$ (**6**) is less pronounced and comparable to that in mono-Cp complex **3**. This weakening of the agostic interaction might be due to either a decreased Lewis acidity of the larger La(III) center or enhanced steric shielding of the metal center by the tetraphenylcyclopentadienyl ligand. Note that the slightly electron-withdrawing property of the phenyl groups should implicate a stronger agostic bonding.

2.3. Molecular structures of lanthanidocene silylamide complexes 4, 5 and 6

Single-crystal X-ray structural determinations were carried out on all three of the metallocene amide complexes **4**, **5** and **6** in order to establish unambiguously the presence of agostic interactions found by IR and ^{1}H-NMR spectroscopy. For ease of comparison, key parameters of these metallocene complexes are listed in Table 2.

All of the complexes display a distorted trigonal planar arrangement of the silylamide and the two cyclopentadienyl ligands of a bent metallocene unit. The molecuar structure of complex $Cp^*_2YN(SiHMe_2)_2$ (**4**) unequivocally proved the presence of a pronounced asymmetric β-SiH monoagostic bonding of the silylamide ligand (Figs. 1 and 2b). The interacting SiH moiety features Y···Si(1) and Y···H distances of 3.0505(8) and 2.40(3) Å, which are comparable to those found in *rac*-$[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]Y[N(SiHMe_2)_2]$ (3.082(1), 2.54(2) Å) and *rac*-$[Me_2Si(2\text{-}Me\text{-}BenzInd)_2]Y[N(SiHMe_2)_2]$ (3.034(1), 2.37(3) Å) exhibiting symmetric diagostic interactions (Fig. 2a) [16]. For comparison, the Ln–Si σ-bond length in $Cp^*_2Sm[SiH(SiMe_3)_2]$ was

Table 2
Selected structural parameters for lanthanidocene complexes

	4 (Ln = Y)	**5** (Ln = Y)	**6** (Ln = La) molecule 1/molecule 2
Bond distances (Å)			
av. Ln–C_{Cp}	2.668	2.650	2.888/2.888
min. Ln–C_{Cp}	2.629(2)	2.612(2)	2.744(4)/2.723(5)
max. Ln–C_{Cp}	2.706(2)	2.684(2)	3.019(5)/3.017(4)
Ln–C_g1 [a]	2.378(2)	2.349(2)	2.616(2)/2.604(2)
Ln–C_g2 [a]	2.383(2)	2.372(2)	2.635(2)/2.644(2)
Ln–Si(a)	3.0505(8)	3.1213(6)	3.261(2)/3.193(2)
Ln–Si(b)	3.5365(7)	3.2887(5)	3.472(2)/3.889(3)
Ln–H(a) [b]	2.40(3)	2.57(3)	2.78(9)/2.59(6)
Ln–H(b) [b]	3.37(3)	2.89(3)	3.21(9)/4.83(6)
Ln–N	2.280(2)	2.277(2)	2.361(5)/2.381(4)
N–Si(a)	1.679(3)	1.678(2)	1.687(5)/1.701(4)
N–Si(b)	1.697(2)	1.677(2)	1.645(5)/1.721(5)
Si(a)–H(a) [b]	1.50(3)	1.48(3)	1.48(9)/1.67(8)
Si(b)–H(b) [b]	1.36(3)	1.48(2)	1.43(6)/1.56(6)
Bond angles (°)			
C_g1–Ln–C_g2 [a]	134.2(1)	131.00(8)	135.2/136.9
Si(a)–N–Si(b)	134.8(1)	139.8(1)	131.6(3)/115.7(2)
Ln–N–Si(a)	99.7(1)	103.19(8)	107.7(2)/101.6(2)
Ln–N–Si(b)	124.9(1)	111.63(9)	117.2(2)/142.5(2)

[a] C_gx = ring centroid, Si/H(a) = Si/H(1) for **4** and **5** and Si/H(1/3) for **6**, Si/H(b) = Si/H(2) for **4** and **5** and Si/H(2/4) for **6**.

[b] Ln–H and Si–H distances have to be discussed carefully due to the difficulties involved in locating hydrogen atoms in close proximity of heavy atoms.

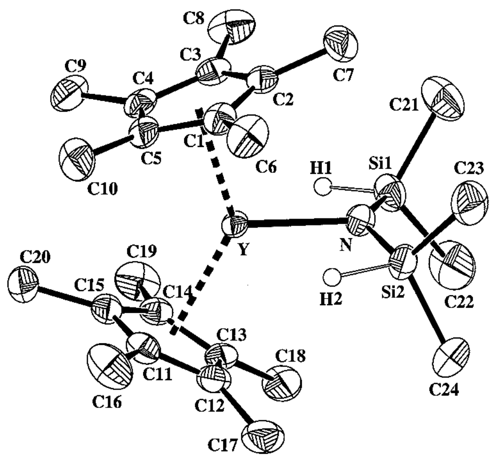


Fig. 1. PLATON [38] drawing of Cp$^*_2$Y[N(SiHMe$_2$)$_2$] (**4**). Atoms are represented by atomic displacement ellipsoids at the 50% level. Except for H(1) and H(2), all hydrogen atoms are omitted for clarity. For selected distances (Å) and angles (°) see Table 2.

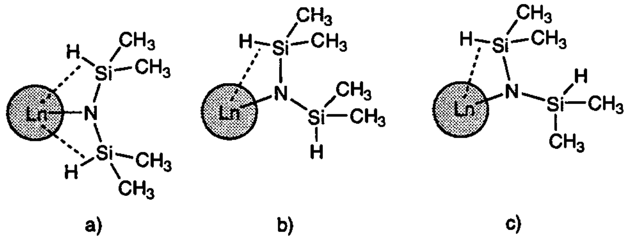


Fig. 2. Monoagostic coordination modes (a) and (b) of the silylamide moiety.

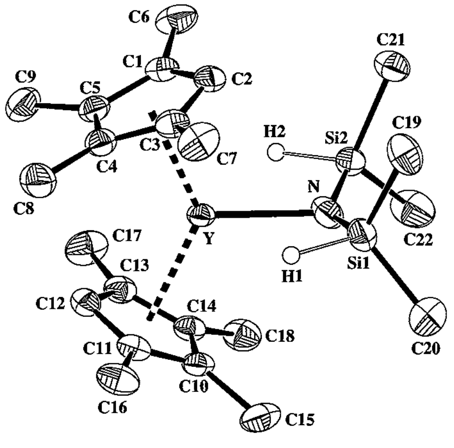


Fig. 3. PLATON [38] drawing of (Me$_4$C$_5$H)$_2$Y[N(SiHMe$_2$)$_2$] (**5**). Atoms are represented by atomic displacement ellipsoids at the 50% level. Except for H(1) and H(2), all hydrogen atoms are omitted for clarity. For selected distances (Å) and angles (°) see Table 2.

reported as 3.0524(8) Å [22]. Further evidence for a monoagostic interaction stems from the presence of one small (99.7(1)°) and one normal (124.9(1)°) Y–N–Si angle, the latter being associated with a longer Y···Si(2) distance of 3.5365(7) Å. The Si(1)–N–Si(2) angle of 134.8(1)° appears significantly widened compared to those in the synthetic precursor complex Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (**1a**) (123.1(2)–125.5(2)°). The Y–C(cyclopentadienyl) bond distances lie in the expected range. The Y–N bond length of 2.280(2) Å in complex **4** correlates well with those in seven-coordinated yttrium amide complexes, e.g., Cp$^*_2$Y[N(SiMe$_3$)$_2$] (2.274(5) Å) [23], {(*R*)-Me$_2$Si(Me$_4$C$_5$)[(−)-menthyl-C$_5$H$_3$]} Y[N(SiMe$_3$)$_2$] (2.211(8), 2.281(8) Å) [24], *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y[N(SiHMe$_2$)$_2$] (2.237(4)Å), and *rac*-[Me$_2$Si(2-Me–BenzInd)$_2$]Y[N(SiHMe$_2$)$_2$] (2.274(3) Å) [16].

The molecular structure of complex (Me$_4$C$_5$H)$_2$Y[N(SiHMe$_2$)$_2$] (**5**) demonstrates impressively the influence of steric factors on the β-SiH agostic bonding of the silylamide moiety (Fig. 3). Exchange of the pentamethylcyclopentadienyl by the tetramethylcyclopentadienyl ligands changes significantly the steric situation at the metal center. Apparently, the decreased steric crowding in complex **5** implies the competition of each of the two SiH groups for the agostic bonding at the metal center. As a consequence, a Y···(SiH) bonding is found which can be described as an intermediate between monoagostic as in complex **4** (Fig. 2b) and diagostic as in *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y[N(SiHMe$_2$)$_2$] (Fig. 2a) [16]. The Y···Si and Y···H bonds average 3.2050 and 2.73 Å, respectively. The enhanced agostic interaction in complex **5** is also revealed by the Y–N–Si and Si(1)–N–Si(2) bond angles: $\Sigma\angle$(Ln–N–Si) of 214.8° is markedly lower than in complex **4** (224.6°) and consequently the Si(1)–N–Si(2) bond angle of 139.8(1)° appears significantly widened. For comparison, an extremely widened $\angle$Si(1)–N–Si(2) of 153.3(2)° was found in *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y[N(SiHMe$_2$)$_2$] [16]. The Y–C(cyclopentadienyl) and Y–N(silylamide) bond lengths are comparable to those in complex **4**. The tetramethylcyclopentadienyl ligands feature a *staggered* 180° configuration, such that the hydrogen atoms of the cyclopentadienyl rings are mutually positioned *anti* resulting in a fully *staggered* arrangement of the five-membered rings. The same structural motif was found in plumbocene (Me$_4$C$_5$H)$_2$Pb [25]. Lanthanide complexes supported by tetramethylcyclopentadienyl ligands have been reported previously [26].

Metallocene complex (Ph$_4$C$_5$H)$_2$La[N(SiHMe$_2$)$_2$] (**6**) is the first structurally characterized lanthanidocene complex featuring tetraphenylcyclopentadienyl as an ancillary ligand, crystallizing with two crystallographically independent molecules in the unit cell (Fig. 4). Like in complex **5** and correponding metallocene complexes (Ph$_4$C$_5$H)$_2$M (M = V, Cr, Fe, Ru Co, Rh, Ni) [27] the two tetrasubstituted cyclopentadientyl ligands of the bent metallocene unit adopt a *staggered* 180° configuration featuring the unsubstituted ring carbon atoms in *anti* position. The cyclopentadienyl rings form inter-ring centroid angles of 135.2 and 136.9° and the phenyl substitutents bend away from the lanthanum

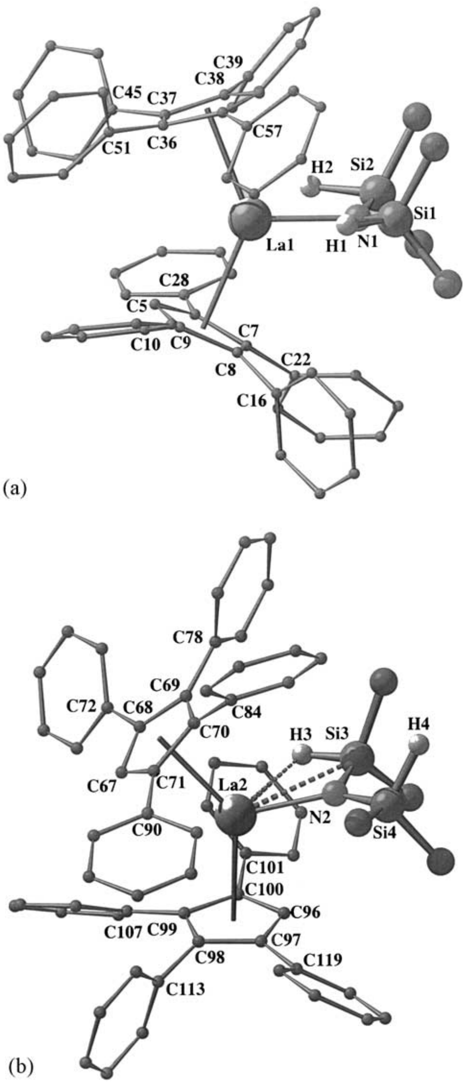


Fig. 4. SCHAKAL [39] drawing of the two crystallographically independent molecules of $(Ph_4C_5H)_2La[N(SiHMe_2)_2]$ (**6**). Except for H(1), H(2), H(3) and H(4), all hydrogen atoms are omitted for clarity. For selected distances (Å) and angles (°) see Tables 2 and 3.

center. An identical coordination behavior was found in $(Ph_4C_5H)_2TiCl$ (C_g1–Ti–C_g2, 136.4(2)°) [28]. However, in titanium complexes $(Ph_4C_5H)_2TiCl$ [28] and $(Ph_4C_5H)_2TiCl_2$ [29] the two unsubstituted carbon atoms of the two C_5 rings are found approximately in the *syn* position ('36° rotamer'). Steric repulsions of the tetraphenylcyclopentadienyl ligands also cause an elongation of the La–C_{Cp} and La–C_g distances, a common feature of such sterically crowded metallocene complexes [28,29]. The La–C_g bonds vary by as much as 0.275 Å (molecule 1) and 0.294 Å (molecule 2). For comparison, the av. La–C_{Cp} and La–C_g distances in $[Me_2Si(C_5Me_4)_2]La[N(SiHMe_2)_2]$ (**8b**) are 2.799 Å (2.738(2)–2.867(3)) and 2.524 Å [16]. The phenyl groups are randomly oriented and the interplanar angles the phenyl groups make with the cyclopentadienyl plane vary from 32.7(3) to 76.6(3)° (Table 3). For comparison, in free tetraphenylcyclopentadiene the phenyl rings are tilted in the direction of the unsubstituted C_5-ring carbon atoms [30], whereas in $(Ph_4C_5H)_2Fe$ the phenyl rings cant in the same direction [27a]. The La–N bond lengths of 2.361(5) and 2.381(4) Å in **6** are significantly shorter than that in **8b** (2.448(3) Å) and compare better with those in eight-coordinated complex $Cp^*_2La(NHMe)(H_2NMe)$ (2.32(1) Å) [31] and its five-coordinated synthetic precursor **1b** (2.395(5)–2.416(5) Å) [14]. Interestingly, the silylamide ligands of the two crystallographically independent molecules of **6** display different coordination modes. Molecule 1 features a $\Sigma\angle$(Ln–N–Si) of 224.9° which equals that in monoagostic complex **4** (224.6°), however, the difference in the Ln···Si contacts, Δ(Ln···Si), of 0.211 Å is less pronounced (**4**, 0.486 Å). In contrast, molecule 2 shows a pronounced monoagostic interaction (Δ(La···Si) of 0.696 Å) involving an unexpected orientation of one silyl group with the silicon hydrogen atom oriented away from the metal center (Fig. 2c). A similar silyl group arrangement was found previously in another sterically encumbered lanthanidocene complex, *rac*-$[Me_2Si(2\text{-}Me\text{-}BenzInd)_2]Lu[N(SiHMe_2)_2]$ [16]. The interacting La···Si and La···H contacts are in the range of those found in diagostic complex **8b** (3.2460(9)/3.2440(9) Å; 2.70(3)/2.66(4) Å) and are slightly elongated compared to σ-bonded silicon [22] and bridging hydride ligands [32], respectively, taking into account the different cation size and coordination number [33]. Similar bonding parameters were recently detected in the single-crystal neutron diffraction structure of the

Table 3
Phenyl ring/cyclopentadienyl ring interplanar angles (°) for lanthanocene complex **6**

Molecule 1								
Cp ring/phenyl ring	Cp1/Ph1	Cp1/Ph2	Cp1/Ph3	Cp1/Ph4	Cp2/Ph5	Cp2/Ph6	Cp2/Ph7	Cp2/Ph8
Interplanar angle (°)	34.7(3)	65.4(3)	45.9(3)	35.5(3)	38.0(3)	64.5(3)	47.7(3)	38.3(3)
Molecule 2								
Cp ring/phenyl ring	Cp3/Ph9	Cp3/Ph10	Cp3/Ph11	Cp3/Ph12	Cp4/Ph13	Cp4/Ph14	Cp4/Ph15	Cp4/Ph16
Interplanar angle (°)	33.6(3)	50.4(3)	49.3(3)	36.5(3)	41.0(3)	32.7(3)	76.6(3)	34.5(3)

Carbon ring planes are defined as: Cp1 (C5–C9), Ph1 (C10–C15), Ph2 (C16–C21), Ph3 (C22–C27), Ph4 (C28–C33); Cp2 (C34–C38), Ph5 (C39–C44), Ph6 (C45–C50), Ph7 (C51–C56), Ph8 (C57–C62); Cp3 (C67–C71), Ph9 (C72–C77), Ph10 (C78–C83), Ph11 (C84–C89), Ph12 (C90–C95); Cp4 (C96–C100), Ph13 (C101–C106), Ph14 (C107–C112), Ph15 (C113–C118), Ph16 (C119–C124).

monoagostic complex Cp*La[CH(SiMe$_3$)$_2$]$_2$ (La···Si, 3.35(1)–3.42(1) Å) [34]. In summary, the extraordinary sterically demanding phenyl substituents of the ancillary Cp ligands in **6** efficiently penetrate the coordination sphere of the bis(dimethylsilyl)amide ligand and counteract an effective approach of the SiH moiety at the trivalent lanthanum center.

3. Conclusions

The 'extended silylamide route' gives access to a variety of nonbridged cyclopentadienyl-derived metallocene bis(dimethylsilyl)amide complexes of the trivalent rare earth elements. According to this strategy, highly substituted cyclopentadiene derivatives such as tetraphenylcylopentadiene can afford lanthanidocene complexes from Ln[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$. In complexes (Me$_4$C$_5$H)$_2$Y[N(SiHMe$_2$)$_2$] and (Ph$_4$C$_5$H)$_2$La[N(SiHMe$_2$)$_2$], the two tetra-substituted cyclopentadienyl ligands adopt a *staggered* 180° configuration featuring the unsubstituted ring carbon atoms in *anti* position. Depending on the metal size and on the substitution pattern of the cyclopentadienyl ring, the bis(dimethylsilyl)amide ligand features various, predominantly monoagostic β-SiH coordination modes. Note that the previously reported *ansa*-bridged lanthanidocene bis(dimethylsilyl)amide complexes revealed a pronounced diagostic β-SiH silylamide bonding. We are currently examining the feasibility of second-order silylamide ligand exchange reactions in order to generate lanthanidocene alkyl and hydride derivatives.

4. Experimental

4.1. General considerations

All air- and moisture-sensitive compounds were manipulated with the rigorous exclusion of oxygen and moisture in flame-dried (180 °C) Schlenk-type glassware using standard high-vacuum technique or an argon-filled glovebox (MBraun) with $O_2/H_2O < 1$ ppm. The solvents were predried, distilled from Na/K alloy and stored in a glovebox. Deuterated solvents were obtained from Deutero GmbH and degassed and dried over Na/K alloy. Pentamethylcyclopentadiene (**2a**) and tetramethylcyclopentadiene (**2b**) were purchased from Aldrich and used as received. Tetraphenylcyclopentadiene (**2c**) was synthesized according to the literature [27b]. Metalation of **2a**, **2b** and that of 1,1,3,3,-tetramethyldisilazane was carried out with NaH or KH in THF. The [bis(dimethylsilyl)amide]lanthanide(III) precursors **1a** and **1b** were prepared as described recently [14]. NMR spectra were recorded either on a Bruker DPX-400 (FT, 400 MHz ^{1}H; 100 MHz ^{13}C) or on a JEOL JNM-GX-400 (FT, 400 MHz ^{1}H; 100 MHz ^{13}C) spectrometer. ^{1}H- and ^{13}C-NMR shifts are referenced to internal solvent resonances and reported relative to TMS. IR spectra were recorded on a Perkin–Elmer 1650-FTIR spectrometer as Nujol mulls. Elemental analyses were performed in the microanalytical laboratory of the institute.

4.2. General procedures for the preparation of lanthanidocene silylamide complexes

4.2.1. Procedure I: 'Extended silylamide route'

In a glovebox, Ln[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (**1**) and the cyclopentadiene derivative were dissolved in toluene (20 ml per mmol silylamide), refluxed for the time mentioned below and evaporated to dryness. For the tetraphenylcyclopentadiene (**2c**), the residue was re-dissolved in mesitylene (20 ml per mmol silylamide) and refluxed a second time. After the solvent was removed in vacuo, the resulting powder was treated in vacuo at 200 °C on an oil bath for 6 h. The resulting powders were extracted with a mixture of *n*-hexane and toluene and cooled to −45 °C, at which temperature pure metallocene amide complexes were obtained as single crystals.

*4.2.1.1. [bis(Dimethylsilylamido)]-bis(η^5-pentamethylcyclopentadienyl)yttrium(III) (**4**).* Following procedure I, **1a** (945 mg, 1.50 mmol) and **2a** (613 mg, 4.50 mmol) yielded **4** (563 mg, 1.15 mmol, 76%) as colourless crystals (24 h of refluxing in toluene). IR (Nujol, cm^{-1}): 2057 m (Si–H); 1827 s (Si–H$_{agostic}$), 1722 w, 1244 s, 1021 s, 908 s, 866 s, 840 s, 788 m, 758 m, 680 w, 591 w, 407 w. Anal. Calc. for $C_{24}H_{44}NSi_2Y$: C, 58.63; H, 9.02; N, 2.85. Found: C, 56.66; H, 9.11; N, 2.28%. ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 4.07 (oct, $^3J_{H,H} \approx {}^3J_{Y,H} = 2.7$ Hz, 2H, Si*H*Me$_2$), 1.97 (s, 30H, Cp–C*H*$_3$), 0.35 (d, $^3J_{H,H} = 3.0$ Hz, 12H, SiH(C*H*$_3$)$_2$). ^{13}C{^{1}H}-NMR (100 MHz, C$_6$D$_6$, 25 °C): d 119.2 (Cp), 11.8 (Cp–*C*H$_3$), 4.47 (SiH(*C*H$_3$)$_2$).

*4.2.1.2. [bis(Dimethylsilylamido)]-bis(η^5-tetramethylcyclopentadienyl)yttrium(III) (**5**).* Following procedure I, **1a** (3150 mg, 5.00 mmol) and **2b** (1222 mg, 10.00 mmol) yielded **5** (1.815 g, 3.91 mmol, 85%) as colourless crystals (18 h of refluxing in toluene). IR (Nujol, cm^{-1}): 2043 m (Si–H), 1823 (Si–H$_{agostic}$), 1729 w, 1677 w, 1244 s, 1086 s, 1022 s, 905 s, 840 s, 785 s, 758 s, 684 m, 620 m, 416 w. Anal. Calc. for $C_{22}H_{40}NSi_2Y$: C, 56.99; H, 8.70; N, 3.02. Found: C, 55.40; H, 8.63; N, 2.75%. ^{1}H-NMR (400 MHz, C$_6$D$_6$, 25 °C): δ 5.94 (s, 2H, Cp–*H*), 3.94 (oct, $^3J_{H,H} \approx {}^3J_{Y,H} = 2.7$ Hz, 2H, Si*H*Me$_2$), 1.99 (s, 12H, Cp–C*H*$_3$), 1.95 (s, 12H, Cp–C*H*$_3$), 0.30 (d, $^3J_{H,H} = 3.0$ Hz, 12H, SiH(C*H*$_3$)$_2$). ^{13}C{^{1}H}-NMR (100 MHz, C$_6$D$_6$, 25 °C): d 121.4, 118.0, 112.8 (Cp), 13.0 (Cp–*C*H$_3$), 11.9 (Cp–*C*H$_3$), 3.7 (SiH(*C*H$_3$)$_2$).

*4.2.1.3. [bis(Dimethylsilylamido)]-bis(η^5-tetraphenylcyclopentadienyl)yttrium(III) (**6**).* Following procedure I, **1b** (680 mg, 1.00 mmol) and **2c** (741 mg, 2.00 mmol) yielded **6** (788 mg, 0.78 mmol, 78%) as yellow prisms (24 h of refluxing in toluene, 24 h of refluxing in mesitylene and 6 h of heating in substance). IR (Nujol, cm^{-1}): 2068 m (Si–H), 1841 m (Si–H$_{\text{agostic}}$), 1596 s, 1246 s, 1155 w, 1073 m, 1028 s, 904 s, 840 m, 788 s, 758 s, 728 s, 695 s, 633 w, 546 w, 530 w, 464 w. Anal. Calc. for $C_{64}H_{56}LaNSi_2$: C, 73.72; H, 5.59; N, 1.38. Found: C, 73.86; H, 5.63; N, 0.98%. ^{1}H-NMR (400 MHz, C_6D_6, 25 °C): δ 7.41–6.75 (m, 48H, Cp–($C_6H_5)_4$), 4.58 (sp, $^3J_{H,H} = 2.7$ Hz, 2H, Si*H*Me$_2$), 2.10 (s, 2H, Cp–*H*), 0.06 (d, $^3J_{H,H} = 2.7$ Hz, 12H, SiH(C*H*$_3)_2$).). ^{13}C{^{1}H}-NMR (100 MHz, C_6D_6, 25 °C): δ 136.4, 136.2, 132.1, 131.7, 130.1, 129.2, 128.9, 127.8, 126.7, 126.4, 125.6, 115.0 (Cp and C(Ph)), 3.0 (NSi(*C*H$_3$).

4.2.2. Procedure II: salt metathetic route

In a glovebox, $YCl_3(THF)_{3.5}$ and two equivalents of the alkali metalated cyclopentadiene were dissolved in tetrahydrofurane (20 ml per mmol yttrium chloride), refluxed for 2.5 h and evaporated to dryness. The resulting slightly yellow powder was dissolved in toluene (10 ml per mmol yttrium chloride). The filtered solution was cooled to −45 °C, upon which the lanthanidocene chloride complexes **7a** and **7b** (contaminated with NaCl or KCl) formed as microcrystalline precipitates. Without further putification complexes **7** were dissolved in toluene (20 ml per mmol metallocene) and reacted with the equimolar amount of K[N(SiHMe$_2)_2$] forming a colourless precipitate. In order to complete the reaction, the mixture was stirred overnight. After the solvent was removed in vacuo, the resulting powder was extracted with *n*-hexane. The filtrated solution was cooled to −45 °C, upon which products **4** and **5** were obtained as crystalline precipitates.

*4.2.2.1. Tetrahydrofurane-bis(η^5-pentamethylcyclopentadienyl)yttrium(III)-chloride (**7a**).* Following procedure II, Na(C_5Me_5) (791 mg, 5.0 mmol) and $YCl_3(THF)_{3.5}$ (1.119 g, 2.5 mmol) yielded **7a** as a colourless powder. ^{1}H-NMR (400 MHz, C_6D_6, 25 °C): δ 3.50 (m, 4H, THF), 2.02 (s, 30H, Cp–C*H*$_3$), 1.56 (m, 4H, THF). Reaction with K[N(SiHMe$_2)_2$] formed **4** as evidenced by IR and NMR spectroscopy.

Table 4
X-ray diffraction collection parameters for lanthanidocene silylamide complexes

	4	**5**	**6**
Formula	$C_{24}H_{44}NSi_2Y$	$C_{22}H_{40}NSi_2Y$	$C_{62}H_{56}LaNSi_2$
Formula weight	491.69	463.64	1010.17
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	8.5516(2)	10.4856(3)	14.7720(2)
b (Å)	9.3743(3)	10.7136(2)	17.3820(3)
c (Å)	18.5896(5)	11.3501(3)	22.0910(3)
α (°)	82.8975(8)	99.8350(10)	100.2577(7)
β (°)	81.8485(15)	98.7970(10)	92.7817(7)
γ (°)	66.4549(14)	91.9650(10)	103.3384(8)
V (Å^3)	1348.68(7)	1239.14(5)	5407.17(14)
Z	2	2	4
ρ_{calc} (g cm^{-3})	1.211	1.243	1.241
μ (mm^{-1})	2.3	2.5	0.9
Crystal size (mm^3)	$0.42 \times 0.47 \times 0.49$	$0.20 \times 0.25 \times 0.45$	$0.19 \times 0.28 \times 0.88$
F(000)	524	492	2080
Temperature (K)	293	173	173
λ(Mo–K$_\alpha$) (Å)	0.71073	0.71073	0.71073
Diffractometer	Nonius-κCCD	Nonius-κCCD	Nonius-κCCD
Scan type	ω- and φ-scans	ω- and φ-scans	ω- and φ-scans
Θ Range (°)	4.7 to 26.4	1.9 to 33.1	2.0 to 25.4
No. of total/unique data ($I > 2\sigma(I)$)	24497/4758	28990/9389	62671/19793
No. of observed data	4586	8227	17481
No. of parameters	261	243	1205
Final R_1 [a]	0.0337	0.0387	0.0517
Final wR_2 [b]	0.0920	0.0914	0.1193
GOF [c]	1.07	1.04	1.14
Difference fourier (e Å^{-3})	0.66/−1.12	0.92/−0.69	2.32/−1.20

[a] $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

[b] $[\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$.

[c] $[\Sigma\, w(F_o^2 - F_c^2)^2/(N_{\text{ref}} - N_{\text{var}})]^{1/2}$.

*4.2.2.2. Tetrahydrofurane-bis(η^5-tetramethylcyclopentadienyl)yttrium(III)-chloride (**7b**).* Following procedure II, $K(C_5Me_4H)$ (1.603 g, 10.0 mmol) and $YCl_3(THF)_{3.5}$ (2.238 g, 5.0 mmol) yielded **7b** as a colourless powder. ^1H-NMR (400 MHz, C_6D_6, 25 °C): d 5.55 (s, 2H, Cp–H), 3.61 (m, 4H, THF), 1.94 (s, 12H, Cp–CH_3), 1.87 (s, 12H, Cp–CH_3), 1.77 (m, 4H, THF). $^{13}C\{^1H\}$-NMR (100 MHz, C_6D_6, 25 °C): δ 119.6, 115.6, 109.4 (Cp), 13.7 (Cp–CH_3), 12.0 (Cp–CH_3). Reaction with $K[N(SiHMe_2)_2]$ formed **5** as evidenced by IR and NMR spectroscopy.

4.3. X-ray crystallography: data collection and refinement

Single crystals of the complexes **4**, **5** and **6** were grown from hexane and toluene solutions at −45 °C. The X-ray diffraction data were collected on a Nonius kappa-CCD-system [35]. Preliminary positions of heavy atoms were found by direct methods [36], while positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least-square refinement [37]. All of the non-hydrogen positions were refined anisotropically. The final least-square refinement was performed using anisotropic thermal parameters for the non-hydrogen atoms of the metal complex and isotropic thermal parameters for the atoms of the solvate molecule. Hydrogen atoms were located from difference Fourier maps and refined isotropically only for Si–H and placed in calculated positions for all other hydrogen atoms. All details of the data collection, the crystal and refinement parameters are summarized in Table 4.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 172525, 171414 and 172415 for compounds **4**, **5** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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