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Organometallic compounds of the lanthanides

Part CIXXX. Synthesis, structure and hydrolysis of 'moderately stable' hydrosilylation catalysts $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Me)]_2$ and $[(\eta^5\text{-}C_5H_4SiMe_2{}^tBu)_2Ln(\mu\text{-}Me)]_2$[☆]

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Abstract

The lanthanidocene chloride complexes $[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Cl)]_2$ ($R = {}^tBu$, $Ln = Y$ (**1a**), Sm (**1b**), Lu (**1c**); $R = Me$, $Ln = Y$ (**2a**), Sm (**2b**), Lu (**2c**)) are prepared from the trichlorides of yttrium, samarium or lutetium and *tert*-butyldimethylsilylcyclopentadienylpotassium or trimethylsilylcyclopentadienylpotassium, respectively. Compounds **1** and **2** react with two equivalents of methyllithium in diethyl ether to give the new dimers $[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Me)]_2$ ($R = {}^tBu$, $Ln = Y$ (**3a**), Sm (**3b**), Lu (**3c**); $R = Me$, $Ln = Y$ (**4a**), Sm (**4b**), Lu (**4c**)) which are 'moderately stable' in atmospheric moisture. The reactions of **2** with methyllithium in a 1:4 molar ratio in THF yield the monomeric lanthanidocene methyl complexes $(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Me)_2Li(THF)_2$ ($Ln = Y$ (**5a**), Sm (**5b**), Lu (**5c**)). Treatment of **3** and **4** with stoichiometric amounts of H_2O in toluene yields the dimeric lanthanidocene hydroxide complexes $[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}OH)]_2$ ($R = {}^tBu$, $Ln = Y$ (**6a**), Sm (**6b**), Lu (**6c**); $R = Me$, $Ln = Y$ (**7a**), Sm (**7b**), Lu (**7c**)). The molecular structures of **1c**, **4a**, and **7c** were determined by single crystal X-ray diffraction. The lanthanidocene methyl complexes **3** and **4** are effective precatalysts for hydrosilylation of alkenes and alkynes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organolanthanide compounds; Metallocenes; Organoyttrium compounds; Organosamarium compounds; Organolutetium compounds; Hydrosilylation

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1. Introduction

Hydrosilylation is an important method for synthesizing monomeric organosilanes and organochlorosilanes as the essential components in silicon chemistry. Since 1957, the year in which Speier [2] showed hexachloroplatinic acid to be a very effective hydrosilylation catalyst, numerous other transition metal compounds were studied with respect to their activity in this field [3]. Investigations of the catalytic activity of lanthanidocenes began in 1990 showing the excellent promoting properties of lanthanidocene alkyl species for hydrosilylation of alkenes and alkynes [4–13]. Insertion of olefins into Ln–H or Ln–C bonds, σ-bond metathesis, and hydrocarbyl protonolysis predestinate lanthanidocenes as useful catalysts for homogeneous catalytic reactions [14,15]. Recently, we gave a report on our investigations of the catalytic abilities of lanthanidocene alkyl compounds bearing the tetramethyl-*iso*-propylcyclopentadienyl ligand [12]. This bulky ligand was chosen in order to reduce the air sensitivity which is normally very high for lanthanidocene alkyl compounds. Continuing our search for catalysts that are 'moderately stable' in atmospheric moisture and

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may be handled in air, at least for a short time, we synthesized lanthanidocene complexes containing silylated cyclopentadienyl ligands. The first complexes of this type, $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Cl)]_2$ or $[(\eta^5\text{-}C_5H_4SiMePh_2)_2Ln(\mu\text{-}Cl)]_2$, were prepared and structurally characterized by Lappert [16,17], Evans [18] and Spirlet [19] or by Watson [20], respectively. Very recently, Voskoboynikov and Beletskaya synthesized $[(\eta^5\text{-}C_5H_4SiMe_3)_2Lu(\mu\text{-}Me)]_2$ and successfully used this compound as a catalyst for hydrosilylation reactions [21]. The utility of the complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Me)]_2$ (Ln = Y, Er) as catalysts for olefin polymerization was already studied in 1978 by Ballard [22].

Lanthanidocene hydroxides have been known since 1988, when Evans and co-workers isolated $(\eta^5\text{-}C_5H_5)_2Y(OH)(THF)$ by reacting $(\eta^5\text{-}C_5H_5)_3Y(THF)$ with NaOH [23]. In the following years, similar complexes like $[(\eta^5\text{-}C_5H_4{}^tBu)_2Nd(\mu\text{-}OH)]_2$ [24], $[O(CH_2CH_2C_5H_4)_2Y\text{-}(\mu\text{-}OH)]_2$ [25], $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2Sm(\mu\text{-}OH)]_2$, $[(\eta^5\text{-}C_5H_4SiMe_3)_2Yb(\mu\text{-}OH)]_2$ [26], $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2Lu(\mu\text{-}OH)]_2$ [27], $[(\eta^5\text{-}C_5H_4CH_2CH_2OMe)_2Er(\mu\text{-}OH)]_2$ [28], $[(\eta^5\text{-}C_5H_4CH_2CH_2OMe)_2Ho(\mu\text{-}OH)]_2$ [29], and $[O(CH_2CH_2C_5H_4)_2Ln(\mu\text{-}N_2C_3HMe_2)\text{-}(\mu\text{-}OH)\text{-}Ln(C_5H_4CH_2CH_2)_2O]$ with Ln = Y and Lu [30] were obtained as products of hydrolysis of appropriate biscyclopentadienyl lanthanide complexes.

2. Results and discussion

2.1. Lanthanidocene chloride complexes $[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Cl)]_2$

The THF adducts of yttrium, samarium, and lutetium trichloride react with a 2-fold molar amount of *tert*-butyldimethylsilylcyclopentadienylpotassium (prepared with a 71% yield from *tert*-butyldimethylsilylcyclopentadiene and potassium hydride) or trimethylsilylcyclopentadienylpotassium in THF at ambient temperatures yielding the dimeric complexes $[(\eta^5\text{-}C_5H_4SiMe_2{}^tBu)_2Ln(\mu\text{-}Cl)]_2$ (Ln = Y **1a**, Sm **1b**, Lu **1c**) and $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Cl)]_2$ (Ln = Y **2a**, Sm **2b**, Lu **2c**) in a 57–63% or 44–75% yield, respectively. The synthesis of **2a** has been previously published [18].

$$2LnCl_3(THF)_x + 4K[C_5H_4SiMe_2R] \rightarrow \underset{\textbf{1a-c; 2a-c}}{[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Cl)]_2} + 4KCl$$

R = ^{t}Bu, Ln = Y **1a**, Sm **1b**, Lu **1c**; R = Me, Ln = Y **2a**, Sm **2b**, Lu **2c**

The yellow colored samarium complexes and the colorless yttrium and lutetium derivatives melt with decomposition and are sensitive to air and moisture. They are soluble in polar solvents like THF and diethyl ether, in aromatic solvents like toluene, and can be crystallized from *n*-hexane. The results of elemental analysis as well as the ^{1}H-NMR, $^{13}C\{^1H\}$-NMR, and mass spectra agree with their molecular formula. The mass spectra show the molecular ion peak as peak of highest mass.

The molecular structure of **1c** was determined by single crystal X-ray diffraction. Suitable crystals were obtained by crystallization from *n*-hexane at −28°C. The crystallographic data are listed in Table 1. The molecular structure is shown in Fig. 1. Each lutetium atom of the dimeric unit is coordinated by two *tert*-butyldimethylsilylcyclopentadienyl ligands and two symmetrically bridging chlorine atoms. Assuming the centroids of the η^5-bonded cyclopentadienyl rings as ligand centers (Cp), the coordination geometry around the lutetium atoms is that of a distorted pseudo tetrahedron with bond angles ranging from 82.95(10)° (Cl–Lu–Cl′) to 133.1(3)° (Cp(1)–Lu–Cp(2)). The lengths of the Lu–Cl bonds of 2.617(3) to 2.619(3) Å are consistent with the Ln–Cl bond lengths in $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2Yb(\mu\text{-}Cl)]_2$ (2.65 Å) and $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2Sc(\mu\text{-}Cl)]_2$ (2.58 Å) [32] considering the different ionic radii of the metal centers. The average Lu–Cp distance of 2.287(7) Å is similar to that in $(\eta^5\text{-}C_5Me_4{}^iPr)_2LuCl(THF)$ (2.355 Å) and $(\eta^5\text{-}C_5Me_4{}^iPr)_2LuMe(THF)$ (2.373 Å) [12]. The cyclopentadienyl rings are planar within the estimated S.D. The ring slippage is 0.064 Å for Cp(1) and 0.017 Å for Cp(2). The Si atoms of the four *tert*-butyldimethylsilyl groups are displaced from the ring planes by 0.195–0.307 Å.

2.2. Lanthanidocene methyl complexes $[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Me)]_2$ and $(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Me)_2Li(THF)_2$

Treatment of the chloro complexes **1** and **2** with two equivalents of methyllithium in diethyl ether at −78°C results in the formation of the corresponding methyl complexes $[(\eta^5\text{-}C_5H_4SiMe_2{}^tBu)_2Ln(\mu\text{-}Me)]_2$ (Ln = Y **3a**, Sm **3b**, Lu **3c**) and $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Me)]_2$ (Ln = Y **4a**, Sm **4b**, Lu **4c**) with yields of 63–77% or 49–58%, respectively. Compound **4a** was already described in [22], the synthesis of **4c** was published last year [21].

$$\underset{\textbf{1, 2}}{[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Cl)]_2} + 2MeLi \rightarrow \underset{\textbf{3a-c; 4a-c}}{[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Me)]_2} + 2LiCl$$

R = ^{t}Bu, Ln = Y **3a**, Sm **3b**, Lu **3c**; R = Me, Ln = Y **4a**, Sm **4b**, Lu **4c**

Reacting **2** with four equivalents of methyllithium in THF at −78°C produced the methyllithium bridged complexes $(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Me)_2Li(THF)_2$ (Ln = Y **5a**, Sm **5b**, Lu **5c**) in a 62–67% yield.

$$[(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Cl)]_2 + 4MeLi$$
$$\rightarrow 2(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Me)_2Li(THF)_2 + 2LiCl$$
5a-c

Ln = Y **5a**, Sm **5b**, Lu **5c**

The complexes **3**, **4**, and **5** are soluble in aprotic solvents like THF, diethyl ether, toluene, or *n*-hexane. The samarium derivatives are yellow colored substances, while the yttrium and lutetium species are colorless compounds. All complexes melt with decomposition in different temperature ranges (**3**: 212–232°C; **4**: 144–174°C; **5**: 32–162°C). In the mass spectra of compounds **3** and **4** the peak of highest mass corresponds to the ion formed by abstraction of one methyl group from the molecular ion, whereas in the spectra of compounds **5** the highest mass peak is to assign to the $[(C_5H_4SiMe_3)_2Ln]^+$ fragment. The NMR spectra of the diamagnetic yttrium and lutetium derivatives show the expected number of proton or carbon signals in the expected shift ranges, whereas the NMR signals of the paramagnetic samarium complexes are broadened and shifted to comparatively higher or lower frequencies. Coupling between yttrium and the protons and carbons of the bridging methyl groups is observed.

The molecular structure determination of **4a** proved its dimeric nature. A crystal of **4a** suitable for X-ray diffraction studies was obtained by crystallisation from *n*-hexane at −28°C. The crystallographic data are listed in Table 1. There are two independent molecules in the unit cell, which differ only little in their structure. Fig. 2 shows the molecular structure of one of the two independent molecules of **4a**. Each of the two yttrium atoms of the dimeric molecule is coordinated by two trimethylsilylcyclopentadienyl ring centroids (Cp) and two symmetrically bridging methyl groups in a distorted pseudo tetrahedral fashion with angles of 90.82(13)° (C(17)–Y(1)–C(17′)) to 130.38(9)° (Cp(1)–Y(1)–Cp(2)). This coordination geometry closely resembles the coordination sphere of the metal centers in $[(\eta^5\text{-}C_5H_5)_2Y(\mu\text{-}Me)]_2$ [33] and $[(\eta^5\text{-}C_5H_3Me_2)_2Y(\mu\text{-}Me)]_2$ [34]. The average Y–Cp distance of 2.380(2) Å is very similar to that in $(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2YI(THF)$ (2.369 Å) [17]. The average length of the Y–C(Me) σ-bond of 2.521(5) Å as well as the Y···Y′ distance of 3.536(9) Å are in good agreement with the corresponding distances in $[(\eta^5\text{-}C_5H_5)_2Y(\mu\text{-}Me)]_2$ (2.545/3.53 Å)

Table 1
Crystal data and structure refinement for **1c**, **4a**, and **7c**

	1c	**4a**	**7c**
Empirical formula	$C_{44}H_{76}Cl_2Lu_2Si_4$	$C_{34}H_{58}Si_4Y_2$	$C_{32}H_{54}Lu_2O_2Si_4$
Formula weight (g mol^{-1})	1138.25	756.98	933.05
T (K)	193(2)	163(2)	163(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions			
a (Å)	11.382(5)	12.193(2)	12.986(3)
b (Å)	14.019(8)	13.424(2)	23.607(10)
c (Å)	16.035(6)	14.643(3)	25.333(8)
α (°)	90.0	62.80(2)	90.0
β (°)	91.30(3)	68.23(2)	102.06(3)
γ (°)	90.0	81.178(14)	90.0
V (Å^3)	2558(2)	1978.2(6)	7595(4)
Z	2	2	8
$D_{calc.}$ (g cm^{-3})	1.478	1.271	1.629
μ (Mo–K$_\alpha$) (mm^{-1})	4.062	3.060	5.320
F(000)	1144	792	3664
Crystal size (mm^3)	$0.24 \times 0.18 \times 0.18$	$0.38 \times 0.33 \times 0.21$	$0.30 \times 0.24 \times 0.18$
$\theta^{min}/\theta^{max}$ (°)	1.79/23.96	1.66/23.93	1.19/23.95
Scan (°)	$1.08 + 0.35\tan\theta$	$0.71 + 0.35\tan\theta$	$0.65 + 0.35\tan\theta$
Aperture (mm)	2.3	2.5	2.2
Ref. reflections (s)	3	3	3
Dataset			
h^{min}/h^{max}	−12/12	0/13	0/14
k^{min}/k^{max}	0/15	−15/15	−7/26
l^{min}/l^{max}	0/18	−15/16	−28/28
Total/unique refl.	4285/3967	6485/6152	12593/11800
Obs. data ($I > 2(\sigma)I$)	3954	6139	11779
N_{ref}, N_{par}	3954, 225	6139, 397	11779, 730
R, wR [$I > 2\sigma(I)$], S	0.0640, 0.1539, 1.003	0.0355, 0.0811, 1.052	0.0473, 0.0940, 1.002
Max. and average shift/error	<0.001	<0.001	<0.001
Max., min. res. density (e Å^{-3})	2.156, −1.853	0.614, −0.594	1.528, −1.377

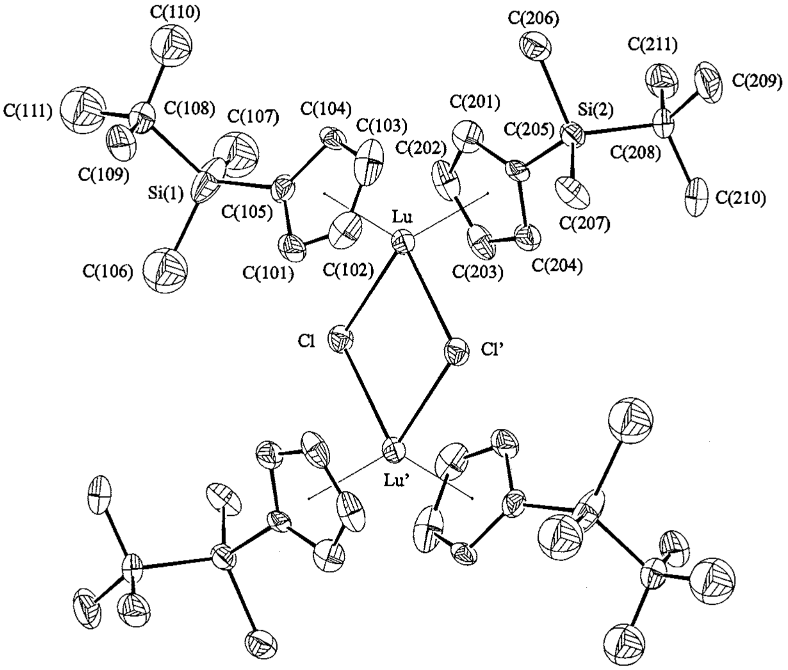

Fig. 1. ORTEP plot [31] of the molecular structure and numbering scheme of **1c** (30% probability thermal ellipsoids). All hydrogen atoms are removed for clarity. Selected distances (Å) and angles (°) with estimated S.D. (Cp denotes the center of the cyclopentadienyl ring): Lu–Cl 2.617(3), Lu–Cl'[a] 2.619(3), Lu–Cp(1)[b] 2.281(7), Lu–Cp(2)[b] 2.292(7), Lu'[a]–Cl 2.618(3), Cl–Lu–Cl'[a] 82.95(10), Lu–Cl–Lu'[a] 97.05(10), Cl–Lu–Cp(1)[b] 108.74(19), Cl'[a]–Lu–Cp(1)[b] 106.4(2), Cl–Lu–Cp(2)[b] 106.50(19), Cl'[a]–Lu–Cp(2)[b] 107.81(19), Cp(1)[b]–Lu–Cp(2)[b] 133.1(3).

[a] Symmetry transformations used to generate equivalent atoms: $-x+1,\ -y,\ -z$.

[b] Cp defines the centroid of the ring atoms Cp(1) [C(101)–C(105)], Cp(2) [C(201)–C(205)].

[33] and in $[(\eta^5\text{-}C_5H_3Me_2)_2Y(\mu\text{-}Me)]_2$ (2.60/3.58 Å) [34] if the different substituents at the cyclopentadienyl rings are taken into consideration. The two trimethylsilyl substituted cyclopentadienyl rings are slipped by 0.033 and 0.010 Å, respectively. The cyclopentadienyl rings are planar within standard deviations. The trimethylsilyl groups are displaced by 0.257–0.277 Å from the ring planes away from the yttrium atom.

In contrast to all known lanthanidocene alkyl complexes including compounds **5**, species **3** and **4** are surprisingly insensitive towards air and do not decompose immediately when brought from the protecting inert gas atmosphere into normal room atmosphere. As could be demonstrated by ^{1}H-NMR measurements of samples of **3** and **4** having been exposed to air at minute intervals, the sensitivity of the complexes to atmospheric humidity decreases with decreasing radius of the lanthanide ion in the series Sm (**b**) > Y (**a**) > Lu (**c**) and also on going from the *tert*-butyldimethylsilylcyclopentadienyl complexes (**3**) to the trimethylsilylcyclopentadienyl complexes (**4**). As shown in Table 2, after 1 min exposure to air, 60% of **3b** and **4b**, 55% of **3a**, but only 15% of **4a**, 23% of **3c**, and 7% of **4c** were decomposed. After 5 min standing on open air, **3b** and **4b** as well as **3a** were completely decomposed, whereas 21% of **3c**, 42% of **4a**, and 75% of **4c** still remained unchanged, thus distinguishing **4c** as the most air-stable complex. The ^{1}H-NMR spectra of all samples exposed to humid air for 1 min show not only the signals of the respective starting complex, but additional signals which for obvious reasons were assigned to the respective hydroxide complexes. To confirm this assignment we synthesized the hydroxide complexes **6** and **7** by stoichiometric hydrolysis of **3** and **4**, and, as expected, their ^{1}H-NMR resonances correspond with those appearing in the spectra of samples of **3** and **4** which had been placed in room atmosphere for 1 min. The data in Table 2 also indicate that the stability of the hydroxide complexes formed in the first step depends in a similar way to the ionic radius of the lanthanide ions and the kind of ligand, since the signals of the free ligand, the last stage of degradation, appear in the spectra of **3a** or **3b** after 2 min, in the spectra of **4a** or **4b** after 5 min, in the spectrum of **3c** after 10 min and not at all in the spectrum of **4c**. In conclusion, the moderate air stability of **4c** should facilitate its use as catalyst in hydrosilylation reactions since it can be handled on open air for at least the short time of weighing and mixing with the reactants without changing the results significantly.

2.3. Lanthanidocene hydroxide complexes $[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}OH)]_2$

The reactions of the lanthanidocene methyl complexes **3** and **4** with two equivalents of degassed water in toluene at room temperature (r.t) produced the corresponding hydroxide complexes $[(\eta^5\text{-}C_5H_4SiMe_2^tBu)_2Ln(\mu\text{-}OH)]_2$ (Ln = Y **6a**, Sm **6b**, Lu **6c**) and $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}OH)]_2$ (Ln = Y **7a**, Sm **7b**, Lu **7c**) with yields of 77–86%.

$$\underset{\mathbf{3,\ 4}}{[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Me)]_2} + 2H_2O$$
$$\rightarrow \underset{\mathbf{6a\text{-}c;\ 7a\text{-}c}}{[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}OH)]_2} + 2CH_4$$

R = ^{t}Bu, Ln = Y **6a**, Sm **6b**, Lu **6c**; R = Me, Ln = Y **7a**, Sm **7b**, Lu **7c**

Compounds **6** and **7** are soluble in THF, diethyl ether, or toluene, but only moderately soluble in *n*-hexane. As expected, the samarium complexes **6b** and **7b** are yellow colored solids while the yttrium and lutetium derivates are colorless substances which all melt with decomposition. In the ^{1}H-NMR spectra of the diamagnetic yttrium and lutetium compounds the signal for the OH proton appears in the range of 0.91–1.39 ppm, whereas the OH resonance of the paramagnetic samarium complexes is shifted to −11.91 for **6b** and to −11.70 ppm for **7b**. The mass spectra of **6** and **7** show the molecular ion as the peak of highest mass.

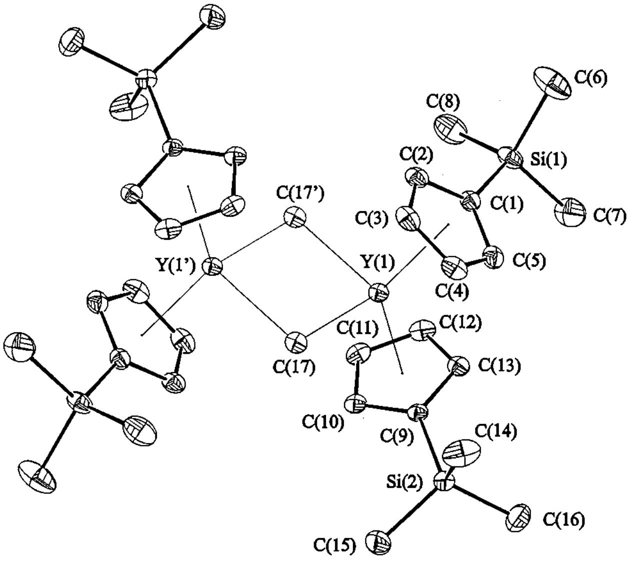

Fig. 2. ORTEP plot [31] of the molecular structure and numbering scheme of **4a** (30% probability thermal ellipsoids). All hydrogen atoms are removed for clarity. Selected distances (Å) and angles (°) with estimated S.D. (Cp denotes the center of the cyclopentadienyl ring): Y(1)–Cp(1)[a] 2.385(2), Y(1)–Cp(2)[a] 2.376(2), Y(1)···Y(1')[b] 3.5361(9), Y(1)–C(17) 2.511(4), Y(1)–C(17')[b] 2.526(5), Y(1')[b]–C(17) 2.526(4), C(17)–Y(1)–Cp(1)[a] 108.23(11), C(17)–Y(1)–Cp(2)[a] 107.22(11), C(17')[b]–Y(1)–Cp(1)[a] 106.22(12), C(17')[b]–Y(1)–Cp(2)[a] 106.83(11), Cp(1)[a]–Y(1)–Cp(2)[a] 130.38(9), C(17)–Y(1)–C(17')[b] 90.82(13), Y(1)–C(17)–Y(1')[b] 89.18(13).

[a] Cp defines the centroid of the ring atoms Cp(1) [C(1)–C(5)], Cp(2) [C(9)–C(13)].

[b] Symmetry transformations used to generate equivalent atoms: $-x+1,\ -y+1,\ -z+1$.

The molecular structure of **7c** was determined by single-crystal X-ray diffraction using a crystal obtained from *n*-hexane at −28°C. The crystal data and refinement parameters are listed in Table 1. The structure of one of the two independent molecules in the unit cell of **7c** is shown in Fig. 3. The monomeric unit is connected to dimers by Lu–O–Lu bridges. Both Lu atoms are in the center of a distorted pseudo tetrahedron built up by the two bridging oxygen atoms and the ring centroids of two η^5-bonded trimethylsilylcyclopentadienyl ligands. Inspecting the molecule containing Lu(1) and Lu(2), among the bond angles of 77.1(3) and 75.5(3)° for the O–Lu–O angles, the average bond angle of 110.0(3)° for the Cp–Lu–O angles, and the bond angles of 129.24(17) and 127.7(2)° for the Cp–Lu–Cp angles, the first most widely deviates from the ideal tetrahedral angle. As is to expect from lanthanide contraction, the average Lu–O bond distance of 2.211(8) Å is shorter than the corresponding Yb–O bond length in $[(\eta^5\text{-}C_5H_4SiMe_3)_2Yb(\mu\text{-}OH)]_2$ (2.29 Å) and the Sm–O bond length in $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)_2Sm(\mu\text{-}OH)]_2$ (2.40 Å) [26], but is comparable to the Y–O bond length in $[O(CH_2CH_2C_5H_4)_2Y(\mu\text{-}N_2C_3HMe_2)\text{-}(\mu\text{-}OH)Y(C_5H_4\text{-}CH_2CH_2)_2O]$ (2.202 Å) [30]. The average Lu–Cp distance of 2.329(6) Å is similar to that in the chloride complex **1c** (2.287(7) Å). The ring slippage is 0.039 Å for Cp(1), 0.028 Å for Cp(2), 0.029 Å for Cp(3), and 0.076 Å for Cp(4). The trimethylsilyl groups are displaced from the planar cyclopentadienyl rings by 0.096–0.289 Å and bent away from the lutetium atoms.

2.4. Activity of 3 and 4 as hydrosilylation precatalysts

To check the potential of lanthanidocene methyl complexes as precatalysts for hydrosilylation reactions, usually their influence on the addition of phenylsilane to commercially available alkenes and alkynes is studied. For this type of hydrosilylation already used to test the activity of $(\eta^5\text{-}C_5Me_5)_2YMe(THF)$ [6,9], $(\eta^5\text{-}C_5Me_5)_2Ln[CH(SiMe_3)_2]$ (Ln = Sm, Yb) [11], $(\eta^5\text{-}C_5Me_4^iPr)_2LnMe(THF)$ (Ln = Y, Lu) [12], or $(\eta^5\text{-}C_5Me_4^iPr)_2Ln[CH(SiMe_3)_2]$ (Ln = Y, Sm) [12], a catalytic cycle via an active dicyclopentadienyllanthanide hydride was outlined [6]. The results obtained with **3** and **4** as precatalysts are summarized in Tables 3 and 4. In the regioselective reactions, the phenylsilyl group is preferentially added to the less hindered carbon atom of the double or triple bond. As expected from previous experiences, the degree of regioselectivity is higher the smaller the size of the lanthanide ion. Thus, the regioselectivity should increase in the series **3b**, **4b** < **3a**, **4a** < **3c**, **4c**. The results of hydrosilylation of norbornene, 1-decene, or 4-methyl-2-hexyne in the presence of **4** confirm this expectation, since for e.g. in the case of 4-methyl-2-hexyne the two regioisomers are generated in a ratio of 3.8:1 for **4b**, of 7.7:1 for **4a**, and of 22.7:1

Table 2
Percentage composition of the reaction products of **3a**, **3b**, **3c**, **4a**, **4b** and **4c** after contact with humid air

Complex	Contact with humid air (min)	$[Cp'_2Ln(\mu\text{-}Me)]_2$ (%)	$[Cp'_2Ln(\mu\text{-}OH)]_2$ (%)	Cp′H (%)
3a	1	45	55	0
	2	0	89	11
	5	0	21	79
	10	0	11	89
3b	1	40	60	0
	2	0	4	96
	5	0	0	100
	10	0	0	100
3c	1	77	23	0
	2	58	42	0
	5	21	79	0
	10	0	24	76
4a	1	85	15	0
	2	76	24	0
	5	42	56	2
	10	7	87	6
4b	1	40	60	0
	2	11	89	0
	5	0	90	10
	10	0	61	39
4c	1	93	7	0
	2	85	15	0
	5	75	25	0
	10	56	44	0

for **4c**, whereas the reactions of phenylsilane with 1-methylene-norbornane or 2-nonyne do not depend of the size of the lanthanide ion. In comparison to the above-mentioned complexes $(\eta^5\text{-}C_5Me_4R)_2LnMe(THF)$ and $(\eta^5\text{-}C_5Me_4R)_2Ln[CH(SiMe_3)_2]$ (R = Me or ^{i}Pr) [6,9,11,12], some hydrosilylation reactions catalyzed by **3** and **4** led to different regioselectivity patterns. For example, the hydrosilylation of 2-nonyne using $(\eta^5\text{-}C_5Me_4{}^iPr)_2LuMe(THF)$ or $(\eta^5\text{-}C_5Me_4{}^iPr)_2Y[CH(SiMe_3)_2]$ as catalysts produced the corresponding regioisomers in ratios of 3.9:1 or 4.0:1 [12], whereas the ratios are 1.0:1 or 1.1:1 using **3** or **4** as catalysts. No dependence on regioselectivity was observed concerning the different substituents of the cyclopentadienyl ligand in **3** and **4**.

3. Experimental

3.1. General

All operations involving organometallics were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled vacuum atmospheres glovebox in dry, oxygen-free solvents. Solvents were freshly distilled from sodium benzophenone ketyl. Melting points were determined in sealed capillaries with a HWS-SG 2000 melting point determination apparatus and are uncorrected. The ^1H- (200 MHz) and $^{13}C\{^1H\}$- (50.32 MHz) NMR spectra were recorded on a Bruker ARX 200 spectrometer. All ^1H- and ^{13}C-NMR chemical shifts are reported in ppm relative to the ^1H- and ^{13}C- residue of the deuterated solvents. Mass spectra (EI, 70 eV) were obtained by using a Varian MAT 311 A instrument. Only characteristic fragments and isotopes of the highest abundance are listed. Elemental analyses were carried out on a Perkin–Elmer Series II CHNS/O Analyser 2400. *tert*-Butyldimethylsilylcyclopentadiene [35], cyclopentadienylsodium [36], trimethylsilylcyclopentadienylpotassium [37], and the lanthanide trichloride THF adducts of yttrium, samarium and lutetium [38] were prepared according to published procedures. Methyllithium and potassium hydride were used as purchased.

3.2. (η^5-tert-Butyldimethylsilylcyclopentadienyl)-potassium

A sample of KH (5.33 g, 132.9 mmol) was added to a stirred solution of 22.33 g (123.8 mmol) of *tert*-butyldimethylsilylcyclopentadiene in 130 ml of THF. The mixture was stirred for 2 h and filtered from solid impurities. The solvent was removed in vacuum and the residue was washed with *n*-hexane. Drying in a vacuum gave the product as a white powder (19.21 g, 71%). ^1H-NMR (pyridine-d_5): δ 6.46 (m, 2H, C_5H_4), 6.40 (m, 2H, C_5H_4), 1.11 (s, 9H, $SiC(CH_3)_3$), 0.34 (s, 6H, $Si(CH_3)_2$). $^{13}C\{^1H\}$-NMR (pyridine-d_5): δ 114.39 (C_5H_4), 108.41 (C_5H_4) 108.21 ($C_5Si(CH_3)_2C(CH_3)_3$), 27.87 ($Si(CH_3)_2C(CH_3)_3$), 18.04 ($Si(CH_3)_2C(CH_3)_3$), −3.03 ($Si(CH_3)_2C(CH_3)_3$). Anal. Calc. for $C_{11}H_{19}KSi$ (218.46 g mol^{-1}): C, 60.48; H, 8.77. Found: C, 59.99; H, 8.72.

3.3. Lanthanidocene chloride complexes $[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Cl)]_2$

*3.3.1. Di(μ-chlorobis(η^5-tert-butyldimethylsilylcyclopentadienyl)yttrium) (**1a**)*

To a suspension of 1.67 g (4.06 mmol) of $YCl_3(THF)_3$ in 70–80 ml of THF were added 1.80 g (8.24 mmol) of $K[C_5H_4SiMe_2{}^tBu]$ at r.t. The reaction mixture was heated to reflux for 3 h. After removal of THF in vacuum, the residue was treated with 75 ml of *n*-hexane. The solution was decanted from undissolved KCl, concentrated to 25 ml and cooled to −28°C to provide 1.23 g (63%) of colorless crystalline **1a**; m.p. 232°C dec. ^1H-NMR (benzene-d_6): δ 6.85 (m, 8H, C_5H_4), 6.47 (m, 8H, C_5H_4), 0.90 (s, 36H, $C_5Si(CH_3)_2C(CH_3)_3$), 0.38 (s, 24H, $C_5Si(CH_3)_2C(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 122.22 ($C_5Si(CH_3)_2C(CH_3)_3$), 121.34 (C_5H_4), 117.34 (C_5H_4), 26.89 ($C_5Si(CH_3)_2C(CH_3)_3$), 17.84 ($C_5Si(CH_3)_2C(CH_3)_3$), −4.81 (C_5Si-

$(C\mathrm{H_3})_2\mathrm{C(CH_3)_3}$). MS (^{89}Y, 245°C) *m/z* (relative intensity, %): 949 (1) $[M\mathrm{-Me}]^+$, 785 (16) $[(\mathrm{C_5H_4Si}^t\mathrm{BuMe_2})_3\mathrm{Y_2Cl_2}]^+$, 482 (2) $[(\mathrm{C_5H_4Si}^t\mathrm{BuMe_2})_2\mathrm{YCl}]^+$, 447 (100) $[(\mathrm{C_5H_4Si}^t\mathrm{BuMe_2})_2\mathrm{Y}]^+$. Anal. Calc. for $\mathrm{C_{44}H_{76}Cl_2Si_4Y_2}$ (966.15 g mol^{-1}): C, 54.70; H, 7.93. Found: C, 54.33; H, 7.80.

3.3.2. *Di(μ-chlorobis(η^5-tert-butyldimethylsilylcyclopentadienyl)samarium) (**1b**)*

In analogy to the preparation of **1a**, 1.72 g (4.29 mmol) of $\mathrm{SmCl_3(THF)_2}$ were reacted with 1.90 g (8.70 mmol) of $\mathrm{K[C_5H_4Si}^t\mathrm{BuMe_2]}$ to give 1.33 g (57%) of yellow crystalline **1b**; m.p. >250°C dec. ^{1}H-NMR (benzene-d_6): δ 18.01 (s, 8H, $\mathrm{C_5}H_4$), 11.74 (s, 8H, $\mathrm{C_5}H_4$), 1.35 (s, 36H, $\mathrm{C_5Si(CH_3)_2C(C}H_3)_3$), −3.48 (s, 24H, $\mathrm{C_5Si(C}H_3)_2\mathrm{C(CH_3)_3}$). ^{13}C{^{1}H}-NMR (benzene-d_6): δ 124.17 ($C_5\mathrm{H_4}$), 118.40 ($C_5\mathrm{Si(CH_3)_2C(CH_3)_3}$), 116.08 ($C_5\mathrm{H_4}$), 26.82 ($\mathrm{C_5Si(CH_3)_2C(}C\mathrm{H_3)_3}$), 16.61 ($\mathrm{C_5Si(CH_3)_2}C\mathrm{(CH_3)_3}$), −8.67 ($\mathrm{C_5Si(}C\mathrm{H_3)_2C(CH_3)_3}$). MS (^{152}Sm, 276°C) *m/z* (relative intensity, %): 1075 (1) $[M\mathrm{-Me}]^+$, 911 (1) $[(\mathrm{C_5H_4Si}^t\mathrm{BuMe_2})_3\mathrm{Sm_2Cl_2}]^+$, 545 (2) $[(\mathrm{C_5H_4Si}^t\mathrm{BuMe_2})_2\mathrm{SmCl}]^+$, 510 (8) $[(\mathrm{C_5H_4Si}^t\mathrm{BuMe_2})_2\mathrm{Sm}]^+$. Anal. Calc. for $\mathrm{C_{44}H_{76}Cl_2Si_4Sm_2}$ (1089.06 g mol^{-1}): C, 48.53; H, 7.03. Found: C, 49.20; H, 6.49.

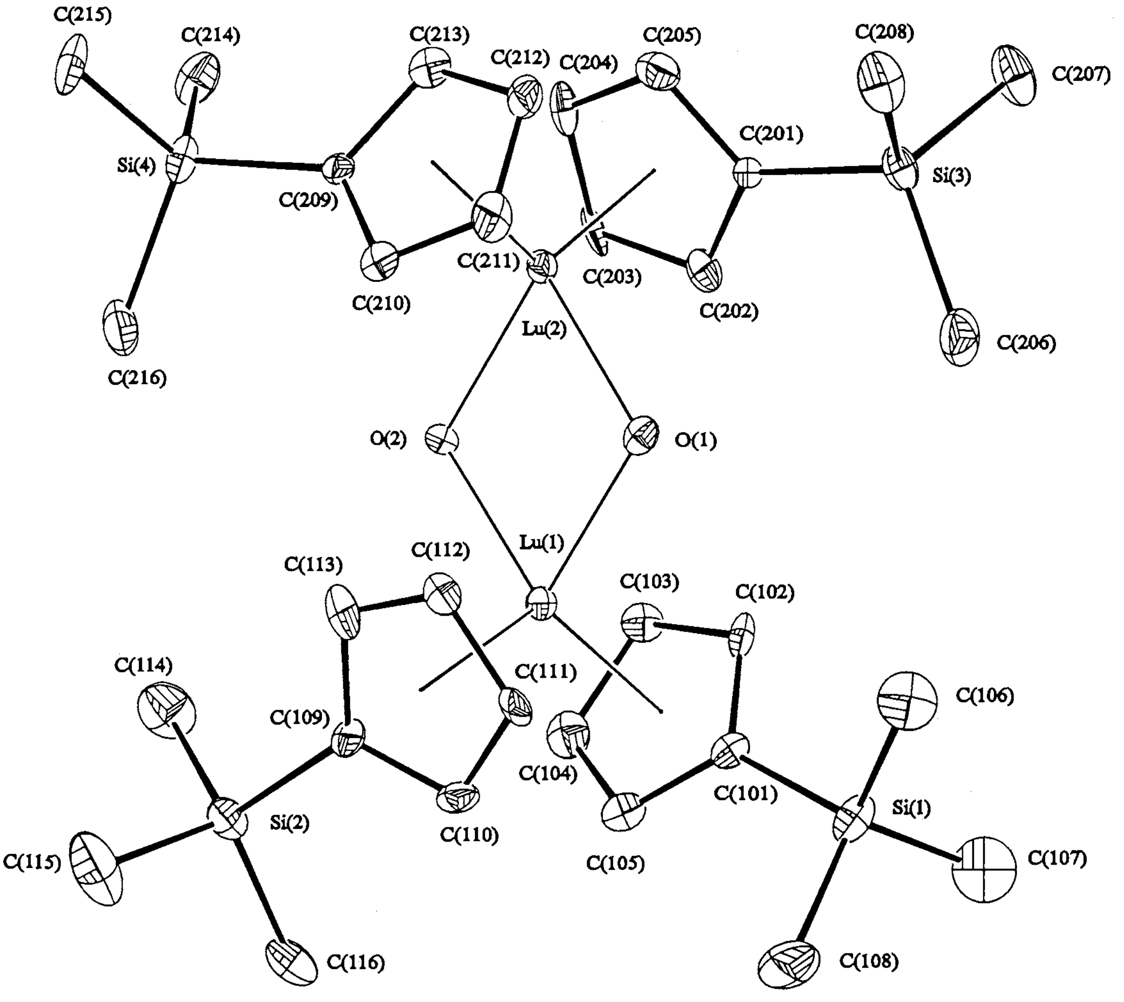

Fig. 3. ORTEP plot [31] of the molecular structure and numbering scheme of **7c** (30% probability thermal ellipsoids). All hydrogen atoms are removed for clarity. Selected distances (Å) and angles (°) with estimated S.D. (Cp denotes the center of the cyclopentadienyl ring): Lu(1)–O(1) 2.183(8), Lu(1)–O(2) 2.200(8), Lu(2)–O(1) 2.227(8), Lu(2)–O(2) 2.232(8), Lu(1)–Cp(1)^a 2.334(6), Lu(1)–Cp(2)^a 2.339(6), Lu(2)–Cp(3)^a 2.325(6), Lu(2)–Cp(4)^a 2.319(5), O(1)–Lu(1)–Cp(1)^a 111.3(3), O(1)–Lu(1)–Cp(2)^a 106.9(2), O(2)–Lu(1)–Cp(1)^a 109.6(2), O(2)–Lu(1)–Cp(2)^a 110.5(2), O(1)–Lu(2)–Cp(3)^a 113.1(3), O(1)–Lu(2)–Cp(4)^a 107.1(2), O(2)–Lu(2)–Cp(3)^a 107.9(2), O(2)–Lu(2)–Cp(4)^a 113.6(2), Cp(1)^a–Lu(1)–Cp(2)^a 129.24(17), Cp(3)^a–Lu(2)–Cp(4)^a 127.7(2), O(1)–Lu(1)–O(2) 77.1(3), O(1)–Lu(2)–O(2) 75.5(3), Lu(1)–O(1)–Lu(2) 104.0(3), Lu(1)–O(2)–Lu(2) 103.3(3).

[a] Cp defines the centroid of the ring atoms Cp(1) [C(101)–C(105)], Cp(2) [C(109)–C(113)], Cp(3) [C(201)–C(205)], Cp(4) [C(209)–C(213)].

Table 3
Hydrosilylation of alkenes and alkynes utilizing $[(\eta^5\text{-}C_5H_4SiMe_2^tBu)_2Ln(\mu\text{-}Me)]_2$ (Ln = Y (**3a**), Sm (**3b**), Lu (**3c**))

Entry	Substrate	Product(s)	Catalyst	Yield (%)[a]
1a	1-Decene	1-(Phenylsilyl)decane, 2-(phenylsilyl)decane	**3a**[b]	98 (40.3:1.0)[c]
1b			**3b**[b]	96 (6.7:1.0)[c]
1c			**3c**[b]	94 (130.2:1.0)[c]
2a	2,4-Dimethyl-1-hexene	2,4-Dimethyl-1-(phenylsilyl)hexane	**3a**[d]	83
2b			**3b**[d]	80
2c			**3c**[d]	84
3a	3,3-Dimethyl-1-hexene	3,3-Dimethyl-1-(phenylsilyl)hexane	**3a**[d]	97
3b			**3b**[d]	96
3c			**3c**[d]	96
4a	1-Methylene-norbornane	1-(Phenylsilyl)methyl-norbornane, 1-methyl-1-(phenylsilyl)-norbornane	**3a**[d]	88 (7.7:1.0)[c]
4b			**3b**[d]	86 (7.6:1.0)[c]
4c			**3c**[d]	96 (9.3:1.0)[c]
5a	Norbornene	*exo*-1-(Phenylsilyl)-norbornane, *endo*-1-(phenylsilyl)-norbornane	**3a**[d]	93 (18.4:1.0)[c]
5b			**3b**[d]	93 (3.6:1.0)[c]
5c			**3c**[d]	94[e]
6a	2-Nonyne	2-(Phenylsilyl)-2-nonene, 3-(phenylsilyl)-2-nonene	**3a**[d]	71 (1.0:1.0)[c]
6b			**3b**[d]	69 (1.1:1.0)[c]
6c			**3c**[d]	85 (1.0:1.0)[c]
7a	4-Methyl-2-hexyne	4-Methyl-2-(phenylsilyl)-2-hexene, 4-methyl-3-(phenylsilyl)-2-hexene	**3a**[d]	85 (8.3:1.0)[c]
7b			**3b**[d]	85 (5.2:1.0)[c]
7c			**3c**[d]	86 (25.2:1.0)[c]

[a] Isolated yields.
[b] 2 h at room temperature.
[c] Ratios were determined on the crude mixture by fused silica capillary gas chromatography.
[d] 12 h at room temperature.
[e] Only *exo*-1-(phenylsilyl)-norbornane was detected.

3.3.3. *Di(μ-chlorobis(η⁵-tert-butyldimethylsilylcyclopentadienyl)lutetium)* (**1c**)

In analogy to the preparation of **1a**, 1.47 g (2.95 mmol) of $LuCl_3(THF)_3$ were reacted with 1.35 g (6.18 mmol) of $K[C_5H_4Si^tBuMe_2]$ to give 1.01 g (60%) of colorless crystalline **1c**; m.p. > 250° C dec. ^{1}H-NMR (benzene-d_6): δ 6.86 (m, 8H, C_5H_4), 6.40 (m, 8H, C_5H_4), 0.90 (s, 36H, $C_5Si(CH_3)_2C(CH_3)_3$), 0.37 (s, 24H, $C_5Si(CH_3)_2C(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 122.01 (C_5H_4), 118.70 ($C_5Si(CH_3)_2C(CH_3)_3$), 115.96 (C_5H_4), 26.58 ($C_5Si(CH_3)_2C(CH_3)_3$), 17.55 ($C_5Si(CH_3)_2C(CH_3)_3$), −5.18 ($C_5Si(CH_3)_2C(CH_3)_3$). MS (^{175}Lu, 277°C) m/z (relative intensity, %): 1121 (1) $[M{-}Me]^+$, 957 (24) $[(C_5H_4Si^tBuMe_2)_3Lu_2Cl_2]^+$, 568 (1) $[(C_5H_4Si^tBuMe_2)_2LuCl]^+$, 533 (74) $[(C_5H_4Si^tBuMe_2)_2Lu]^+$. Anal. Calc. for $C_{44}H_{76}Cl_2Lu_2Si_4$ (1138.27 g mol^{-1}): C, 46.43; H, 6.73. Found: C, 46.89; H, 6.58.

3.3.4. *Di(μ-chlorobis(η⁵-trimethylsilylcyclopentadienyl)yttrium)* (**2a**)

In analogy to the preparation of **1a**, 1.34 g (3.26 mmol) of $YCl_3(THF)_3$ were reacted with 1.15 g (6.52 mmol) of $K[C_5H_4SiMe_3]$ to give 0.98 g (75%) of colorless crystalline **2a**; m.p. 128°C dec. ^{1}H-NMR (benzene-d_6): δ 6.78 (m, 8H, C_5H_4), 6.45 (m, 8H, C_5H_4), 0.30 (s, 36H, $C_5Si(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 123.50 ($C_5Si(CH_3)_3$), 121.03 (C_5H_4), 116.98 (C_5H_4), 0.27 ($C_5Si(CH_3)_3$). MS (^{89}Y, 140°C) m/z (relative intensity, %): 796 (13) $[M]^+$, 659 (89) $[(C_5H_4SiMe_3)_3Y_2Cl_2]^+$, 398 (1) $[(C_5H_4SiMe_3)_2YCl]^+$, 363 (100) $[(C_5H_4SiMe_3)_2Y]^+$. Anal. Calc. for $C_{32}H_{52}Cl_2Si_4Y_2$ (797.82 g mol^{-1}): C, 48.17; H, 6.57. Found: C, 49.18; H, 6.16.

*3.3.5. Di(μ-chlorobis(η^5-trimethylsilylcyclopentadienyl)samarium) (**2b**)*

In analogy to the preparation of **1a**, 1.56 g (3.89 mmol) of $SmCl_3(THF)_2$ were reacted with 1.38 g (7.82 mmol) of $K[C_5H_4SiMe_3]$ to give 0.90 g (50%) of yellow crystalline **2b**; m.p. 151°C dec. ^{1}H-NMR (benzene-d_6): δ 18.13 (s, 8H, C_5H_4), 11.61 (s, 8H, C_5H_4), −2.36 (s, 36H, $C_5Si(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 123.32 (C_5H_4), 119.70 ($C_5Si(CH_3)_3$), 118.20 (C_5H_4), −2.84 ($C_5Si(CH_3)_3$). MS (^{152}Sm, 140°C) m/z (relative intensity, %): 922 (3) $[M]^+$, 785 (21) $[(C_5H_4SiMe_3)_3Sm_2Cl_2]^+$, 461 (1) $[(C_5H_4SiMe_3)_2SmCl]^+$, 426 (100) $[(C_5H_4SiMe_3)_2Sm]^+$. Anal. Calc. for $C_{32}H_{52}Cl_2Si_4Sm_2$ (920.73 g mol^{-1}): C, 41.74; H, 5.69. Found: C, 40.47; H, 5.82.

*3.3.6. Di(μ-chlorobis(η^5-trimethylsilylcyclopentadienyl)lutetium) (**2c**)*

In analogy to the preparation of **1a**, 1.27 g (2.55 mmol) of $LuCl_3(THF)_3$ were reacted with 0.90 g (2.55 mmol) of $K[C_5H_4SiMe_3]$ to give 0.55 g (44%) of colorless crystalline **2c**; m.p. 194°C dec. ^{1}H-NMR (benzene-d_6): δ 6.78 (m, 8H, C_5H_4), 6.39 (m, 8H, C_5H_4), 0.30 (s, 36H, $C_5Si(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 121.68 ($C_5Si(CH_3)_3$), 121.12 (C_5H_4), 115.93 (C_5H_4), 0.44 ($C_5Si(CH_3)_3$). MS (^{175}Lu, 160°C) m/z (relative intensity, %): 968 (5) $[M]^+$, 831 (46) $[(C_5H_4SiMe_3)_3Lu_2Cl_2]^+$, 484 (2) $[(C_5H_4SiMe_3)_2LuCl]^+$, 449 (100) $[(C_5H_4SiMe_3)_2Lu]^+$. Anal. Calc. for $C_{32}H_{52}Cl_2Lu_2Si_4$ (969.95 g mol^{-1}): C, 39.63; H, 5.40. Found: C, 40.01; H, 5.69.

3.4. Lanthanidocene methyl complexes $[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}Me)]_2$ and $(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Me)_2Li(THF)_2$

*3.4.1. Di(bis(η^5-tert-butyldimethylsilylcyclopentadienyl)-μ-methylyttrium) (**3a**)*

To a solution of 0.79 g (0.82 mmol) of **1a** in 75 ml of diethyl ether was added dropwise 1.1 ml of a 1.6 M ethereal solution of methyllithium (1.76 mmol) at

Table 4
Hydrosilylation of alkenes and alkynes utilizing $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ln(\mu\text{-}Me)]_2$ (Ln = Y (**4a**), Sm (**4b**), Lu (**4c**))

Entry	Substrate	Product(s)	Catalyst	Yield (%)[a]
8a	1-Decene	1-(Phenylsilyl)decane, 2-(phenylsilyl)decane	**4a**[b]	88 (48.9:1.0)[c]
8b			**4b**[b]	89 (7.6:1.0)[c]
8c			**4c**[b]	86 (95.0:1.0)[c]
9a	2,4-Dimethyl-1-hexene	2,4-Dimethyl-1-(phenylsilyl)hexane	**4a**[d]	80
9b			**4b**[d]	81
9c			**4c**[d]	88
10a	3,3-Dimethyl-1-hexene	3,3-Dimethyl-1-(phenylsilyl)hexane	**4a**[d]	93
10b			**4b**[d]	94
10c			**4c**[d]	96
11a	1-Methylene-norbornane	1-(Phenylsilyl)methyl-norbornane,	**4a**[d]	85 (7.7:1.0)[c]
11b		1-methyl-1-(phenylsilyl)-norbornane	**4b**[d]	79 (7.6:1.0)[c]
11c			**4c**[d]	80 (7.7:1.0)[c]
12a	Norbornene	*exo*-1-(Phenylsilyl)-norbornane,	**4a**[d]	91 (11.5:1.0)[c]
12b		*endo*-1-(phenylsilyl)-norbornane	**4b**[d]	85 (2.0:1.0)[c]
12c			**4c**[d]	97[e]
13a	2-Nonyne	2-(Phenylsilyl)-2-nonene, 3-(phenylsilyl)-2-nonene	**4a**[d]	75 (1.1:1.0)[c]
13b			**4b**[d]	71 (1.1:1.0)[c]
13c			**4c**[d]	77 (1.0:1.0)[c]
14a	4-Methyl-2-hexyne	4-Methyl-2-(phenylsilyl)-2-hexene,	**4a**[d]	83 (7.7:1.0)[c]
14b		4-methyl-3-(phenylsilyl)-2-hexene	**4b**[d]	86 (3.8:1.0)[c]
14c			**4c**[d]	86 (22.7:1.0)[c]

[a] Isolated yields.

[b] 2 h at room temperature.

[c] Ratios were determined on the crude mixture by fused silica capillary gas chromatography.

[d] 12 h at room temperature.

[e] Only *exo*-1-(phenylsilyl)-norbornane was detected.

−78°C. The reaction mixture was stirred for 3 h at this temperature. After warming to r.t., the solvent was removed in vacuum and the residue was extracted with 80 ml of *n*-hexane. The clear *n*-hexane solution was concentrated to 25 ml and cooled to −28°C to provide 0.52 g (69%) of colorless crystalline **3a**; m.p. 212°C dec. ^{1}H-NMR (benzene-d_6): δ 6.78 (m, 8H, C_5H_4), 6.32 (m, 8H, C_5H_4), 0.90 (s, 36H, $C_5Si(CH_3)_2C(CH_3)_3$), 0.33 (s, 24H, $C_5Si(CH_3)_2C(CH_3)_2$), −0.74 (t, $^2J(^{89}Y,^1H) = 3$ Hz, 6H, YCH_3). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 121.06 (C_5H_4), 115.76 ($C_5Si(CH_3)_2C(CH_3)_3$), 114.30 (C_5H_4), 26.34 ($C_5Si(CH_3)_2C(CH_3)_3$), 25.04 (t, $^1J(^{89}Y,^{13}C) = 50$ Hz, YCH_3), 17.37 ($C_5Si(CH_3)_2C(CH_3)_3$), −5.19 ($C_5Si(CH_3)_2C(CH_3)_3$). MS (^{89}Y, 210°C) m/z (relative intensity, %): 909 (34) $[(C_5H_4Si^tBuMe_2)_4Y_2Me]^+$, 745 (5) $[(C_5H_4Si^tBuMe_2)_3Y_2Me_2]^+$, 447 (100) $[(C_5H_4Si^tBuMe_2)_2Y]^+$. Anal. Calc. for $C_{46}H_{82}Si_4Y_2$ (925.31 g mol^{-1}): C, 59.71; H, 8.93. Found: C, 59.22; H, 8.66.

3.4.2. Di(bis(η^5-tert-butyldimethylsilylcyclopentadienyl)-μ-methylsamarium) (3b)

In analogy to the preparation of **3a**, 0.78 g (0.72 mmol) of **1b** were reacted with 1.0 ml of a 1.6 M ethereal solution of methyllithium (1.60 mmol) to give 0.58 g (77%) of yellow crystalline **3b**; m.p. 232°C dec. ^{1}H-NMR (benzene-d_6): δ 15.76 (s, 8H, C_5H_4), 10.36 (s, 8H, C_5H_4), 1.45 (s, 36H, $C_5Si(CH_3)_2C(CH_3)_3$), −2.39 ($C_5Si(CH_3)_2C(CH_3)_3$), −26.04 (s, 6H, $SmCH_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 126.37 (C_5H_4), 123.66 ($C_5Si(CH_3)_2C(CH_3)_3$), 116.46 (C_5H_4), 26.98 ($C_5Si(CH_3)_2C(CH_3)_3$), 17.26 ($C_5Si(CH_3)_2C(CH_3)_2$), −7.36 ($C_5Si(CH_3)_2C(CH_3)_3$). MS (^{152}Sm, 241°C) m/z (relative intensity, %): 1035 (12) $[(C_5H_4Si^tBuMe_2)_4Sm_2Me]^+$, 871 (3) $[(C_5H_4Si^tBuMe_2)_3Sm_2Me_2]^+$, 510 (100) $[(C_5H_4Si^tBuMe_2)_2Sm]^+$. Anal. Calc. for $C_{46}H_{82}Si_4Sm_2$ (1048.22 g mol^{-1}): C, 52.71; H, 7.88. Found: C, 53.01; H, 7.72.

3.4.3. Di(bis(η^5-tert-butyldimethylsilylcyclopentadienyl)-μ-methyllutetium) (3c)

In analogy to the preparation of **3a**, 0.95 g (0.83 mmol) of **1c** were reacted with 1.1 ml of a 1.6 M ethereal solution of methyllithium (1.76 mmol) to give 0.57 g (63%) of colorless crystalline **3c**; m.p. 225°C dec. ^{1}H-NMR (benzene-d_6): δ 6.76 (m, 8H, C_5H_4), 6.22 (m, 8H, C_5H_4), 0.90 (s, 36H, $C_5Si(CH_3)_2C(CH_3)_3$), 0.33 (s, 24H, $C_5Si(CH_3)_2C(CH_3)_3$), −0.31 (s, 6H, $LuCH_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 121.64 (C_5H_4), 114.12 ($C_5Si(CH_3)_2C(CH_3)_3$), 113.55 (C_5H_4), 29.29 ($LuCH_3$), 26.60 ($C_5Si(CH_3)_2C(CH_3)_3$), 17.66 ($C_5Si(CH_3)_2C(CH_3)_3$), −5.01 ($C_5Si(CH_3)_2C(CH_3)_3$). MS (^{175}Lu, 273°C) m/z (relative intensity, %): 1081 (1) $[(C_5H_4Si^tBuMe_2)_4Lu_2Me]^+$, 917 (5) $[(C_5H_4Si^tBuMe_2)_3Lu_2Me_2]^+$, 548 (10) $[(C_5H_4Si^tBuMe_2)_2LuMe]^+$, 533 (100) $[(C_5H_4Si^tBuMe_2)_2Lu]^+$. Anal. Calc. for $C_{46}H_{82}Lu_2Si_4$ (1097.43 g mol^{-1}): C, 50.35; H, 7.53. Found: C, 50.10; H, 7.42.

3.4.4. Di(bis(η^5-trimethylsilylcyclopentadienyl)-μ-methylyttrium) (4a)

In analogy to the preparation of **3a**, 0.90 g (1.13 mmol) of **2a** were reacted with 1.4 ml of a 1.6 M ethereal solution of methyllithium (2.24 mmol) to give 0.48 g (56%) of colorless crystalline **4a**; m.p. 174°C dec. ^{1}H-NMR (benzene-d_6): δ 6.72 (m, 8H, C_5H_4), 6.31 (m, 8H, C_5H_4), 0.29 (s, 36H, $C_5Si(CH_3)_3$), −0.75 (t, $^2J(^{89}Y,^1H) = 1$ Hz, 6H, YCH_3). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 120.63 (C_5H_4), 118.75 ($C_5Si(CH_3)_3$), 114.62 (C_5H_4), 24.64 (t, $^1J(^{89}Y,^{13}C) = 25$ Hz, YCH_3), 0.63 ($C_5Si(CH_3)_3$). MS (^{89}Y, 200°C) m/z (relative intensity, %): 756 (1) $[M]^+$, 741 (57) $[(C_5H_4SiMe_3)_4Y_2Me]^+$, 619 (2) $[(C_5H_4SiMe_3)_3Y_2Me_2]^+$, 363 (100) $[(C_5H_4SiMe_3)_2Y]^+$. Anal. Calc. for $C_{34}H_{58}Si_4Y_2$ (756.99 g mol^{-1}): C, 53.95; H, 7.72. Found: C, 54.36; H, 7.75.

3.4.5. Di(bis(η^5-trimethylsilylcyclopentadienyl)-μ-methylsamarium) (4b)

In analogy to the preparation of **3a**, 0.94 g (1.02 mmol) of **2b** were reacted with 1.3 ml of a 1.6 M ethereal solution of methyllithium (2.08 mmol) to give 0.52 g (58%) of yellow crystalline **4b**; m.p. 144°C dec. ^{1}H-NMR (benzene-d_6): δ 15.55 (s, 8H, C_5H_4), 10.43 (s, 8H, C_5H_4), −1.36 (s, 36H, $C_5Si(CH_3)_3$), −25.95 (s, 6H, $SmCH_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 122.78 (C_5H_4), 116.83 ($C_5Si(CH_3)_3$), 116.56 (C_5H_4), −1.30 ($C_5Si(CH_3)_3$). MS (^{152}Sm, 180°C) m/z (relative intensity, %): 867 (2) $[(C_5H_4SiMe_3)_4Sm_2Me]^+$, 852 (2) $[(C_5H_4SiMe_3)_4Sm_2]^+$, 426 (100) $[(C_5H_4SiMe_3)_2Sm]^+$, 289 (41) $[(C_5H_4SiMe_3)Sm]^+$. Anal. Calc. for $C_{34}H_{58}Si_4Sm_2$ (879.90 g mol^{-1}): C, 46.41; H, 6.64. Found: C, 46.56; H, 7.19.

3.4.6. Di(bis(η^5-trimethylsilylcyclopentadienyl)-μ-methyllutetium) (4c)

In analogy to the preparation of **3a**, 0.89 g (0.92 mmol) of **2c** were reacted with 1.2 ml of a 1.6 M ethereal solution of methyllithium (1.92 mmol) to give 0.42 g (49%) of colorless crystalline **4c**; m.p. 169°C dec. ^{1}H-NMR (benzene-d_6): δ 6.70 (m, 8H, C_5H_4), 6.23 (m, 8H, C_5H_4), 0.29 (s, 36H, $C_5Si(CH_3)_3$), −0.29 (s, 6H, $LuCH_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 121.00 (C_5H_4), 115.87 ($C_5Si(CH_3)_3$), 113.64 (C_5H_4), 28.68 ($LuCH_3$), 0.64 ($C_5Si(CH_3)_3$). MS (^{175}Lu, 200°C) m/z (relative intensity, %): 913 (38) $[(C_5H_4SiMe_3)_4Lu_2Me]^+$, 776 (1) $[(C_5H_4SiMe_3)_3Lu_2Me]^+$, 449 (100) $[(C_5H_4SiMe_3)_2Lu]^+$. Anal. Calc. for $C_{34}H_{58}Lu_2Si_4$ (929.11 g mol^{-1}): C, 43.95; H, 6.29. Found: C, 43.39; H, 6.52.

3.4.7. Bis(η^5-trimethylsilylcyclopentadienyl)yttriumbis(μ-methyl)lithiumbis(THF) (**5a**)

To a solution of 1.23 g (1.54 mmol) of **2a** in 75 ml THF were added dropwise 3.9 ml of a 1.6 M ethereal solution of methyllithium (6.24 mmol) at −78°C. The reaction mixture was stirred for 3 h at this temperature. After warming to r.t., the volatiles were removed in vacuum and the remaining residue was extracted with 80 ml of diethyl ether. The clear solution was concentrated to 25 ml and was cooled to −28°C to provide 1.08 g (64%) of colorless crystalline **5a**; m.p. 53°C dec. ^{1}H-NMR (benzene-d_6): δ 6.61 (m, 4H, C_5H_4), 6.44 (m, 4H, C_5H_4), 3.40 (m, 8H, THF), 1.26 (m, 8H, THF), 0.49 (s, 18H, $C_5Si(CH_3)_3$), −0.99 (s, 6H, YCH_3). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 117.43 (C_5H_4), 116.25 ($C_5Si(CH_3)_3$), 112.96 (C_5H_4), 68.26 (THF), 25.29 (THF), 10.33 (d, $^1J(^{89}Y,^{13}C) = 34$ Hz, YCH_3), 1.00 ($C_5Si(CH_3)_3$). MS (^{89}Y, 75°C) m/z (relative intensity, %): 363 (80) $[(C_5H_4SiMe_3)_2Y]^+$. Anal. Calc. for $C_{26}H_{48}LiO_2Si_2Y$ (544.68 g mol^{-1}): C, 57.33; H, 8.88. Found: C, 56.97; H, 8.63.

3.4.8. Bis(η^5-trimethylsilylcyclopentadienyl)-samariumbis(μ-methyl)lithiumbis(THF) (**5b**)

In analogy to the preparation of **5a**, 1.11 g (1.21 mmol) of **2b** were reacted with 3.1 ml of a 1.6 M ethereal solution of methyllithium (4.96 mmol) to give 0.99 g (67%) of yellow crystalline **5b**; m.p. 32°C dec. ^{1}H-NMR (benzene-d_6): δ 10.05 (s, 4H, C_5H_4), 7.20 (s, 4H, C_5H_4), 4.63 (m, 8H, THF), 1.83 (m, 8H, THF), −0.45 (s, 18H, $C_5Si(CH_3)_3$), −4.31 (s, 6H, $SmCH_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 115.79 (C_5H_4), 113.15 ($C_5Si(CH_3)_3$), 110.99 (C_5H_4), 69.71 (THF), 26.07 (THF), −0.01 ($C_5Si(CH_3)_3$). MS (^{152}Sm, 22°C) m/z (relative intensity, %): 426 (5) $[(C_5H_4SiMe_3)_2Sm]^+$, 289 (41) $[(C_5H_4SiMe_3)Sm]^+$. Anal. Calc. for $C_{26}H_{48}LiO_2Si_2Sm$ (606.14 g mol^{-1}): C, 51.52; H, 7.98. Found: C, 50.94; H, 7.71.

3.4.9. Bis(η^5-trimethylsilylcyclopentadienyl)-lutetiumbis(μ-methyl)lithiumbis(THF) (**5c**)

In analogy to the preparation of **5a**, 0.95 g (0.98 mmol) of **2c** were reacted with 2.5 ml of a 1.6 M ethereal solution of methyllithium (4.00 mmol) to give 0.77 g (62%) of colorless crystalline **5c**; m.p. 162°C dec. ^{1}H-NMR (benzene-d_6): δ 6.54 (m, 4H, C_5H_4), 6.34 (m, 4H, C_5H_4), 3.38 (m, 8H, THF), 1.27 (m, 8H, THF), 0.46 (s, 18H, $C_5Si(CH_3)_3$), −0.89 (s, 6H, $LuCH_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 118.08 (C_5H_4), 114.39 ($C_5Si(CH_3)_3$), 112.11 (C_5H_4), 68.33 (THF), 25.29 ($LuCH_3$), 16.10 (THF), 1.08 ($C_5Si(CH_3)_3$). MS (^{175}Lu, 139°C) m/z (relative intensity, %): 449 (30) $[(C_5H_4SiMe_3)_2Lu]^+$. Anal. Calc. for $C_{26}H_{48}LiLuO_2Si_2$ (630.74 g mol^{-1}): C, 49.51; H, 7.67. Found: C, 49.01; H, 7.22.

3.5. Lanthanidocene hydoxide complexes $[(\eta^5\text{-}C_5H_4SiMe_2R)_2Ln(\mu\text{-}OH)]_2$

3.5.1. Di(bis(η^5-tert-butyldimethylsilylcyclopentadienyl)-μ-hydroxoyttrium) (**6a**)

A total 17 µl (0.94 mmol) of degassed H_2O was added to a solution of 0.43 g (0.46 mmol) of **3a** in 70–75 ml of toluene at r.t. The mixture was stirred for 4 h. After removal of the volatiles in vacuum, the residue was washed with 30 ml of *n*-hexane and was again dissolved in 20 ml of toluene. Concentration of the solution to 15 ml and cooling to −28°C provided 0.33 g (77%) of colorless crystalline **6a**; m.p. 222°C dec. ^{1}H-NMR (benzene-d_6): δ 6.74 (m, 8H, C_5H_4), 6.28 (m, 8H, C_5H_4), 1.07 (s, 2H, OH), 0.95 (s, 36H, $C_5Si(CH_3)_2C(CH_3)_3$), 0.32 (s, 24H, $C_5Si(CH_3)_2C(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 122.04 (C_5H_4), 120.03 ($C_5Si(CH_3)_2C(CH_3)_3$), 114.54 (C_5H_4), 27.03 ($C_5Si(CH_3)_2C(CH_3)_3$), 17.61 ($C_5Si(CH_3)_2C(CH_3)_3$), −4.61 ($C_5Si(CH_3)_2C(CH_3)_3$). MS (^{89}Y, 231°C) m/z (relative intensity, %): 913 (2) $[M{-}Me]^+$, 749 (100) $[(C_5H_4Si^tBuMe_2)_3Y_2(OH)_2]^+$, 464 (2) $[(C_5H_4Si^tBuMe_2)_2YOH]^+$, 447 (35) $[(C_5H_4Si^tBuMe_2)_2Y]^+$. Anal. Calc. for $C_{44}H_{78}O_2Si_4Y_2$ (929.26 g mol^{-1}): C, 56.87; H, 8.46. Found: C, 56.37; H, 8.21.

3.5.2. Di(bis(η^5-tert-butyldimethylsilylcyclopentadienyl)-μ-hydroxosamarium) (**6b**)

In analogy to the preparation of **6a**, 0.49 g (0.47 mmol) of **3b** were reacted with 18 µl (1.00 mmol) of degassed H_2O. In total 0.39 g (79%) of yellow crystalline **6b** were obtained from 25 ml of toluene at −28°C; m.p. 192°C dec. ^{1}H-NMR (benzene-d_6): δ 18.85 (s, 8H, C_5H_4), 10.44 (s, 8H, C_5H_4), 1.03 (s, 36H, $C_5Si(CH_3)_2C(CH_3)_3$), −4.11 (s, 24H, $C_5Si(CH_3)_2C(CH_3)_3$), −11.91 (s, 2H, OH). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 127.10 (C_5H_4), 124.06 ($C_5Si(CH_3)_2C(CH_3)_3$), 116.59 (C_5H_4), 27.33 ($C_5Si(CH_3)_2C(CH_3)_3$), 16.11 ($C_5Si(CH_3)_2C(CH_3)_3$), −7.90 ($C_5Si(CH_3)_2C(CH_3)_3$). MS (^{152}Sm, 208°C) m/z (relative intensity, %): 1039 (5) $[M{-}Me]^+$, 875 (89) $[(C_5H_4Si^tBuMe_2)_3Sm_2(OH)_2]^+$, 527 (12) $[(C_5H_4Si^tBuMe_2)_2SmOH]^+$, 510 (100) $[(C_5H_4Si^tBuMe_2)_2Sm]^+$. Anal. Calc. for $C_{44}H_{78}O_2Si_4Sm_2$ (1052.16 g mol^{-1}): C, 50.23; H, 7.47. Found: C, 49.98; H, 7.44.

3.5.3. Di(bis(η^5-tert-butyldimethylsilylcyclopentadienyl)-μ-hydroxolutetium) (**6c**)

In analogy to the preparation of **6a**, 0.53 g (0.48 mmol) of **3c** were reacted with 18 µl (1.00 mmol) of degassed H_2O. In total 0.44 g (83%) of colorless crystalline **6c** were obtained from 25 ml of toluene at −28°C; m.p. 203°C dec. ^{1}H-NMR (benzene-d_6): δ 6.75 (m, 8H, C_5H_4), 6.26 (m, 8H, C_5H_4), 1.39 (s, 2H, OH), 0.94 (s, 36H, $C_5Si(CH_3)_2C(CH_3)_3$), 0.31 (s, 24H, $C_5Si(CH_3)_2C(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ

121.44 (C_5H_4), 115.74 ($C_5Si(CH_3)_2C(CH_3)_3$), 113.83 (C_5H_4), 26.51 ($C_5Si(CH_3)_2C(CH_3)_3$), 17.43 ($C_5Si(CH_3)_2$-$C(CH_3)_3$), −4.81 ($C_5Si(CH_3)_2C(CH_3)_3$). MS (^{175}Lu, 258°C) m/z (relative intensity, %): 1100 (1) $[M]^+$, 921 (100) $[(C_5H_4Si^tBuMe_2)_3Lu_2(OH)_2]^+$, 550 (1) $[(C_5H_4Si$-$^tBuMe_2)_2LuOH]^+$, 533 (4) $[(C_5H_4Si^tBuMe_2)_2Lu]^+$. Anal. Calc. for $C_{44}H_{78}Lu_2O_2Si_4$ (1101.38 g mol^{-1}): C, 47.98; H, 7.14. Found: C, 47.21; H, 6.89.

3.5.4. Di(bis(η^5-trimethylsilylcyclopentadienyl)-μ-hydroxoyttrium) (7a)

Following the procedure described for **6a**, 0.45 g (0.59 mmol) of **4a** were reacted with 22 µl (1.22 mmol) of degassed H_2O. In total 0.37 g (82%) of colorless crystalline **7a** were obtained from 25 ml of toluene at −28°C; m.p. 218°C dec. ^{1}H-NMR (benzene-d_6): δ 6.71 (m, 8H, C_5H_4), 6.30 (m, 8H, C_5H_4), 1.08 (s, 2H, OH), 0.27 (s, 36H, $C_5Si(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 120.33 (C_5H_4), 120.02 ($C_5Si(CH_3)_3$), 114.86 (C_5H_4), 0.43 ($C_5Si(CH_3)_3$). MS (^{89}Y, 156°C) m/z (relative intensity, %): 760 (2) $[M]^+$, 623 (100) $[(C_5H_4SiMe_3)_3Y_2(OH)_2]^+$, 380 (4) $[(C_5H_4SiMe_3)_2YOH]^+$, 363 (6) $[(C_5H_4SiMe_3)_2Y]^+$. Anal. Calc. for $C_{32}H_{54}O_2Si_4Y_2$ (760.93 g mol^{-1}): C, 50.51; H, 7.15. Found: C, 49.76; H, 6.70.

3.5.5. Di(bis(η^5-trimethylsilylcyclopentadienyl)-μ-hydroxosamarium) (7b)

Following the procedure described for **6a**, 0.56 g (0.64 mmol) of **4b** were reacted with 23 µl (1.28 mmol) of degassed H_2O. A total of 0.47 g (83%) of yellow crystalline **7b** were obtained from 25 ml of toluene at −28°C; m.p. 202°C dec. ^{1}H-NMR (benzene-d_6): δ 18.84 (s, 8H, C_5H_4), 10.48 (s, 8H, C_5H_4), −2.82 (s, 36H, $C_5Si(CH_3)_3$), −11.70 (s, 2H, OH). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 124.22 (C_5H_4), 117.61 ($C_5Si(CH_3)_3$), 116.17 (C_5H_4), −2.55 ($C_5Si(CH_3)_3$). MS (^{152}Sm, 202°C) m/z (relative intensity, %): 886 (1) $[M]^+$, 749 (100) $[(C_5H_4SiMe_3)_3Sm_2(OH)_2]^+$, 443 (5) $[(C_5H_4SiMe_3)_2SmOH]^+$, 426 (8) $[(C_5H_4SiMe_3)_2Sm]^+$. Anal. Calc. for $C_{32}H_{54}O_2Si_4Sm_2$ (883.84 g mol^{-1}): C, 43.49; H, 6.16. Found: C, 43.01; H, 6.00.

3.5.6. Di(bis(η^5-trimethylsilylcyclopentadienyl)-μ-hydroxolutetium) (7c)

Following the procedure described for **6a**, 0.43 g (0.46 mmol) of **4c** were reacted with 18 µl (1.00 mmol) of degassed H_2O. In total 0.37 g (86%) of colorless crystalline **7c** were obtained from 25 ml of toluene at −28°C; m.p. 162°C dec. ^{1}H-NMR (benzene-d_6): δ 6.72 (m, 8H, C_5H_4), 6.27 (m, 8H, C_5H_4), 0.91 (s, 2H, OH), 0.26 (s, 36H, $C_5Si(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6): δ 120.59 (C_5H_4), 118.53 ($C_5Si(CH_3)_3$), 113.86 (C_5H_4), 0.44 ($C_5Si(CH_3)_3$). MS (^{175}Lu, 207°C) m/z (relative intensity, %): 932 (2) $[M]^+$, 795 (100) $[(C_5H_4SiMe_3)_3Lu_2(OH)_2]^+$, 658 (19) $[(C_5H_4SiMe_3)_2Lu_2(OH)_2]^+$, 449 (4) $[(C_5H_4SiMe_3)_2Lu]^+$. Anal. Calc. for $C_{32}H_{54}Lu_2O_2Si_4$ (933.06 g mol^{-1}): C, 41.19; H, 5.83. Found: C, 41.52; H, 5.51.

3.6. Catalytic hydrosilylation reactions

In a typical procedure the organolanthanide precatalyst (0.05 mmol), 2 ml of cyclohexane, the alkene (1.0 mmol) or the alkyne (1.0 mmol), and H_3SiPh (1.1 mmol) were loaded into a 10 ml flask equipped with an Ace needle valve. The homogeneous mixture was stirred for 1–12 h at r.t. (Tables 3 and 4). After filtration through a plug of Florisil, the solvent was removed in vacuum and the crude product was flash chromatographed with SiO_2 and n-hexane as eluant. All hydrosilylation products were identified by comparison of their NMR spectra (^{1}H-, $^{13}C\{^1H\}$-) with those from the literature [6,7,9,11,12].

4. X-ray structure determination of 1c, 4a and 7c

Suitable crystals of **1c** were obtained from n-hexane. A colorless, block-shaped crystal was selected by using a device similar to that reported by Veith and Bärnighausen [39], glued with grease onto the top of a glass fiber, and transferred directly into the cold nitrogen stream of the low temperature unit mounted to an Enraf–Nonius CAD-4 automatic diffractometer (graphite crystal monochromator, Mo–K_α radiation = 71.069 pm) controlled by a PC. The cell parameters were obtained from the angles of 25 reflections (scan type ω–2θ) in the range of $5.23 < \theta < 12.04°$. Reflections were scanned with variable scan time, depending on intensities, with two-thirds of the time used for scanning the peak and each one-sixth measuring the left and right background. The intensities of three check reflections monitored after 2 h showed only statistical fluctuations during the course of the data collection. The crystal orientation was checked every 200 intensity measurements by scanning three reflections. A new orientation matrix was automatically calculated from a list of 25 recentered reflections in case the angular change was greater than 0.1°. The raw data were corrected for Lorentz and polarisation effects [40]. Refinements in space group $P2_1/c$ were successful. The position of the Lu-atom was determined from a three-dimensional Patterson synthesis (SHELXS86) [41]. The calculated difference Fourier map (SHELXL93) [42] revealed all other missing non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The C–H hydrogen atoms were calculated in idealized positions (C–H 0.96 Å, $U_{iso} = 0.08$ Å^2). Scattering factors were taken from the literature [43]. After all atoms were added to the model of the structure, an empirical absorption correction was applied (DIFABS [44]; min.: 0.690, max.: 1.645, average: 1.056). Final residual of least squares is R 6.40%. The geometrical aspects of the structure were analysed by using the PLUTON program [45].

Suitable colorless, block-shaped crystals of **4a** and **7c** were obtained from *n*-hexane. The general procedure for solving the structure is outlined above. The cell parameters were obtained from the angles of 25 reflections (scan type ω–2θ) in the range of $6.30 < \theta < 13.60°$ (**4a**) and $7.83 < \theta < 11.92°$ (**7c**), respectively. The intensities of three check reflections monitored every 2 h showed only statistical fluctuations during the data collection. Refinements in space group $P\bar{1}$ (**4a**) and $P2_1/c$ (**7c**) were successful. The structures were solved with direct methods (SHELXS86) [41]. Final residual of least squares are R 3.55% (**4a**) and R 4.73% (**7c**). Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-410287 (**1c**), CSD-410285 (**4a**), CSD-410286 (**7c**), the authors, and the full citation of the journal.

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