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Organometallic compounds of the lanthanides. CXXIII[1]. Lanthanide bent-sandwich complexes with the bulky tetramethyl-*iso*-propylcyclopentadienyl ligand—synthesis, structures and catalytic activity for the hydrosilylation of alkenes/alkynes

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Abstract

The trichlorides of yttrium, samarium and lutetium react with two equivalents of Na[$C_5Me_4{}^iPr$] in THF to form [(η^5-$C_5Me_4{}^iPr)_2LnCl(THF)$] (Ln = Y (**1**), Sm (**2**), Lu (**3**)). Metathesis of **1**–**3** with $LiCH_3$ in diethyl ether and $LiCH(SiMe_3)_2$ in toluene gives [(η^5-$C_5Me_4{}^iPr)_2LnCH_3(THF)$] (Ln = Y (**4**), Lu (**5**)) and [(η^5-$C_5Me_4{}^iPr)_2Ln\{CH(SiMe_3)_2\}$] (Ln = Y (**6**), Sm (**7**)), respectively. The 1:2 reaction of $LnI_2(THF)_x$ (Ln = Sm, Yb) with Na[$C_5Me_4{}^iPr$] in THF results in the formation of the divalent metallocenes [(η^5-$C_5Me_4{}^iPr)_2Ln(THF)$] (Ln = Sm (**8**), Yb (**9**)). The new compounds with the bulky tetramethyl-*iso*-propylcyclopentadienyl ligands were characterized by C, H analysis, mass spectrometry and NMR spectroscopy. Additionally, single crystal X-ray structure determination of the lutetium complexes **3** and **5** was performed. It has been shown that the alkyl complexes **4**–**7** are effective precatalysts for the hydrosilylation of alkenes and alkynes. The results of the described investigations are discussed.

Keywords: Lanthanidocene; Catalytic activity; Hydrosilylation

1. Introduction

The discovery of hexachloroplatinic acid as an efficient catalyst for hydrosilylation reactions by Speier in 1957 [2] became a starting point for one of the most effective and elegant methods for synthesizing organosilicon compounds. Homogeneous catalysis of hydrosilylation has subsequently been studied with transition metal compounds containing metals other than platinum [3]. Recently, it has been found that lanthanidocene complexes like [(η^5-$C_5Me_5)_2LnCH_3$ (THF)] and [(η^5-$C_5Me_5)_2Ln\{CH(SiMe_3)_2\}$] are efficient promoters for the addition of hydrosilanes to alkenes and alkynes [4]. The catalytic activity of the lanthanides is based on insertion reactions into Ln–H or Ln–C bonds, σ-bond metathesis, and hydrocarbyl protonolysis. Unlike the electron-rich transition metal-catalyzed processes, the organolanthanide-catalyzed processes are typically not directed by polar groups, but appear purely steric in their selectivity patterns ([4](a), [5]). The generation of the formally 14 electron complex '[(η^5-$C_5Me_5)_2LnH$]' as the active catalyst has been investigated, as well as each single step of the catalytic cycle of hydrosilylation [6].

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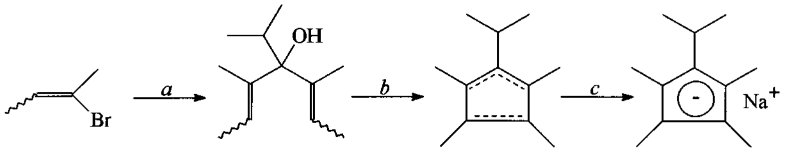

^{a} (1) 2 equiv Li, (2) ^{i}PrCOOEt, (3) H_2O. ^{b} $C_7H_7SO_3H$ (cat.). ^{c} $NaNH_2$.

Scheme 1. Preparation of the tetramethyl-*iso*-propylcyclopentadienyl ligand according to the synthesis of the pentamethylcyclopentadienyl ligand [7].

The focus of the present research was the synthesis of lanthanidocene catalysts with bulky cyclopentadienyl ligands and to use the steric properties of these complexes for selective hydrosilylation. In this paper we present the results of our investigations in this area of tetramethyl-*iso*-propylcyclopentadienyllanthanide complexes.

2. Results and discussion

2.1. Synthesis

The bulky tetramethyl-*iso*-propylcyclopentadienyl ligand was prepared according to the synthesis of the pentamethylcyclopentadienyl ligand [7], by starting from 2-bromo-2-butene (*cis* + *trans* mixture), as shown in Scheme 1.

Reaction of sodium tetramethyl-*iso*-propylcyclopentadienide with Y, Sm and Lu trichloride in THF with a molar ratio of 2:1 cleanly gave the metallocene chlorides $[(\eta^5\text{-}C_5Me_4{}^iPr)_2LnCl(THF)]$ (**1**–**3**) with 70–75% yield.

$$LnCl_3(THF)_x + 2Na[C_5Me_4{}^iPr]$$
$$\rightarrow [(\eta^5\text{-}C_5Me_4{}^iPr)_2LnCl(THF)] + 2NaCl,$$
$$(Ln = Y\ (\mathbf{1}),\ Sm\ (\mathbf{2}),\ Lu\ (\mathbf{3})).$$

The orange Sm complex and the colorless Y and Lu derivatives are air- and moisture-sensitive and soluble in polar solvents (e.g. THF or diethyl ether), in aromatic solvents (e.g. toluene) and in non-polar hydrocarbons. Crystals of **1**–**3** were obtained by cooling saturated *n*-hexane solutions to −28°C. The presence of THF in **1**–**3** was proven by elemental analysis, by NMR spectroscopy (^1H, $^{13}C\{^1H\}$), and by single crystal X-ray structure determination of the lutetium complex **3**.

Treating these metallocene chlorides with one equivalent of methyllithium in diethyl ether or with a stoichiometric amount of bis(trimethylsilyl)methyllithium in toluene results in the corresponding methyl complexes **4** and **5** in 36 and 43% yield, respectively, or the bis(trimethylsilyl)methyl compounds **6** and **7** in 60 and 40% yield, respectively.

$$[(\eta^5\text{-}C_5Me_4{}^iPr)_2LnCl(THF)] + LiCH_3$$
$$\rightarrow [(\eta^5\text{-}C_5Me_4{}^iPr)_2LnCH_3(THF)] + LiCl,$$
$$(Ln = Y\ (\mathbf{4}),\ Lu\ (\mathbf{5})).$$

$$[(\eta^5\text{-}C_5Me_4{}^iPr)_2LnCl(THF)] + LiCH(SiMe_3)_2$$
$$\rightarrow [(\eta^5\text{-}C_5Me_4{}^iPr)_2Ln\{CH(SiMe_3)_2\}] + LiCl,$$
$$(Ln = Y\ (\mathbf{6}),\ Sm\ (\mathbf{7})).$$

The colorless compounds **4**–**6** and the red Sm derivative **7** are soluble in aprotic organic solvents like THF, toluene, benzene or *n*-hexane. All four alkyl complexes were obtained in a crystalline form from an *n*-hexane solution at low temperature. In contrast to the expected shielding of the Lewis acidic lanthanide metal center against traces of water by the bulky cyclopentadienyl ligand system, **4**–**7** show the same extreme sensitivity towards moisture and air than the corresponding pentamethylcyclopentadienyllanthanide alkyl derivatives. They react with water yielding lanthanide hydroxide, tetramethyl-*iso*-propylcyclopentadiene and methane or bis(trimethylsilyl)methane, respectively.

The complexes **4**–**7** were characterized by ^1H and $^{13}C\{^1H\}$ and MS data and by elemental analysis. A single crystal X-ray structure determination was performed on compound **5**.

The NMR spectra of the diamagnetic Y and Lu alkyl derivatives show the proton and carbon signals with expected chemical shifts and proton intensity; whereas the signals in the ^1H and $^{13}C\{^1H\}$ spectrum of the paramagnetic Sm alkyl complex, **7**, are partially broadened and shifted to higher/lower frequencies. The signal for the $C\mathit{H}(SiMe_3)_2$ proton in the ^1H NMR spectrum has, for example, a line width of 35 Hz and is shifted to δ 19.7 ppm. Similar values have been observed for the derivatives $[(\eta^5\text{-}C_5Me_4R)_2Sm\{CH(SiMe_3)_2\}]$ (R = Me, Et) ([5](d), [8]). In case of the metallocene bis(trimethylsilyl)methyl complexes **6** and **7**, the number of cyclopentadienyl resonances in the NMR spectra indicates non-equivalent cyclopentadienyl rings. This behavior is expected for a fixed non-planar α-carbon geometry of the alkyl group. No evidence for a static α-agostic C–H interaction is observed in the NMR spectra of the methyl compounds **4** and **5**. The ^1H NMR and the $^{13}C\{^1H\}$ NMR spectra show only one set

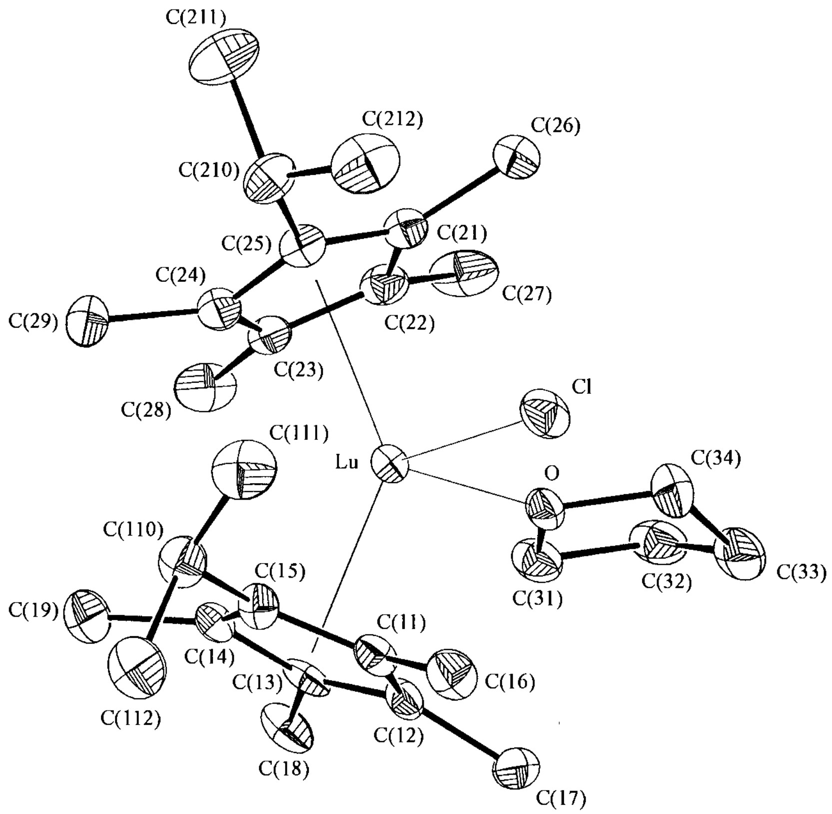

Fig. 1. Crystal structure of **3** (ZORTEP plot [10]). Selected distances [Å] and angles [°] with estimated S.D. (Cp denotes the center of the cyclopentadienyl ring): Lu–Cp(1) 2.352(3), Lu–C(11) 2.644(6), Lu–C(12) 2.656(6), Lu–C(13) 2.649(6), Lu–C(14) 2.648(6), Lu–C(15) 2.624(6), Lu–Cp(2) 2.358(3), Lu–C(21) 2.695(6), Lu–C(22) 2.631(6), Lu–C(23) 2.594(6), Lu–C(24) 2.628(7), Lu–C(25) 2.678(6), Lu–Cl 2.516(2), Lu–O 2.314(5); Cp(1)–Lu–Cp(2) 137.22(11), Cp(1)–Lu–Cl 106.87(9), Cp(1)–Lu–O 102.97(14), Cp(2)–Lu–Cl 106.27(10), Cp(2)–Lu–O 104.95(14), Cl–Lu–O 87.17(12).

of signals for two tetramethyl-*iso*-propylcyclopentadienyl rings. This is in agreement with observations from the NMR spectra of [(η^5-C_5Me_5)$_2$YCH$_3$(THF)] [9]. The NMR spectra of the Y derivatives **4** and **6** show coupling between ^{89}Y and the protons of the α-C of the alkyl ligand and several carbon atoms, respectively. The mass spectra of **4** and **5** show the molecular ion without THF and the spectra of **6** and **7** show the fragment [($C_5Me_4{}^i$Pr)$_2$Ln]$^+$ as the peak with the highest mass.

Metallocene complexes with the divalent Sm and Yb centers and the bulky tetramethyl-*iso*-propylcyclopentadienyl ligands were obtained by a 2:1 reaction of sodium tetramethyl-*iso*-propylcyclopentadienide and Sm and Yb di-iodide in THF.

$$\mathrm{LnI_2(THF)}_x + 2\mathrm{Na[C_5Me_4{}^iPr]}$$

$$\rightarrow [(\eta^5\text{-}\mathrm{C_5Me_4{}^iPr})_2\mathrm{Ln(THF)}] + 2\mathrm{NaCl},$$

Ln = Sm (**8**), Yb (**9**)).

The dark compounds **8** and **9** show good solubility in THF, toluene, benzene and *n*-hexane. Both extremely air- and moisture-sensitive complexes could be isolated as crystals with 75 and 71% yield, respectively.

The presence of one molecule of THF per bis(tetramethyl-*iso*-propylcyclopentadienyl)lanthanide unit was detected by elemental analysis and by the NMR spectra (^{1}H and ^{13}C{^{1}H}) of the diamagnetic Yb complex **9**. The mass spectra of **8** and **9** show the fragment [($C_5Me_4{}^i$Pr)$_2$Ln]$^+$ as the peak with the highest mass and the fragment [($C_5Me_4{}^i$Pr)Ln]$^+$ as the base peak.

2.2. Molecular structure of 3 and 5

Crystals suitable for single crystal X-ray structure determination of **3** and **5** were obtained by recrystallization from *n*-hexane solution at −28°C. The molecular structures, numbering schemes, selected bond distances and bond angles are shown in Figs. 1 and 2.

In [(η^5-$C_5Me_4{}^i$Pr)$_2$LuCl(THF)], the two tetramethyl-*iso*-propylcyclopentadienyl ring centroids, the THF oxygen atom and the chlorine atom coordinate the lutetium ion in a roughly tetrahedral fashion with angles from 87.17(12)° (Cl–Lu–O) to 137.22(11)° (Cp(1)–Lu–Cp(2)). The structure is typical of bent metallocene species that contain two additional ligands. The average Lu–Cp distance (2.355(3) Å), the value of the Lu–Cl bond (2.516(2) Å) and the Lu–O(THF) bond

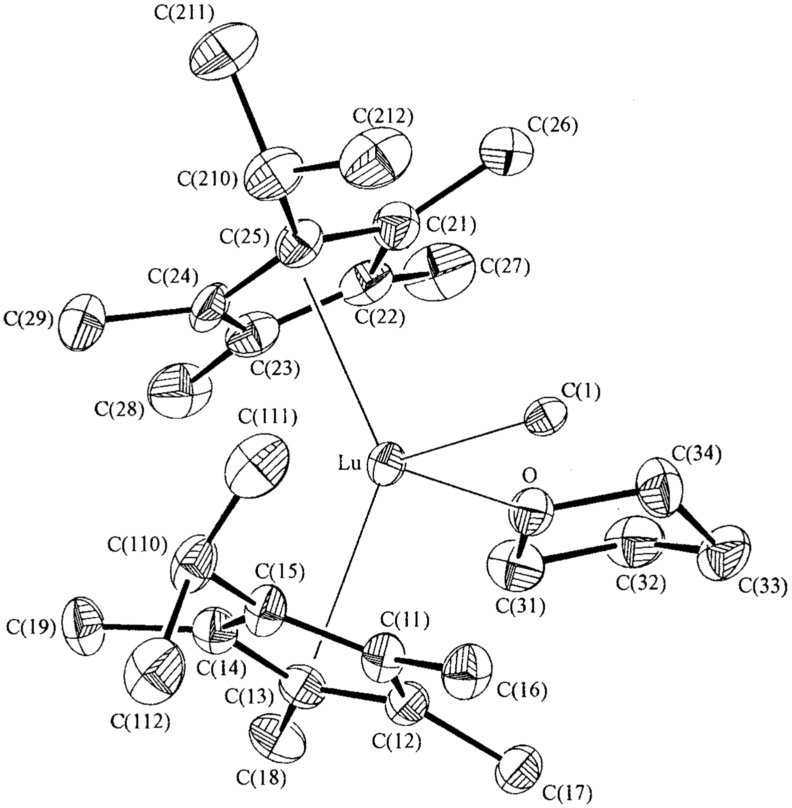

Fig. 2. Crystal structure of **5** (ZORTEP plot [10]). Selected distances [Å] and angles [°] with estimated S.D. (Cp denotes the center of the cyclopentadienyl ring): Lu–Cp(1) 2.369(3), Lu–C(11) 2.655(6), Lu–C(12) 2.663(6), Lu–C(13) 2.662(6), Lu–C(14) 2.665(6), Lu–C(15) 2.649(6), Lu–Cp(2) 2.377(3), Lu–C(21) 2.707(7), Lu–C(22) 2.655(6), Lu–C(23) 2.610(6), Lu–C(24) 2.654(6), Lu–C(25) 2.690(6), Lu–C(1) 2.390(5), Lu–O 2.325(4); Cp(1)–Lu–Cp(2) 137.62(11), Cp(1)–Lu–C(1) 105.7(2), Cp(1)–Lu–O 102.92(13), Cp(2)–Lu–C(1) 106.5(2), Cp(2)–Lu–O 105.10(13), C(1)–Lu–O 87.9(2).

(2.314(5) Å) are consistent with the corresponding bond lengths in [(η^5-C_5Me_5)$_2$YCl(THF)] (d(Y–Cp) = 2.380(1) Å, d(Y–Cl) = 2.578(3) Å, d(Y–O(THF)) = 2.410(7) Å) [11] and [(η^5-C_5Me_5)$_2$LuCl(THF)] (d(Lu–Cp) = 2.34 Å, d(Lu–Cl) = 2.53 Å) [12]. The ring slippage in **3** has a value of 0.03 Å (Cp(1)) and 0.11 Å (Cp(2)). The ring planes defined by the atoms C(11)–C(15) and C(21)–C(25) are planar within the range of their estimated S.D. The pendant alkyl groups of the $C_5Me_4{}^i$Pr rings are significantly bent from the ring planes (0.105(12)–0.370(10) Å), lying on the opposite sides of the C_5 rings from the lutetium ion.

The geometry around the lanthanide center in **5** is, with angles from 87.9(2)° (C(1)–Lu–O) to 137.62(11)° (Cp(1)–Lu–Cp(2)), very similar to that around the metal center of **3**. The average Lu–Cp distance (2.373(3) Å), Lu–C σ-bond (2.390(5) Å) and the Lu–O(THF) distance (2.325(4) Å) are similar to the corresponding distances in the complexes [(η^5-C_5H_5)$_2$YbMe(THF)] (d(Yb–Cp) = 2.368 Å, d(Yb–C(Me)) = 2.362(11) Å, d(Yb–O(THF)) = 2.311(6) Å) [13] and [(η^5-C_5Me_5)$_2$YMe(THF)] (d(Y–Cp) = 2.38(1) Å, d(Y–C(Me)) = 2.44(2) Å, d(Y–O(THF)) = 2.379(8) Å) [9], when the different ionic radii of the metal centers and the different substituents on the cyclopentadienyl rings are taken in consideration. The two tetramethyl-*iso*-propylcyclopentadienyl ligands in **5** are slipped 0.014 and 0.102 Å from the centroid of the ring and the ring planes are planar within the range of their S.D. As in the molecular structure of **3**, the pendant alkyl groups of the tetramethyl-*iso*-propylcyclopentadienyl ligands are displaced by 0.118(11)–0.349(12) Å from the planes of the C_5 rings.

In both solid state structures the two bulky tetramethyl-*iso*-propylcyclopentadienyl rings are in a staggered conformation. The five torsional angles of the type C(110)–Cp(1)–Cp(2)–C(210) average 25.0° in **3** and 26.1° in **5**.

2.3. Hydrosilylation

We checked the catalytic activity of the lanthanide alkyl complexes **4**–**7** for hydrosilylation in the reaction of phenylsilane with selected commercially available alkenes and alkynes. Most of these addition reactions had been performed before with other organolanthanide catalysts. In a typical hydrosilylation reaction, the unsaturated substrate and 1.1 equivalents of phenyl-

Table 1
Hydrosilylation of alkenes and alkynes utilizing catalytic [(η^5-$C_5Me_4{}^iPr)_2LnR(THF)_x$] (R = Me, $x = 1$, Ln = Y (**4**), Lu (**5**); R = $CH(SiMe_3)_2$, $x = 0$, Ln = Y (**6**), Sm (**7**))

Entry	Substrate	Product(s)	Catalyst	Yield (%)[a]
1a	1-decene	1-(phenylsilyl)decane	**4**[b]	96
1b			**5**[b]	95
1c			**6**[b]	95
1d			**7**[b]	93
2a	2-nonene	3-(phenylsilyl)nonane 2-(phenylsilyl)nonane 1-(phenylsilyl)nonane	**4**[c]	23 (1.6:1.0)[d,e]
2b			**5**[c]	25 (1.5:1.0)[d,e]
2c			**6**[c]	21 (1.5:1.0)[d,e]
2d			**7**[c]	66 (0.7:1.0)[d,e]
3a	(*R*)-(+)-limonene	(*R*)-(+)-4-[1-((phenylsilyl)methyl)ethyl]-1-methyl-1-cyclohexene	**4**[f]	40
3b			**5**[f]	51
3c			**6**[f]	42
3d			**7**[f]	82
4a	1,5-hexadiene	[(phenylsilyl)methyl]cyclopentane	**4**[g]	96
4b			**5**[g]	94
4c			**6**[g]	94
4d			**7**[g]	97
5a	2-nonyne	2-(phenylsilyl)-2-nonene 3-(phenylsilyl)-2-nonene	**4**[h]	83 (3.2:1.0)[e]
5b			**5**[h]	77 (3.9:1.0)[e]
5c			**6**[h]	78 (4.0:1.0)[e]
5d			**7**[h]	77 (2.7:1.0)[e]
6a	4-methyl-2-hexyne	4-methyl-2-(phenylsilyl)-2-hexene	**4**[h]	69
6b			**5**[h]	74
6c			**6**[h]	72
6d			**7**[h]	75

[a] Isolated yields; [b] 2 h at r.t.; [c] 36 h at r.t.; [d] ratio of 3-(phenylsilyl)nonane and 2-(phenylsilyl)nonane:1-(phenylsilyl)nonane; [e] ratios were determined on the crude mixture by fused silica capillary GC; [f] 96 h at r.t.; [g] 1 h at r.t.; [h] 12 h at 50°C.

silane were stirred in the presence of the organolanthanide precatalyst in an inert atmosphere over a period of 1–96 h. The hydrosilylation products were recovered by filtration through a plug of Florisil and purified by flash chromatography. The results are summarized in Table 1. The reactions take place with high regioselectivity, wherein the silyl group is delivered preferentially to the less hindered carbon atom of the double or triple bond. These results are in agreement with the earlier findings that [(η^5-$C_5Me_5)_2YMe(THF)$] and [(η^5-$C_5Me_5)_2Ln\{CH(SiMe_3)_2\}$] mediate the 1,2 addition of the Si–H bond to the unsaturated compounds with high selectivity [4c, 4f, 4h]. The olefin 2-nonene (entry 2) with an internal double bond yields in a side reaction an addition product with a terminal silyl group, what can be explained by an organolanthanide-catalyzed migration of the double bond. (*R*)-(+)-Limonene (entry 3) was cleanly hydrosilylated in the presence of the precatalysts **4**–**7** only at the terminal C=C bond ([4]c). As expected no disilyl product is formed in the presence of excess of hydrosilane, even at elevated temperatures. In the case of 1,5-hexadiene (entry 4), the organolanthanide catalyst cyclizes the diene in the first step and hydrosilylates the cyclized product in a second step. Similar observations have been made before with [(η^5-$C_5Me_5)_2YMe(THF)$] as the precatalyst ([4]d).

In conclusion, [(η^5-$C_5Me_4{}^iPr)_2LnR(THF)_x$] (R = Me, $x = 1$, Ln = Y, Lu; R = $CH(SiMe_3)_2$, $x = 0$, Ln = Y, Sm) complexes are efficient precatalysts for the hydrosilylation of several alkenes and alkynes. However, there is no significant difference in the selectivity or reactivity using the precatalysts **4**–**7** or the corresponding pentamethylcyclopentadienyllanthanide complexes for the hydrosilylation of alkenes and alkynes. For example, in the hydrosilylation of 2-nonyne with the yttrium methyl compound **4** (entry 5a) and [(η^5-$C_5Me_5)_2YMe(THF)$], the two regioisomers are generated with the same ratio of 4.1:1 under the same conditions. Variation of the lanthanide size, using the Y and Lu compounds instead of the corresponding Sm derivative, has only a minor influence on the selectivity of the reaction (entries 2 and 5). Further studies regarding the synthesis of organolanthanide catalysts and their application in hydrosilylation reactions continue in these laboratories.

3. Experimental section

General Comments. All experiments were carried out in an atmosphere of dried, oxygen-free nitrogen by using standard Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres glovebox. Solvents were freshly distilled from sodium benzophenone ketyl. ^{1}H-NMR (200 MHz) and ^{13}C{^{1}H}-NMR spectra (50.23 MHz) were recorded on a Bruker ARX 200 or a Bruker AM 400 spectrometer at ambient temperature. The chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the NMR solvent. Mass spectra were obtained at 70 eV on a Varian MAT 311A spectrometer. Elemental analyses were carried out on a Perkin-Elmer Series II CHNS/O Analyser 2400. Melting points were determined in sealed capillaries with a HWS-SG 2000 melting point determination apparatus and are uncorrected.

Materials. 2-Bromo-2-butene (*cis* + *trans*) was passed through a short column of aluminium oxide prior to use. All other reagents for the synthesis of the ligands were used as purchased. $LiCH(SiMe_3)_2$ [14], the lanthanide trichloride THF adducts of yttrium, samarium and lutetium[3] [15], and the lanthanide di-iodide THF adducts of samarium and ytterbium [16] were synthesized as described in the literature. The alkynes 2-nonyne and 4-methyl-2-hexyne and the alkenes 1-decene, (*R*)-(+)-limonene, 2-nonene and 1,5-hexadiene were commercial samples dried over activated 4-Å molecular sieves, vacuum-transferred, and freeze/pump/thaw-degassed.

Table 2
Crystallographic data for **3** and **5**

	3	**5**
Empirical formula	$C_{31}H_{53}ClOLu$	$C_{32}H_{56}OLu$
Formula weight (g mol^{-1})	652.2	631.7
Temperature (K)	193(2)	240(2)
Radiation (Mo–K_α) (Å)	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.728(6)	10.747(3)
b (Å)	25.765(9)	25.726(7)
c (Å)	11.055(2)	11.132(2)
β (°)	93.69(4)	92.89(2)
V (Å^3)	3049(2)	3073.9(12)
Z	4	4
D_{calc} (g cm^{-3})	1.421	1.365
Absorption coefficient (mm^{-1})	3.345	3.104
F(000)	1340	1296
Crystal size (mm^3)	$0.12 \times 0.21 \times 0.21$	$0.16 \times 0.16 \times 0.26$
2θ range (°)	$3 < 2\theta < 48$	$1 < 2\theta < 50$
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Aperture (mm)	2.70	2.20
Scan angle (°)	$(0.70 + 0.35 \cdot \tan\theta)$	$(0.92 + 0.35 \cdot \tan\theta)$
Reflections collected	5132	5792
Reflections unique	4756	5376
Reflections observed [$I > 2\sigma(I)$]	3868	4145
Data/restraints/parameters	4724/0/307	5303/0/307
$R1$ [$I > 2\sigma(I)$]/all data[a]	0.036/0.054	0.035/0.062
$wR2$ [$I > 2\sigma(I)$]/all data[b]	0.086/0.126	0.0804/0.231
Goodness of fit[c]	1.224	1.106
Min./max. density (eÅ^{-3})	−2.678/1.328	−1.110/1.714

[a] $R_1 = \sum\left((|F_o| - |F_c|)/\sum|F_o|\right)$; [b] $wR_2 = \left[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\right]^{1/2}$; [c] $\mathrm{GOOF} = \left[\sum w(|F_o| - |F_c|)^2/(n-p)\right]^{1/2}$

3.1. $Na[C_5Me_4{}^iPr]$

The following preparation of tetramethyl-*iso*-propylcyclopentadiene is based on the procedure for a similar compound (pentamethylcyclopentadiene) reported by Bercaw and Bergman [7]. A 7.65 g (1.102 mol.) portion of lithium wire, cut to small pieces, was covered with 100 ml diethyl ether and the reaction was initiated by addition of 15 ml of 2-bromo-2-butene. The reaction mixture was stirred vigorously, and the remainder of the 148.51 g (1.100 mol) of 2-bromo-2-butene in 200 ml of diethyl ether was added at a rate that the ether barely boiled. After the addition was complete, the yellow reaction mixture was stirred at room temperature for 1 h, followed by the addition of 63.89 g (0.550 mol.) of ethyl isobutyrate over a period of 45 min. The resulting orange solution was poured into 500 ml of saturated ammonium chloride solution, the aqueous layer was separated and extracted with three 150 ml portions of diethyl ether. After the combined organic layers had been dried over magnesium sulfate and evaporated to ca. 100 ml, the mixture was added slowly to a solution of 4.50 g (0.024 mol) of *p*-toluenesulfonic acid monohydrate in 200 ml of diethyl ether at room temperature. The solution was stirred for 1 h, quenched with 100 ml of saturated, aqueous sodium bicarbonate, and extracted with three 100 ml portions of diethyl ether. The ether extracts were combined and dried over magnesium sulfate. The ether was removed under reduced pressure, followed by fractional distillation. The resulting colorless liquid[4] (wt. 42.70 g, b.p. 68°C/1 Torr) was dissolved in 250 ml of THF. A 10.14 g (0.260 mol) portion of sodium amide was added while stirring at room temperature. After the mixture had been

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[3] The dry rare earth chlorides were purified by extraction with THF yielding $LnCl_3THF_x$ adducts with the given amount of THF.

[4] The following NMR data for tetramethyl-*iso*-propylcyclopentadiene were assigned from a mixture of three isomers. ^{1}H-NMR (benzene-d_6) δ 2.8, 2.2 (2m, 1H, $CHMe_2$), 2.5 (m, 1H, C_5H), 1.7–1.9, 0.8–1.2 (2m, 18H, C_5CH_3 and $CH(CH_3)_2$).

Table 3
Atomic coordinates and equivalent isotropic displacement parameters for **3**

Atom	x [10^{-4}]	y [10^{-4}]	z [10^{-4}]	U_{eq} [10^{-3} Å^2]
Lu	2255(1)	1556(1)	4833(1)	24(1)
Cl	3278(2)	2113(1)	6481(1)	40(1)
C(11)	3841(6)	2083(3)	3571(5)	31(1)
C(12)	2653(6)	2195(2)	3013(5)	28(1)
C(13)	2157(6)	1733(3)	2468(5)	30(1)
C(14)	3086(6)	1335(2)	2689(5)	30(1)
C(15)	4099(5)	1547(2)	3385(6)	28(1)
C(16)	4714(6)	2491(3)	4127(6)	41(2)
C(17)	2096(6)	2732(3)	2915(6)	39(2)
C(18)	1040(7)	1686(3)	1600(6)	43(2)
C(19)	3040(7)	838(3)	1980(6)	42(2)
C(110)	5317(6)	1260(3)	3691(7)	40(2)
C(111)	5815(7)	1315(3)	4996(8)	56(2)
C(112)	6303(7)	1413(3)	2813(8)	56(2)
C(21)	1575(6)	1004(2)	6753(6)	32(1)
C(22)	594(6)	976(3)	5849(6)	35(2)
C(23)	1005(6)	694(2)	4854(6)	32(1)
C(24)	2247(7)	545(3)	5157(6)	36(2)
C(25)	2613(6)	741(2)	6318(6)	31(1)
C(26)	1446(8)	1245(3)	7986(6)	48(2)
C(27)	−741(6)	1140(3)	6014(8)	52(2)
C(28)	184(7)	508(3)	3774(7)	49(2)
C(29)	2978(7)	139(3)	4509(7)	46(2)
C(210)	3773(7)	555(3)	7057(7)	43(2)
C(211)	3439(8)	63(3)	7749(8)	65(2)
C(212)	4429(8)	935(3)	7940(8)	60(2)
O	558(4)	2110(2)	4844(4)	32(1)
C(31)	−550(6)	2108(3)	4017(6)	39(2)
C(32)	−1491(7)	2445(3)	4608(6)	46(2)
C(33)	−668(7)	2850(3)	5231(7)	52(2)
C(34)	437(7)	2537(3)	5713(7)	44(2)
C(41)	3075(11)	4057(4)	4778(11)	93(3)
C(42)	3644(10)	4557(4)	4402(9)	81(3)
C(43)	4687(9)	4756(4)	5189(8)	69(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

stirred for further 12 h, the solution was filtered from unreacted sodium amide, and the solvent was next removed under reduced pressure. The resulting residue was washed with n-hexane (2 × 100 ml); yield 40.98 g (40%) of white solid. M.p. 59°C (decomposition). Anal. found: C, 77.66; H, 10.49. $C_{12}H_{19}Na$ calc.: C, 77.38; H, 10.28%. ^{1}H-NMR (pyridine-d_5) δ 3.45 (sep, $^3J(^1H,^1H) =$ 7 Hz, 1H, CHMe$_2$), 2.48 (s, 6H, C_5CH_3), 2.40 (s, 6H, C_5CH_3), 1.56 (d, $^3J(^1H,^1H) = 7$ Hz, 6H, CH(CH_3)$_2$); $^{13}C\{^1H\}$-NMR (pyridine-d_5) δ 117.60 ($C_5{}^iPr$), 105.60 (C_5Me), 104.09 (C_5Me), 27.88 (CHMe$_2$), 25.21 (CH(CH$_3$)$_2$), 12.82 (C_5CH_3), 11.91 (C_5CH_3).

3.2. $[(C_5Me_4{}^iPr)_2YCl(THF)]$ (**1**)

A 1.73 g (4.20 mmol) amount of $YCl_3(THF)_3$ was suspended in 70 ml of THF and 1.64 g (8.80 mmol) of $Na[C_5Me_4{}^iPr]$ were added at room temperature. The reaction mixture was stirred and heated at reflux for 12 h. After the solvent had been removed under vacuum, the residue was treated with 75 ml of n-hexane, stirred, allowed to settle, and the clear solution was decanted off. Concentration to 25 ml and cooling to −28°C gave the product in a crystalline form; yield 1.65 g (75%) of colorless crystals. M.p. 98°C (decomposition). Anal. found: C, 63.90; H, 8.55. $C_{28}H_{46}ClOY$ calc.: C, 64.30; H, 8.86%. ^{1}H-NMR (benzene-d_6) δ 3.60 (m, 4H, THF), 3.16 (sep, $^3J(^1H,^1H) = 7$ Hz, 2H, CHMe$_2$), 2.18 (s, 12H, C_5CH_3), 1.98 (s, 12H, C_5CH_3), 1.31 (d, $^3J(^1H,^1H) = 7$ Hz, 12H, CH(CH_3)$_2$), 1.22 (m, 4H, THF); $^{13}C\{^1H\}$-NMR (benzene-d_6) δ 118.67 (d, $^1J(^{89}Y,^{13}C) = 1.4$ Hz, $C_5{}^iPr$), 118.33 (d, $^1J(^{89}Y,^{13}C) = 1.2$ Hz, C_5Me), 72.24 (THF), 27.57 (CHMe$_2$), 25.27 (THF), 23.37 (CH(CH$_3$)$_2$), 12.63 (C_5CH_3), 11.80 (C_5CH_3). MS (140°C); m/z (%): 450 ([M–THF]$^+$, 60), 415 ($[(C_5Me_4{}^iPr)_2Y]^+$, 7), 287 ($[(C_5Me_4{}^iPr)YCl]^+$, 100), 252 ($[(C_5Me_4{}^iPr)Y]^+$, 1) and additional fragments.

Table 4
Atomic coordinates and equivalent isotropic displacement parameters for **5**

Atom	x [10^{-4}]	y [10^{-4}]	z [10^{-4}]	U_{eq} [10^{-3} Å^2]
Lu	2213(1)	1561(1)	4746(1)	26(1)
C(1)	3168(5)	2107(2)	6266(5)	27(1)
C(11)	3827(5)	2085(2)	3483(6)	33(1)
C(12)	2644(6)	2207(2)	2946(5)	32(1)
C(13)	2159(6)	1746(3)	2392(5)	33(1)
C(14)	3047(6)	1346(3)	2588(6)	33(1)
C(15)	4081(5)	1552(2)	3282(6)	35(1)
C(16)	4719(6)	2485(3)	4041(6)	42(2)
C(17)	2079(6)	2740(2)	2872(6)	40(2)
C(18)	1025(6)	1702(3)	1538(6)	44(2)
C(19)	3003(7)	843(3)	1885(6)	44(2)
C(110)	5286(6)	1253(3)	3559(7)	42(2)
C(111)	5785(7)	1300(3)	4853(7)	58(2)
C(112)	6260(7)	1410(3)	2668(8)	61(2)
C(21)	1556(6)	1010(3)	6686(6)	39(2)
C(22)	566(6)	967(3)	5800(6)	38(2)
C(23)	990(6)	686(3)	4821(6)	40(2)
C(24)	2247(6)	542(2)	5112(6)	37(2)
C(25)	2600(6)	751(2)	6246(6)	37(2)
C(26)	1428(8)	1242(3)	7915(6)	55(2)
C(27)	−756(6)	1134(3)	5986(8)	61(2)
C(28)	188(7)	496(3)	3739(7)	57(2)
C(29)	2987(8)	146(3)	4450(7)	55(2)
C(210)	3758(7)	566(3)	6974(7)	49(2)
C(211)	3427(8)	76(3)	7674(8)	65(2)
C(212)	4401(8)	950(3)	7832(8)	67(2)
O	485(4)	2105(2)	4739(4)	36(1)
C(31)	−632(6)	2100(3)	3938(6)	44(2)
C(32)	−1563(6)	2432(3)	4577(7)	49(2)
C(33)	−740(7)	2842(3)	5178(7)	53(2)
C(34)	368(7)	2522(3)	5628(7)	48(2)
C(41)	3064(11)	4066(5)	4735(11)	106(4)
C(42)	3631(11)	4556(5)	4445(12)	106(4)
C(43)	4677(10)	4756(4)	5148(9)	80(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.3. $[(C_5Me_4{}^iPr)_2SmCl(THF)]$ (**2**)

Following the procedure described for **1**, 0.89 g (2.22 mmol) of $SmCl_3(THF)_2$ were treated with 0.83 g (4.44 mmol) of $Na[C_5Me_4{}^iPr]$; yield 0.91 g (70%), orange crystals. M.p. 92°C (decomposition). Anal. found: C, 57.00; H, 7.53. $C_{28}H_{46}ClOSm$ calc.: C, 57.54; H, 7.93%. ^{1}H-NMR (benzene-d_6) δ 2.9 (sep, 2H, C*H*Me$_2$), 2.2 (s, lw = 22 Hz, 12H, C_5CH_3), 1.2 (s, lw = 31 Hz, 12H, C_5CH_3), −0.4 (d, 12H, $CH(CH_3)_2$), −0.9 (m, 4H, THF), −1.3 (m, 4H, THF); $^{13}C\{^1H\}$-NMR (benzene-d_6) δ 125.86 ($C_5{}^iPr$), 117.50 (C_5Me), 65.56 (THF), 31.86 (*C*HMe$_2$), 21.77 (THF), 19.43 (C_5CH_3), 19.26 (C_5CH_3), 17.70 ($CH(CH_3)_2$). MS (250°C, ^{152}Sm); *m*/*z* (%): 513 ([M–THF]$^+$, 19), 478 ($[(C_5Me_4{}^iPr)_2Sm]^+$, 9), 350 ($[(C_5Me_4{}^iPr)SmCl]^+$, 59), 315 ($[(C_5Me_4{}^iPr)Sm]^+$, 15), 149 ($[(C_5Me_4{}^iPr)H–CH_3]^+$, 100) and additional fragments.

3.4. $[(C_5Me_4{}^iPr)_2LuCl(THF)]$ (**3**)

Following the procedure described for **1**, 1.09 g (2.20 mmol) of $LuCl_3(THF)_3$ were treated with 0.88 g (4.55 mmol) of $Na[C_5Me_4{}^iPr]$; yield 0.95 g (71%), colorless crystals. M.p. 65°C (decomposition). Anal. found: C, 54.81; H, 7.48. $C_{28}H_{46}ClLuO$ calc.: C, 55.21; H, 7.61%. ^{1}H-NMR (benzene-d_6) δ 3.65 (m, 4H, THF), 3.17 (sep, $^3J(^1H,^1H) = 7$ Hz, 2H, C*H*Me$_2$), 2.19 (s, 12H, C_5CH_3), 1.98 (s, 12H, C_5CH_3), 1.30 (d, $^3J(^1H,^1H) = 7$ Hz, 12H, $CH(CH_3)_2$), 1.24 (m, 4H, THF); $^{13}C\{^1H\}$-NMR (benzene-d_6) δ 118.37 ($C_5{}^iPr$), 117.57 (C_5Me), 73.09 (THF), 27.63 (*C*HMe$_2$), 25.47 (THF), 23.31 ($CH(CH_3)_2$), 12.82 (C_5CH_3), 11.97 (C_5CH_3). MS (200°C, ^{175}Lu); *m*/*z* (%): 536 ([M–THF]$^+$, 79), 501 ($[(C_5Me_4{}^iPr)_2Lu]^+$, 5), 373 ($[(C_5Me_4{}^iPr)LuCl]^+$, 89), 338 ($[(C_5Me_4{}^iPr)Lu]^+$, 1) 149 ($[(C_5Me_4{}^iPr)H–CH_3]^+$, 100) and additional fragments.

3.5. $[(C_5Me_4{}^iPr)_2YMe(THF)]$ (**4**)

To a suspension of 1.04 g (1.99 mmol) of **1** in 70 ml of diethyl ether cooled to −78°C, were added dropwise with stirring 1.3 ml (2.08 mmol) of methyllithium (1.6 M in diethyl ether). The reaction mixture was stirred for 3 h at this temperature. After the solvent of the suspension had been removed under vacuum, the residue was extracted with 75 ml of *n*-hexane. The clear *n*-hexane solution was concentrated to 15 ml and cooled to −28°C, providing the product in a crystalline form; yield 0.36 g (36%) of colorless crystals. M.p. 137°C (decomposition). Anal. found: C, 68.97; H, 9.76. $C_{29}H_{49}OY$ calc.: C, 69.30; H, 9.83%. ^{1}H-NMR (benzene-d_6) δ 3.24 (m, 4H, THF), 3.06 (sep, $^3J(^1H,^1H) = 7$ Hz, 2H, C*H*Me$_2$), 2.19 (s, 12H, C_5CH_3), 1.99 (s, 12H, C_5CH_3), 1.21 (d, $^3J(^1H,^1H) = 7$ Hz, 12H, $CH(CH_3)_2$), 1.06 (m, 4H, THF), −0.95 (d, $^2J(^{89}Y,^1H) = 2.1$ Hz, 3H, YCH_3); $^{13}C\{^1H\}$-NMR (benzene-d_6) δ 125.92 ($C_5{}^iPr$), 116.08 (C_5Me), 115.85 (C_5Me), 70.13 (THF), 27.23 (*C*HMe$_2$), 24.93 (THF), 23.34 ($CH(CH_3)_2$), 16.80 (d, $^1J(^{89}Y,^{13}C) = 50.4$ Hz, YCH_3), 12.45 (C_5CH_3), 11.62 (C_5CH_3). MS (120°C); *m*/*z* (%): 430 ([M–THF]$^+$, 1), 415 ($[(C_5Me_4{}^iPr)_2Y]^+$, 100) and additional fragments.

3.6. $[(C_5Me_4{}^iPr)_2LuMe(THF)]$ (**5**)

Following the procedure described for **4**, 0.79 g (1.30 mmol) of **3** were treated with 0.8 ml (1.28 mmol) of methyllithium (1.6 M in diethyl ether); yield 0.33 g (43%), colorless crystals. M.p. 113°C (decomposition). Anal. found: C, 58.77; H, 8.11. $C_{29}H_{49}LuO$ calc.: C, 59.17; H, 8.39%. ^{1}H-NMR (benzene-d_6) δ 3.36 (m, 4H, THF), 3.09 (sep, $^3J(^1H,^1H) = 7$ Hz, 2H, C*H*Me$_2$), 2.15 (s, 12H, C_5CH_3), 1.96 (s, 12H, C_5CH_3), 1.28 (d, $^3J(^1H,^1H) = 7$ Hz, 12H, $CH(CH_3)_2$), 1.15 (m, 4H, THF), −0.57 (s, 3H, $LuCH_3$); $^{13}C\{^1H\}$-NMR (benzene-d_6) δ 125.35 ($C_5{}^iPr$), 116.07 (C_5Me), 115.73 (C_5Me), 70.75 (THF), 27.30 (*C*HMe$_2$), 25.51 ($LuCH_3$), 25.04 (THF), 23.50 ($CH(CH_3)_2$), 12.56 (C_5CH_3), 11.85 (C_5CH_3). MS (100°C, ^{175}Lu); *m*/*z* (%): 516 ([M–THF]$^+$, 1), 501 ($[(C_5Me_4{}^iPr)_2Lu]^+$, 100) and additional fragments.

3.7. $[(C_5Me_4{}^iPr)_2Y\{CH(SiMe_3)_2\}]$ (**6**)

A 0.31 g (1.88 mmol) amount of $LiCH(SiMe_3)_2$ was added to a solution of 0.98 g (1.87 mmol) of **1** in 70 ml of toluene at −78°C. The reaction mixture was stirred and allowed to warm to room temperature over 5 h. After removal of the volatiles under vacuum, the residue was extracted with 75 ml of *n*-hexane. The clear solution was concentrated to 15 ml and cooled to −28°C, providing the product in a crystalline form; yield 0.65 g (60%) of colorless crystals. M.p. 167°C (decomposition). Anal. found: C, 63.25; H, 9.55. $C_{31}H_{57}Si_2Y$ calc.: C, 64.77; H, 9.99%. ^{1}H-NMR (benzene-d_6) δ 2.98 (sep, $^3J(^1H,^1H) = 7$ Hz, 2H, C*H*Me$_2$), 2.21 (s, 6H, C_5CH_3), 2.16 (s, 6H, C_5CH_3), 1.97 (s, 6H, C_5CH_3), 1.84 (s, 6H, C_5CH_3), 1.10 (d, $^3J(^1H,^1H) = 7$ Hz, 6H, $CH(CH_3)_2$), 1.07 (d, $^3J(^1H,^1H) = 7$ Hz, 6H, $CH(CH_3)_2$), 0.23 (s, 18H, $Si(CH_3)_3$), −0.13 (d, $^2J(^{89}Y,^1H) = 2$ Hz, 1H, $CH(SiMe_3)_2$); $^{13}C\{^1H\}$-NMR (benzene-d_6) δ 127.66 (d, $^1J(^{89}Y, ^{13}C) = 1$ Hz, $C_5{}^iPr$), 120.89 (d, $^1J(^{89}Y,^{13}C) = 1$ Hz, C_5Me), 120.60 (d, $^1J(^{89}Y,^{13}C) = 1$ Hz, C_5Me), 120.39 (d, $^1J(^{89}Y,^{13}C) = 1$ Hz, C_5Me), 119.47 (d, $^1J(^{89}Y,^{13}C) = 1$ Hz, C_5Me), 27.21 (*C*HMe$_2$), 24.54 (d, $^1J(^{89}Y, ^{13}C) = 36$ Hz, $CH(SiMe_3)_2$), 22.96 ($CH(CH_3)_2$), 22.81 ($CH(CH_3)_2$), 13.37 (C_5CH_3), 13.11 (C_5CH_3), 12.39 (C_5CH_3), 12.05 (C_5CH_3), 5.17 ($Si(CH_3)_3$). MS (160°C); *m*/*z* (%): 415 ($[(C_5Me_4{}^iPr)_2Y]^+$, 100) and additional fragments.

3.8. $[(C_5Me_4{}^iPr)_2Sm\{CH(SiMe_3)_2\}]$ (7)

Following the procedure described for **6**, 0.90 g (1.54 mmol) of **2** were treated with 0.26 g (1.56 mmol) of $LiCH(SiMe_3)_2$; yield 0.39 g (40%), red crystals. M.p. 139°C (decomposition). Anal. found: C, 58.38; H, 9.22. $C_{31}H_{57}Si_2Sm$ calc.: C, 58.51; H, 9.03%. ^{1}H-NMR (benzene-d_6) δ 19.7 (s, lw = 35 Hz, 1H, $CH(SiMe_3)_2$), 4.0 (s, lw = 20 Hz, 6H, C_5CH_3), 3.8 (s, lw = 20 Hz, 6H, C_5CH_3), 2.8 (sep, 1H, $CHMe_2$), 1.5 (sep, 1H, $CHMe_2$), −0.4 (s, lw = 13 Hz, 6H, C_5CH_3), −0.6 (s, lw = 12 Hz, 6H, C_5CH_3), −3.2 (d, 6H, $CH(CH_3)_2$), −3.8 (d, 6H, $CH(CH_3)_2$), −4.0 (s, lw = 30 Hz, 18H, $Si(CH_3)_3$). $^{13}C\{^1H\}$-NMR (benzene-d_6) δ 127.29 ($C_5{}^iPr$), 124.52 ($C_5{}^iPr$), 123.33 (C_5Me), 122.55 (C_5Me), 119.59 (C_5Me), 118.99 (C_5Me), 31.35 ($CHMe_2$), 29.92 ($CH(SiMe_3)_2$), 24.13 ($CH(CH_3)_2$), 23.87 ($CH(CH_3)_2$), 18.58 (C_5CH_3), 18.31 (C_5CH_3), 15.96 (C_5CH_3), 15.55 (C_5CH_3), −2.39 ($Si(CH_3)_2$). MS (140°C, ^{152}Sm); m/z (%): 478 ($[(C_5Me_4{}^iPr)_2Sm]^+$, 100) and additional fragments.

3.9. $[(C_5Me_4{}^iPr)_2Sm(THF)]$ (**8**)

A 1.32 g (2.40 mmol) amount of $SmI_2(THF)_2$ was suspended in 70 ml of THF and 0.92 g (4.94 mmol) of $Na[C_5Me_4{}^iPr]$ added at room temperature. The reaction mixture was stirred for 3 h. After the solvent of the suspension had been removed under vacuum, the residue was extracted with 75 ml of n-hexane. The clear solution was concentrated to 30 ml and cooled to −28°C, providing the product in a crystalline form; yield 1.12 g (75%) of dark red crystals. M.p. 153°C (decomposition). Anal. found: C, 61.53; H, 8.47. $C_{28}H_{46}OSm$ calc.: C, 61.25; H, 8.44%. MS (98°C, ^{152}Sm); m/z (%): 478 ($[(C_5Me_4{}^iPr)_2Sm]^+$, 60), 315 ($[(C_5Me_4{}^iPr)Sm]^+$, 100) and additional fragments.

3.10. $[(C_5Me_4{}^iPr)_2Yb(THF)]$ (**9**)

Following the procedure described for **8**, 2.30 g (4.01 mmol) $YbI_2(THF)_2$ were treated with 1.52 g (8.16 mmol) of $Na[C_5Me_4{}^iPr]$; yield 1.56 g (71%), dark green crystals. M.p. 167°C (decomposition). Anal. found: C, 57.60; H, 8.39. $C_{28}H_{46}OYb$ calc.: C, 58.82; H, 8.11%. ^{1}H-NMR (benzene-d_6) δ 3.65 (m, 4H, THF), 3.05 (sep, $^3J(^1H,^1H) = 7$ Hz, 2H, $CHMe_2$), 1.99 (s, 12H, C_5CH_3), 1.92 (s, 12H, C_5CH_3), 1.60 (m, 4H, THF), 1.23 (d, $^3J(^1H,^1H) = 7$ Hz, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$-NMR (benzene-d_6) δ 111.17 ($C_5{}^iPr$), 110.72 (C_5Me), 67.44 (THF), 27.01 ($CHMe_2$), 25.41 (THF), 23.54 ($CH(CH_3)_2$), 11.83 (C_5CH_3), 11.46 (C_5CH_3). MS (121°C, ^{174}Yb); m/z (%): 500 ($[(C_5Me_4{}^iPr)_2Yb]^+$, 68), 337 ($[(C_5Me_4{}^iPr)Yb]^+$, 100) and additional fragments.

3.11. 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 50-ml flask equipped with an Ace needle valve. The homogeneous mixture was stirred for 1–96 h at room temperature or elevated temperature (Table 1). After filtration through a plug of Florisil, the solvent was removed and the crude product was flash chromatographed with SiO_2 and n-hexane as eluant. All hydrosilylation products were identified by comparison with NMR spectra (^{1}H, $^{13}C\{^1H\}$) from the literature ([4]c, [4]d, [4]f).

3.12. Single crystal X-ray structure determination of **3** and **5**

A summary of the crystal data, data collection and refinement parameters for **3** and **5** is given in Table 2. Crystals suitable for X-ray structure determination were mounted on a glass fiber and transferred to an Enraf Nonius CAD-4 automatic diffractometer equipped with a low temperature device. Lattice parameters were derived from the setting angles of 25 reflections in the range of $19 \leq 2\theta \leq 34$ for **3** and $19 \leq 2\theta \leq 29$ for **5**. Data were collected in the ω-2θ scan mode. After every 200 reflections for **3** and **5**, three strong reflections well-distributed in reciprocal space were monitored, and the crystal reoriented in case of deviation larger than 0.1%. The intensities of three check reflections monitored every 2 h showed only statistical fluctuations during the data collection for **3** and **5**. Intensity data were corrected for Lorentz and polarization effects [17].

The space group of **3** and **5** is $P2_1/n$. Structure solution was performed by Pattersson methods (SHELXS 86) [18] and subsequent difference Fourier synthesis (SHELXL 93) [19]. Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL 93). One half of an n-hexane solvent molecule was found in the asymmetric unit of **3** and **5**. The n-hexane molecule lies on the center of symmetry. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model with $d(C–H) = 0.96$ Å and $U_{iso} = 0.08$ Å^2. Scattering factors were taken from Refs. [20–22]. The final residual of least-squares is $R = 3.6\%$ for **3** and $R = 3.5\%$ for **5**. Geometrical calculations were performed with PLATON [23]. For all ZORTEP [10] illustrations, thermal ellipsoids were scaled to 40% probability level. Final positional and equivalent isotropic thermal parameters are given in Table 3 for **3** and in Table 4 for **5**. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-407190 for **3** and CSD-407189 for **5**.

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