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Organometallic Compounds of the Lanthanides. 156.[1] ω-Alkenyl-Functionalized Cyclopentadienyl Complexes of Yttrium, Samarium, Ytterbium, and Lutetium[†]

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YCl_3, $SmCl_3$, $LuCl_3$, and YbI_2 react with the lithium, sodium, and potassium salts of 1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadiene, yielding $[(CH_2{=}CHCH_2CH_2C_5Me_4)_2LnCl]_2$ (Ln = Y (**3a**), Sm (**3b**), Lu (**3c**)) and $(CH_2{=}CHCH_2CH_2C_5Me_4)_2Yb$ (**6**), respectively. The monomeric THF adducts $(CH_2{=}CHCH_2CH_2C_5Me_4)_2LnCl(THF)$ (Ln = Y (**2a**), Sm (**2b**)) crystallize from hexane. $Li[C_5Me_4CH_2CH_2CH_2CH{=}CH_2]$ reacts with $SmCl_3$, yielding $(CH_2{=}CHCH_2CH_2CH_2C_5Me_4)_2SmCl(THF)$ (**5b**). The reaction of YCl_3, $SmCl_3$, and $LuCl_3$ with 1 equiv of $M[C_5Me_4CH_2CH_2CH{=}CH_2]$ followed by $M[C_5Me_5]$ (M = Na, K) gives $[(CH_2{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)LnCl]_2$ (Ln = Y (**9a**), Sm (**9b**), Lu (**9c**)). The NaCl adduct $(CH_2{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)Y(\mu\text{-}Cl)_2Na(Et_2O)_2$ (**8a**) crystallizes from Et_2O. The cyclopentadienyllanthanide halides **3a**,**b** and **9b** react with LiMe, $LiCH(SiMe_3)_2$, and $LiN(SiMe_3)_2$, forming the corresponding unstable alkyl derivatives $(CH_2{=}CHCH_2CH_2C_5Me_4)_2LnR$ (Ln = Y, R = Me (**10a**), $CH(SiMe_3)_2$ (**11a**); Ln = Sm, R = $CH(SiMe_3)_2$ (**11b**)), and $(CH_2{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)YCH(SiMe_3)_2$ (**12a**), as well as $(CH_2{=}CHCH_2CH_2C_5Me_4)_2SmN(SiMe_3)_2$ (**13b**). **10a**, **11a**,**b**, and **12a** have been characterized by mass spectrometry, whereas all data of **13b** have been obtained. The trichlorides of Y, Sm, and Lu react with 2 equiv of the sodium and potassium salts of 1-(4-methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadiene, yielding $[(Me_2C{=}CHCH_2CH_2C_5Me_4)_2LnCl]_2$ (Ln = Y (**15a**), Sm (**15b**), Lu (**15c**)) or with 1 equiv of $M[C_5Me_4CH_2CH_2CH{=}CMe_2]$ followed by $M[C_5Me_5]$ (M = Na, K), yielding $[(Me_2C{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)LnCl]_2$ (Ln = Y (**17a**), Sm (**17b**), Lu (**17c**)). The monomeric NaCl adduct $(Me_2C{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)Lu(\mu\text{-}Cl)_2Na(OEt_2)_2$ (**16c**) crystallizes from Et_2O. The structures of **2a**,**b**, **8a**, **13b**, and **16c** were determined by single-crystal X-ray diffraction.

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Introduction

Cyclopentadienyllanthanide complexes possess unique properties in homogeneous catalysis. They play an important role as catalysts in polymerization, hydrogenation, and epoxidation reactions.[2] Recent research was especially focused on the synthesis of complexes with substituted cyclopentadienyl ligands containing strong donor atoms such as nitrogen,[3] oxygen,[3d,4] and sulfur[5] in their side chains. The additional intramolecular coordination stabilizes the otherwise very labile lanthanidocenes, leading to moderately stable and solvent-free complexes. Therefore, it was of special interest whether an alkenyl substituent tethered to the cyclopentadienyl ligand would coordinate and protect the metal from deactivation. Considering the missing ability of the lanthanides to carry out π-electron back-donation, the weakly binding donor "double bond" should be displaced by an incoming substrate in order to ensure the catalytic activity of the complexes. Furthermore, the alkenyl site chain offers the possibility to copolymerize metallocenes with other comonomers.[6] Copolymerization of alkenyl-substituted lanthanidocenes would produce the first immobilized olefin polymerization catalysts containing lanthanide metals.

Until now only very few olefin complexes of the lanthanides have been known[7] or proven by NMR

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[†] Dedicated to Professor Gottfried Hüttner on the occasion of his 65th birthday.

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spectroscopy.[8] Recently, Casey demonstrated that even propene is able to coordinate yttrium, yielding a reasonable stable complex.[9] Here we report the synthesis and X-ray structural analyses of a number of yttrium(III), samarium(III), lutetium(III), and ytterbium(II) complexes containing the 1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl, 1-(pent-4-enyl)-2,3,4,5-tetramethylcyclopentadienyl, and the 1-(4-methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl ligands. Analogous lanthanide complexes with vinylcyclopentadienyl and other alkenylcyclopentadienyl ligands will be reported in an additional paper.[10]

Experimental Section

All operations involving organometallic compounds were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques in dry, oxygen-free solvents. Melting points were measured in sealed capillaries with a Büchi 510 melting point determination apparatus and are uncorrected. The NMR spectra were recorded on a Bruker ARX 200 (^{1}H, 200 MHz; ^{13}C, 50.32 MHz) or ARX 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz) spectrometer at 298 K. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the deuterated solvents. Mass spectra (EI, 70 eV) were obtained by using a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities are given in parentheses. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. 1-(But-3-enyl)-2,3,4,5-tetramethylcyclopentadiene (**1**),[11] lithium bis(trimethylsilyl)methyl,[12] potassium bis(trimethylsilyl)amide,[13] and $YbI_2(THF)_2$[14] were prepared according to published procedures. Anhydrous YCl_3, $SmCl_3$, and $LuCl_3$ were prepared from the pure oxides by reaction with NH_4Cl and Soxhlet extraction with THF.[15]

[1-(But-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]sodium (1b). To a solution of 1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadiene (**1**; 5.46 g, 31 mmol) in tetrahydrofuran (80 mL) was added sodium amide (1.33 g, 34 mmol) at room temperature. The suspension was stirred for 24 h and filtered, and the solvent was removed under vacuum (10^{-2} mbar), leaving a beige solid which was washed with ether/*n*-hexane (1:5) and several times with *n*-hexane, yielding 3.99 g (65%) of a pyrophoric white powder of **1b**; mp 225 °C. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 6.24−6.14 (m, 1 H, $-CH=$), 5.13 (d, $^{3}J_{trans} = 17.1$ Hz, 1 H, $=CH_2$), 4.97 (d, $^{3}J_{cis} = 10.1$ Hz, 1 H, $=CH_2$), 2.90 (t, $^{3}J = 7.5$ Hz, 2 H, CH_2), 2.47 (q, $^{3}J = 7.4$ Hz, 2 H, CH_2), 2.41 (s, 6 H, CH_3), 2.39 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 100.64 MHz): δ 141.49 ($-CH=$), 112.59 ($=CH_2$), 111.01 ($C-C_4H_7$), 105.37 ($C-CH_3$), 104.89 ($C-CH_3$), 38.68 (CH_2), 27.50 (CH_2), 12.00 (CH_3), 11.94 (CH_3). MS (188 °C; *m*/*z* (%)): 176 (28) $[C_{13}H_{20}]^+$, 175 (2) $[C_{13}H_{19}]^+$, 161 (12), 159 (5), 151 (24), 135 (100), 119 (23), 105 (23), 91 (24), 55 (20).

[1-(But-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]potassium (1c). To a solution of 1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadiene (**1**; 7.25 g, 41 mmol) in tetrahydrofuran (150 mL) was added potassium hydride (1.65 g, 41 mmol) at room temperature. The suspension was stirred for 12 h at room temperature and warmed to 60 °C. Beige needles crystallize after cooling to 25 °C. Filtering, washing of the residue with pentane, and drying under vacuum (10^{-2} mbar) yields 4.75 g (54%) of a pyrophoric beige powder of **1c**; mp 221 °C. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 6.17−6.00 (m, 1 H, $-CH=$), 5.17 (d, $^{3}J_{trans} = 17.1$ Hz, 1 H, $=CH_2$), 5.07 (d, $^{3}J_{cis} = 10.1$ Hz, 1 H, $=CH_2$), 2.73−2.66 (m, 2 H, CH_2), 2.38−2.26 (m, 2 H, CH_2), 2.19 (s, 6 H, CH_3), 2.14 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 100.64 MHz): δ 141.47 ($-CH=$), 113.39 ($=CH_2$), 111.55 ($C-C_4H_7$), 105.88 ($C-CH_3$), 105.69 ($C-CH_3$), 37.96 (CH_2), 26.37 (CH_2), 11.25 (CH_3). MS (284 °C; *m*/*z* (%)): 214 (7) $[M]^+$, 176 (18) $[C_{13}H_{20}]^+$, 175 (44) $[C_{13}H_{19}]^+$, 159 (16), 145 (34), 133 (29), 119 (44), 105 (19), 91 (17), 55 (11), 39 (100). Anal. Calcd for $C_{13}H_{19}K$ (mol wt 214.39): C, 72.83; H, 8.93. Found: C, 71.15; H, 9.10.

Bis[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]yttrium Chloride (3a). To a suspension of YCl_3 (1.17 g, 6 mmol) in THF (80 mL) was added $K[C_5Me_4CH_2CH_2CH=CH_2]$ (**1c**; 2.57 g, 12 mmol) at room temperature, and the reaction mixture was stirred for 12 h. After removal of the solvent under vacuum, the residue was extracted with diethyl ether. The resulting ether solution was evaporated and the residue washed twice with *n*-hexane (30 mL), dissolved in toluene (50 mL), and refluxed for 2 h. The hot solution was filtered and cooled to room temperature to provide 2.37 g (83%) of a beige powder of **3a**; mp 258 °C dec. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 6.00−5.80 (m, 2 H, $-CH=$), 5.06 (d, $^{3}J_{cis} = 16.9$ Hz, 2 H, $=CH_2$), 4.97 (d, $^{3}J_{trans} = 9.2$ Hz, 2 H, $=CH_2$), 2.60−2.50 (m$_{br}$, 4 H, CH_2Cp), 2.15−2.05 (m$_{br}$, 4 H, CH_2), 2.01 (s, 12 H, CH_3), 1.95 (s, 12 H, CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 139.04 ($-CH=$), 121.55 (d, $^{1}J_{YC} = 1.3$ Hz, $C-C_4H_7$), 117.64 (d, $^{1}J_{YC} = 1.2$ Hz, $C-CH_3$), 117.04 (d, $^{1}J_{YC} = 1.2$ Hz, $C-CH_3$), 114.10 ($=CH$), 35.16 (CH_2Cp), 26.36 (CH_2), 11.25 (CH_3), 11.20 (CH_3). MS (172 °C; *m*/*z* (%)): 474 (11) [M(monomer)]$^+$, 439 (2) $[C_{26}H_{38}Y]^+$, 433 (12) $[C_{23}H_{32}YCl]^+$, 299 (100) $[C_{13}H_{19}YCl]^+$, 257 (6) $[C_{10}H_{13}YCl]^+$, 176 (8), 135 (42). Anal. Calcd for $C_{26}H_{38}ClY$ (mol wt 474.95): C, 65.75; H, 8.06. Found: C, 65.86; H, 8.44.

The *n*-hexane portions used in the washing process of the first reaction product were evaporated, yielding a few yellowish crystals of **2a**, suitable for X-ray diffraction. ^{1}H NMR (benzene-d_6, 200 MHz): δ 6.00−5.80 (m, 2 H, $-CH=$), 5.08 (d, $^{3}J_{cis} = 17.0$ Hz, 2 H, $=CH_2$), 4.97 (d, $^{3}J_{trans} = 10.6$ Hz, 2 H, $=CH_2$), 3.53−3.47 (m$_{br}$, CH_2, THF), 2.69−2.61 (m, 4 H, CH_2Cp), 2.21−2.13 (m, 4 H, CH_2), 2.07 (s, 12 H, CH_3), 1.99 (s, 12 H, CH_3), 1.25−1.16 (m$_{br}$, CH_2, THF).

Bis[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]samarium Chloride (3b). In analogy to the preparation of **3a**, $SmCl_3$ (1.54 g, 6 mmol) in THF (80 mL) was reacted with $K[C_5Me_4CH_2CH_2CH=CH_2]$ (**1c**; 2.57 g, 12 mmol) to provide 2.60 g (81%) of an orange powder of **3b**; mp 223 °C dec. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.49−6.30 (m, 2 H, $-CH=$), 5.31 (d, $^{3}J_{cis} = 17.1$ Hz, 2 H, $=CH_2$), 5.16 (d, $^{3}J_{trans} = 10.0$ Hz, 2 H, $=CH_2$), 3.35−3.25 (m$_{br}$, 4 H, CH_2Cp), 2.00−1.97 (m$_{br}$, 4 H, CH_2), 1.45 (s, 12 H, CH_3), 1.23 (s, 12 H, CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 139.26 ($-CH=$), 120.31 ($C-C_4H_7$), 116.11 ($C-CH_3$), 114.54 ($C-CH_3$), 114.54 ($=CH$), 31.91 (CH_2Cp), 31.86 (CH_2), 16.95 (CH_3), 16.78 (CH_3). MS (^{152}Sm, 145 °C; *m*/*z* (%)): 537.2 (21) [M(monomer)]$^+$, 502 (3) $[C_{26}H_{38}Sm]^+$, 496 (13) $[C_{23}H_{32}SmCl]^+$, 364 (100) $[C_{13}H_{19}SmCl]^+$, 327 (6) $[C_{13}H_{19}Sm]^+$, 321 (25) $[C_{10}H_{13}SmCl]^+$, 187 (30) $[SmCl]^+$, 176 (8), 135 (29). Anal. Calcd for $C_{26}H_{38}ClSm$ (mol wt 536.40): C, 58.22; H, 7.14. Found: C, 58.03; H, 6.74.

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The *n*-hexane portions used in the washing process of the first reaction product were evaporated, yielding a few yellow crystals of **2b**, suitable for X-ray diffraction. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.45−6.25 (m, 2 H, −CH=), 5.26 (d, $^3J_{\rm cis}$ = 17.1 Hz, 2 H, =CH$_2$), 5.04 (d, $^3J_{\rm trans}$ = 10.0 Hz, 2 H, =CH$_2$), 3.64 (m$_{\rm br}$, CH$_2$, THF), 3.25−3.14 (m, 4 H, CH$_2$Cp), 2.56 (s$_{\rm br}$, 4 H, CH$_2$), 1.89 (s, 12 H, CH$_3$), 1.69 (s, 12 H, CH$_3$), 1.61 (m, CH$_2$, THF).

Bis[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]-lutetium Chloride (3c). In analogy to the preparation of **3a**, LuCl$_3$(THF)$_3$ (1.76 g, 3.53 mmol) in THF (80 mL) was reacted with K[C$_5$Me$_4$CH$_2$CH$_2$CH=CH$_2$] (**1c**; 1.51 g, 7.07 mmol) to provide 1.66 g (84%) of a beige powder of **3c**; mp 243 °C dec. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.00−5.80 (m, 2 H, −CH=), 5.06 (d, $^3J_{\rm cis}$ = 17.1 Hz, 2 H, =CH$_2$), 4.96 (d, $^3J_{\rm trans}$ = 10.7 Hz, 2 H, =CH$_2$), 2.58−2.50 (m, 4 H, CH$_2$Cp), 2.15−2.08 (m, 4 H, CH$_2$), 2.01 (s, 6 H, CH$_3$), 1.98 (s, 6 H, CH$_3$), 1.95 (s, 6 H, CH$_3$), 1.93 (s, 6 H, CH$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 139.11 (−CH=), 120.79 (*C*−C$_4$H$_7$), 116.97 (*C*−CH$_3$), 116.90 (*C*−CH$_3$), 116.44 (*C*−CH$_3$), 116.22 (*C*−CH$_3$), 114.05 (=CH), 35.06 (CH$_2$Cp), 26.50 (CH$_2$), 11.40 (CH$_3$), 11.32 (CH$_3$). MS (^{175}Lu, 105 °C; *m/z* (%)): 560 (21) [M(monomer)]$^+$, 525 (3) [C$_{26}$H$_{38}$Lu]$^+$, 519 (19) [C$_{23}$H$_{33}$LuCl]$^+$, 385 (100) [C$_{13}$H$_{19}$LuCl]$^+$, 343 (14) [C$_{10}$H$_{13}$-LuCl]$^+$, 176 (0.5), 135 (3). Anal. Calcd for C$_{26}$H$_{38}$ClLu (mol wt 561.01): C, 55.67; H, 6.83. Found: C, 55.20; H, 6.95.

[1-(Pent-4-enyl)-2,3,4,5-tetramethylcyclopentadienyl]-lithium (4a). Tetramethylcyclopent-2-enone (10.10 mL, 67 mmol) in diethyl ether (20 mL) was dropped into a Grignard reagent made from 5-bromo-1-pentene (10.0 g, 67 mmol) and magnesium (1.63 g, 67 mmol) in diethyl ether (80 mL) within 15 min. After 2 h of refluxing, pouring on ice, diluting with concentrated HCl (30 mL), and 15 min of stirring, the aqueous phase was separated and extracted twice with diethyl ether (50 mL each). The combined organic phases were washed four times with 10% NaHCO$_3$ (40 mL each) and twice with saturated NaCl solution (50 mL each) and dried over MgSO$_4$. Evaporation of the solvent and distillation yielded 11.96 g (95%) of 1-(pent-4-enyl)-2,3,4,5-tetramethylcyclopentadiene (mixture of isomers) (**4**): bp 55−60 °C, 10^{-2} mbar.

To a solution of **4** (3.92 g, 21 mmol) in *n*-hexane (50 mL) was dropped *n*-butyllithium (12.86 mL, 1.6 M in *n*-hexane) at 0 °C. The reaction mixture was stirred for 12 h at room temperature and filtered, and the white solid was washed twice with *n*-hexane (15 mL each) and dried under vacuum (10^{-2} mbar), yielding 2.66 g (66%) of a pyrophoric white powder of **4a**; mp 198 °C. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.07−5.89 (m, 1 H, −CH=), 5.08 (d, $^3J_{\rm trans}$ = 17.1 Hz, 1 H, =CH$_2$), 4.96 (d, $^3J_{\rm cis}$ = 10.1 Hz, 1 H, =CH$_2$), 2.73 (t, ^3J = 7.0 Hz, 2 H, CH$_2$), 2.28 (s, 12 H, CH$_3$), 1.82−1.67 (m, 4 H, CH$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 140.18 (−CH=), 113.48 (=CH$_2$), 111.71 (*C*−C$_5$H$_9$), 105.86 (*C*−CH$_3$), 105.48 (*C*−CH$_3$), 34.36 (CH$_2$), 32.80 (CH$_2$), 26.40 (CH$_2$), 11.25 (CH$_3$).

[1-(Pent-4-enyl)-2,3,4,5-tetramethylcyclopentadienyl]-sodium (4b). In analogy to the preparation of **1b**, **4** (11.96 g, 62 mmol) in THF (150 mL) was reacted with sodium amide (2.45 g, 62 mmol) to provide 5.67 g (43%) of a pyrophoric white powder of **4b**; mp 189 °C. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.05−5.84 (m, 1 H, −CH=), 5.02 (d, $^3J_{\rm trans}$ = 18.4 Hz, 1 H, =CH$_2$), 4.93 (d, $^3J_{\rm cis}$ = 10.1 Hz, 1 H, =CH$_2$), 2.80 (t, ^3J = 7.3 Hz, 2 H, CH$_2$), 2.42 (s, 6 H, CH$_3$), 2.40 (s, 6 H, CH$_3$), 1.86−1.73 (m, 4 H, CH$_2$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 140.30 (−CH=), 113.29 (=CH$_2$), 111.68 (*C*−C$_5$H$_9$), 105.28 (*C*−CH$_3$), 104.95 (*C*−CH$_3$), 34.32 (CH$_2$), 33.41 (CH$_2$), 27.29 (CH$_2$), 12.11 (CH$_3$).

Bis[1-(pent-4-enyl)-2,3,4,5-tetramethylcyclopentadienyl]-(tetrahydrofuran)samarium Chloride (5b). To a suspension of SmCl$_3$(THF)$_{0.4}$ (1.12 g, 3.92 mmol) in THF (80 mL) was added Li[C$_5$Me$_4$CH$_2$CH$_2$CH$_2$CH=CH$_2$] (**4a**; 1.54 g, 7.84 mmol) at room temperature, and the reaction mixture was stirred for 12 h. After removal of the solvent under vacuum, the residue was extracted with *n*-hexane (50 mL). The *n*-hexane solution was concentrated to 15 mL, treated with THF (5 mL), and cooled to −30 °C to provide after 2 weeks 1.04 g (42%) of an orange powder of **5b**; mp 197 °C. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.18−5.93 (m, 2 H, −CH=), 5.13 (d, $^3J_{\rm cis}$ = 16.9 Hz, ^2J = 1.8 Hz, 2 H, =CH$_2$), 5.00 (d, $^3J_{\rm trans}$ = 10.0 Hz, ^2J = 2.0 Hz, 2 H, =CH$_2$), 3.65 (m, 4 H, THF), 2.48 (s$_{\rm br}$, 8 H, CH$_2$), 2.36 (s$_{\rm br}$, 4 H, CH$_2$), 1.85 (s, 12 H, CH$_3$), 1.76 (s, 12 H, CH$_3$), 1.60 (4 H, THF). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 139.65 (−CH=), 114.38 (*C*−C$_5$H$_9$), 113.93 (=CH$_2$), 113.66 (*C*−CH$_3$), 113.20 (*C*−CH$_3$), 67.45 (CH$_2$, THF), 34.20 (CH$_2$), 31.28 (CH$_2$), 28.03 (CH$_2$), 25.43 (CH$_2$, THF), 16.65 (CH$_3$). MS (^{152}Sm, 233 °C; *m/z* (%)): 567 (12) [M − THF]$^+$, 541 (5) [C$_{26}$H$_{40}$Sm]$^+$, 532 (3) [C$_{28}$H$_{42}$Sm]$^+$, 376 (94) [C$_{14}$H$_{21}$SmCl]$^+$, 341 (9) [C$_{14}$H$_{21}$Sm]$^+$, 321 (21) [C$_{10}$H$_{13}$SmCl]$^+$, 190 (25) [C$_{14}$H$_{22}$]$^+$, 175 (38) [C$_{13}$H$_{19}$]$^+$, 160 (13) [C$_{12}$H$_{16}$]$^+$, 147 (22) [C$_{11}$H$_{15}$]$^+$, 135 (48) [C$_{10}$H$_{15}$]$^+$. Anal. Calcd for C$_{32}$H$_{50}$ClOSm (mol wt 636.56): C, 60.38; H, 7.92. Found: C, 60.34; H, 7.75.

Bis[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]ytterbium (6). To a suspension of YbI$_2$(THF)$_2$ (0.72 g, 1.27 mmol) in THF (50 mL) was added K[C$_5$Me$_4$CH$_2$CH$_2$CH=CH$_2$] (**1c**; 0.54 g, 2.55 mmol) at room temperature, and the reaction mixture was stirred for 12 h. After removal of the solvent under vacuum, the residue was extracted with *n*-hexane (50 mL). The *n*-hexane solution was concentrated to 10 mL, precipitating 0.35 g (53%) of a black solid of **6**; mp 179 °C. ^{1}H NMR (benzene-d_6, 400 MHz): δ 5.85−5.75 (m, 2 H, −CH=), 4.78 (d, $^3J_{\rm cis}$ = 19.0 Hz, 2 H, =CH$_2$), 4.73 (d, $^3J_{\rm trans}$ = 11.2 Hz, 2 H, =CH$_2$), 2.51 (t, ^3J = 6.1 Hz, 4 H, CH$_2$−Cp), 2.10 (s, 12 H, CH$_3$), 2.08 (t, ^3J = 6.2 Hz, 4 H, CH$_2$), 1.98 (s, 12 H, CH$_3$). ^{13}C-{^{1}H} NMR (benzene-d_6, 100.64 MHz): δ 147.78 (−CH=), 119.02 (*C*−C$_4$H$_7$), 113.87 (=CH$_2$), 112.61 (*C*−CH$_3$), 111.51 (*C*−CH$_3$), 36.27 (CH$_2$), 23.89 (CH$_2$), 11.36 (CH$_3$), 11.28 (CH$_3$). MS (^{174}Yb, 136 °C; *m/z* (%)): 524 (61) [M]$^+$, 349 (100) [C$_{13}$H$_{41}$Yb]$^+$, 307 (17) [C$_{10}$H$_{13}$Yb]$^+$, 176 (17) [C$_{13}$H$_{20}$]$^+$, 135 (54) [C$_{10}$H$_{15}$]$^+$. Anal. Calcd for C$_{26}$H$_{38}$Yb (mol wt 523.63): C, 59.64; H, 7.31. Found: C, 59.01; H, 6.71.

Bis{(μ-chloro)[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl](pentamethylcyclopentadienyl)yttrium} (9a). To a stirred suspension of YCl$_3$ (1.32 g, 6.76 mmol) in THF (80 mL) at room temperature was added first K[C$_5$Me$_4$CH$_2$-CH$_2$CH=CH$_2$] (**1c**; 1.44 g, 6.76 mmol) and then after 1 h Na-[C$_5$Me$_5$] (1.06 g, 6.76 mmol), and the reaction mixture was stirred for 12 h. After removal of the solvent under vacuum, the residue was extracted with diethyl ether (70 mL). The resulting ether solution was evaporated and the residue washed with *n*-hexane (20 mL), dissolved in toluene (100 mL), and refluxed for 4 h. Part of the solvent is evaporated each 20 min by vacuum, to concentrate the solution to 100 mL. The hot solution was filtered and cooled to room temperature to provide 2.0 g (68%) of a beige powder of **9a**; mp 319 °C dec. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.00−5.80 (m, 2 H, −CH=), 5.07 (d, $^3J_{\rm cis}$ = 16.4 Hz, 2 H, =CH$_2$), 4.97 (d, $^3J_{\rm trans}$ = 10.1 Hz, 2 H, =CH$_2$), 2.65−2.52 (m, 4 H, CH$_2$Cp), 2.19−2.05 (m, 4 H, CH$_2$), 2.03 (s, 12 H, CH$_3$), 2.00 (s, 12 H, CH$_3$), 1.96 (s, 30 H, CH$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 139.06 (−CH=), 121.47 (*C*−C$_4$H$_7$), 117.53 (*C*−CH$_3$), 116.95 (*C*−CH$_3$), 114.10 (=CH), 35.18 (CH$_2$Cp), 26.31 (CH$_2$), 11.24 (CH$_3$), 11.16 (CH$_3$). MS (258 °C; *m/z* (%)): 434 (19) [M(monomer)]$^+$, 399 (6) [C$_{23}$H$_{34}$Y]$^+$, 394 (13) [C$_{20}$H$_{29}$YCl]$^+$, 299 (100) [C$_{13}$H$_{19}$YCl]$^+$, 259 (47) [C$_{10}$H$_{15}$YCl]$^+$, 257 (20) [C$_{10}$H$_{13}$YCl]$^+$, 176 (3) [C$_{13}$H$_{20}$]$^+$, 135 (25) [C$_{10}$H$_{15}$]$^+$. Anal. Calcd for C$_{46}$H$_{68}$Cl$_2$Y$_2$ (mol wt 869.76): C, 63.52; H, 7.88. Found: C, 63.31; H, 7.39.

Bis{(μ-chloro)[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl](pentamethylcyclopentadienyl)samarium} (9b). In analogy to the preparation of **9a**, SmCl$_3$(THF)$_3$ (1.13 g, 2.82 mmol) in THF (80 mL) was reacted with Na[C$_5$Me$_4$-CH$_2$CH$_2$CH=CH$_2$] (**1b**; 0.56 g, 2.82 mmol) and K[C$_5$Me$_5$] (0.5 g, 2.82 mmol) to provide 1.05 g (75%) of a yellow powder of **9b**; mp 287 °C dec. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.52−6.27 (m, 2 H, −CH=), 5.30 (d, $^3J_{\rm cis}$ = 17.1 Hz, 2 H, =CH$_2$), 5.14 (d, $^3J_{\rm trans}$ = 10.3 Hz, 2 H, =CH$_2$), 3.29 (s$_{\rm br}$, 4 H, CH$_2$Cp),

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1.94 (s_{br}, 4 H, CH_2), 1.45 (s, 12 H, CH_3), 1.31 (s, 30 H, CH_3), 1.22 (s, 12 H, CH_3). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 50.32 MHz): δ 139.20 (−CH=), 120.00 ($C-C_4H_7$), 115.9 (s_{br}, $C-CH_3$), 114.38 (=CH_2), 31.80 (CH_2), 16.89 (CH_3, Cp*), 16.86 (CH_3), 16.63 (CH_3). MS (^{152}Sm, 304 °C; *m/z* (%)): 499 (9) [M(monomer)]$^+$, 462 (3) $[C_{23}H_{34}Sm]^+$, 457 (18) $[C_{20}H_{28}Sm]^+$, 364 (26) $[C_{13}H_{19}SmCl]^+$, 327 (5) $[C_{13}H_{19}Sm]^+$, 323 (50) $[C_{10}H_{15}SmCl]^+$, 321 (48) $[C_{10}H_{13}SmCl]^+$, 287 (14) $[C_{10}H_{15}Sm]^+$, 189 (42) $[SmCl]^+$, 176 (21) $[C_{13}H_{19}]^+$, 135 (100) $[C_{10}H_{15}]^+$. Anal. Calcd for $C_{46}H_{68}Cl_2Sm_2$ (mol wt 992.68): C, 55.66; H, 6.90. Found: C, 55.92; H, 7.20.

Bis{(*μ*-chloro)[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl](pentamethylcyclopentadienyl)lutetium} (9c). In analogy to the preparation of **9a**, $LuCl_3(THF)_3$ (2.21 g, 4.44 mmol) in THF (80 mL) was reacted with $Na[C_5Me_4CH_2CH_2CH{=}CH_2]$ (**1b**; 0.88 g, 4.44 mmol) and $K[C_5Me_5]$ (0.77 g, 4.44 mmol) to provide 1.69 g (73%) of a beige powder of **9c**; mp 274 °C dec. ^1H NMR (pyridine-d_5, 200 MHz): δ 5.99−5.79 (m, 2 H, −CH=), 5.06 (d, $^3J_{cis}$ = 17.1 Hz, 2 H, =CH_2), 4.97 (d, $^3J_{trans}$ = 10.1 Hz, ^2J = 2.1 Hz, 2 H, =CH_2), 2.60−2.47 (m_{br}, 4 H, CH_2Cp), 2.18−2.04 (m_{br}, 4 H, CH_2), 2.00 (s_{br}, 12 H, CH_3), 1.92 (s, 42 H, CH_3). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 50.32 MHz): δ 139.13 (−CH=), 120.70 ($C-C_4H_7$), 116.81 ($C-CH_3$), 116.72 ($C-CH_3$), 114.06 (=CH), 35.09 (CH_2Cp), 26.44 (CH_2), 11.39 (CH_3). MS (^{175}Lu, 218 °C; *m/z* (%)): 520 (27) [M(monomer)]$^+$, 485 (4) $[C_{23}H_{34}Lu]^+$, 479 (18) $[C_{20}H_{28}LuCl]^+$, 385 (100) $[C_{13}H_{19}LuCl]^+$, 345 (42) $[C_{10}H_{15}LuCl]^+$, 343 (32) $[C_{10}H_{13}LuCl]^+$, 135 (8) $[C_{10}H_{15}]^+$. Anal. Calcd for $C_{46}H_{68}Cl_2Lu_2$ (mol wt 1041.88): C, 53.03; H, 6.58. Found: C, 52.85; H, 6.05.

Bis[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]methylyttrium (10a). To a solution of **3a** (0.48 g, 0.5 mmol) in diethyl ether (80 mL) was added MeLi (0.67 mL, 1 mmol, 1.5 M in Et_2O) at −78 °C, and the reaction mixture was stirred for 12 h. A white solid precipitates, which could not be purified by either recrystallization or extraction with toluene. MS (171 °C; *m/z* (%)): 534 (23), 532 (17), 510 (15), 454 (33) [M]$^+$, 453 (60) [M − 1]$^+$, 452 (100) [M − 2]$^+$, 439 (28) $[C_{26}H_{38}Y]^+$, 438 (46) $[C_{26}H_{37}Y]^+$, 437 (47) $[C_{26}H_{36}Y]^+$, 423 (29), 399 (17), 398 (17), 397 (16), 358 (15), 317 (20), 316 (12), 315 (21), 304 (27), 303 (25), 302 (30), 301 (24), 233 (22), 226 (28), 223 (16), 219 (28), 185 (12), 175 (11), 135 (93); $C_{27}H_{41}Y$ (mol wt 454.53).

Bis[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl][bis(trimethylsilyl)methyl]yttrium (11a). In analogy to the preparation of **10a**, **3a** (0.98 g, 1.03 mmol) in diethyl ether (80 mL) was reacted with $(Me_3Si)_2CHLi$ (0.34 g, 2.06 mmol) to give a white solid. MS (23 °C; *m/z* (%)): 599 (5) [M]$^+$, 439 (61) $[M - CH(SiMe_3)_2]^+$, 423 (2) $[M - C_{13}H_{19}]^+$, together with signals of **3a**; $C_{33}H_{57}YSi_2$ (mol wt 598.88).

Bis[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl][bis(trimethylsilyl)methyl]samarium (11b). In analogy to the preparation of **10a**, **3b** (0.65 g, 0.60 mmol) in diethyl ether (80 mL) was reacted with $(Me_3Si)_2CHLi$ (0.20 g, 1.21 mmol) to give a white solid. MS (^{152}Sm, 117 °C; *m/z* (%)): 662 (0.03) [M]$^+$, 502 (11) $[M - CH(SiMe_3)_2]^+$, 486 (0.14) $[M - C_{13}H_{19}]^+$, 327 (9) $[SmC_{13}H_{19}]^+$, 286 (3) $[SmC_{10}H_{14}]^+$, 176 (4) $[C_{13}H_{19}]^+$, 145 (100) $[C_6H_{17}Si_2]^+$, 135 (17) $[C_{10}H_{15}]^+$; $C_{33}H_{57}SmSi_2$ (mol wt 660.34).

[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl][bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)yttrium (12a). In analogy to the preparation of **10a**, **9a** (0.28 g, 0.32 mmol) in diethyl ether (25 mL) was reacted with $(Me_3Si)_2CHLi$ (0.11 g, 0.64 mmol) to give a white solid. MS (123 °C; *m/z* (%)): 599 (1.4) [M]$^+$, 399 (100) $[C_{23}H_{34}Y]^+$, 359 (57) $[C_{20}H_{30}Y]^+$, 265 (10) $[C_{13}H_{19}Y]^+$, 223 (32) $[C_{10}H_{13}Y]^+$, 179 (16), 176 (8) $[C_{13}H_{20}]^+$, 145 (0) $[C_6H_{16}Si_2]^+$, 135 (44) $[C_{10}H_{15}]^+$; $C_{30}H_{53}YSi_2$ (mol wt 558.83).

Bis[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]samarium Bis(trimethylsilyl)amide (13b). To a solution of **3b** (2.35 g, 2.19 mmol) in diethyl ether (80 mL) was added $K[N(SiMe_3)_2]$ (0.87 g, 4.39 mmol) at −78 °C, and the reaction mixture was stirred for 12 h. After filtration of the precipitated KCl and removal of the solvent under vacuum, the residue was diluted in *n*-hexane and filtered and the *n*-hexane solution cooled to −78 °C, providing 1.27 g (44%) of deep red crystals of **13b**; mp 65 °C dec. ^1H NMR (benzene-d_6, 400 MHz): δ 6.58−6.53 (m, 2 H, −CH=), 5.44 (d, $^3J_{cis}$ = 17.1 Hz, 2 H, =CH_2), 5.21 (d, $^3J_{trans}$ = 9.9 Hz, 2 H, =CH_2), 3.85 (s_{br}, 4 H, CH_2Cp), 1.88 (s_{br}, 4 H, CH_2), 0.70 (s, 24 H, CH_3), −6.39 (s, 18 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.64 MHz): δ 139.02 (−CH=), 123.70 ($C-C_4H_7$), 120.21 ($C-CH_3$), 119.84 ($C-CH_3$), 115.09 (=CH), 36.90 (CH_2Cp), 28.65 (CH_2), 21.80 (CH_3), 21.69 (CH_3), −2.69 ($SiCH_3$). MS (^{152}Sm, 117 °C; *m/z* (%)): 662 (0.5) [M]$^+$, 502 (1) $[C_{26}H_{38}Sm]^+$, 487 (93) $[M - C_{13}H_{19}]^+$, 312 (29) $[M - C_{26}H_{38}]^+$, 176 (26) $[C_{13}H_{20}]^+$, 135 (96) $[C_{10}H_{15}]^+$. Anal. Calcd for $C_{32}H_{56}NSi_2Sm$ (mol wt 661.33): C, 58.12; H, 8.53; N, 2.12. Found: C, 58.80; H, 8.78; N, 2.15.

[1-(4-Methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]sodium (14b). Into a solution of the Grignard reagent $Me_2C{=}CHCH_2CH_2MgBr$, made from 5-bromo-2-methyl-2-pentene (4.75 g, 29 mmol) and Mg (0.71 g, 29 mmol) in diethyl ether (80 mL), was dropped within 15 min 2,3,4,5-tetramethylcyclopent-2-enone (4.39 mL, 4.01 g, 29 mmol) in diethyl ether (20 mL). After 2 h of refluxing the yellow reaction mixture is poured on ice, treated with concentrated HCl (30 mL), and stirred for 15 min at room temperature. After separation, the aqueous phase is extracted four times with diethyl ether (50 mL each) and the combined ethereal solutions are washed four times with 10% aqueous $NaHCO_3$ (40 mL each) and twice with 50% aqueous NaCl (50 mL each). Drying over $MgSO_4$, evaporation of the solvent, and distillation resulted in 5.62 g (94%) of 1-(4-methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadiene (**14**) (mixture of isomers); bp 58−65 °C/10^{-2} mbar. To **14** (5.62 g, 27 mmol) in tetrahydrofuran (100 mL) was added sodium amide (1.07 g, 27 mmol) at room temperature. The suspension was stirred for 24 h and filtered, and the solvent was removed under vacuum (10^{-2} mbar), leaving a white solid which was washed with ether/hexane (1:5) and several times with *n*-hexane, yielding 2.63 g (43%) of a pyrophoric white powder of **14b**; mp 149 °C. ^1H NMR (pyridine-d_5, 200 MHz): δ 5.63−5.50 (m, 1 H, −CH=), 2.94−2.86 (m, 2 H, CH_2), 2.46−2.35 (m, 2 H, CH_2), 2.46 (s, 6 H, CH_3), 2.42 (s, 6 H, CH_3), 1.69 (s, 3 H, =CH_3(trans)), 1.65 (s, 3 H, CH_3(cis)). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 50.32 MHz): δ 129.03 (=$C(CH_3)_2$), 127.21 (−CH=), 111.81 ($C-C_6H_{11}$), 105.33 ($C-CH_3$), 104.90 ($C-CH_3$), 33.20 (CH_2), 28.26 (CH_2), 25.57 (=CH_3(trans)), 17.43 (=$CH_{3/cis}$), 12.11 (CH_3), 12.05 (CH_3). MS (303 °C; *m/z* (%)): 226 (2.5) [M]$^+$, 204 (17) $[C_{15}H_{24}]^+$, 203 (5) $[C_{15}H_{23}]^+$, 134 (100) $[C_{10}H_{15}]^+$, 122 (8), 119 (18), 107 (11). Anal. Calcd for $C_{15}H_{23}Na$ (mol wt 226.34): C, 79.60; H, 10.24. Found: C, 79.58; H, 8.84.

[1-(4-Methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]potassium (14c). In analogy to the preparation of **14b**, to **14** (13.1 g, 64 mmol) in tetrahydrofuran (150 mL) was added potassium hydride (2.58 g, 64 mmol) at room temperature to provide 12.36 g (80%) of a pyrophoric yellow powder of **14c**, mp 147 °C. ^1H NMR (pyridine-d_5, 400 MHz): δ 5.50−5.45 (m, 1 H, -CH=), 2.69−2.63 (m, 2 H, CH_2), 2.25−2.16 (m, 2 H, CH_2), 2.22 (s, 6 H, CH_3), 2.21 (s, 6 H, CH_3), 1.72 (s, 3 H, =CH_3(trans)), 1.71 (s, 3 H, CH_3(cis)). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 100.64 MHz): δ 129.82 (=$C(CH_3)_2$), 126.31 (−CH=), 112.29 ($C-C_6H_{11}$), 105.84 ($C-CH_3$), 105.52 ($C-CH_3$), 32.65 (CH_2), 27.45 (CH_2), 25.48 (=CH_3(trans)), 17.39 (=CH_3(cis)), 11.27 (CH_3), 11.25 (CH_3). MS (288 °C; *m/z* (%)): 242 (16) [M]$^+$, 204 (10) $[C_{15}H_{24}]^+$, 203 (17) $[C_{15}H_{23}]^+$, 147 (22), 135 (78), 134 (94), 120 (13), 119 (87), 107 (9), 105 (15), 91 (18), 69 (27). Anal. Calcd for $C_{15}H_{23}K$ (mol wt 242.45): C, 74.31; H, 9.56. Found: C, 72.59; H, 9.58.

Bis{(*μ*-chloro)bis[1-(4-methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]yttrium} (15a). In analogy to the preparation of **3a**, YCl_3 (0.78 g, 4 mmol) in THF (80 mL) was reacted with $K[C_5Me_4CH_2CH_2CH{=}CMe_2]$ (**14c**; 1.93 g, 8 mmol) to provide 1.73 g (82%) of a beige powder of **15a**; mp

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101 °C dec. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 5.25$-$5.20 (m, 4 H, $-\mathrm{CH}=$), 2.56$-$2.50 (m, 8 H, CH_2Cp), 2.13$-$2.03 (m, 8 H, CH_2), 2.03 (s, 24 H, CH_3), 1.96 (s, 12 H, CH_3), 1.48 (s, 12 H, CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 100.64 MHz): δ 130.92 ($=C(CH_3)_2$), 124.76 ($-\mathrm{CH}=$), 122.00 ($C-C_6H_{11}$), 117.60 ($C-CH_3$), 117.03 ($C-CH_3$), 29.55 (CH_2Cp), 26.82 (CH_2), 25.34 (CH_3), 17.00 (CH_3), 11.16 (CH_3, Cp), 11.13 (CH_3, Cp). MS (^{89}Y, 266 °C; *m/z* (%)): 530 (5) [M(monomer)]$^+$, 495 (5) $[C_{30}H_{46}Y]^+$, 461 (5) $[C_{25}H_{37}YCl]^+$, 327 (100) $[C_{15}H_{23}YCl]^+$, 259 (23) $[C_{10}H_{14}YCl]^+$, 204 (5), 135 (47). Anal. Calcd for $C_{60}H_{92}Cl_2Y_2$ (mol wt 1062.1): C, 67.85; H, 8.73. Found: C, 67.36; H, 8.97.

Bis{(μ-chloro)bis[1-(4-methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]samarium} (15b). In analogy to the preparation of **3a**, $SmCl_3$ (0.93 g, 3.62 mmol) in THF (80 mL) was reacted with $K[C_5Me_4CH_2CH_2CH{=}CMe_2]$ (**14c**; 1.75 g, 7.24 mmol) to provide 1.67 g (78%) of an orange powder of **15b**; mp 124 °C dec. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 5.69$-$5.62 (m, 4 H, $-\mathrm{CH}=$), 3.20$-$3.10 (m_{br}, 8 H, CH_2Cp), 1.94$-$1.84 (m, 8 H, CH_2), 1.89 (s, 12 H, CH_3), 1.80 (s, 12 H, CH_3), 1.46 (s, 24 H, CH_3), 1.27 (s, 24 H, CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 131.31 ($=C(CH_3)_2$), 124.94 ($-\mathrm{CH}=$), 120.57 ($C-C_6H_{11}$), 116.08 ($C-CH_3$), 115.92 ($C-CH_3$), 32.28 (CH_2Cp), 26.13 (CH_2), 25.56 (CH_3), 17.44 (CH_3), 16.90 (CH_3, Cp), 16.76 (CH_3, Cp). MS (^{152}Sm, 269 °C; *m/z* (%)): 77 (0.5) $[C_{30}H_{46}Sm_2Cl_2]^+$, 593 (7) $[C_{30}H_{46}SmCl]^+$, 558 (4) $[C_{30}H_{46}Sm]^+$, 524 (8) $[C_{25}H_{37}SmCl]^+$, 392 (65) $[C_{15}H_{23}SmCl]^+$, 355 (3) $[C_{15}H_{23}Sm]^+$, 323 (19) $[C_{10}H_{14}SmCl]^+$, 204 (12), 187 (23) $[SmCl]^+$, 135 (100). Anal. Calcd for $C_{60}H_{92}Cl_2Sm_2$ (mol wt 1185.02): C, 60.81; H, 7.83. Found: C, 60.46; H, 7.75.

Bis{(μ-chloro)bis[1-(4-methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]lutetium} (15c). In analogy to the preparation of **3a**, $LuCl_3(THF)_3$ (1.89 g, 3.78 mmol) in THF (80 mL) was reacted with $K[C_5Me_4CH_2CH_2CH{=}CMe_2]$ (**14c**; 1.83 g, 7.59 mmol) to provide 1.96 g (84%) of a beige powder of **15c**; mp 98 °C dec. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 5.27$-$5.19 (m, 4 H, $-\mathrm{CH}=$), 2.58$-$2.45 (m, 8 H, CH_2Cp), 2.15$-$2.04 (m, 8 H, CH_2), 2.04 (s, 24 H, CH_3), 1.96 (s, 24 H, CH_3), 1.62 (s, 12 H, CH_3), 1.48 (s, 12H, CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 130.88 ($=C(CH_3)_2$), 124.85 ($-\mathrm{CH}=$), 121.26 ($C-C_6H_{11}$), 117.01 ($C-CH_3$), 116.87 ($C-CH_3$), 116.35 ($C-CH_3$), 116.33 ($C-CH_3$), 29.55 (CH_2Cp), 27.06 (CH_2), 25.42 (CH_3), 17.09 (CH_3), 11.39 (CH_3, Cp). MS (^{175}Lu, 207 °C; *m/z* (%)): 616 (7) [M(monomer)]$^+$, 581 (1) $[C_{30}H_{46}Lu]^+$, 547 (4) $[C_{25}H_{37}LuCl]^+$, 413 (100) $[C_{15}H_{23}LuCl]^+$, 345 (38) $[C_{10}H_{14}LuCl]^+$, 204 (1), 135 (14). Anal. Calcd for $C_{60}H_{92}Cl_2Lu_2$ (mol wt 1234.24): C, 58.39; H, 7.51. Found: C, 57.70; H, 7.59.

Bis{(μ-chloro)[1-(4-methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl](pentamethylcyclopentadienyl)yttrium} (17a). In analogy to the preparation of **9a**, YCl_3 (0.48 g, 2.47 mmol) in THF (80 mL) was reacted with $Na[C_5Me_4CH_2CH_2CH{=}CMe_2]$ (**14b**; 0.56 g, 2.47 mmol) and $Na[C_5Me_5]$ (0.39 g, 2.47 mmol) to provide 0.62 g (54%) of a beige powder of **17a**; mp 200 °C dec. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 5.30$-$5.18 (m, 2 H, $-\mathrm{CH}=$), 2.59$-$2.47 (m, 4 H, CH_2-Cp), 2.15$-$2.05 (m, 4 H, CH_2), 2.03 (s, 12 H, CH_3), 1.93 (s, 12 H, CH_3), 1.93 (s, 30 H, CH_3), 1.63 (s_{br}, 6 H, CH_3(trans)), 1.49 (s_{br}, 6 H, CH_3(cis)). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 130.92 ($=C(CH_3)_2$), 124.79 ($-\mathrm{CH}=$), 122.02 (d, $^{1}J_{^{89}Y,^{13}C} = 1.3$ Hz, $C-C_6H_{11}$), 117.57 (d, $^{1}J_{^{89}Y,^{13}C} = 1.2$ Hz, $C-CH_3$), 117.48 (d, $^{1}J_{^{89}Y,^{13}C} = 1.3$ Hz, $C-CH_3$, Cp*), 117.02 (d, $^{1}J_{^{89}Y,^{13}C} = 1.2$ Hz, $C-CH_3$), 29.65 (CH_2-Cp), 26.86 (CH_2), 25.43 ($=CCH_3$(trans)), 17.10 ($=CCH_3$(cis)), 11.21 (CH_3). MS (191 °C; *m/z* (%)): 462 (19) [M(monomer)]$^+$, 427 (4) $[C_{25}H_{38}Y]^+$, 393 (17) $[C_{20}H_{28}YCl]^+$, 327 (100) $[C_{15}H_{23}YCl]^+$, 259 (39) $[C_{10}H_{15}YCl]^+$, 204 (1) $[C_{15}H_{24}]^+$, 135 (13) $[C_{10}H_{15}]^+$. Anal. Calcd for $C_{50}H_{76}Cl_2Y_2$ (mol wt 925.88): C, 64.86; H, 8.27. Found: C, 65.27; H, 7.83.

Bis{(μ-chloro)[1-(4-methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl](pentamethylcyclopentadienyl)samarium} (17b). In analogy to the preparation of **9a**, $SmCl_3$ (1.08 g, 4.21 mmol) in THF (80 mL) was reacted with $K[C_5Me_4CH_2CH_2CH{=}CMe_2]$ (**14c**; 0.95 g, 4.21 mmol) and $Na[C_5Me_5]$ (0.66 g, 4.21 mmol) to provide 0.97 g (44%) of an orange powder of **17b**; mp 232 °C dec. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 5.68$-$5.61 (m, 2 H, $-\mathrm{CH}=$), 3.17$-$3.10 (m_{br}, 4 H, CH_2-Cp), 1.86 (s, 6 H, CH_3), 1.78 (s, 6 H, CH_3), 1.80$-$1.72 (m, 4 H, CH_2), 1.60$-$1.10 (m_{br}, 54 H, CH_3). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 129.02 ($=C(CH_3)_2$), 125.37 ($-\mathrm{CH}=$), 120.50 ($C-C_6H_{11}$), 115.99 ($C-CH_3$), 32.17 (CH_2-Cp), 25.46 (CH_3), 25.35 (CH_2), 17.34 (CH_3), 16.76 (CH_3, Cp), 16.54 (CH_3, Cp). MS (^{152}Sm, 61 °C; *m/z* (%)): 525 (5) [M(monomer)]$^+$, 490 (1) $[C_{25}H_{38}Sm]^+$, 456 (3) $[C_{20}H_{28}SmCl]^+$, 390 (34) $[C_{15}H_{23}SmCl]^+$, 323 (15) $[C_{10}H_{15}SmCl]^+$, 204 (20) $[C_{15}H_{24}]^+$, 135 (100) $[C_{10}H_{15}]^+$. Anal. Calcd for $C_{50}H_{76}Cl_2Sm_2$ (mol wt 1048.78): C, 57.26; H, 7.30. Found: C, 56.93; H, 7.53.

Bis{(μ-chloro)[1-(4-methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl](pentamethylcyclopentadienyl)lutetium} (17c). In analogy to the preparation of **9a**, $LuCl_3$ (0.85 g, 1.71 mmol) in THF (80 mL) was reacted with $Na[C_5Me_4CH_2CH_2CH{=}CMe_2]$ (**14b**; 0.38 g, 1.71 mmol) and $Na[C_5Me_5]$ (0.27 g, 1.71 mmol) to provide 0.45 g (49%) of a beige powder of **17c**; mp 212 °C dec. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 5.30$-$5.18 (m, 2 H, $-\mathrm{CH}=$), 2.54$-$2.46 (m, 4 H, CH_2-Cp), 2.02 (s, 12 H, CH_3), 1.93 (s, 12 H, CH_3), 1.92 (s, 30 H, CH_3), 1.82$-$1.70 (m, 4 H, CH_2), 1.63 (s_{br}, 6 H, CH_3(trans)), 1.49 (s_{br}, 6 H, CH_3(cis)). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 130.88 ($=C(CH_3)_2$), 124.86 ($-\mathrm{CH}=$), 121.23 ($C-C_6H_{11}$), 116.94 ($C-CH_3$), 116.79 ($C-CH_3$, Cp*), 116.27 ($C-CH_3$), 29.56 (CH_2-Cp), 27.02 (CH_2), 25.42 ($C-CH_3$(trans)), 17.09 ($C-CH_{3/cis}$), 11.38 (CH_3). MS (^{175}Lu, 203 °C; *m/z* (%)): 548 (22) [M(monomer)]$^+$, 513 (3) $[C_{25}H_{38}Lu]^+$, 479 (23) $[C_{20}H_{28}LuCl]^+$, 413 (100) $[C_{15}H_{23}LuCl]^+$, 345 (53) $[C_{10}H_{15}LuCl]^+$, 204 (3) $[C_{15}H_{24}]^+$, 135 (27) $[C_{10}H_{15}]^+$. Anal. Calcd for $C_{50}H_{76}Cl_2Lu_2$ (mol wt 1097.99): C, 54.70; H, 6.98. Found: C, 55.08; H, 6.12.

The *n*-hexane portions used in the washing process of the first reaction product were evaporated, yielding a few colorless crystals of **16c**, suitable for X-ray diffraction.

X-ray Structure Determination. The crystal data and details of data collections of **2a**,**b**, **8a**, **13b**, and **16c** are given in Table 1. Data sets were collected at 173 K on a Siemens SMART CCD diffractometer[16] (ω scans, $\lambda = 0.710\,73$ Å, Mo Kα). The structures were solved by direct methods using SHELXS-97[17] and refined on F^2 using all reflections with SHELXL-97.[18] All non-hydrogen atoms of **2a**,**b**, **8a**, and **13b** were refined anisotropically. One ethyl chain of each of the coordinated diethyl ether solvent molecules in **16c** showed disorder and was refined isotropically. SADABS[19] was used to perform area detector scaling and absorption corrections. Further material is part of the Supporting Information. The geometrical aspects of the structures were analyzed by using PLATON software.[20]

Results and Discussion

[1-(But-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]- and [1-(Pent-4-enyl)-2,3,4,5-tetramethylcyclopentadienyl]lanthanide Chlorides. The trichlorides of yttrium, samarium, and lutetium react in THF at room temperature with 2 equiv of alkali-metal salts of 1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadiene (alkali metal = Li (**1a**), Na (**1b**), K (**1c**)), which are

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Table 1. Crystal Structure Determination of 2a,b, 8a, 13b, and 16c

	2a	**2b**	**8a**	**13b**	**16c**
empirical formula	$C_{30}H_{46}ClOY$	$C_{30}H_{46}ClOSm$	$C_{31}H_{54}Cl_2NaO_2Y$	$C_{32}H_{56}NSi_2Sm$	$C_{33}H_{58}Cl_2NaO_2Lu$
fw	547.1	608.5	641.5	661.3	755.7
cryst size (mm^3)	0.50 × 0.50 × 0.40	0.90 × 0.36 × 0.25	0.36 × 0.24 × 0.18	0.70 × 0.30 × 0.20	0.52 × 0.44 × 0.40
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$C2/c$	$P2_1/n$
Z (formula units)	2	2	4	4	4
a (Å)	8.49780(10)	8.52810(10)	14.1843(13)	19.2718(2)	15.8983(2)
b (Å)	11.0340(10)	11.1139(2)	14.829(3)	14.55600(10)	15.8069(2)
c (Å)	16.67060(10)	16.7786(2)	16.330(3)	14.25320(10)	16.44610(10)
α (deg)	74.6320(10)	74.3790(10)	90	90	90
β (deg)	81.7780(10)	81.88000(10)	92.993(10)	121.7950(10)	117.4770(10)
γ (deg)	75.6650(10)	75.7590(10)	90	90	90
V (Å^3)	1455.32(2)	1479.68(4)	3430.2(9)	3398.41(4)	3666.74(7)
D(calcd) (g/cm^3)	1.248	1.366	1.242	1.293	1.349
F(000)	580	626	1360	1380	1508
μ(Mo Kα) (mm^{-1})	2.114	2.093	1.892	1.818	2.874
2θ range (deg)	$3 \le 2\theta \le 55$	$4 \le 2\theta \le 55$	$4 \le 2\theta \le 70$	$4 \le 2\theta \le 55$	$3 \le 2\theta \le 55$
no. of collected rflns	11 184	11 481	35 788	12 899	26 760
no. of unique rflns	6573	6741	12 724	3904	8368
abs cor (SADABS): max/min	0.4985/0.4074	0.4769/0.3228	0.5027/0.3477	0.5930/0.4234	0.1129/0.0454
no. of obsd rflns, $I > 2\sigma(I)$	5759	6232	8007	3508	5253
no. of data/restraints/params	6573/0/306	6741/0/306	12724/0/347	3890/0/276	8343/2/360
R1: $I > 2\sigma(I)$/all data[a]	0.0322/0.0418	0.0317/0.0355	0.0477/0.1016	0.0245/0.0313	0.0480/0.0953
wR2: $I > 2\sigma(I)$/all data[b]	0.0731/0.0769	0.0788/0.0807	0.0910/0.1088	0.0574/0.0629	0.0944/0.1159
goodness of fit[c]	1.060	1.008	1.016	1.012	1.109
wt details a/b[d]	0.0314/0.2437	0.0477/0	0.0441/0.3095	0.0327/1.5159	0.0298/0
diff peak/hole, e Å^{-3}	0.649/−0.404	1.518/−2.580	0.409/−0.668	0.963/−1.051	2.505/−2.809

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $S = [\sum w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$. [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

prepared from **1** and butyllithium,[11] sodium amide, or potassium hydride. Evaporation of the solvent under vacuum (10^{-2} mbar) after 12 h leads to the crude bis(butenyltetramethylcyclopentadienyl)lanthanide chlorides (lanthanide = Y (**3a**), Sm (**3b**), Lu (**3c**)). The remaining oils are extracted with diethyl ether, and after removal of the second solvent different observations can be made. When **1a** is used for the reaction, an oil is obtained, whereas the application of **1b** or **1c** leads to a solid. Even though all residues are washed with hexane, no solid can be obtained in the first case. Subsequent crystallization from toluene leads to **3a**−**c** in reasonable yields only if the reaction is carried out with the sodium and potassium salts of **1** (Scheme 1). Obviously, the formed lithium chloride prevents a satisfactory purification of the metallocenes.

The beige to orange complexes melt with decomposition, and when exposed to air, they are pyrophoric. The low solubility in nonpolar, noncoordinating solvents such as hexane, benzene, and toluene has hindered successful cryoscopic molecular weight determinations, NMR spectroscopy, or growing crystals for X-ray crystallography, and therefore information about a monomeric or dimeric chlorine-bridged structure is lacking. In the mass spectra of **3a**−**c** the monomer is detected as the molecular ion peak, but there is evidence for a dimeric structure from elemental analyses and the NMR data in *d*-pyridine. In polar solvents such as THF and pyridine, the complexes show good solubility, since the solvent molecule breaks the dimeric form, resulting in the solvent-coordinated monomers $(CH_2{=}CHCH_2CH_2C_5Me_4)_2LnCl(L)$ (L = THF, pyridine). However, if the three complexes **3a**−**c** were monomeric, they would contain either THF, which could be detected in the ^{1}H NMR spectrum, or coordinate alkali-metal chloride, which could be found in the elemental analyses. Indeed, the ^{1}H NMR spectra show no signals for coordinated solvent. This demonstrates that the monomeric THF complexes, which are formed during the reaction, lose their coordinated THF molecule when evaporated, resulting in the chlorine-bridged dimers $[(CH_2{=}CHCH_2CH_2C_5Me_4)_2LnCl]_2$. Surprisingly, the lutetium derivative **3c** shows four signals for four inequivalent CH_3 groups in the ^{1}H NMR spectra and also four signals for the cyclopentadienyl carbon atoms carrying the methyl groups in the ^{13}C NMR spectra, whereas the spectra of **3a**,**b** show only two peaks each, which may be caused by a hindered rotation of the cyclopentadienyl rings around the somewhat smaller lutetium in relation to yttrium (**3a**) and samarium (**3b**). A possible coordination of the olefinic double bond to the metal, which would also stabilize the monomeric form, cannot be detected in the ^{1}H NMR spectrum because of the reasons discussed above.

Furthermore, it was not possible to grow crystals for a structural determination of the solvent adducts from THF and pyridine solutions. Only from the first hexane fraction of the washing procedure could a few crystals of the compounds $(CH_2{=}CHCH_2CH_2C_5Me_4)_2YCl(THF)$ (**2a**) and $(CH_2{=}CHCH_2CH_2C_5Me_4)_2SmCl(THF)$ (**2b**) be obtained. The molecular structures of these isomorphous and isostructural complexes **2a**,**b** show monomers with the metal atoms coordinated by two cyclopentadienyl ligands, the chlorine, and the THF oxygen in a slightly distorted tetrahedral arrangement (Figures 1 and 2). Bonding distances and angles are in accordance with those of $(C_5Me_5)_2LnCl(THF)$.[21,22] The olefinic double bond does not coordinate to the metal.

Assuming that an increase of the alkene chain length

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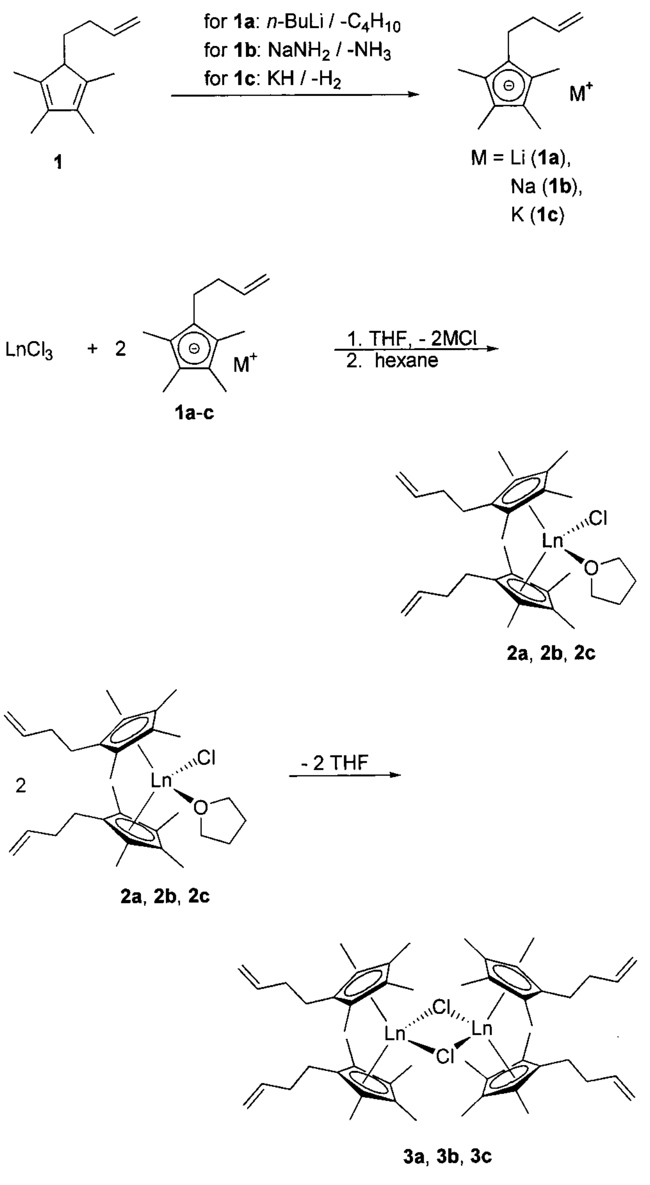
Scheme 1



Ln = Y (**2a**, **3a**), Sm (**2b**, **3b**), Lu (**2c**, **3c**)

would provide better coordination conditions for the double bond, the pentenyl-substituted cyclopentadiene **4** was prepared according to the synthesis of the butenyl-substituted cyclopentadiene **1**.[11] Compound **4** is converted into the metal salts (metal = Li (**4a**), Na (**4b**)), which react with the trichlorides of yttrium, samarium, and lutetium as outlined earlier. After the purification procedure, the products are oils regardless of which metal salt (**4a**,**b**) is used. Crystallization from toluene cannot be achieved, and attempts to obtain pure compounds via sublimation lead to decomposition. Only the samarium derivative **5b** could be isolated from a THF−hexane mixture at −30 °C, as an amorphous precipitate and characterized by ^{1}H and ^{13}C NMR, MS, and elemental analysis to be $(CH_2{=}CHCH_2CH_2CH_2C_5Me_4)_2SmCl(THF)$ (**5b**) (Scheme 2).

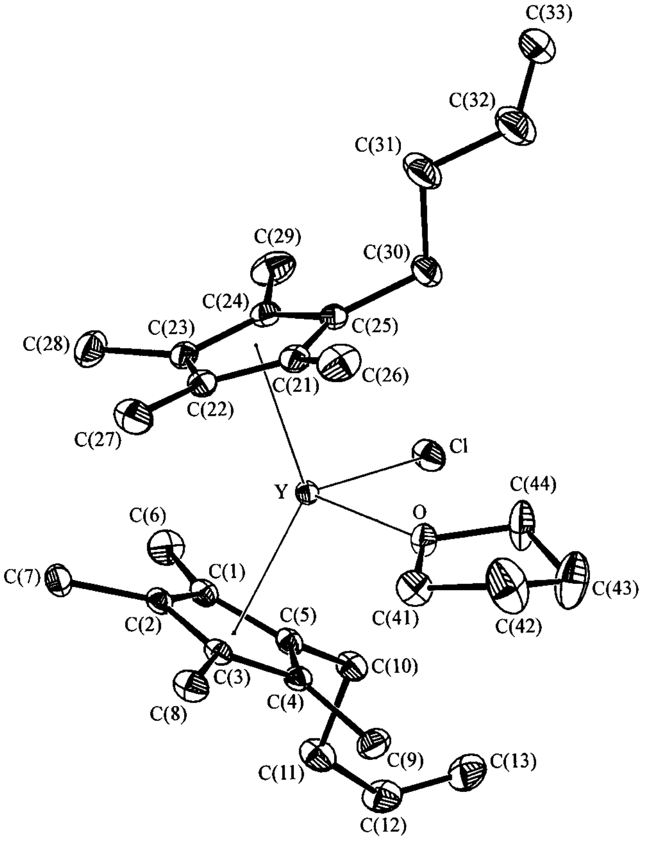


Figure 1. ORTEP plot[23] of the molecular structure and the numbering scheme of **2a** with 40% probability thermal ellipsoids. The hydrogen atoms are not depicted. Selected bond lengths (Å) and bond angles (deg), with estimated standard deviations in parentheses (Cp(1) and Cp(2) define the centroid positions of the ring atoms C(1−5) and C(21−25), respectively): Cp(1)−Y = 2.3833(9), Cp(2)−Y = 2.3859(9), Y−Cl = 2.5973(5), Y−O = 2.3677(14); Cp(1)−Y−Cp(2) = 135.28(3), Cp(1)−Y−Cl = 106.59(3), Cp(2)−Y−Cl = 105.69(3), Cp(1)−Y−O = 104.81(4), Cp(2)−Y−O = 104.81(5), O−Y−Cl = 90.97(4).

To answer the question of the behavior of alkenyl-substituted cyclopentadienyl complexes of divalent lanthanides, 2 equiv of $K[C_5Me_4CH_2CH_2CH{=}CH_2]$ (**1c**) was added to suspensions of samarium(II) and ytterbium(II) iodides in THF at room temperature. In the case of samarium, the bis(butenyltetramethylcyclopentadienyl) complex decomposes during the reaction. Oxidation of Sm(II) to Sm(III) is observed by color changes from black to orange. Too many byproducts do not allow a satisfying characterization of the product mixture. In comparison to samarium, the black bis[1-(but-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]ytterbium(II) (**6**) can be obtained as an amorphous precipitate from hexane (Scheme 3). The mass spectrum shows the molecular ion peak and the fragment containing ytterbium with only one ligand as the mass peak. The NMR spectrum, recorded in noncoordinating *d*-benzene, shows no signals for coordinated THF but also no indication for a coordination of the alkenyl group to the unsaturated metal center.

The chelating effect of cyclopentadienyl ligands containing strong donors such as oxygen can stabilize monocyclopentadienyl complexes of the lanthanides.[3d,4] If the ligand has no second donor functionality, mono(cyclopentadienyl) complexes stabilize themselves via coordination of alkali metal halides.[24] After the reaction

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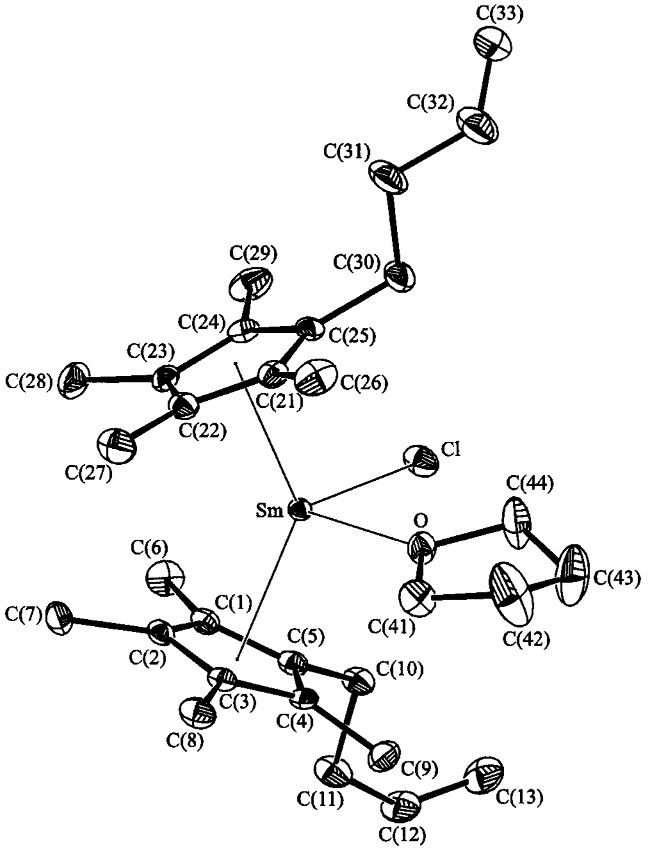
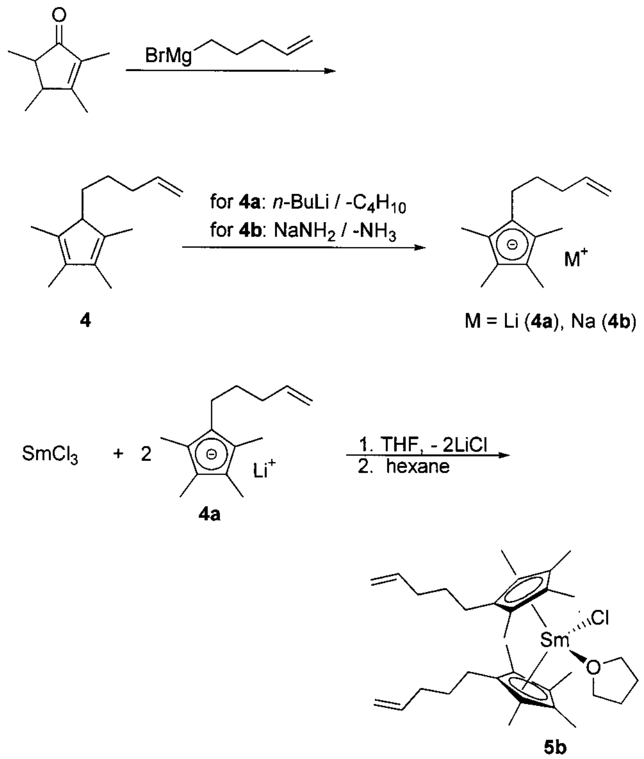


Figure 2. ORTEP plot[23] of the molecular structure and the numbering scheme of **2b** with 40% probability thermal ellipsoids. The hydrogen atoms are not depicted. Selected bond lengths (Å) and bond angles (deg), with estimated standard deviations in parentheses (Cp(1) and Cp(2) define the centroid positions of the ring atoms C(1−5) and C(21−25), respectively): Cp(1)−Sm = 2.4491(2), Cp(2)−Sm = 2.4526(1), Sm−Cl = 2.6607(7), Y−O = 2.450(2); Cp(1)−Sm−Cp(2) = 134.98(1), Cp(1)−Sm−Cl = 106.60(2), Cp(2)−Sm−Cl = 105.71(2), Cp(1)−Sm−O = 105.02(5), Cp(2)−Sm−O = 104.64(5), O−Sm−Cl = 91.42 (6).

of $LnCl_3$ (Ln = Y, Sm, Lu) with equimolar amounts of $M[C_5Me_4CH_2CH_2CH{=}CH_2]$ (M = Na (**1b**), K (**1c**)) in THF at room temperature, the corresponding mono(cyclopentadienyl) lanthanide complexes $(CH_2{=}CHCH_2CH_2C_5Me_4)LnCl_2$ (**7a**−**c**) are formed but could not be isolated pure enough for characterization. However, coordination of the double bond seems to be unlikely, since recently published results show that the complex $(CH_2{=}CHCH_2CMePrC_5H_4)LnCl_2$ could only be isolated as a $MgCl_2$ adduct of the type $(CH_2{=}CHCH_2CMePrC_5H_4)LnCl_2MgCl_2(THF)$ (Ln = La, Nd, Sm, Gd).[7f]

The complexes **7a**−**c** react in situ with equimolar amounts of $M[C_5Me_5]$ (M = Na, K), resulting in monomeric alkali metal chloride stabilized lanthanidocenes, as proven by the molecular structure of $(CH_2{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)Y(\mu\text{-}Cl)_2Na(Et_2O)_2$ (**8a**) (Figure 3). **8a** was obtained from diethyl ether after extraction of the crude reaction mixture, whereas crystallization of compounds **8** in polar solvents remains unsuccessful. Treatment of the evaporated residues with nonpolar solvents such as hexane and toluene leads to the loss of the alkali metal chloride and to the solvent-free dimers $[(CH_2{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)LnCl]_2$ (**9a**−**c**) (Scheme 4).

Scheme 2



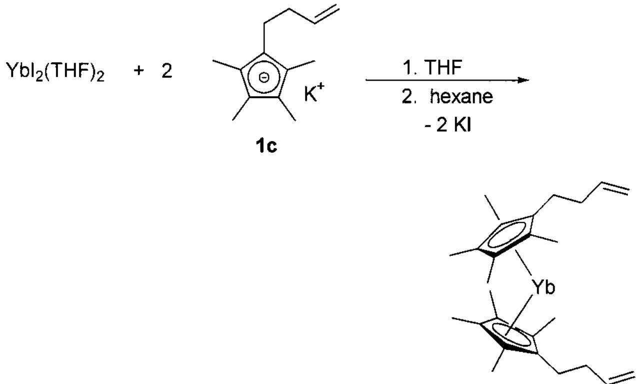
4

M = Li (**4a**), Na (**4b**)

4a

5b

Scheme 3



1c

6

All three yellow to beige complexes are highly air- and moisture-sensitive. They are soluble in polar solvents such as THF and pyridine, but the solubility in aliphatic and aromatic hydrocarbons such as benzene and toluene is very poor. For this reason, it is not possible to use cryoscopic molecular weight determinations, noncoordinating solvents for NMR spectroscopy, or growth of X-ray-compatible crystals to get information about the coordination as outlined earlier. In the mass spectra the molecular ion peaks appear to be the monomer, indicating weak chlorine bridges. In the crude products traces of the fragments $[(CH_2{=}CHCH_2CH_2C_5Me_4)_2LnCl]$ and $[(C_5Me_5)_2LnCl]$ can be detected. Elemental analyses and NMR spectra in *d*-pyridine show the expected data for chlorine-bridged, solvent-free dimers, $[(CH_2{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)LnCl]_2$.

With complex **8a** the only X-ray-compatible crystals of these lanthanidocene derivatives are isolated via very slow evaporation of the diethyl ether used to extract the reaction residue. The complex crystallizes in the monoclinic space group $P2_1/n$ with four crystallographically

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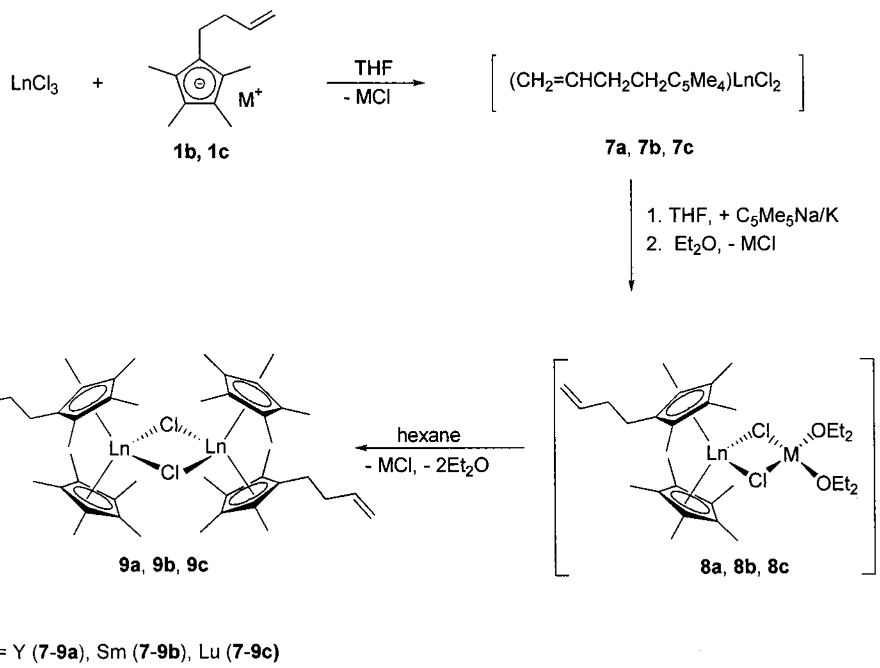
Scheme 4



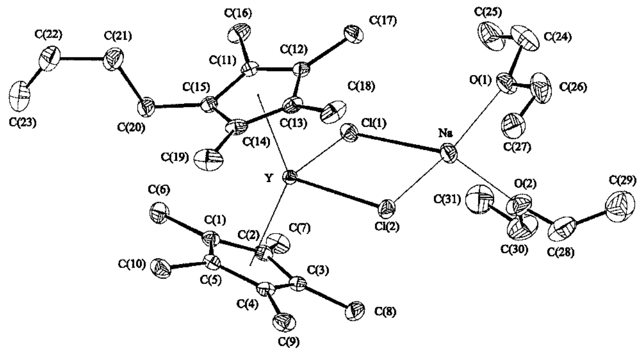


Figure 3. ORTEP plot[23] of the molecular structure and the numbering scheme of **8a** with 30% probability thermal ellipsoids. The hydrogen atoms are not depicted. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations in parentheses (Cp(1) and Cp(2) define the centroid positions of the ring atoms C(1−5) and C(11−15), respectively): Cp(1)−Y = 2.39(8), Cp(2)−Y = 2.39(7), Y−Cl(1) = 2.6310(6), Y−Cl(2) = 2.6350(6), Cl(1)−Na = 2.6909(11), Cl(2)−Na = 2.6805(12), Na−O(1) = 2.3084(19), Na−O(2) = 2.278(2); Cp(1)−Y−Cp(2) = 137(3), Cp(1)−Y−Cl(1) = 106(2), Cp(1)−Y−Cl(2) = 104(2), Cp(2)−Y−Cl(1) = 104.6(6), Cp(2)−Y−Cl(2) = 105.1(6), Cl(1)−Y−Cl(2) = 88.81(2), Y−Cl(1)−Na = 91.86(3), Y−Cl(2)−Na = 92.01(3), O(1)−Na−O(2) = 97.17(8), Cl(1)−Na−Cl(2) = 86.62(3), O(1)−Na−Cl(1) = 125.36(6), O(1)−Na−Cl(2) = 111.97(6), O(2)−Na−Cl(1) = 120.23(7), O(2)−Na−Cl(2) = 116.71(7).

independent molecules in the asymmetric unit. The solid-state structure is shown in Figure 3.

The structure shows a distorted tetrahedral environment for both metals, yttrium and sodium. The yttrium atom is surrounded by two bridging chlorine atoms and the centroids of the two different cyclopentadienyl ligands. There is no coordination of the olefinic double bond of the $CH_2{=}CHCH_2CH_2C_5Me_4$ ligand to the yttrium center. The Cp−Y (2.39(8) and 2.39(7) Å) and Cl−Y (2.6310(6) and 2.6350(6) Å) distances are in accordance with comparable values in $(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (2.66 and 2.65 Å, respectively),[25] as are the distances Na−Cl (2.6805(12) and 2.6909(11) Å) with those in $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(DME)_2$ (2.801 Å), taking into account the different distorted octahedral environment of the sodium atom in that case.[26]

[1-(But-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]lanthanide Alkyls and Amides. The symmetrically substituted cyclopentadienyllanthanide chlorides (lanthanide = Y (**3a**), Sm (**3b**), and Lu (**3c**)) as well as the complexes **9a**−**c** with two different cyclopentadienyl ligands react in diethyl ether at −78 °C with methyllithium as well as [bis(trimethylsilyl)methyl]lithium, forming the corresponding alkyl derivatives $(CH_2{=}CHCH_2CH_2C_5Me_4)_2LnR$ (R = Me (**10**), $CH(SiMe_3)_2$ (**11**)) and $(CH_2{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)YCH(SiMe_3)_2$ (**12a**) (Scheme 5), respectively. The reaction products are extremely sensitive and decompose even at −78 °C in an inert atmosphere within a few minutes. Only the methyl derivative **10a** and the bis(trimethylsilyl)methyl derivatives **11a**,**b** and **12a** could be characterized by mass spectrometry out of the crude reaction mixture. Therefore, the diethyl ether is evaporated immediately after addition of the lithium alkyl at −78 °C. Exchange of the ether to nonpolar solvents such as cyclohexane, benzene, and toluene at the same temperature or carrying out the reaction in deuterated solvents followed by NMR studies do not lead to interpretable NMR spectra. Increasing amounts of insoluble polymeric precipitates appear during those manipulations, indicating that the products are already catalytically active. Most likely, the intramolecular coordination of the double bond to the metal center causes CH activation followed by insertion of the alkene moiety into the σ-Ln−C bond comparable to studies by Watson[27] and Bercaw[28] with several lanthanidocene alkyl complexes. Intensive investigations of mechanistic details are in progress.

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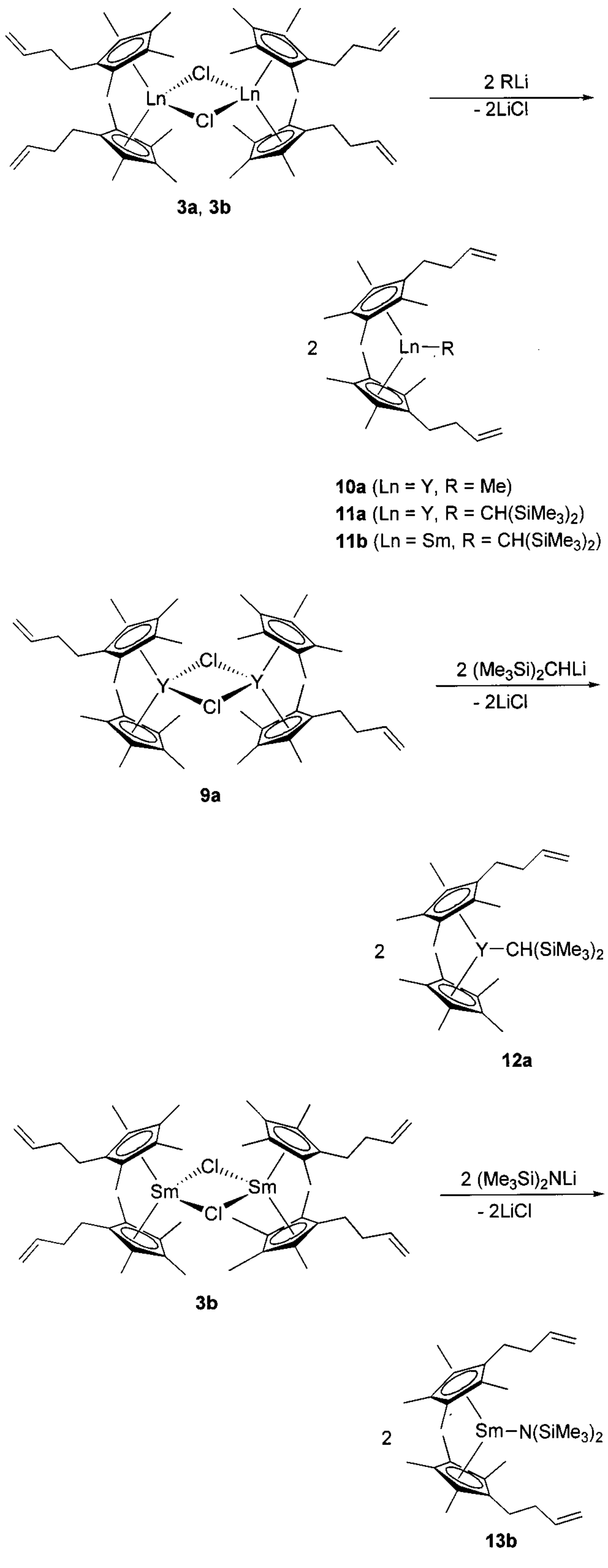
Scheme 5



In this context we investigated the synthesis of $(CH_2{=}CHCH_2CH_2C_5Me_4)_2SmN(SiMe_3)_2$ (**13b**) to get information about the stability of the alkenyl-substituted lanthanidocenes in the presence of a Ln−N bond. The dark red bis(trimethylsilyl)amido samarocene was prepared from $[(CH_2{=}CHCH_2CH_2C_5Me_4)_2SmCl]_2$ (**3b**) and $KN(SiMe_3)_2$ in diethyl ether at −78 °C (Scheme 5). The complex has to be stored as a solid below 0 °C but is stable in solution at room temperature without the observed decomposition reactions of the lanthanide alkyl derivatives. The ^1H NMR data in *d*-benzene show no interaction between the olefinic double bond and the samarium center. The signals for the vinylic protons appear as doublets at 5.44 and 5.21 ppm for the CH_2 group and as a multiplet between 6.58 and 6.53 ppm for the CH unit. In the mass spectrum the molecular ion peak is found, in addition to the mass peak for the fragment $[(C_4H_7C_5Me_4)SmN(SiMe_3)_2]$, as is known for the analogous complexes $[(C_5Me_4Et)_2LnN(SiMe_3)_2]$ (Ln = Y, Nd, Sm, Lu).[29]

Crystals suitable for X-ray structure determination were obtained from hexane at −78 °C. Complex **13b** crystallizes in the monoclinic space group *C*2/*c* with four independent molecules in the asymmetric unit. The solid-state structure is shown in Figure 4.

In the structure of **13b** the samarium atom with formal coordination number 7 is surrounded in a pseudo trigonal planar fashion by the two cyclopentadienyl ligands and the bis(trimethylsilyl)amido moiety. The largest deviation of the ideal 120° angle is, with respect to the large butenyl substituent on the cyclopentadienyl ligands, slightly smaller for Cp−Sm−Cp (130.49(4)°) than in $(C_5Me_4Et)_2YN(SiMe_3)_2$ (Cp−Y−Cp = 132.59°)[29] and in $(C_5Me_5)_2SmN(SiMe_3)_2$ (Cp−Sm−Cp = 132.8°).[30] There is no coordination of the olefinic double bond of the $CH_2{=}CHCH_2CH_2C_5Me_4$ ligand to the samarium center. The distances C(Cp)−Sm (2.747 Å) and N−Sm (2.331(3) Å) are in the expected range. Samarium, nitrogen, and both silicon atoms are occupying the same plane. Both trimethylsilyl groups force themselves into an ecliptic arrangement. The conformation of the amido ligands is remarkable. The angle N−Si−C(14) (105.82(13)°) is clearly smaller than the angles N−Si−C(15) (114.08(13)°) and N−Si−C(16) (114.82(14)°), which is in accordance with the situation in $(C_5Me_4Et)_2YN(SiMe_3)_2$ (107.4/115.1°)[29] and in $(C_5Me_5)_2SmN(SiMe_3)_2$ (106.3/114.6°).[30] These distortions are the consequence of *γ*-agostic interactions between the methyl groups of the bis(trimethylsilyl)amido ligand and the unsaturated samarium center, as was discussed also in the cases of $(C_5Me_4Et)_2YN(SiMe_3)_2$[29] and $(C_5Me_5)_2SmN(SiMe_3)_2$.[30] The closest Sm···H−CH2−Si and Sm···CH2−Si distances, Sm···H(14A) (3.015(8) Å and Sm···C(14) (3.255(4) Å) are comparable with those in $(C_5Me_5)_2SmN(SiMe_3)_2$ (2.97/3.216 Å).[30]

[1-(4-Methylpent-3-enyl)-2,3,4,5-tetramethylcyclopentadienyl]lanthanide Chlorides. In butenyl- as well as pentenyl-substituted tetramethylcyclopentadienyl lanthanide chlorides no coordination of the olefinic double bond to the metal center can be observed, due to the presence of the chlorine as the better ligand, resulting in dimerization via chlorine bridges. The corresponding alkyl derivatives Cp_2LnR (R = Me, CH-

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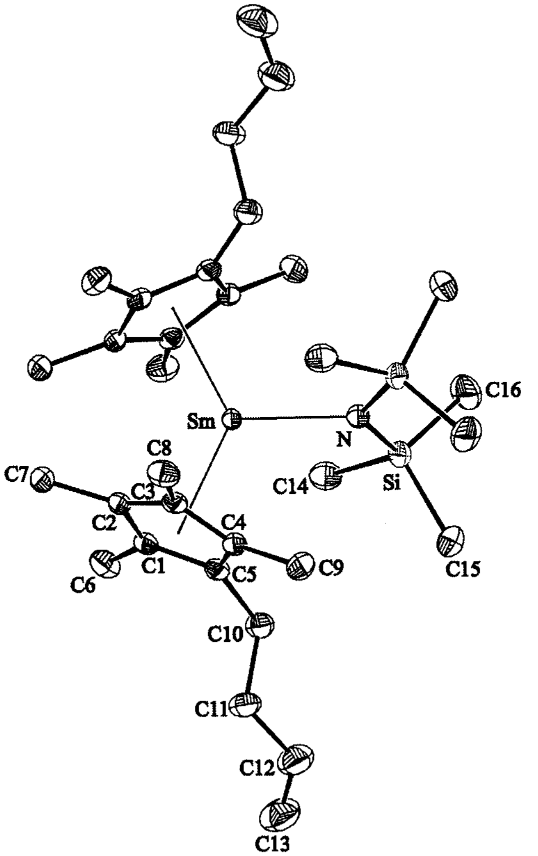
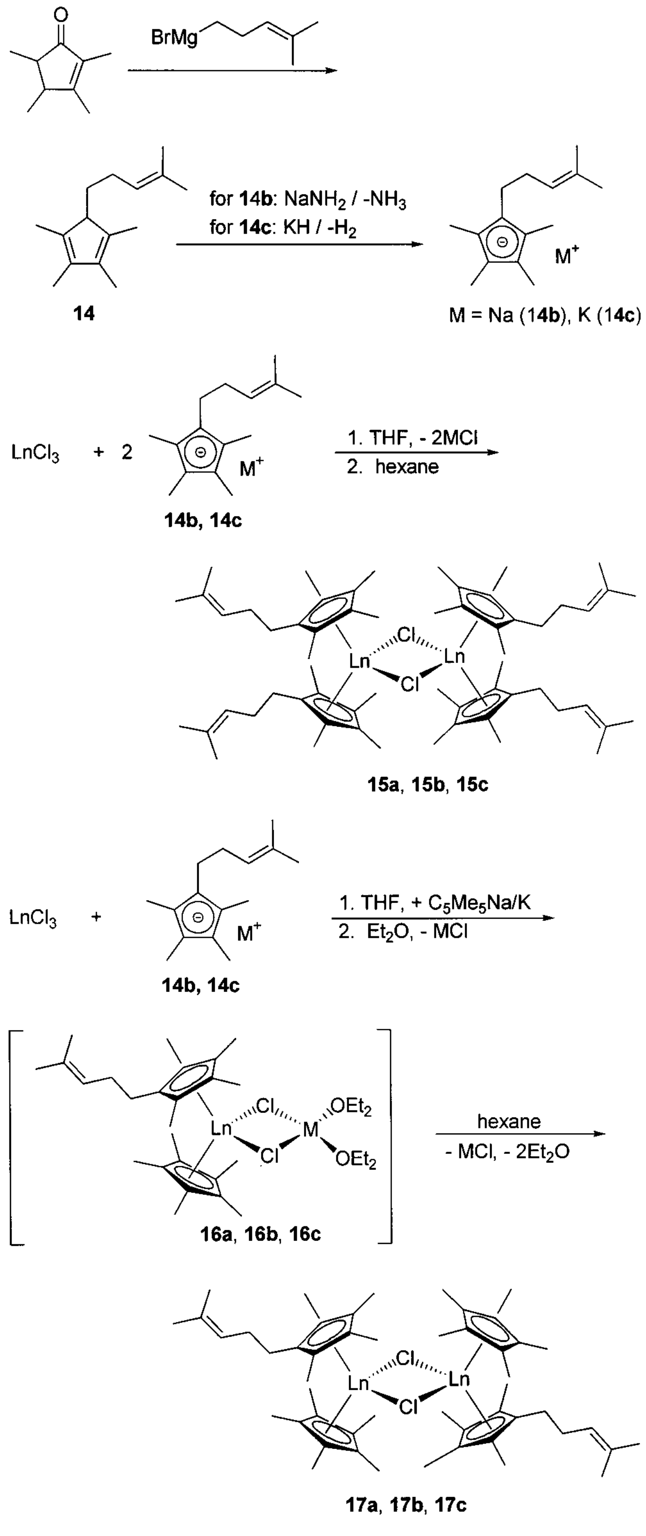


Figure 4. ORTEP plot[23] of the molecular structure and the numbering scheme of **13b** with 40% probability thermal ellipsoids. The hydrogen atoms are not depicted. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations (Cp defines the centroid position of the ring atoms C(1−5)): Cp−Sm = 2.4690(11), Sm−N = 2.331(3), Si−N = 1.6933(13), Si−C(16) = 1.873(3), Si−C(15) = 1.876(3), Si−C(14) = 1.882(3), Sm−C(14) = 3.255(4), Sm−H(14A) = 3.015(8), Sm−H(14C) = 3.263(9), Cp−Sm−Cp = 130.49(4), Cp−Sm−N = 114.75(2), Si−N−Sm = 116.08(8), Si−N−Si′ = 127.8(2), N−Si−C(16) = 114.82(14), N−Si−C(15) = 114.08(13), N−Si−C(14) = 105.82(13), Sm−H(14A)−C(14) = 96(3), Sm−H(14C)−C(14) = 81(4).

Scheme 6



Ln = Y (**15-17a**), Sm (**15-17b**), Lu (**15-17c**)

($SiMe_3)_2$) decompose shortly after preparation, induced by insertion of the double bond into the σ-Ln−C bond. Even the bulky $(Me_3Si)_2CH$ group does not prevent decomposition of the alkyl complex $(CH_2{=}CHCH_2CH_2C_5Me_4)_2LnCH(SiMe_3)_2$. Considering the four-center transition state postulated by Watson for CH activation processes,[27c] substituents at the olefinic double bond should suppress insertion reactions. To verify this hypothesis, we synthesized the alkali metal salts of $M[(CH_3)_2C{=}CHCH_2CH_2C_5Me_4]$ (M = Na (**14b**), K (**14c**)) according to the procedure described earlier (Scheme 6).

The trichlorides of yttrium, samarium, and lutetium react in THF at room temperature with 2 equiv of **14b**,**c** as well as 1 equiv of **14b**,**c** and 1 equiv of $M[C_5Me_5]$ (M = Na, K), yielding between 44% and 84% of the corresponding complexes $[(Me_2C{=}CHCH_2CH_2C_5Me_4)_2LnCl]_2$ (Ln = Y (**15a**), Sm (**15b**), Lu (**15c**)) and $[(Me_2C{=}CHCH_2CH_2C_5Me_4)(C_5Me_5)LnCl]_2$ (Ln = Y (**17a**), Sm (**17b**), Lu (**17c**)), respectively. The properties of the beige and orange complexes are the same as for the analogous complexes **3**, **5**, and **9**. They are characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. Like before, the primary formation of mononuclear, alkali metal halide stabilized complexes $Cp_2Ln(\mu\text{-}Cl)_2ML_2$ can be considered, since a few single crystals of the lutetium derivative **16c** could be isolated from the hexane washing solution during purification. The molecular structure shows $(Me_2C{=}CHCH_2CH_2C_5Me_4)_2Lu(\mu\text{-}Cl)_2Na(Et_2O)_2$ (**16c**) crystallizing in the monoclinic space group $P2_1/n$ with four molecules in the asymmetric unit (Figure 5). The lutetium atom is

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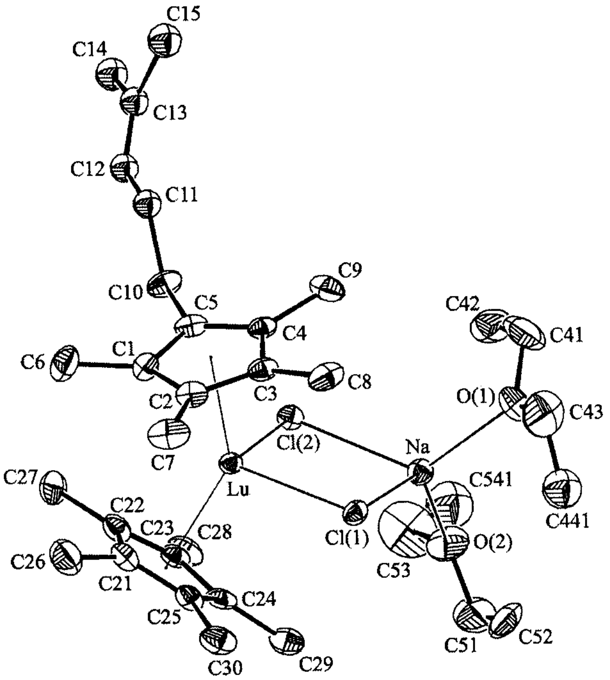

Figure 5. ORTEP plot[23] of the molecular structure and the numbering scheme of **16c** with 40% probability thermal ellipsoids. For clarity, all hydrogens are not depicted. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations in parentheses (Cp(1) and Cp(2) define the centroid positions of the ring atoms C(1−5), and C(21−25), respectively): Cp(1)−Lu = 2.350(3), Cp(2)−Lu = 2.343(3), Lu−Cl(1) = 2.589(2), Lu−Cl(2) = 2.581(2), Cl(1)−Na = 2.688(3), Cl(2)−Na = 2.687(3), Na−O(1) = 2.305(5), Na−O(2) = 2.300(5); Cp(1)−Lu−Cp(2) = 137.19(11), Cp(1)−Lu−Cl(1) = 105.62(8), Cp(1)−Lu−Cl(2) = 104.62(9), Cp(2)−Lu−Cl(1) = 88.99(4), Cp(2)−Lu−Cl(2) = 105.72(8), Lu−Cl(1)−Na = 92.97(8), Lu−Cl(2)−Na = 93.17(8).

surrounded by two η^5-bonded cyclopentadienyl ligands and two bridging Cl atoms in a slightly distorted tetrahedral arrangement. The $LuCl_2Na$ core is nearly planar with angles Cl(1)−Lu−Cl(2) = 88.99°, Lu−Cl(1)−Na = 92.97°, Lu−Cl(2)−Na = 93.17°, and Cl(1)−Na−Cl(2) = 84.78°. All the other distances and angles are in accordance with those in analogous complexes. The alkenyl substituent is orientated away from the metal core, showing no interaction of the double bond with the metal center.

After the reactions of compounds **15** and **17** with alkylating reagents such as methyllithium and the bulkier [bis(trimethylsilyl)methyl]lithium in diethyl ether at −78 °C the same observations as described for lanthanidocenes **3** and **9** with unsubstituted double bonds are made. Continuous precipitation of polymer-like decomposition products occurs independent of reaction time, temperature, or solvent. This means that even a sterically demanding double bond is not able to prevent activation followed by insertion reactions. Changing the electronic properties of the alkyl carbon from sp^3 via sp^2 to sp using phenyllithium or lithium acetylide to exchange the chlorine also does not allow the isolation of well-defined alkyl complexes of alkenyl-substituted lanthanide alkyl derivatives.

Conclusion

The first ω-alkenyl-functionalized bis(cyclopentadienyl) lanthanidocenes were prepared from YCl_3, $SmCl_3$, $LuCl_3$, and YbI_2. The alkenyl side chain as a chelating donor did not coordinate to the metal center in bis(cyclopentadienyl)lanthanide chlorides. Instead, the complexes stabilized themselves by formation of alkali metal halide adducts, coordination of additional donor molecules, or dimerization. Substitution of chloride by transmetalation with lithium alkyls resulted in unstable lanthanidocene alkyl complexes. After the formation of the σ-Ln−C bond, interactions between the metal center and the alkenyl moiety led to insertion of the double bond into the σ-Ln−C bond. Neither the size of the alkyl group and the electronegativity of its σ-bonded carbon atom nor steric changes at the double bond prevented autocatalytic decomposition reactions. Some of these lanthanidocene alkyl complexes were detected by mass spectrometry. Nevertheless, butenyl-substituted bis(cyclopentadienyl)samarium amide was isolated and demonstrated that the olefinic double bond did not insert into the Ln−N bond.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (Graduiertenkolleg “Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren”).

Supporting Information Available: Full details of the X-ray structural analyses of the complexes **2a**,**b**, **8a**, **13b**, and **16c**, including tables of crystal data, atomic coordinates, bond lengths and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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