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# Organometallic Compounds of the Lanthanides. 158.[1] Alkenyl-Functionalized Cyclopentadienyl Complexes of Yttrium, Samarium, and Lutetium and Their Hydroboration

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$YCl_3$, $SmCl_3$, and $LuCl_3$ react with (tetramethylvinylcyclopentadienyl)lithium (**1a**), yielding $(CH_2{=}CHC_5Me_4)_2Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$ (Ln = Y (**2a**), Sm (**2b**), Lu (**2c**)). $LuCl_3$ and the analogous potassium salt **1b** form oligomeric $[(CH_2{=}CHC_5Me_4)_2Lu(\mu_3\text{-}Cl)_2K(THF)]_n$ (**3**). Methylation of the yttrium complex **2a** with MeLi gives $(CH_2{=}CHC_5Me_4)_2Y(\mu\text{-}CH_3)_2Li(THF)$ (**4**). Hydroboration of the complexes **2a**−**c** with 9-BBN results in the formation of $(C_8H_{14}BCH_2CH_2C_5Me_4)_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Ln = Y (**5a**), Sm (**5b**), Lu (**5c**)). The reaction of $YCl_3$ with 2 equiv of $K[C_5H_4CH{=}C_6H_{10}]$ (**6**) or $K[C_5H_4CH{=}CMe_2]$ (**10**) affords the dimeric complexes $[(C_6H_{10}{=}CHC_5H_4)_2Y(\mu\text{-}Cl)]_2$ (**7**) and $[(Me_2C{=}CHC_5H_4)_2Y(\mu\text{-}Cl)]_2$ (**11**), whereas $SmCl_3$ reacts with 2 equiv of **6** or **10**, yielding the tris(cyclopentadienyl) derivatives $(C_6H_{10}{=}CHC_5H_4)_3Sm(THF)$ (**9**) and $(Me_2C{=}CHC_5H_4)_3Sm(THF)$ (**13**), respectively. Methylation of **7** with MeLi yields unstable $[(C_6H_{10}{=}CHC_5H_4)_2Y(\mu\text{-}CH_3)]_2$ (**7a**). $SmI_2$ and **6** react with formation of $(C_6H_{10}{=}CHC_5H_4)_2Sm(THF)_2$ (**8**). Hydrolysis during crystallization of **11** caused by some water in the solvent leads to decomposition, forming the oxygen-bridged complex $[(Me_2C{=}CHC_5H_4)_2Y(Et_2O)]_2(\mu\text{-}O)$ (**12**). The *ansa*-lanthanidocene chloride $[H_2C{=}C(CH_2C_5H_4)_2]LuCl(THF)$ (**15**) was prepared from $LuCl_3$ and the new ligand $K_2[H_2C{=}C(CH_2C_5H_4)_2]$ (**14**). The structures of **2a**, **3**, **5b**, **7**, and **12** were determined by single-crystal X-ray diffraction.

## Introduction

Organolanthanide chemistry has produced an impressive number of highly active homogeneous catalysts. Various alkene and alkyne transformations are effectively catalyzed by lanthanidocenes.[2] Among them, the most active catalysts are organolanthanide hydrides of the type $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$ which can be generated from the respective halide precursors $[(C_5Me_5)_2Ln(\mu\text{-}Cl)]_2$. More than 90% of the known organolanthanide complexes contain cyclopentadienyl groups as the most powerful ligand in this field, and substantial research activities are focused on the modification of the coordination sphere of the lanthanide metals by variation of the substituents at the cyclopentadienyl ligands in order to achieve better catalytic properties.[3]

Recently, we reported on the properties of organolanthanide complexes with ω-alkenyl-substituted cyclopentadienyl ligands.[4] Compared to complexes with cyclopentadienyls containing strong donor atoms such as nitrogen, oxygen, and sulfur in their side chains,[5−7] the olefinic double bond is not able to stabilize the metal center by intramolecular coordination. In this context and for the following reasons, we started to synthesize and to investigate lanthanide complexes with vinyl-substituted cyclopentadienyl ligands. First, the vinyl side chain is shorter than a dangling ω-alkenyl group and should therefore promote the crystallization of such complexes. Second, vinyl side chains should be capable of copolymerizing metallocenes with other monomers[8] suitable for polymerization, thus leading to immobilized olefin polymerization catalysts containing lanthanide

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(1) Part 157: Schumann, H.; Freckmann, D. M. M.; Dechert, S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2422.

(2) (a) *Applied Homogeneous Catalysis with Organometallic Compounds*; Corniels, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996. (b) *Metallocenes;* Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

(3) Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 247.

(4) Schumann, H.; Heim, A.; Demtschuk, J.; Mühle, S. H. *Organometallics* **2002**, *21*, 3323.

(5) (a) Jutzi, P.; Dahlhaus, J.; Kristen, M. O. *J. Organomet. Chem.* **1993**, *450*, C1. (b) Herrmann, W. A.; Anwander, R.; Munck, F. C.; Scherer, W. *Chem. Ber.* **1993**, *126*, 331. (c) Anwander, R.; Herrmann, W. A.; Scherer, W.; Munck, F. C. *J. Organomet. Chem.* **1993**, *462*, 163. (d) Schumann, H.; Erbstein, F.; Herrmann, K.; Demtschuk, J.; Weimann, R. *J. Organomet. Chem.* **1998**, *562*, 255. (e) Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J.; Molander, G. A. *Organometallics* **1998**, *17*, 5324. (f) Schumann, H.; Erbstein, F.; Karasiak, D. F.; Fedushkin, I. L.; Demtschuk, J.; Girgsdies, F. *Z. Anorg. Allg. Chem.* **1999**, *625*, 781. (g) Schumann, H.; Erbstein, F.; Demtschuk, J.; Weimann, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1457. (h) Schumann, H.; Rosenthal, E. C. E.; Demtschuk, J.; Mühle, S. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2161. (i) Fedushkin, I. L.; Dechert, S.; Schumann, H. *Organometallics* **2000**, *19*, 4066.

(6) (a) Deng, D.; Li, B.; Qian, C. *Polyhedron* **1990**, *12*, 1453. (b) Deng, D.; Qian, C.; Wu, G.; Zheng, P. *J. Chem. Soc., Chem. Commun.* **1990**, 880. (c) Qian, C.; Zhu, D.; Li, D. *J. Organomet. Chem.* **1992**, *430*, 175. (d) Laske, D. A.; Duchateau, R.; Teuben, J. H.; Spek, A. L. *J. Organomet. Chem.* **1993**, *462*, 149. (e) Qian, C.; Zou, G.; Sun, J. *J. Organomet. Chem.* **1998**, *566*, 21.

(7) Schumann, H.; Hermann, K.; Demtschuk, J.; Mühle, S. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1107.

(8) Pfeifer, B.; Milius, W.; Alt, H. G. *J. Organomet. Chem.* **1998**, *553*, 205.

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metals. Third, the vinyl substituent can be used for a further functionalization of the cyclopentadienyl ligand: for example, by the introduction of a borane group via hydroboration.[9] Following the concept of zwitterionic metallocenes,[10] such a second *Lewis* acidic borane moiety could cause a huge impact on the catalytic properties of the lanthanidocenes. Furthermore, we wanted to use the tool of hydroboration to link two vinyl side chains, thus generating a borane-bridged cyclopentadienyl ligand system. So far, only borane-bridged *ansa* ligands are known in which the boron atom is directly bonded to two cyclopentadienyl units.[11]

Here we report the synthesis of a number of yttrium(III), samarium(II/III), and lutetium(III) complexes containing cyclopentadienyl ligands with differently substituted vinyl side chains and one bridging allylic ligand system. The successful hydroboration of the bis(tetramethylvinylcyclopentadienyl)lanthanide chlorides (Ln = Y, Sm, Lu) demonstrates the potential of (vinylcyclopentadienyl)lanthanide complexes for further functionalization.

## 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. (Tetramethylvinylcyclopentadienyl)lithium (**1a**),[12] (2,4-cyclopentadien-1-ylidenemethyl)cyclohexane,[13] 5-isobutylidenecyclopentadiene,[13] and SmI$_2$(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$_4$Cl followed by Soxhlet extraction of the trichlorides formed with THF.[15]

**(Tetramethylvinylcyclopentadienyl)potassium (1b).** To a solution of the isomeric mixture of tetramethylvinylcyclopentadiene and 5-ethylidene-1,2,3,4-tetramethyl-1,3-cyclopentadiene[12] (5.63 g, 38 mmol) in tetrahydrofuran (150 mL) was added K[N(SiMe$_3$)$_2$] (7.58 g, 38 mmol) at −78 °C. The reaction mixture was stirred for 12 h at room temperature. After removal of the solvent under vacuum ($10^{-2}$ mbar), the remaining beige solid was washed several times with hexane, leaving 5.43 g (77%) of a pyrophoric gray-white powder of **1b**; mp 241 °C. $^{1}$H NMR (pyridine-$d_5$, 200 MHz): $\delta$ 7.26 (dd, $^{3}J_{\mathrm{trans}}$ = 17.5 Hz, $^{3}J_{\mathrm{cis}}$ = 10.6 Hz, 1 H, CH=), 5.10 (dd, $^{3}J_{\mathrm{trans}}$ = 17.5 Hz, $^{2}J$ = 2.7 Hz, 1 H, =CH$_2$), 4.64 (dd, $^{3}J_{\mathrm{cis}}$ = 10.6 Hz, $^{2}J$ = 2.6 Hz, 1 H, =CH$_2$), 2.42 (s, 6 H, CH$_3$), 2.25 (s, 6 H, CH$_3$). $^{13}$C{$^{1}$H} NMR (pyridine-$d_5$, 50.32 MHz): $\delta$ 135.17 (−CH=), 112.67 (*C*−C$_2$H$_3$), 111.02 (*C*−CH$_3$), 110.31 (*C*−CH$_3$), 93.34 (=CH$_2$), 12.82 (CH$_3$), 11.40 (CH$_3$). MS (296 °C; *m*/*z* (%)): 148 (68) [C$_{11}$H$_{16}$]$^+$, 147 (21) [C$_{11}$H$_{15}$]$^+$, 134 (12), 133 (100), 131 (16), 119 (13), 117 (13), 115 (11), 105 (27), 91 (23), 41 (15). Anal. Calcd for C$_{11}$H$_{15}$K (mol wt 186.34): C, 70.90; H, 8.11. Found: C, 70.60; H, 7.85.

**Bis(diethyl ether)lithium Bis($\mu$-Chloro)bis(tetramethylvinylcyclopentadienyl)yttrium (2a).** To a suspension of YCl$_3$ (1.50 g, 7.7 mmol) in THF (80 mL) was added Li[C$_5$Me$_4$-CH=CH$_2$] (**1a**; 2.37 g, 15.4 mmol) at room temperature, and the reaction mixture was stirred for 6 h. After removal of the solvent under vacuum ($10^{-2}$ mbar), the residue was extracted with diethyl ether (70 mL). The resulting ether solution was concentrated and cooled to 0 °C, yielding 2.1 g (45%) of pale yellow crystals of **2a**; mp 97 °C dec. $^{1}$H NMR (benzene-$d_6$, 200 MHz): $\delta$ 6.92 (dd, $^{3}J_{\mathrm{trans}}$ = 18.0 Hz, $^{3}J_{\mathrm{cis}}$ = 11.6 Hz, 2 H, −CH=), 5.38 (dd, $^{3}J_{\mathrm{trans}}$ = 18.0 Hz, $^{2}J$ = 2.2 Hz, 2 H, =CH$_2$), 5.04 (dd, $^{3}J_{\mathrm{cis}}$ = 11.6 Hz, $^{2}J$ = 2.2 Hz, 2 H, =CH$_2$), 3.19 (q, $^{3}J$ = 7.0 Hz, 8 H, CH$_2$(Et$_2$O), 2.24 (s, 12 H, CH$_3$), 2.08 (s, 12 H, CH$_3$), 0.99 (t, $^{3}J$ = 7.0 Hz, 12 H, CH$_3$(Et$_2$O)). $^{13}$C{$^{1}$H} NMR (benzene-$d_6$, 50.32 MHz): $\delta$ 133.59 (−CH=), 120.49 (d, $^{1}J(^{89}\mathrm{Y},^{13}\mathrm{C})$ = 1.3 Hz, *C*−CH$_3$), 119.59 (d, $^{1}J(^{89}\mathrm{Y},^{13}\mathrm{C})$ = 1.3 Hz, *C*−CH$_3$), 117.04 (d, $^{1}J(^{89}\mathrm{Y},^{13}\mathrm{C})$ = 1.4 Hz, *C*−C$_2$H$_3$), 107.59 (=CH$_2$), 65.83 (CH$_2$, Et$_2$O), 14.86 (CH$_3$, Et$_2$O), 12.82 (CH$_3$), 11.60 (CH$_3$). MS (313 °C; *m*/*z* (%)): 420 (54) [M − LiClC$_8$H$_{20}$]$^+$, 418 (71) [M − LiClC$_8$H$_{22}$]$^+$, 403 (100) [C$_{21}$H$_{26}$YCl]$^+$, 382 (10) [C$_{22}$H$_{28}$Y]$^+$, 273 (76) [C$_{11}$H$_{15}$YCl]$^+$, 271 (92) [C$_{11}$H$_{13}$YCl]$^+$, 148 (11) [C$_{11}$H$_{16}$]$^+$, 135 (73) [C$_{10}$H$_{15}$]$^+$. Anal. Calcd for C$_{30}$H$_{50}$Cl$_2$LiO$_2$Y (mol wt 609.48): C, 59.12; H, 8.27. Found: C, 58.90; H, 7.31 (Calcd for C$_{22}$H$_{30}$Cl$_2$LiY(OC$_4$H$_{10}$) after losing one molecule of diethyl ether under vacuum: C, 58.33; H, 7.53).

**Bis(diethyl ether)lithium Bis($\mu$-Chloro)bis(tetramethylvinylcyclopentadienyl)samarium (2b).** In analogy to the preparation of **2a**, SmCl$_3$ (1.43 g, 5.6 mmol) in THF (80 mL) was reacted with Li[C$_5$Me$_4$CH=CH$_2$] (**1a**; 1.72 g, 11.14 mmol) to provide 2.10 g (56%) of orange crystals of **2b**; mp 112 °C dec. $^{1}$H NMR (benzene-$d_6$, 200 MHz): $\delta$ 7.03 (dd$_{\mathrm{br}}$, $^{3}J_{\mathrm{cis}}$ = 11.3 Hz, $^{3}J_{\mathrm{trans}}$ = 17.6 Hz, 2 H, −CH=), 5.16 (d$_{\mathrm{br}}$, $^{3}J_{\mathrm{trans}}$ = 17.6 Hz, 2 H, =CH$_2$), 4.84 (d$_{\mathrm{br}}$, $^{3}J_{\mathrm{cis}}$ = 11.3 Hz, 2 H, =CH$_2$), 3.30 (q, 8 H, CH$_2$, Et$_2$O), 1.71 (s$_{\mathrm{br}}$, 12 H, CH$_3$), 1.12 (s, 12 H, CH$_3$), 1.03 (t, 12 H, CH$_3$, Et$_2$O). $^{13}$C{$^{1}$H} NMR (benzene-$d_6$, 50.32 MHz): $\delta$ 141.09 (−CH=), 120.96 (*C*−CH$_3$), 117.74 (*C*−CH$_3$), 116.75 (*C*−C$_2$H$_3$), 103.99 (=CH$_2$), 65.79 (CH$_2$, Et$_2$O), 17.55 (CH$_3$), 17.48 (CH$_3$), 14.90 (CH$_3$, Et$_2$O). MS ($^{152}$Sm, 403 °C; *m*/*z* (%)): 481 (2) [M − LiClC$_8$H$_{20}$]$^+$, 445 (2) [M − LiCl$_2$C$_8$H$_{22}$]$^+$, 335 (4) [C$_{11}$H$_{15}$SmCl]$^+$, 299 (3) [C$_{11}$H$_{15}$Sm]$^+$, 148 (29) [C$_{11}$H$_{16}$]$^+$, 135 (73) [C$_{10}$H$_{15}$]$^+$. Anal. Calcd for C$_{30}$H$_{50}$Cl$_2$LiO$_2$Sm (mol wt 670.93): C, 53.71; H, 7.51. Found: C, 50.43; H, 5.92 (Calcd for C$_{22}$H$_{30}$Cl$_2$LiSm after losing two molecules of diethyl ether under vacuum: C, 50.55; H, 5.79).

**Bis(diethyl ether)lithium Bis($\mu$-Chloro)bis(tetramethylvinylcyclopentadienyl)lutetium (2c).** In analogy to the preparation of **2a**, LuCl$_3$(THF)$_3$ (2.23 g, 4.5 mmol) in THF (80 mL) was reacted with Li[C$_5$Me$_4$CH=CH$_2$] (**1a**; 1.38 g, 8.96 mmol) to provide 1.88 g (60%) of pale yellow crystals of **2c**; mp 117 °C dec. $^{1}$H NMR (benzene-$d_6$, 200 MHz): $\delta$ 6.93 (dd, $^{3}J_{\mathrm{trans}}$ = 18.0 Hz, $^{3}J_{\mathrm{cis}}$ = 11.6 Hz, 2 H, −CH=), 5.35 (dd, $^{3}J_{\mathrm{trans}}$ = 18.0 Hz, $^{4}J$ = 2.2 Hz, 2 H, =CH$_2$), 5.02 (dd, $^{3}J_{\mathrm{cis}}$ = 11.6 Hz, $^{4}J$ = 2.2 Hz, 2 H, =CH$_2$), 3.19 (q, $^{3}J$ = 7.0 Hz, 8 H, CH$_2$(Et$_2$O),

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[9] Erker, G.; Aul, R. *Chem. Ber.* **1991**, *124*, 1301.

[10] Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13.

[11] (a) Reetz, M. T.; Brümmer, H.; Kessler, M.; Kuhnigk, J. *Chimia* **1995**, *49*, 501. (b) Bochmann, M.; Lancaster, S. J.; Robinson, O. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2081. (c) Duchateau, R.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1997**, *16*, 4995. (d) Lancaster, S. J.; Thornton-Pett, M.; Dawson, D. M.; Bochmann, M. *Organometallics* **1998**, *17*, 3829. (e) Ruwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem.* **1996**, *108*, 108; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80. (f) Larkin, S. A.; Golden, J. T.; Shapiro, P. J.; Yap, G. P. A.; Foo, D. M. J.; Rheingold, A. L. *Organometallics* **1996**, *15*, 287. (g) Rufanov, K. A.; Kotov, V. V.; Kazennova, N. B.; Lemenovskii, D. A.; Avtomonov, E. V.; Lorberth, J. *J. Organomet. Chem.* **1996**, *525*, 287. (h) Stelck, D. S.; Shapiro, P. J.; Basickes, N.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4546. (i) Rufanov, K. A.; Avtomonov, E. V.; Kazennova, N. B.; Kotov, V. V.; Khvorost, A.; Lemenovskii, D. A.; Lorberth, J. *J. Organomet. Chem.* **1997**, *536*, 361. (j) Reetz, M. T.; Willuhn, M.; Psiorz, C.; Goddard, R. *Chem. Commun.* **1999**, 1105.

[12] (a) Macomber, D. W.; Spink, W. C.; Rausch, M. D. *J. Organomet. Chem.* **1983**, *250*, 311. (b) Bensley, D. M.; Mintz, E. A. *J. Organomet. Chem.* **1988**, *250*, 311.

[13] Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.

[14] Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999.

[15] Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; F. Enke Verlag: Stuttgart, Germany, 1962; Vol. 2, p 1002.

2.23 (s, 12 H, $CH_3$), 2.09 (s, 12 H, $CH_3$), 0.99 (t, $^{3}J$ = 7.0 Hz, 12 H, $CH_3(Et_2O)$). $^{13}C\{^{1}H\}$ NMR (benzene-$d_6$, 50.32 MHz): δ 134.04 (−CH═), 119.80 ($C{-}CH_3$), 119.02 ($C{-}CH_3$), 116.76 ($C{-}C_2H_3$), 107.28 (═$CH_2$), 65.82 ($CH_2$, $Et_2O$), 14.88 ($CH_3$, $Et_2O$), 12.99 ($CH_3$), 11.78 ($CH_3$). MS ($^{175}$Lu, 334 °C; *m/z* (%)): 504 (66) $[M - LiClC_8H_{20}]^+$, 489 (56) $[C_{21}H_{27}LuCl]^+$, 469 (4) $[C_{22}H_{30}Lu]^+$, 357 (100) $[C_{11}H_{15}LuCl]^+$, 148 (84) $[C_{11}H_{16}]^+$. Anal. Calcd for $C_{30}H_{50}Cl_2LiLuO_2$ (mol wt 695.54): C, 51.81; H, 7.25. Found: C, 50.28; H, 6.35 (Calcd for $C_{22}H_{30}Cl_2LiLu(OC_4H_{10})$ after losing one molecule diethyl ether under vacuum: C, 50.25; H, 6.49).

**(Tetrahydrofuran)potassium Bis(μ-Chloro)bis(tetramethylvinylcyclopentadienyl)lutetium (3).** To a suspension of $LuCl_3(THF)_3$ (3.31 g, 6.65 mmol) in THF (80 mL) was added $K[C_5Me_4CH{=}CH_2]$ (**1b**; 2.47 g, 13.3 mmol) at room temperature, and the reaction mixture was stirred for 12 h. After filtration and removal of the solvent under vacuum ($10^{-2}$ mbar) 2.30 g (53%) of a pale yellow powder of **3** were obtained; mp 247 °C dec. $^{1}H$ NMR (pyridine-$d_5$, 200 MHz): δ 6.68 (dd, $^{3}J_{trans}$ = 18.0 Hz, $^{3}J_{cis}$ = 11.6 Hz, 2 H, −CH═), 5.17 ($d_{br}$, $^{3}J_{trans}$ = 18.0 Hz, 2 H, ═$CH_2$), 5.04 ($d_{br}$, $^{3}J_{cis}$ = 11.6 Hz, 2 H, ═$CH_2$), 3.65 ($s_{br}$, 4 H, $CH_2$(THF)), 2.30−1.70 (m, 24 H, $CH_3$), 1.61 ($s_{br}$, 4 H, $CH_2$(THF)). $^{13}C\{^{1}H\}$ NMR (pyridine-$d_5$, 50.32 MHz): δ 132.16 (−CH═), 121.16, 119.89, 118.28, 117.77, 117.58 ($C{-}CH_3$, $C{-}C_2H_3$), 109.21 (═$CH_2$), 67.84 ($CH_2$, THF), 25.82 ($CH_2$, THF), 13.86, 12.96, 12.52, 12.07, 11.74, 11.50 ($CH_3$). MS ($^{175}$Lu, 334 °C; *m/z* (%)): 504 (66) $[M - KClC_4H_8]^+$, 489 (56) $[C_{21}H_{27}LuCl]^+$, 469 (4) $[C_{22}H_{30}Lu]^+$, 357 (100) $[C_{11}H_{15}LuCl]^+$, 148 (84) $[C_{11}H_{16}]^+$. Anal. Calcd for $C_{26}H_{38}Cl_2KLuO$ (mol wt 651.56): C, 47.93; H, 5.88. Found: C, 47.63; H, 5.83.

**(Tetrahydrofuran)lithium Bis(μ-Methyl)bis(tetramethylvinylcyclopentadienyl)yttrium (4).** To a solution of $YCl_3$ (0.24 g, 1.21 mmol) in tetrahydrofuran (50 mL) was added $Li[C_5Me_4CH{=}CH_2]$ (**1a**; 0.37 g, 2.42 mmol), and the mixture was refluxed for 2 h. After removal of the solvent under vacuum ($10^{-2}$ mbar), the residue was extracted with diethyl ether (50 mL). The extract was cooled to −78 °C, followed by slow addition of MeLi (1.5 M in diethyl ether, 0.81 mL, 1.21 mmol). After the reaction mixture was stirred for 12 h, it was filtered and the solvent was removed from the filtrate under vacuum ($10^{-2}$ mbar). The remaining pale yellow powder was extracted with hexane (40 mL). The extract was concentrated and stored at −78 °C, yielding a few pale yellow crystals of **4**, which decompose immediately at room temperature. $^{1}H$ NMR (pyridine-$d_5$, 200 MHz, −40 °C): δ 7.13 (dd, $^{3}J_{trans}$ = 17.8 Hz, $^{3}J_{cis}$ = 11.6 Hz, 2 H, −CH═), 5.36 (dd, $^{3}J_{trans}$ = 17.8 Hz, $^{2}J$ = 2.5 Hz, 2 H, ═$CH_2$), 5.04 (dd, $^{3}J_{cis}$ = 11.6 Hz, $^{2}J$ = 2.5 Hz, 2 H, ═$CH_2$), 3.67 (m, 4 H, THF), 2.44 (s, 12 H, $CH_3$), 2.32 (s, 12 H, $CH_3$), 1.66 (m, 4 H, THF), −0.775 (d, $^{2}J(^{89}Y,^{1}H)$ = 2 Hz, 6 H, $CH_3$). $^{13}C\{^{1}H\}$ NMR (pyridine-$d_5$, 50.32 MHz): δ 134.76 (−CH═), 115.65 ($C{-}CH_3$), 113.90 ($C{-}C_2H_3$), 112.92 ($C{-}CH_3$), 103.54 (═$CH_2$), 67.52 ($CH_2$, THF), 25.49 ($CH_2$, THF), 18.17 ($CH_3$), 17.18 ($CH_3$), 12.88 ($CH_3$), 11.91 ($CH_3$).

**Bis(tetrahydrofuran)lithium Bis(μ-Chloro)bis{(2-(9-borabicyclo[3.3.1]non-9-yl)ethyl)tetramethylcyclopentadienyl}yttrium (5a).** To a solution of **2a** (1.39 g, 2.28 mmol) in toluene (80 mL) was added 9-BBN (9.12 mL 0.5 M in THF, 4.56 mmol) slowly at room temperature. After the reaction mixture was stirred for 12 h, it was filtered. Removal of the solvent from the filtrate under vacuum ($10^{-2}$ mbar) left a residue which was washed only once with pentane (10 mL) and was then dissolved in hexane. Cooling of the hexane solution to 0 °C caused precipitation of 1.33 g (69%) of colorless crystals of **5a**; mp 128 °C. $^{1}H$ NMR (benzene-$d_6$, 200 MHz): δ 3.54 ($m_{br}$, 8 H, THF), 3.10−2.99 (m, 4 H, $CH_2$), 2.34 (s, 12 H, $CH_3$), 2.25 (s, 12 H, $CH_3$), 2.00−1.62 (m, 32 H, CH, $CH_2$), 1.32 ($m_{br}$, 8 H, THF). $^{13}C\{^{1}H\}$ NMR (benzene-$d_6$, 50.32 MHz): δ 124.81 ($C{-}C_2H_4$-9-BBN), 118.24 (d, $^{1}J(^{89}Y,^{13}C)$ = 1.2 Hz, $C{-}CH_3$), 116.28 ($C{-}CH_3$), 68.36 ($CH_2$, THF), 33.53 ($CH_2$, 9-BBN), 31.70 (CH, 9-BBN), 30.55 ($CH_2$), 25.36 ($CH_2$, THF), 23.67 ($CH_2$, 9-BBN), 23.57 ($CH_2$, 9-BBN), 21.46 ($CH_2$), 12.08 ($CH_3$), 11.92 ($CH_3$). MS (211 °C; *m/z* (%)): 662 (2) [M − (LiCl, 2THF)]$^+$, 393 (4) $[M - C_{19}H_{30}B]^+$, 270 (25) $[C_{19}H_{31}B]^+$, 256 (6) $[C_{18}H_{29}B]^+$, 230 (4), 194 (4), 162 (10), 148 (18) $[C_{11}H_{18}]^+$, 135 (100) $[C_{10}H_{15}]^+$, 122 (42) [9-BBN]$^+$, 108 (11). Anal. Calcd for $C_{46}H_{76}B_2YCl_2LiO_2$ (mol wt 849.48): C, 65.04; H, 9.02. Found: C, 64.02; H, 8.22 (Calcd for $C_{38}H_{60}B_2YCl_2Li$ after loss of two molecules of THF under vacuum: C, 64.72; H, 8.57).

**Bis(tetrahydrofuran)lithium Bis(μ-Chloro)bis{(2-(9-borabicyclo[3.3.1]non-9-yl)ethyl)tetramethylcyclopentadienyl}samarium (5b).** In analogy to the preparation of **5a**, compound **2b** (0.64 g, 0.95 mmol) dissolved in toluene (30 mL) was reacted with 9-BBN (3.81 mL, 0.5 M in THF, 1.9 mmol) to provide 0.70 g (81%) of yellow crystals of **5b**; mp 139 °C. $^{1}H$ NMR (benzene-$d_6$, 400 MHz): δ 3.95 ($s_{br}$, 8 H, THF), 1.94 ($s_{br}$, 4 H, $CH_2$), 1.85−1.39 (m, 60 H, CH, $CH_2$, $CH_3$), 1.10 ($s_{br}$, 4 H, $CH_2$). $^{13}C\{^{1}H\}$ NMR (benzene-$d_6$, 100.64 MHz): δ 122.83 ($C{-}C_2H_4$-9-BBN), 117.74 ($C{-}CH_3$), 115.01 ($C{-}CH_3$), 68.70 ($CH_2$, THF), 33.32 ($CH_2$, 9-BBN), 31.44 (CH, 9-BBN), 26.78 ($CH_2$), 26.52 ($CH_2$), 27.11 ($CH_2$, THF), 23.49 ($CH_2$, 9-BBN), 18.27 ($CH_3$), 18.10 ($CH_3$). MS ($^{152}$Sm, 234 °C; *m/z* (%)): 725 (0.4) [M − (LiCl, 2THF)]$^+$, 457 (0.6) $[M - C_{19}H_{30}B]^+$, 336 (2) $[M - C_{27}H_{44}B_2]^+$, 270 (33) $[C_{19}H_{31}B]^+$, 256 (21) $[C_{18}H_{29}B]^+$, 230 (22), 194 (7), 162 (9), 148 (13) $[C_{11}H_{16}]^+$, 135 (100) $[C_{10}H_{15}]^+$, 122 (82) [9-BBN]$^+$, 107 (49), 94 (100), 79 (68), 67 (72), 53 (65), 41 (97). Anal. Calcd for $C_{46}H_{76}B_2SmCl_2LiO_2$ (mol wt 910.94): C, 60.65; H, 8.41. Found: C, 59.87; H, 8.49.

**Bis(tetrahydrofuran)lithium Bis(μ-Chloro)bis{(2-(9-borabicyclo[3.3.1]non-9-yl)ethyl)tetramethylcyclopentadienyl}lutetium (5c).** In analogy to the preparation of **5a**, compound **2c** (0.34 g, 0.48 mmol) dissolved in toluene (30 mL) was reacted with 9-BBN (1.95 mL 0.5 M in THF, 0.96 mmol) to provide 0.39 g (87%) of pale yellow crystals of **5c**; mp 141 °C. $^{1}H$ NMR (benzene-$d_6$, 200 MHz): δ 3.52 ($m_{br}$, 8 H, THF), 3.12−3.00 (m, 4 H, $CH_2$), 2.34 (s, 12 H, $CH_3$), 2.26 (s, 12 H, $CH_3$), 2.00−1.65 (m, 32 H, CH, $CH_2$), 1.34 ($m_{br}$, 8 H, THF). $^{13}C\{^{1}H\}$ NMR (benzene-$d_6$, 50.32 MHz): δ 124.07 ($C{-}C_2H_4$-9BBN), 117.49 ($C{-}CH_3$), 115.42 ($C{-}CH_3$), 68.31 ($CH_2$, THF), 33.53 ($CH_2$, 9-BBN), 31.62 (CH, 9-BBN), 30.53 ($CH_2$), 25.41 ($CH_2$, THF), 23.69 ($CH_2$, 9-BBN), 21.67 ($CH_2$), 12.25 ($CH_3$), 12.11 ($CH_3$). MS ($^{175}$Lu, 217 °C; *m/z* (%)): 748 (0.8) [M − (LiCl, 2THF)]$^+$, 479 (2) $[M - C_{19}H_{30}B]^+$, 358 (2) $[M - C_{27}H_{44}B_2]^+$, 270 (29) $[C_{19}H_{31}B]^+$, 256 (5) $[C_{18}H_{29}B]^+$, 230 (4), 162 (11), 148 (20) $[C_{11}H_{16}]^+$, 135 (100) $[C_{10}H_{15}]^+$, 122 (45) [9-BBN]$^+$, 107 (17), 93 (28), 79 (24), 67 (18), 53 (22). Anal. Calcd for $C_{46}H_{76}B_2LuCl_2LiO_2$ (mol wt 935.54): C, 59.06; H, 8.19. Found: C, 57.26; H, 7.72 (Calcd for $C_{38}H_{60}B_2LuCl_2Li$ after losing two molecules of THF under vacuum: C, 57.68; H, 7.64).

**((Cyclohexylidenemethyl)cyclopentadienyl)potassium (6).** To a solution of (2,4-cyclopentadien-1-ylidenemethyl)cyclohexane (5.03 g, 31 mmol) in tetrahydrofuran (150 mL), precooled to −20 °C, was added $K[N(SiMe_3)_2]$ (6.27 g, 31 mmol). The reaction mixture was stirred for 2 h at room temperature. Then the solvent was removed under vacuum ($10^{-2}$ mbar), leaving a viscous brown oil, to which hexane (40 mL) was added. The mixture was stirred for 30 min, and then the solvent was decanted and the remaining oily residue was dried under vacuum. Again hexane (30 mL) was added. After prolonged stirring 5.61 g (91%) of pyrophoric, gray-white, powdery **6** precipitated; mp 205 °C. $^{1}H$ NMR (pyridine-$d_5$, 200 MHz): δ 6.51 (s, 1 H, CH), 6.36−6.32 (m, 2 H, CH), 6.30−6.26 (m, 2 H, CH), 2.90−2.80 ($m_{br}$, 2 H, $CH_2$), 2.40−2.30 ($m_{br}$, 2 H, $CH_2$), 1.67−1.50 ($m_{br}$, 6 H, $CH_2$). $^{13}C\{^{1}H\}$ NMR (pyridine-$d_5$, 100.64 MHz): δ 125.29 (−C═), 123.29 (CH), 119.07 ($C{-}C_7H_{11}$), 107.34 (CH, Cp), 106.10 (CH, Cp), 38.20 ($CH_2$), 30.01 ($CH_2$), 29.03 ($CH_2$), 27.63 ($CH_2$), 27.27 ($CH_2$). MS (284 °C; *m/z* (%)): 198 (7) [M]$^+$, 159 (30) $[C_{12}H_{15}]^+$, 143 (5), 129 (21), 115 (22), 103 (5), 91 (37), 79 (25), 67 (14), 39 (100). Anal. Calcd for $C_{12}H_{15}K$: (mol wt 198.35): C, 72.67; H, 7.62. Found: C, 73.31; H, 8.12.

**Bis((cyclohexylidenemethyl)cyclopentadienyl)yttrium Chloride (7).** To a suspension of $YCl_3$ (0.78 g, 4 mmol) in THF (75 mL) was added $K[C_5H_4CH{=}C_6H_{10}]$ (**6**; 1.59

g, 8 mmol) at room temperature, and the reaction mixture was stirred for 12 h. After removal of the solvent under vacuum ($10^{-2}$ mbar), the residue was extracted with hexane (60 mL). The resulting hexane extract was concentrated and cooled to −25 °C, yielding 0.85 g (48%) of colorless crystals of **7**; mp 92 °C. $^{1}H$ NMR (benzene-$d_6$, 200 MHz): $\delta$ 6.44−6.41 (m, 8 H, CH), 6.23−6.20 (m, 8 H, CH), 6.16 (s, 4 H, CH), 2.56−2.50 (m, 8 H, $CH_2$), 2.26−2.20 (m, 8 H, $CH_2$), 1.67−1.42 (m, 24 H, $CH_2$). $^{13}C\{^{1}H\}$ NMR (benzene-$d_6$, 50.32 MHz): $\delta$ 141.06 ($-C{=}$), 126.80 (d, $^{1}J(^{89}Y,^{13}C) = 1.1$ Hz, $C-C_7H_{11}$), 116.90 (CH), 113.41 (d, $^{1}J(^{89}Y,^{13}C) = 1.1$ Hz, CH, Cp), 113.18 (d, $^{1}J(^{89}Y,^{13}C) = 1.0$ Hz, CH, Cp), 38.24 ($CH_2$), 30.39 ($CH_2$), 29.04 ($CH_2$), 27.88 ($CH_2$), 26.91 ($CH_2$). MS (217 °C; *m/z* (%)): 886 (1) $[M]^+$, 727 (42) $[C_{36}H_{45}Y_2Cl_2]^+$, 567 (1) $[C_{24}H_{30}Y_2Cl_2]^+$, 443 (0.3) [M(monomer)]$^+$, 407 (100) $[C_{24}H_{30}Y]^+$, 283 (4) $[C_{12}H_{15}YCl]^+$, 247 (1) $[C_{12}H_{14}Y]^+$, 1600 (8) $[C_{12}H_{16}]^+$. Anal. Calcd for $(C_{24}H_{30}YCl)_2$ (mol wt 885.72): C, 65.09; H, 6.83. Found: C, 65.19; H, 6.60.

**Bis[((cyclohexylidenemethyl)cyclopentadienyl)methylyttrium] (7a).** To a solution of **7** (0.166 g, 0.187 mmol) in toluene (15 mL) was added MeLi (0.12 mL, 1.5 M in $Et_2O$) at −78 °C, and the reaction mixture was stirred for 6 h. The solvent was removed under vacuum ($10^{-2}$ mbar), leaving a colorless solid which could not be purified by crystallization. $^{1}H$ NMR (benzene-$d_6$, 200 MHz): $\delta$ −0.61 (t, 6H, $^{2}J(^{89}Y,^{1}H) = 3.1$ Hz) and signals of the educt. MS (205 °C; *m/z* (%)): 709 (0.4) $[(C_{12}H_{14})_3Y_2Me_2]^+$, 421 (0.3) $[(C_{12}H_{14})_3Y_2Me]^+$, 407 (110) $[C_{24}H_{30}Y]^+$, and educt signals.

**Bis((cyclohexylidenemethyl)cyclopentadienyl)bis(tetrahydrofuran)samarium (8).** To a suspension of $SmI_2(THF)_2$ (1.23 g, 2.24 mmol) in THF (50 mL) was added $K[C_5H_4CH{=}C_6H_{10}]$ (**6**; 0.88 g, 4.48 mmol) at room temperature. After the reaction mixture was stirred for 12 h, it was filtered. Then the solvent was removed from the filtrate under vacuum ($10^{-2}$ mbar). The remaining black oil was washed with pentane (20 mL) and dried, yielding 0.59 g (43%) of a black powder of **8**; mp 98 °C. $^{1}H$ NMR (pyridine-$d_5$, 200 MHz): $\delta$ 13.33 ($s_{br}$, 4 H, CH, Cp), 12.56 ($s_{br}$, 4 H, CH, Cp), 3.66 (m, 8 H, THF), 2.35 ($s_{br}$, 2 H, CH), 1.63 (m, 8 H, THF), (m, 20 H, $CH_2$). $^{13}C\{^{1}H\}$ NMR (pyridine-$d_5$, 50.32 MHz): $\delta$ 131.44 (CH), 127.68 ($-C{=}$), 115.62 ($C_{qu}$, Cp), 105.50 (CH, Cp), 103.57 (CH, Cp), 67.43 ($CH_2$, THF), 38.44 ($CH_2$), 30.23 ($CH_2$), 26.91 ($CH_2$), 26.39 ($CH_2$), 26.34 ($CH_2$), 25.41 ($CH_2$, THF). MS ($^{152}Sm$, 204 °C; *m/z* (%)): 472 (100) $[M + 2H, - 2THF]^+$, 470 (99) $[M - 2THF]^+$, 311 (26) $[C_{12}H_{15}Sm]^+$, 160 (42) $[C_{12}H_{16}]^+$, 145 (9), 131 (20), 117 (24), 104 (5). Anal. Calcd for $C_{32}H_{46}SmO_2$ (mol wt 613.02): C, 62.69; H, 7.56. Found: C, 61.92; H, 6.72.

**Tris((cyclohexylidenemethyl)cyclopentadienyl)(tetrahydrofuran)samarium (9).** To a suspension of $SmCl_3$ (0.58 g, 2.26 mmol) in THF (80 mL) was added $K[C_5H_4CH{=}C_6H_{10}]$ (**6**; 1.35 g, 6.8 mmol) was added at room temperature, and the reaction mixture was stirred for 12 h. After removal of the solvent under vacuum ($10^{-2}$ mbar), the residue was washed with pentane (20 mL) and extracted with toluene (50 mL). The toluene extract was concentrated and cooled to −25 °C, yielding 1.13 g (71%) of red crystals of **9**; mp 109 °C. $^{1}H$ NMR (benzene-$d_6$, 200 MHz): $\delta$ 13.96 ($s_{br}$, 6 H, CH, Cp), 13.50 ($s_{br}$, 6 H, CH, Cp), 2.77 (s, 3 H, CH), 2.35−2.25 (m, 6 H, $CH_2$), 1.60−0.87 (m, 24 H, $CH_2$), −2.50 ($s_{br}$, 4 H, THF), −4.20 ($s_{br}$, 4 H, THF). $^{13}C\{^{1}H\}$ NMR (benzene-$d_6$, 50.32 MHz): $\delta$ 132.05 (CH), 128.29 ($-C{=}$), 115.37 ($C-C_7H_{11}$), 105.95 (CH, Cp), 105.06 (CH, Cp), 67.36 ($CH_2$, THF), 38.90 ($CH_2$), 30.61 ($CH_2$), 27.42 ($CH_2$), 26.86 ($CH_2$), 26.83 ($CH_2$), 19.30 ($CH_2$, THF). MS ($^{152}Sm$, 84 °C; *m/z* (%)): 629 (8) $[M - THF]^+$, 470 (100) $[C_{24}H_{30}Sm]^+$, 311 (29) $[C_{12}H_{15}Sm]^+$, 160 (84) $[C_{12}H_{16}]^+$, 145 (16), 131 (33), 117 (40), 104 (20). Anal. Calcd for $C_{40}H_{53}SmO$ (mol wt 700.22): C, 68.61; H, 7.63. Found: C, 68.37; H, 7.48.

**(2-Methyl-1-propenylcyclopentadienyl)potassium (10).** In analogy to the preparation of **6**, 5-(2-methyl-1-propenyl)cyclopentadiene (4.74 g, 39 mmol) was reacted with $K[N(SiMe_3)_2]$ (7.78 g, 39 mmol) in THF (150 mL) to provide 6.01 g (97%) of a pyrophoric beige powder of **10**; mp 146 °C. $^{1}H$ NMR (pyridine-$d_5$, 200 MHz): $\delta$ 6.51 (s, 1 H, CH), 6.28−6.21 (m, 4 H, CH), 2.03 (s, 3 H, $CH_3$), 1.91 (s, 3 H, $CH_3$). $^{13}C\{^{1}H\}$ NMR (pyridine-$d_5$, 50.32 MHz): $\delta$ 126.10 ($-C{=}$), 123.12 (CH), 115.76 ($C-C_4H_7$), 107.01 (CH, Cp), 106.19 (CH, Cp), 27.52 ($CH_3$), 20.09 ($CH_3$). MS (197 °C; *m/z* (%)): 158 (0.4) $[M]^+$, 120 (71) $[C_9H_{11}]^+$, 105 (100), 91 (38), 77 (29), 65 (8), 51 (10), 39 (13). Anal. Calcd for $C_9H_{11}K$ (mol wt 158.28): C, 68.29; H, 7.00. Found: C, 68.46; H, 6.57.

**Bis(2-methyl-1-propenylcyclopentadienyl)yttrium Chloride (11).** In analogy to the preparation of **7**, $YCl_3$ (1.20 g, 6.14 mmol) suspended in THF (80 mL) was reacted with $K[C_5H_4CH{=}CMe_2]$ (**10**; 1.94 g, 12.3 mmol). After removal of the solvent under vacuum ($10^{-2}$ mbar), the residue was extracted with diethyl ether (60 mL). The clear solution was decanted, the diethyl ether removed under vacuum ($10^{-2}$ mbar), and the residue washed twice with pentane (2 × 10 mL), yielding 0.93 g (42%) of a beige powder of **11**; mp 85 °C. $^{1}H$ NMR (benzene-$d_6$, 200 MHz): $\delta$ 6.41−6.39 (m, 8 H, CH), 6.21−6.17 (m, 8 H, CH), 6.19 (s, 4 H, CH), 1.87 (s, 6 H, $CH_3$), 1.86 (s, 6 H, $CH_3$), 1.79 (s, 6 H, $CH_3$), 1.78 (s, 6 H, $CH_3$). $^{13}C\{^{1}H\}$ NMR (benzene-$d_6$, 50.32 MHz): $\delta$ 132.48 ($-C{=}$), 127.23 ($C-C_4H_7$), 119.99 (CH), 113.38 (CH, Cp), 112.74 (CH, Cp), 27.31 ($CH_3$), 20.09 ($CH_3$). MS (169 °C; *m/z* (%)): 724 (1.5) $[M]^+$, 607 (42) $[C_{27}H_{33}Y_2Cl_2]^+$, 362 (1) [M(monomer)]$^+$, 327 (100) $[C_{18}H_{22}Y]^+$, 273 (7) $[C_{14}H_{16}Y]^+$, 243 (5) $[C_9H_{11}YCl]^+$, 207 (9) $[C_9H_{11}Y]^+$, 160 (8), 120 (18) $[C_9H_{12}]^+$, 105 (20). Anal. Calcd for $(C_{18}H_{22}YCl)_2$ (mol wt 725.46): C, 59.60; H, 6.11. Found: C, 59.24; H, 6.17.

During the purification process of **11**, a few colorless crystals of the hydrolyzation product $[(Me_2C{=}CHC_5H_4)_2Y(Et_2O)]_2(\mu\text{-}O)$ (**12**) were isolated and characterized by X-ray diffraction analysis.

**Tris((2-methyl-1-propenyl)cyclopentadienyl)(tetrahydrofuran)samarium (13).** In analogy to the preparation of **11**, $SmCl_3$ (0.75 g, 3 mmol) suspended in THF (80 mL) was reacted with $K[C_5H_4CH{=}CMe_2]$ (**10**: 1.40 g, 9 mmol) to provide 1.05 g (61%) of red crystals of **13**; mp 91 °C dec. $^{1}H$ NMR (benzene-$d_6$, 400 MHz): $\delta$ 13.72 ($s_{br}$, 6 H, CH, Cp), 13.57 ($s_{br}$, 6 H, CH, Cp), 3.35 (s, 3 H, CH), 1.14 (s, 9 H, $CH_3$), 0.46 (s, 9 H, $CH_3$), −2.46 ($s_{br}$, 4 H, THF), −4.12 ($s_{br}$, 4 H, THF). $^{13}C\{^{1}H\}$ NMR (benzene-$d_6$, 100.64 MHz): $\delta$ 130.91 ($-C{=}$), 122.16 (CH), 115.62 ($C-C_4H_7$), 104.80 (CH, Cp), 104.63 (CH, Cp), 64.30 (br, $CH_2$, THF), 27.50 ($CH_3$), 19.93 ($CH_3$), 18.61 ($CH_2$, THF). MS ($^{152}Sm$, 132 °C; *m/z* (%)): 509 (14) $[M - THF]^+$, 390 (100) $[C_{18}H_{22}Sm]^+$, 271 (42) $[C_{12}H_{15}Sm]^+$, 119 (15) $[C_9H_{11}]^+$, 105 (13). Anal. Calcd for $C_{31}H_{41}SmO$ (mol wt 580.03): C, 64.19; H, 7.12. Found: C, 64.28; H, 6.71.

**(1,1-Bis(methylenecyclopentadienyl)ethene)dipotassium (14).** To a solution of $Na[C_5H_5]$ (21.13 g, 240 mmol) in THF (180 mL) was added 3-chloro-2-(chloromethyl)-1-propene (9.26 mL, 80 mmol) at −20 °C. After it was stirred for 24 h at −20 °C, the reaction mixture was filtered and the solvent was removed from the filtrate under vacuum ($10^{-2}$ mbar). The remaining oily residue was stirred for 2 h under vacuum and was then extracted with hexane (120 mL). Removal of hexane from the extract left a yellow liquid (11.36 g, 61.5 mmol), which was immediately dissolved in THF (150 mL). Then potassium hydride (4.94 g, 123 mmol) was added to this solution at −20 °C. The brown reaction mixture was stirred for 24 h at this temperature and was then filtered at room temperature and the filtrate concentrated to 30 mL. After addition of hexane (50 mL) the mixture was again stirred for 1 h. The yellow sticky residue remaining after removal of the solvents by decantation was washed twice with a mixture (1:1 v/v) of hexane and diethyl ether (50 mL), yielding 13.74 g (66%) of **14** as a yellow pyrophoric powder; mp 223 °C dec. $^{1}H$ NMR (pyridine-$d_5$, 200 MHz): $\delta$ 6.11−6.08 (m, 4 H, CH), 5.98−5.93 (m, 4 H, CH), 5.23 (s, 2 H, $=CH_2$), 3.86 (s, 4 H, $CH_2$). $^{13}C\{^{1}H\}$ NMR (pyridine-$d_5$, 50.32 MHz): $\delta$ 155.25 ($-C{=}$), 119.01 ($=CH_2$), 109.0 ($C-Cp$), 104.89 (CH, Cp), 103.69 (CH, Cp), 40.02 ($CH_2$). MS (147 °C; *m/z* (%)): 184 (82) $[C_{14}H_{16}]^+$, 169 (82)

**Table 1. Crystal Structure Determination of 3, 5b, and 7**

| | 3 | 5b | 7 |
|---|---|---|---|
| formula | $C_{26}H_{38}KOLuCl_2$ | $C_{46}H_{76}B_2LiO_2SmCl_2$ | $C_{48}H_{60}Y_2Cl_2 \cdot C_7H_8$ |
| fw | 651.6 | 910.9 | 488.9 |
| cryst size (mm$^3$); color | 0.40 × 0.24 × 0.08; yellow | 0.30 × 0.05 × 0.20; yellow | 0.40 × 0.26 × 0.22; colorless |
| cryst syst | monoclinic | monoclinic | triclinic |
| space group | *Cc* | *C*2/*c* | $P\bar{1}$ |
| *Z* (formula units) | 4 | 4 | 1 |
| *a* (Å) | 11.3332(2) | 29.5008(3) | 6.5351(2) |
| *b* (Å) | 27.3575(3) | 12.8306(2) | 12.4006(4) |
| *c* (Å) | 8.8820(2) | 13.53190(10) | 15.4309(6) |
| α (deg) | 90 | 90 | 104.2920(10) |
| $\beta$ (deg) | 103.5380(10) | 115.6220(10) | 95.3160(10) |
| $\gamma$ (deg) | 90 | 90 | 96.8640(10) |
| *V* (Å$^3$) | 2677.33(8) | 4618.33(9) | 1193.38(7) |
| $d_{calcd}$ (g cm$^{-3}$) | 1.611 | 1.310 | 1.361 |
| *F*(000) | 1296 | 1908 | 510 |
| $\mu$ (mm$^{-1}$) | 4.058 | 1.422 | 2.567 |
| $2\theta$ range (deg) | 3−52 | 3−55 | 3−55 |
| no. of rflns collected | 7615 | 17 220 | 9011 |
| no. of unique rflns | 4911 | 5303 | 5392 |
| abs cor, max/min | 1.0000/0.4382 | 0.8253/0.5959 | 0.6647/0.5006 |
| no. of obsd rflns, $I > 2\sigma(I)$ | 3686 | 4557 | 3453 |
| no. of data/restraints/params | 4911/63/276 | 5301/0/249 | 5392/0/264 |
| R1 ($I > 2\sigma(I)$, all data)[a] | 0.0567/0.0740 | 0.0404/0.0561 | 0.0560/0.1117 |
| wR2 ($I > 2\sigma(I)$, all data)[b] | 0.1214/0.1262 | 0.0717/0.0765 | 0.0950/0.1128 |
| goodness of fit[c] | 0.932 | 1.089 | 0.969 |
| weighting const *a*/*b*[d] | 0.0105/0 | 0.0214/1.2687 | 0.0168/0 |
| diff peak/hole (e Å$^{-3}$) | 2.348/−3.156 | 0.963/−1.274 | 0.885/−1.067 |

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

$[C_{13}H_{13}]^+$, 155 (31), 143 (27), 135 (14), 128 (44), 117 (36), 104 (40), 91 (55), 77 (58), 66 (16), 51 (20), 41 (26), 39 (27). Anal. Calcd for $C_{14}H_{14}K_2$: (mol wt 260.46): C, 64.56; H, 5.42. Found: C, 64.36; H, 5.90.

***ansa*-[1,1-Bis(methylenecyclopentadienyl)ethene]-(tetrahydrofuran)lutetium Chloride (15).** To a suspension of $LuCl_3(THF)_3$ (1.15 g, 2.31 mmol) in THF (50 mL) was added $K_2[H_2C{=}C(CH_2C_5H_4)_2]$ (**14**; 0.6 g, 2.31 mmol) at room temperature. The reaction mixture was stirred for 6 h and was then filtered. After removal of the solvent from the filtrate under vacuum ($10^{-2}$ mbar), the residue was extracted with diethyl ether (50 mL). The resulting ether solution was evaporated, yielding 0.15 g (14%) of a white powder of **15**; mp 192 °C dec. $^1H$ NMR (pyridine-$d_5$, 200 MHz): $\delta$ 6.14 (s, 4 H, CH), 6.10 (s, 4 H, CH), 5.06 (s, 2 H, $=CH_2$), 3.64 (m, 4 H, THF), 3.38 (s, 4 H, $CH_2$), 1.59 (m, 4 H, THF). $^{13}C\{^1H\}$ NMR (pyridine-$d_5$, 50.32 MHz): $\delta$ 147.89 ($C{=}CH_2$), 113.41 (CH), 112.57 ($=CH_2$), 109.85 (CH), 67.38 ($CH_2$, THF), 36.66 ($CH_2$), 25.33 ($CH_2$, THF). MS ($^{175}$Lu, 238 °C; $m/z$ (%)): 392 (47) $[M - THF]^+$, 356 (100) $[C_{14}H_{14}Lu]^+$, 313 (12), 302 (18) $[C_{10}H_8Lu]^+$, 291 (8) $[C_9H_{10}Lu]^+$, 277 (25) $[C_8H_8Lu]^+$, 238 (13) $[C_5H_5Lu]^+$, 184 (89) $[C_{14}H_{16}]^+$, 169 (70), 155 (36), 141 (40), 129 (46), 117 (59), 104 (75), 91 (53), 77 (70). Anal. Calcd for $C_{18}H_{22}LuClO$ (mol wt 464.79): C, 46.51; H, 4.77. Found: C, 46.71; H, 5.48.

**Table 2. Crystal Structure Determination of 2a and 12**

| | 2a | 12 |
|---|---|---|
| formula | $C_{30}H_{50}LiO_2YCl_2$ | $C_{44}H_{64}O_3Y_2$ |
| fw | 609.5 | 818.8 |
| cryst size (mm$^3$); color | 0.40 × 0.32 × 0.25; pale yellow | 0.80 × 0.50 × 0.40; pale yellow |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/n$ |
| *Z* (formula units) | 4 | 2 |
| *a* (Å) | 15.953(7) | 11.3097(3) |
| *b* (Å) | 14.702(6) | 15.4902(4) |
| *c* (Å) | 13.952(6) | 11.8711(2) |
| $\beta$ (deg) | 92.66(3) | 100.257(1) |
| *V* (Å$^3$) | 3269(2) | 2046.46(8) |
| $d_{calcd}$ (g cm$^{-3}$) | 1.238 | 1.329 |
| *F*(000) | 1288 | 860 |
| $\mu$ (mm$^{-1}$) | 1.970 | 2.858 |
| $2\theta$ range (deg) | 4−55 | 4−61 |
| no. of rflns collected | 7764 | 15 217 |
| no. of unique rflns | 7455 | 4707 |
| abs cor, max/min | none | 0.4490/0.2568 |
| no. of obsd rflns, $I > 2\sigma(I)$ | 3742 | 3562 |
| no. of data/restraints/params | 7455/1/337 | 4707/0/229 |
| R1 ($I > 2\sigma(I)$, all data)[a] | 0.0703/0.1763 | 0.0350/0.0736 |
| wR2 ($I > 2\sigma(I)$, all data)[b] | 0.1763/0.2217 | 0.0585/0.0827 |
| goodness of fit[c] | 1.023 | 1.037 |
| weighting const *a*/*b*[d] | 0.1139/0 | 0.0339/0.7952 |
| diff peak/hole (e Å$^{-3}$) | 1.296/−0.818 | 0.887/−0.427 |

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

**X-ray Structure Determination.** The crystal data and details of data collection of **2a**, **3**, **5b**, **7**, and **12** are given in Tables 1 and 2. Data sets were collected at 173 K on a Siemens SMART CCD diffractometer[16] ($\omega$ scans, $\lambda$ = 0.710 73 Å, graphite-monochromated Mo Kα radiation). The structures were solved by direct methods using SHELXS-97[17] and were refined on $F^2$ using all observed reflections with SHELXL-97.[18] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions (C−H = 0.96 Å) and assigned to an isotropic displacement parameter of 0.08 Å$^2$). SADABS[19] was used to perform area detector scaling and absorption corrections for the data of **3**, **5b**, **7**, and **12**. In **3**, one cyclopentadienyl ligand as well as the vinyl group attached to the second cyclopentadienyl ligand were disordered and were therefore refined with isotropic displacement parameters. Further material is part of the Supporting Informa-

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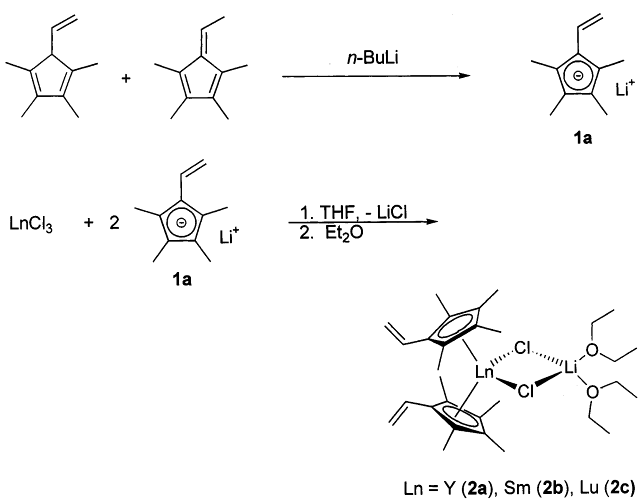
[16] SMART and SAINT. DataCollection and Processing Software for SMART System; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

[17] Sheldrick, G. M. SHELXS-97, Program for Crystral Structure Determination; Universität Göttingen, Göttingen, Germany, 1997.

[18] Sheldrick, G. M. SHELXL-97, Program for Crystral Structure Determination; Universität Göttingen, Göttingen, Germany, 1997.

[19] Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction of Area Detector Data; Universität Göttingen, Göttingen, Germany, 1996.

**Scheme 1**



tion. The geometrical aspects of the structures were analyzed by using PLATON software.[20]

## Results and Discussion

**Bis(tetramethylvinylcyclopentadienyl)lanthanide Chlorides.** The trichlorides of yttrium, samarium, and lutetium react in THF at room temperature with 2 equiv of (tetramethylvinylcyclopentadienyl)lithium (**1a**), which in turn is prepared from butyllithium and the isomeric mixture of tetramethylvinylcyclopentadiene and 5-ethylidene-1,2,3,4-tetramethyl-1,3-cyclopentadiene,[12] to give the crystalline lithium chloride adducts $(CH_2{=}CHC_5Me_4)_2Ln(\mu\text{-}Cl)_2Li(OEt_2)_2$ (Ln = Y (**2a**), Sm (**2b**), Lu (**2c**)) in 45–60% yield (Scheme 1).

The pale yellow (**2a**,**c**) or orange complexes (**2b**) melt with decomposition and are slightly pyrophoric. Depending on the duration of the drying process of the crystals under vacuum, the analytical data of the complexes indicate some loss of diethyl ether, as already stated earlier for other compounds of this type.[21] The new complexes **2a**–**c** are soluble in polar solvents and in aromatic hydrocarbons. In contrast to the noncrystalline products which we isolated from the reactions of $LnCl_3$ with $Li[C_5Me_4CH_2CH_2CH{=}CH_2]$,[4] the complexes **2** readily crystallize from diethyl ether below 0 °C. Obviously, the dangling butenyl substituents prevent crystallization. The yttrium complex **2a** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure (Figure 1) shows for both metals, the yttrium and the lithium atom, the typical distorted-tetrahedral ligand arrangement. The dicyclopentadienyllanthanide unit and the lithium dietherate moiety are bridged by two chlorine atoms. The bond lengths $Cp_c$–Y (2.39 Å), Cl–Y (2.62 Å), and Li–Cl (2.41 Å) are in accordance with the respective values in $(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2$.[22]

In contrast to the above-described reactions, no monomeric complex is formed when $LuCl_3(THF)_3$ is reacted in THF with 2 equiv of (tetramethylvinylcyclopentadienyl)potassium (**1b**), the latter being prepared from $K[N(SiMe_3)_2]$ and the isomeric mixture of tetramethylvinylcyclopentadiene and 5-ethylidene-1,2,3,4-tetramethyl-1,3-cyclopentadiene (Scheme 2). The reaction affords a pale yellow powder which is soluble in boiling toluene but almost insoluble in ether and other donor solvents such as THF and pyridine. Whereas cooling of the toluene solution did not afford a crystalline product, pale yellow crystals separated from the ethereal solution obtained by extraction of the solid immediately after isolation from the reaction mixture. The crystals proved to be suitable for X-ray diffraction analysis. The result of the structure determination shows the monosolvated complex $[(CH_2{=}CHC_5Me_4)_2Lu(\mu\text{-}Cl)_2K(THF)]_n$ (**3**) (Figure 2a), forming polymeric chains (Figure 2b).

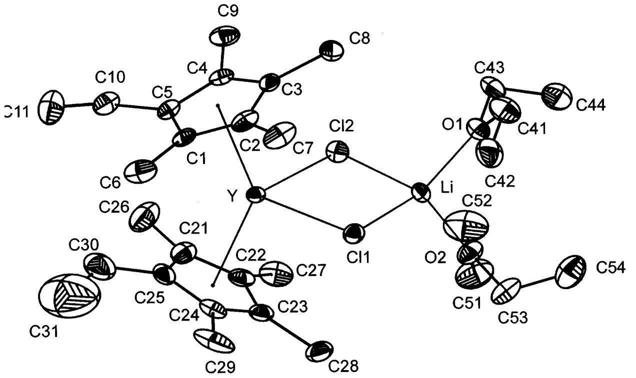
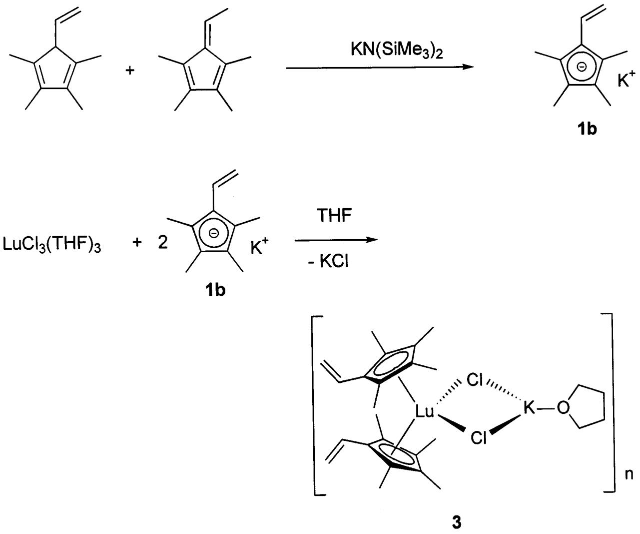


**Figure 1.** ORTEP plot[23] of the molecular structure and the numbering scheme of **2a** with 30% probability thermal ellipsoids. The hydrogen atoms are not depicted. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations in parentheses (Cp(1) and Cp(2) define the centroid positions of the ring atoms C(1–5), and C(21–25), respectively): Y–Cp(1) = 2.386(3), Y–Cp(2) = 2.386(3), Y–Cl(1) = 2.628(2), Y–Cl(2) = 2.621(2), Cl(1)–Li = 2.396(11), Cl(2)–Li = 2.420(11), Li–O(1) = 1.946(11), Li–O(2) = 1.935(12); Cp(1)–Y–Cp(2) = 137.03(11), Cl(1)–Y–Cp(1) = 106.98(9), Cl(1)–Y–Cp(2) = 104.84(9), Cl(2)–Y–Cp(2) = 106.53(9), Cl(2)–Y–Cp(1) = 104.37(9), Cl(1)–Y–Cl(2) = 84.91(7), Li–Cl(1)–Y = 90.3(3), Li–Cl(2)–Y = 90.0(3).

**Scheme 2**



As in the solid-state structure of the yttrium complex **2a**, the coordination geometry around the lutetium atom is that of a distorted tetrahedron formed by the ring centroids of the two cyclopentadienyl ligands and by two bridging chlorine atoms, whereas the coordination

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(20) Spek, A. L. PLATON. *Acta Crystallogr.* **1990**, *4*, C34.

(21) Schumann, H.; Albrecht, I.; Loebel, J.; Hahn, E.; Bilayet Hossain, M.; van der Helm, D. *Organometallics* **1986**, *5*, 1296.

(22) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 1120.

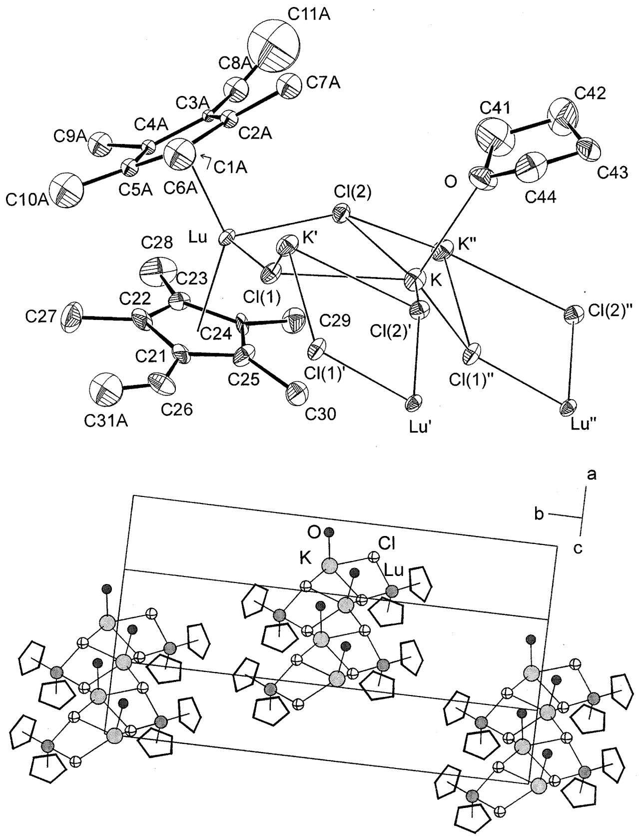

**Figure 2.** (a, top) ORTEP plot[23] of the molecular structure and the numbering scheme of **3** with 30% probability thermal ellipsoids. The hydrogen atoms and the disorder are not depicted. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations in parentheses (Cp(1A), Cp(1B), and Cp(2) define the centroid positions of the ring atoms C(1A−5A), C(1B−5B), and C(21−25), respectively): Lu−Cp(1A) = 2.318(8), Lu−Cp(1B) = 2.332(12), Lu−Cp(2) = 2.343(7), Lu−Cl(1) = 2.571(3), Lu−Cl(2) = 2.579(3), K−O = 2.665(12), K−Cl(1) = 3.116(5), K−Cl(1)″ = 3.123(5), K−Cl(2)′ = 3.157(5), K−Cl(2) = 3.163(4), K−K′ = 4.635(2); Cp(1A)−Lu−Cp(2) = 134.8(2), Cp(1B)−Lu−Cp(2) = 134.6(3), Cp(1A)−Lu−Cl(1) = 106.3(2), Cp(1A)−Lu−Cl(2) = 105.97(14), Cp(1B)−Lu−Cl(1) = 106.5(2), Cp(1B)−Lu−Cl(2) = 106.0(2), Cp(2)−Lu−Cl(1) = 105.9(2), Cp(2)−Lu−Cl(2) = 105.9(2), Cl(1)−Lu−Cl(2) = 88.48(11), Cl(1)−K−Cl(2) = 69.82(10), Cl(1)−K−Cl(1)″ = 124.0(2), Cl(1)−K−Cl(2)′ = 80.37(11), Cl(1)″−K−Cl(2)′ = 130.36(13), Cl(1)″−K−Cl(2) = 80.18(11), Cl(2)′−K−Cl(2) = 146.81(14), O−K−Cl(1) = 116.0(3), Cl(1)″−K−O = 113.4(3), O−K−Cl(2) = 96.4(3), O−K−Lu = 115.2(3), Lu−Cl(1)−K = 100.51(12), Lu−Cl(2)−K = 99.12(12), Lu−Cl(1)−K′ = 148.08(14), Lu−Cl(2)−K″ = 141.84(14), K−Cl(1)−K′ = 95.97(11), K″−Cl(2)−K = 94.35(9). Applied symmetry operations: (′) *x*, −*y*, *z* + 0.5; (″) *x*, −*y*, *z* − 0.5. (b, bottom) Unit cell plot[23] of $[(CH_2{=}CHC_5Me_4)_2Lu(\mu_3{-}Cl)_2K(THF)]_n$ (**3**), showing three chains along the *c* axis.

geometry of the respective alkali metal changes from a distorted tetrahedron in **2a** to a highly distorted trigonal bipyramid in **3**. Each potassium atom is coordinated by one THF molecule and four chlorine atoms which belong to three different monomeric units. Each chlorine atom is $\mu_3$-coordinated to one lutetium and two potassium atoms. The only complex in the literature which shows the same remarkable structure is the cerium compound $[(C_5Me_5)_2Ce(\mu_3{-}Cl)_2K(THF)_n$.[24] The angles Cp$_c$−Lu−Cp$_c$, Cl(1)−Lu−Cl(2), and Lu−Cl(1/2)−K of 135, 88.5, and 99.8°, respectively, correspond very well with the respective values of the cerium complex (136, 86.5, and 98.3°). The Cp$_c$−Lu−Cl angles, ranging from 105.9 to 106.5°, are almost identical with those of the cerium compound (105.4−106.2°). Due to the difference in the ionic radii of Lu(III) and Ce(III), the bond distances Lu−C(Cp) (2.58−2.68 Å) and Lu−Cl (2.57 and 2.58 Å) are shorter than the Ce−C(Cp) (2.77−2.83 Å) and the Ce−Cl distances (2.77 and 2.78 Å). The trigonal-bipyramidal coordination geometry around the potassium atom is formed by the Cl(2) and Cl(2)′ atoms in the axial positions and by Cl(1), Cl(1)″, and the oxygen of the THF ligand occupying the corners of the equatorial plane. The Cl(1)−K−Cl(1)″, Cl(1)−K−O, and Cl(1)″−K−O angles of 124, 116, and 113.4° estimated for **3** are closer to the ideal value of 120° than the comparable values of the cerium complex (128.7, 104.3, and 124.6°). However, the Cl(2)−K−Cl(2)′ angles of 146.8° for **3** and 156.1° for the cerium complex are far from the 180° angle demanded for a regular trigonal bipyramid.

The very broadened signals in the NMR spectra of **3** indicate the existence of oligomeric structures even in solution. All attempts to remove the potassium chloride from **3** in order to get the complex $[(CH_2{=}CHC_5Me_4)_2LuCl]_n$ were unsuccessful. Sublimation of **3** or its treatment with polar solvents caused decomposition or formation of insoluble products, respectively.

**Bis(tetramethylvinylcyclopentadienyl)lanthanide Alkyls.** Alkyl lanthanide complexes play a key role as precatalysts in organolanthanide-mediated reactions.[2] Our recent results concerning the alkylation of $\omega$-alkenyl-functionalized cyclopentadienyllanthanide chlorides indicate that it is very difficult to generate stable $\sigma$-Ln−C bonds in the presence of alkenyl substituents at the cyclopentadienyl ligands.[4] The expected alkyl complexes are unstable in solution and decompose via insertion reactions.[4] Despite these discouraging experiences, but aware of the better crystallization properties of (vinylcyclopentadienyl)lanthanide complexes, we investigated the metathetical reactions of the complexes **2a**−**c** with methyllithium and (bis(trimethylsilyl)methyl)lithium in order to get the corresponding alkyl derivatives $(CH_2{=}CHC_5Me_4)_2LnR$ (R = Me, $CH(SiMe_3)_2$). The reactions were conducted in diethyl ether at −78 °C. The products formed are extremely sensitive and decompose even under an inert atmosphere at this low temperature within a few minutes. The exchange of diethyl ether for nonpolar solvents such as cyclohexane, benzene, and toluene, or carrying out the reactions in deuterated solvents in order to get interpretable NMR spectra immediately after the end of the reactions, does not lead to satisfying results. Increasing amounts of insoluble polymeric solids precipitate during these manipulations, thus indicating that the products themselves are already catalytically active and self-polymerizing. Comparable to the results of Watson[25] and

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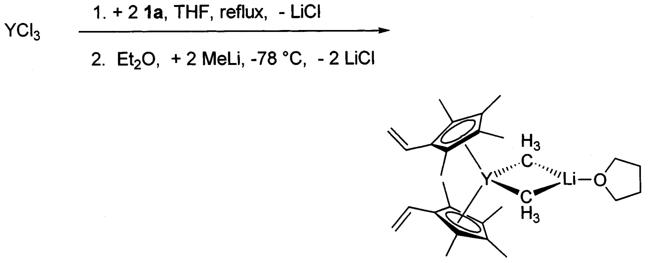
[23] Bergerhoff, G.; Brandenburg, K.; Berndt, M., DIAMOND, Visuelles Informationssystem für Kristallstrukturen; Universität Bonn, Bonn, Germany, 1996.

[24] Evans, W. J.; Olofson, J. M.; Zhang, H.; Atwood, J. L. *Organometallics* **1988**, *7*, 629.

[25] (a) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (b) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (c) Watson, P. L. In *Selective Hydrocarbon Activation*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990.

**Scheme 3**



Bercaw[26] concerning several lanthanidocene alkyl complexes, the spatial vicinity of the double bonds to the metal center will probably cause CH activation followed by insertion of the alkene moiety into the $\sigma$-Ln–C bond. The only compound from which we could isolate a few crystals is the yttrium methyl derivative $(CH_2{=}CHC_5Me_4)_2Y(\mu\text{-}CH_3)_2Li(THF)_2$ (**4**), stabilized by 1 equiv of methyllithium (Scheme 3). This "ate" complex could be definitely characterized only by NMR spectroscopy, since its extremely low thermal stability prevents the application of all other analytical methods, including X-ray diffraction. The crystals decompose slowly even at −78 °C.

Whereas the reactions of **2a**–**c** with $KN[(SiMe_3)_2]$, which are expected to generate the amide complexes $(CH_2{=}CHC_5Me_4)_2LnN(SiMe_3)_2$, take the same complex course as the alkylation reactions, the isolation of $(CH_2{=}CHCH_2CH_2C_5Me_4)_2SmN(SiMe_3)_2$ was successful.[4] We assume that the vinyl group is more reactive than the 3-butenyl moiety and inserts even into a Ln–N bond.

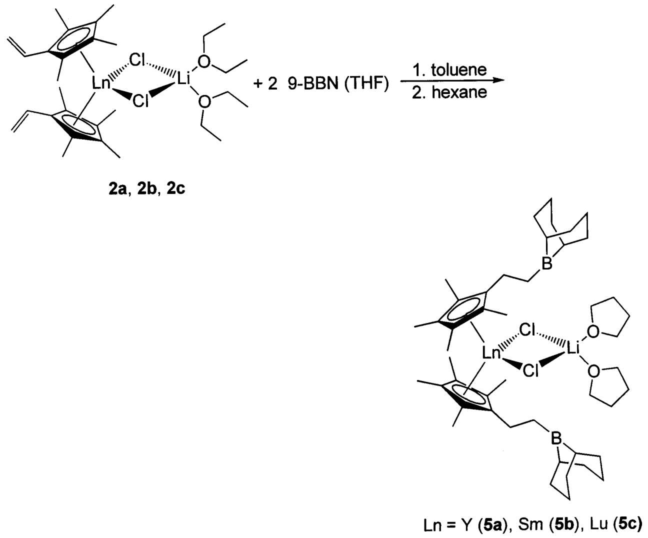
**Bis{(2-(9-borabicyclo[3.3.1]non-9-yl)ethyl)-tetramethylcyclopentadienyl}lanthanide Chlorides.** The vinyl substituents of the cyclopentadienyl ligands of the bis(tetramethylvinylcyclopentadienyl)-lanthanide chlorides **2a**–**c** should be suitable for the introduction of borane groups via hydroboration. Since our previous experiences showed that a further functionalization of the alkenyl side chains of lanthanidocenes and, especially, the isolation of the respective products is rather difficult, the highly selective 9-borabicyclo[3.3.1]nonane (9-BBN) was chosen as hydroboration agent.

The three complexes **2a**–**c** react with 2 equiv of 9-BBN in toluene at room temperature, producing the crystalline compounds $(C_8H_{14}BCH_2CH_2C_5Me_4)_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Ln = Y (**5a**), Sm (**5b**), Lu (**5c**)) in yields of 70–90% (Scheme 4). No isomeric products are formed. The borane selectively attacks the terminal vinylic carbon atom.

The colorless (**5a**) or yellow crystals (**5b**,**c**) are not pyrophoric like their vinyl precursors **2a**–**c** and melt without decomposition at 128, 139, and 141 °C, respectively. They are soluble in polar (diethyl ether, THF) and aromatic solvents (toluene) and crystallize from hexane or toluene at 0 °C. According to the results of the elemental analyses of **5a**,**c**, both complexes lose the two lithium-coordinated THF molecules under vacuum.

The molecular structure of $(C_8H_{14}BCH_2CH_2C_5Me_4)_2Sm(\mu\text{-}Cl)_2Li(THF)_2$ (**5b**) (Figure 3) shows a distorted-tetrahedral ligand arrangement around both the samarium atom (two cyclopentadienyl groups and two chlorine atoms) and the lithium atom (two chlorine atoms and two THF molecules), which is typical of alkali-metal halide adducts of lanthanide complexes of this type. When the difference in the ionic radii of Sm(III) and Y(III) is taken into account, the bond distances and bond angles in **5b** are in accordance with those estimated for $(CH_2{=}CHC_5Me_4)_2Y(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**2a**).

**Scheme 4**



The attempts to synthesize the *ansa*-lanthanidocene complexes $RB(CH_2CH_2C_5Me_4)_2LnCl$ were not successful. The reactions of **2a**–**c** with $BH_3(THF)$, $ClBH_2(SMe_2)$, or $Me_2CHCMe_2BH_2$ did not allow the isolation of any identificable hydroboration products. The obviously nonregioselective course of the reactions led to product mixtures which could not be separated into their components either by crystallization or by sublimation.

In view of the fact that in **5a**–**c** the alkenyl functions of the starting lanthanidocene chlorides **2a**–**c** are saturated by addition of the 9-BBN borane, the alkylation of these hydroborated complexes should be more promising, since C–H activation followed by insertion reactions can no longer disturb the course of the alkylation reactions. However, although the NMR spectra of the crude products obtained from the reactions of **5a**–**c** with $LiCH(SiMe_3)_2$ as the alkylating agent give some indication of the formation of complexes such as $(C_8H_{14}BCH_2CH_2C_5Me_4)_2LnCH(SiMe_3)_2$, no pure and crystalline products could be isolated.

**(Cyclohexylidenemethyl)cyclopentadienyl and (2-Methyl-1-propenyl)cyclopentadienyl Complexes of Yttrium and Samarium.** Since the synthesis of borane-bridged *ansa*-lanthanidocenes via hydroboration of the unsubstituted vinyl functions of the complexes **2a**–**c** did not achieve satisfying results, we postulated that the use of lanthanidocenes containing already substituted vinyl groups could still make this plan succeed. To that purpose, first the potassium salts of (2,4-cyclopentadien-1-ylidenemethyl)cyclohexane (**6**) and 5-isobutylidenecyclopentadiene (**10**) were prepared by deprotonation of the corresponding fulvene derivatives[13] with $K[N(SiMe_3)_2]$, which then were reacted with $YCl_3$ in THF at room temperature, giving the dimeric complexes $[(C_6H_{10}{=}CHC_5H_4)_2Y(\mu\text{-}Cl)]_2$ (**7**) and $[(Me_2C{=}CHC_5H_4)_2Y(\mu\text{-}Cl)]_2$ (**11**) in yields of 48 and 42%, respec-

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(26) St. Clair, M.; Santersiero, B. D.; Bercaw, J. E. *Organometallics* **1989**, *8*, 17.

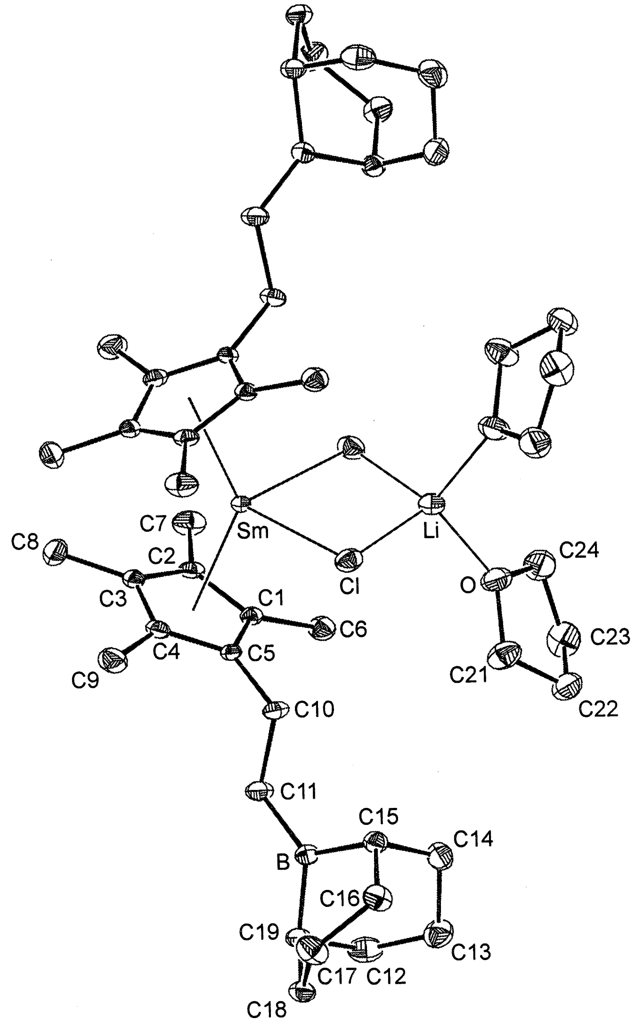
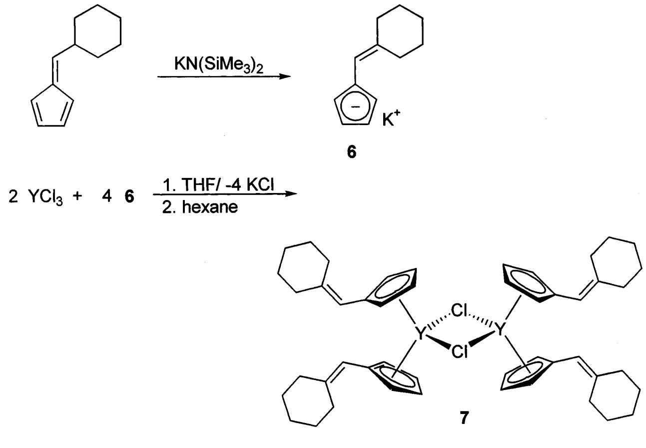
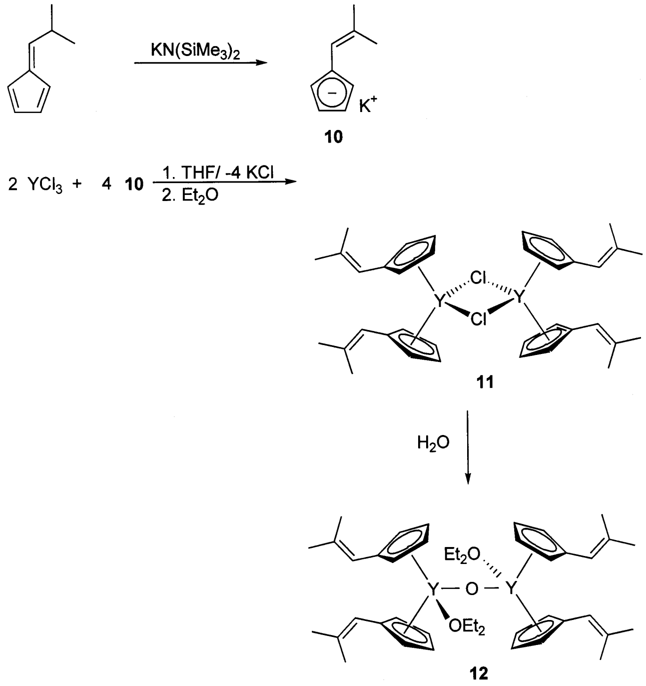


**Figure 3.** ORTEP plot[23] of the molecular structure and the numbering scheme of **5b** with 30% probability thermal ellipsoids. The hydrogen atoms are not depicted. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations in parentheses (Cp defines the centroid position of the ring atoms C(1−5)): Sm−Cp = 2.467(2), Sm−Cl = 2.7094(8), Cl−Li = 2.370(6), Li−O = 1.931(6), B−C(11) = 1.582(5), B−C(15) = 1.587(5), B−C(19) = 1.572(5); Cp−Sm−Cp′ = 136.77(5), Cp-Sm−Cl = 105.98(4), Cp-Sm−Cl′ = 105.47(4), Cl−Sm−Cl′ = 85.25(4), Li−Cl−Sm = 86.6(2), O′−Li−O = 106.0(5), O−Li−Cl′ = 116.39(10), O−Li−Cl = 108.47(9), Cl′−Li−Cl = 101.5(3), C(11)−B−C(15) = 125.0(3), C(19)−B−C(11) = 122.5(3), C(19)−B−C(15) = 111.8(3). Applied symmetry operations: (′) $-x + 1, y, -z + 0.5$.

**Scheme 5**



**Scheme 6**



tively (Schemes 5 and 6).While **7** is soluble in polar and nonpolar solvents and can be crystallized from toluene at −25 °C, the low solubility of **11** in nonpolar solvents such as hexane and toluene prevents its crystallization.

The single-crystal X-ray structural analysis of **7** (Figure 4) shows a distorted-tetrahedral ligand arrangement around each yttrium atom, as usually found for these types of dimeric bis(cyclopentadienyl)lanthanide halides.[27] The bond distances and bond angles of **7** (Y−Cl = 2.68 Å, Y−$Cp_c$ = 2.34 Å; $Cp_c$−Y−$Cp_c$ = 129°, Cl−Y−Cl′ = 82°) correspond well with the values of $[(Me_3SiC_5H_4)_2Y(\mu\text{-}Cl)]_2$ (2.69, 2.34 Å; 130, 81.6°).[28] Due to steric reasons, the two cyclohexylidenemethyl substituents of each $Cp_2YCl$ unit are trans-positioned.

In the course of our attempts to crystallize complex **11** from different solvents, we isolated a few crystals, which, however, turned out to be the hydrolyzation product of **11**, $[(Me_2C{=}CHC_5H_4)_2Y(OEt_2)]_2(\mu\text{-}O)$ (**12**) (Figure 5), probably formed by slight traces of water being present when changing solvents. This fact demonstrates impressively the extremely high oxophilicity of such lanthanidocenes.

The most interesting parameters of the molecular structure of **12** are the Y−O(1)−Y angle of 180° and the short Y−O(1) distance of 2.05 Å, which, however, correspond very well with the respective data for $[(C_5H_5)_2Lu(THF)]_2(\mu\text{-}O)$ (180°/2.00 Å).[29]

The sterically demanding $C_6H_{10}{=}CH$ moiety at the cyclopentadienyl ligands of the yttrium compound **7** probably will prevent interactions of the double bond

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(27) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.

(28) Evans, W. J.; Sollberger, M. S.; Shreeve, J. L.; Olofson, J. M.; Hain, J. H.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 2492.

(29) Schumann, H.; Palamidis, E.; Loebel, J. *J. Organomet. Chem.* **1990**, *384*, C49.

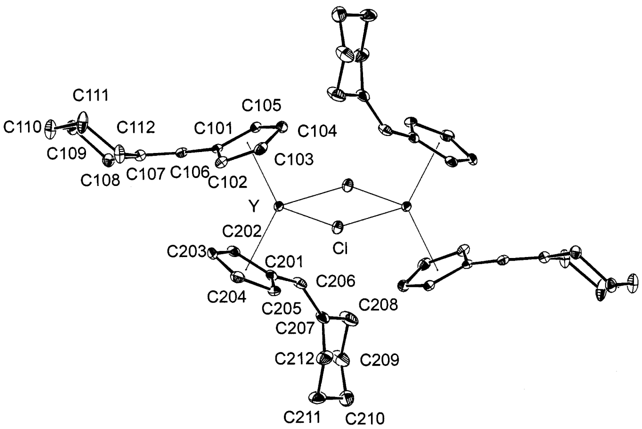


**Figure 4.** ORTEP plot[23] of the molecular structure and the numbering scheme of **7** with 30% probability thermal ellipsoids. The hydrogen atoms are not depicted. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations in parentheses (Cp(1) and Cp(2) define the centroid positions of the ring atoms C(101−105), and C(201−205), respectively): Y−Cp(1) = 2.334(2), Y−Cp(2) = 2.349(2), Y−Cl = 2.6749(11), Y−Cl′ = 2.6934(11); Cp(1)−Y−Cp(2) = 128.92(7), Cp(1)−Y−Cl = 107.48(6), Cp(1)−Y−Cl′ = 107.05(6), Cp(2)−Y−Cl = 107.28(6), Cp(2)−Y−Cl′ = 113.85(6), Cl−Y−Cl′ = 82.03(4), Y−Cl−Y′ = 97.97(4). Applied symmetry operations: (′) $-x+2$, $-y+1$, $-z+2$.

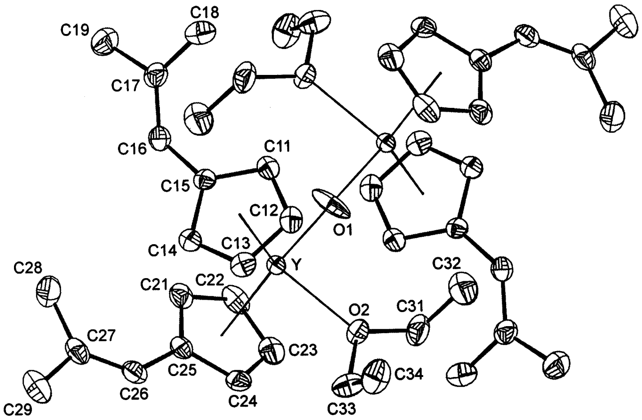
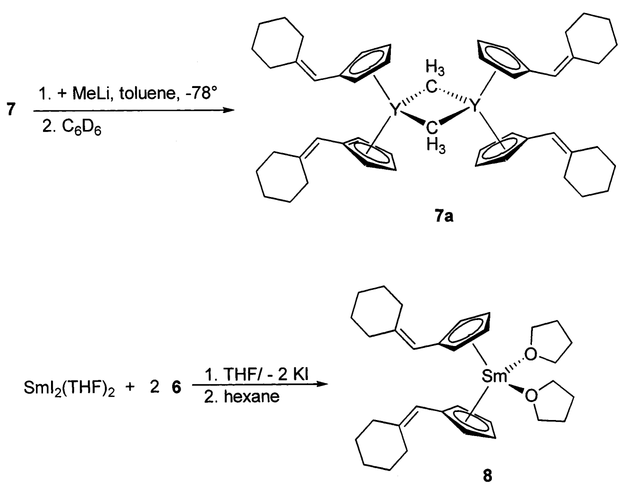


**Figure 5.** ORTEP plot[23] of the molecular structure and the numbering scheme of **12** with 30% probability thermal ellipsoids. The hydrogen atoms are not depicted. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations in parentheses (Cp(1) and Cp(2) define the centroid positions of the ring atoms C(1−5), and C(21−25), respectively): Y−Cp(1) = 2.4267(11), Y−Cp(2) = 2.4325(12), Y−O(1) = 2.0466(2), Y−O(2) = 2.3918(18); Cp(1)−Y−Cp(2) = 129.77(4), Y−O(1)−Y′ = 180.0, Cp(1)−Y−O(2) = 102.11(5), Cp(2)−Y−O(2) = 101.95(6), O(1)−Y−Cp(1) = 109.24(3), O(1)−Y−Cp(2) = 110.66(3), O(1)−Y−O(2) = 97.09(5). Applied symmetry operations: (′) $1-x$, $1-y$, $1-z$.

with the σ-Y−C bonds which should be formed by alkylation of the complex. To answer this question, we investigated the reaction of **7** with methyllithium in toluene at −78 °C. After a reaction time of 6 h, the solvent was removed under vacuum and replaced by benzene-$d_6$ to get a solution suitable for $^1$H NMR spectroscopic measurements. The appearance of a signal at −0.61 ppm, split into a triplet by $^1$H$^{89}$Y coupling ($^2J$ = 3.1 Hz), clearly proves the existence of the methyl-bridged dimer $[(C_6H_{10}{=}CHC_5H_4)_2Y(\mu\text{-}CH_3)]_2$ (**7a**) (Scheme 7). Thesignals expected for the protons of the cyclopentadienyl ligands of **7a** cannot be assigned because of superposition with the respective signals of the educt **7**. Further proof for the formation of the methyl complex is the presence of the monomeric methyl fragment $[(C_7H_{11}C_5H_4)_2YCH_3]$ in the mass spectrum. In conclusion it can be noted that, at least in this case, the substitution of a β-vinyl proton by a space-demanding group slows down the interactions between the double bond and the metal center, although autocatalytic decomposition reactions prevent the isolation of the methyl complex **7a**.

**Scheme 7**



In the frame of our investigations concerning the behavior of samarium halides toward the potassium salts **6** and **10**, we started with the reaction of $SmI_2$ with 2 equiv of **6** (Scheme 7), keeping in mind that it was not possible to isolate the analogous ω-butenyl-substituted bis(cyclopentadienyl)samarium(II) derivative.[4] The resulting black solid is soluble in toluene and THF but rather insoluble in hexane and diethyl ether. Elemental analysis and NMR and mass spectra prove its formulation as the THF-stabilized Sm(II) derivative $(C_6H_{10}{=}CHC_5H_4)_2Sm(THF)_2$ (**8**). The remarkable upfield shift of the $^1$H NMR signal of the single proton at the double bond from 6.51 ppm in the potassium salt **6** to 2.35 ppm may indicate a participation of the double bond in the coordination to the metal center. Unfortunately, all attempts to get single crystals of **8** suitable for X-ray analysis failed.

The reactions of $SmCl_3$ with 2 equiv of the ligand salts **6** and **10** do not afford the respective bis(cyclopentadienyl)samarium chlorides but their redistribution products, the tris(cyclopentadienyl)samarocenes $(C_6H_{10}{=}CHC_5H_4)_3Sm(THF)$ (**9**) and $(Me_2C{=}CHC_5H_4)_3Sm(THF)$ (**13**) (Scheme 8). Such redistribution behavior is also known for the complexes of the early lanthanides with unsubstituted cyclopentadienyl ligands.[30] On the other hand, the (methylcyclopentadienyl)samarium complex $[(MeC_5H_4)_2Sm(\mu\text{-}Cl)(THF)]_2$ proved to be a stable compound.[31] The red complexes **9** and **13** are soluble in polar and in aromatic solvents. Whereas **9** melts without

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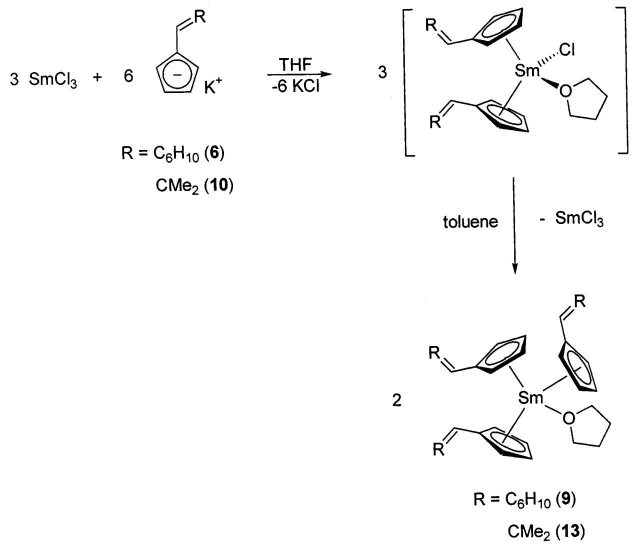
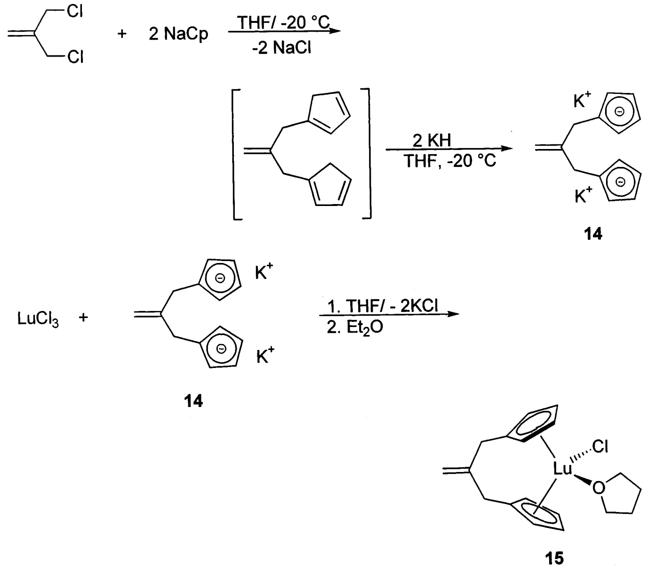
(30) Edelmann, F. T.; Poremba, P. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Brauer, G., Eds.; G. Thieme: Stuttgart, New York, 1997.

(31) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *J. Organomet. Chem.* **1993**, *450*, 115.

**Scheme 8**



**Scheme 9**



decomposition at 109 °C, **13** decomposes already at 91 °C. As in the $^1$H NMR spectrum of the above-described Sm(II) complex **8**, the $^1$H NMR spectra of **9** and **13** show an extreme upfield shift of the signal of the single proton at the double bond from 6.51 ppm in the potassium salts **6** and **10** to 2.77 ppm for **9** and 3.35 ppm for **13**. Again, this fact may be interpreted as the participation of the double bond in coordination to the samarium center. Regardless of the kind of solvent, the complexes **9** and **13** are always obtained as amorphous powders, thus preventing the estimation of their molecular structure.

***ansa*-[1,1′-Bis(methylenecyclopentadienyl)ethene](tetrahydrofuran)lutetium Chloride.** The hydroboration of the organolanthanide complexes **7**, **9**, **11**, and **13** containing substituted vinyl groups turned out to be not regioselective and hence generates inseparable product mixtures. Therefore, we changed our approach in looking for a vinylic ligand system suitable to produce *ansa*-lanthanidocenes. Such vinylic ansa complexes should probably allow the synthesis of well-defined hydroboration products with the borane group attached to the backbone of the bridging ligand system. For these reasons, we synthesized the dipotassium salt $K_2[(C_5H_4CH_2)_2C{=}CH_2]$ (**14**) in two steps starting with the reaction of 3-chloro-2-(chloromethyl)-1-propene with cyclopentadienylsodium, followed by deprotonation of the hydrocarbon formed with potassium hydride. The dipotassium salt **14**, a yellow pyrophoric powder, reacts with equimolar amounts of $LuCl_3$ in THF at room temperature, producing the ansa complex $[H_2C{=}C(CH_2C_5H_4)_2]LuCl(THF)$ (**15**), but only in yields of 14% (Scheme 9). The complex can be isolated from the crude residue remaining after the removal of the solvent from the reaction mixture, by extraction with diethyl ether. The main part of the residue, consisting of polymers, is insoluble. Unfortunately, the hydroboration of complex **15** does not afford clearly defined borane derivatives.

## Conclusion

The first vinyl-functionalized bis(cyclopentadienyl)lanthanide chlorides were prepared from $YCl_3$, $SmI_2$, $SmCl_3$, and $LuCl_3$ by their reaction with the alkali-metal salts of the respective functionalized cyclopentadiene. The complexes are stabilized either by formation of alkali-metal halide adducts or by dimerization. The substitution of the chloride by transmetalation with lithium or potassium alkyls resulted in the formation of extremely unstable lanthanidocene alkyl complexes. After the formation of the $\sigma$-Ln−C bond, interactions between the metal center and the alkenyl moiety are assumed, which cause insertion of the vinylic group into the $\sigma$-Ln−C bond. In the case of the divalent samarium complex, the steric conditions at the double bond prevented autocatalytic decomposition reactions. Bis(cyclopentadienyl)lanthanidocenes with unsubstituted vinyl side chains at the cyclopentadienyl ligands reacted regioselectively with 9-BBN, forming stable complexes. These first hydroborations of lanthanidocenes demonstrate the potential of (alkenylcyclopentadienyl)lanthanide complexes in further functionalization.

**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 **2a**, **3**, **5b**, **7**, and **12**, 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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