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Alkyl Complexes of Rare-Earth Metals That Contain a Furyl-Functionalized Cyclopentadienyl Ligand: Alkyl Cation Formation and Unexpected Ring-Opening Reaction of the Furyl Group

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Rare-earth metal complexes of the type $[Ln\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2(C_4H_3O\text{-}2)\}(CH_2SiMe_3)_2(THF)]$ (Ln = Y, Lu) were prepared by σ-bond metathesis of $[Ln(CH_2SiMe_3)_3(THF)_2]$ with the 2-furyl-functionalized tetramethylcyclopentadiene $(C_5Me_4H)SiMe_2(C_4H_3O\text{-}2)$ and isolated as colorless crystals. Single-crystal X-ray structure analysis of the lutetium complex confirmed the coordination of the furyl group and THF to give a molecule of trigonal bipyramidal geometry with the oxygen donor atoms in the apical positions. The lability of the oxygen donor atoms results in fluxional behavior. Reaction with triphenylborane in THF gave thermally robust mono(alkyl) cations $[Ln\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2(C_4H_3O\text{-}2)\}(CH_2SiMe_3)(THF)_n]^+$. Unexpectedly, the reaction of $[Ln(CH_2SiMe_3)_3(THF)_2]$ with the 5-methylfuryl-functionalized tetramethylcyclopentadiene $(C_5Me_4H)SiMe_2\{(C_4H_2MeO\text{-}5)\text{-}2\}$ gave yne-enolate complexes $[Ln\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2C{\equiv}CCH{=}CMeO)\}(CH_2SiMe_3)]_2$ under elimination of 2 equiv of $SiMe_4$. Single-crystal X-ray structure analysis of the yttrium complex revealed that a ring-opening of the 5-methylfuryl group had occurred.

Introduction

Organometallic complexes of the rare-earth metals are conventionally supported by bis(cyclopentadienyl) ligand frameworks.[1] The formal exchange of one cyclopentadienyl ligand by an X ligand (X = H, alkyl) results in the electronically more unsaturated and sterically more open mono(cyclopentadienyl) complexes $[Ln(C_5R_5)X_2(L)_x]$ (X = H, alkyl). Mono(cyclopentadienyl) alkyl and hydrido derivatives are still fairly rare species, partly due to the synthetic difficulty of their preparation.[2,3] Their pronounced sensitivity adds to the difficulty of handling this class of complexes, although the expected high electrophilicity makes them attractive. Owing to the even higher unsaturation, cationic half-sandwich alkyls of the type $[Ln(C_5R_5)R(L)_x]^+$ so far have only been reported in few instances,[4,5] while hydrido cations remain unknown to date. We have recently developed a straightforward synthetic methodology to prepare the linked amido-cyclopentadienyl complexes $[Ln(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NR)(CH_2SiMe_3)(THF)]$, where Ln = Y, Yb, Lu; R = ^{t}Bu, ^{t}Pe.[6,7] Yttrium complexes of the type $[Y(\eta^5\text{-}C_5Me_4SiMe_2X)(CH_2SiMe_3)_2(THF)_x]$, where X = Me, Ph, C_6F_5, o-C_6H_4OMe,[6a,8] $CH_2CH{=}CH_2$,[10b] became acces-

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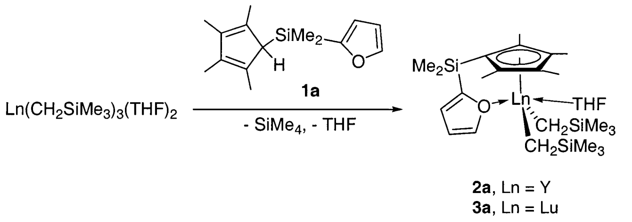
Scheme 1



sible also by this method, but their low melting points and extreme temperature, air, and moisture sensitivity precluded detailed exploration of their reactivity.[2] We describe here that a furyl function[9a] as an additional donor in the side chain of the cyclopentadienyl moiety[9b,c] results in more stable bis(alkyl) derivatives and that alkyl cations can be generated fairly straightforwardly.

Results and Discussion

When the 2-furyl-functionalized tetramethylcyclopentadiene $(C_5Me_4H)SiMe_2(C_4H_3O)$-2 (**1a**) was treated with $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Y, Lu),[10a] the bis(alkyl) complexes $[Ln\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2(C_4H_3O\text{-}2)\}(CH_2SiMe_3)_2(THF)]$ (Ln = Y, **2a**; Lu, **3a**) were formed in good yield (Scheme 1) and isolated as thermally somewhat unstable, colorless crystals (**3a** has a half-life of 5.5 h at 40 °C). The ^1H and ^{13}C NMR spectra indicate a C_{2v}-symmetry at room temperature. Thus, the ^1H NMR spectrum of the yttrium complex **2a** in C_6D_6 at room temperature shows only one signal at 0.55 ppm for the $SiMe_2$ and two signals at 1.91 and 2.15 ppm for the C_5Me_4 group. The methylene protons at the two equivalent CH_2SiMe_3 groups appear as a doublet at −0.86 ppm with $^2J_{YH} = 2.9$ Hz. These features are comparable to those of the complexes of the type $[Y\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)_nSiMe_2NCMe_3\}(CH_2SiMe_3)(THF)]$ ($n = 0, 1$)[6] or $[Y(\eta^5\text{-}C_5Me_4SiMe_2X)(CH_2SiMe_3)_2(THF)_x]$.[6a,8] Temperature-dependent ^1H NMR spectra of **2a** suggest a fluxionality that is caused by the presence of both a dissociatively labile THF and a labile interaction of the furyl oxygen donor. At −80 °C the methylene protons of the CH_2SiMe_3 groups are diastereotopic. Moreover, the resonance of the 5-furyl proton at −80 °C is recorded at 8.19 ppm, significantly low-field shifted from that in the free cyclopentadiene **1a** found at 7.42 ppm. These data are compatible with a trigonal bipyramidal structure of C_s-symmetry with both the THF and the furyl function coordinated at the metal center. The lutetium complex **3a** shows an analogous pattern. The ^1H NMR spectrum of **3a** is depicted at the bottom of Figure 1.

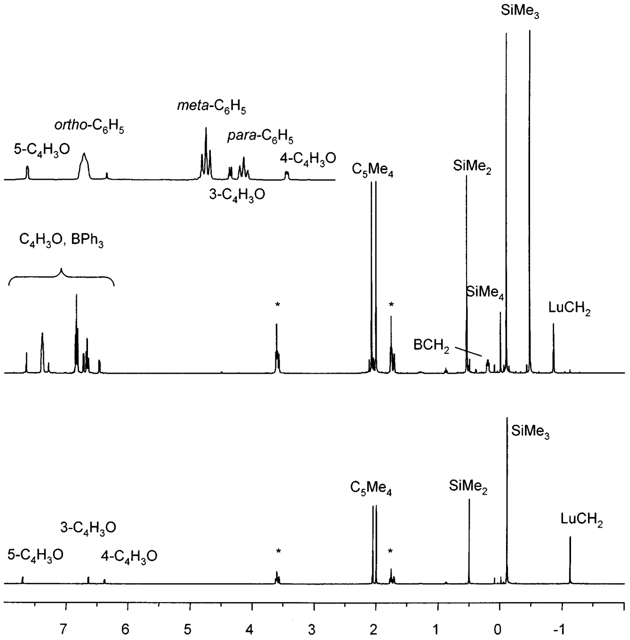


Figure 1. ^1H NMR spectra of the bis(alkyl) lutetium complex **3a** (bottom) and cationic mono(alkyl) complex **5** (top) in THF-d_8 at 25 °C. Signals denoted with (*) are due to THF and residual protons of THF-d_8.

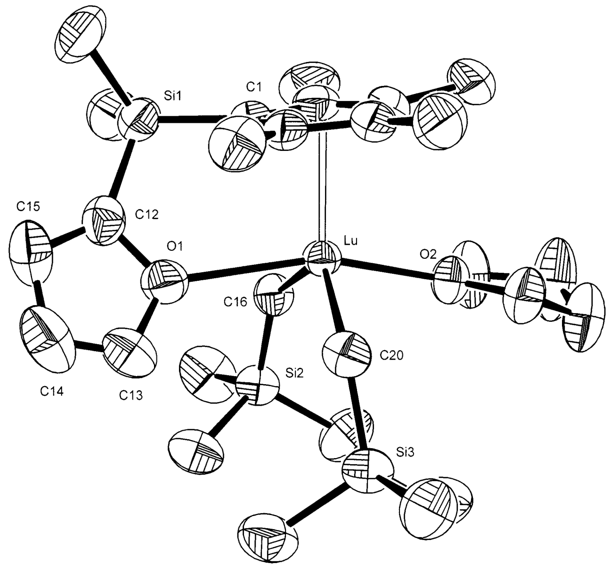


Figure 2. ORTEP diagram of the bis(alkyl) lutetium complex **3a**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Lu−Cp_{cent} 2.367(4), Lu−C16 2.373(4), Lu−C20 2.381(4), Lu−O1 2.659(3), Lu−O2 2.305(3), O1−Lu−O2 162.0(1), C16−Lu−C20 124.4(2).

The trigonal bipyramidal structure of the lutetium derivative **3a** was confirmed by a single-crystal X-ray structure analysis (Figure 2). The oxygen atoms are shown to adopt the axial positions with the angle at lutetium O1−Lu−O2 of 162.0(1)°. The angle at lutetium C16−Lu−C20 for the two alkyl ligands in the equatorial plane is 124.4(2)°. The lutetium−oxygen bond distance for the furyl group is 2.659(3) Å, whereas the lutetium−oxygen bond distance for the THF ligand is 2.305(3) Å. The large difference in the lutetium−oxygen bond lengths is partially a consequence of the stronger basicity of the THF ligand,[11] although the constraint of the chelating ligand system is mainly responsible for this effect.[9b] The lutetium−carbon bond lengths for the two trimethylsilylmethyl ligands of 2.373(4) and 2.381(4) Å are within the expected range.[12]

Reaction of the bis(alkyl) complexes **2a** and **3a** with triphenylborane as a mild Lewis acid in THF resulted

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(10) (a) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 126. (b) Evans, W. J.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 7711.

(11) (a) Evans, W. J.; Fujimoto, Cy H.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2002**, *21*, 1825. (b) Relative basicities based on hydrogen-bond affinity for THF and furan were given as $pK_{HB}(THF) = 1.28$, $pK_{HB}(furan) = -0.40$, see: Berthelot, M.; Besseau, F.; Laurence, C. *Eur. J. Org. Chem.* **1998**, 925.

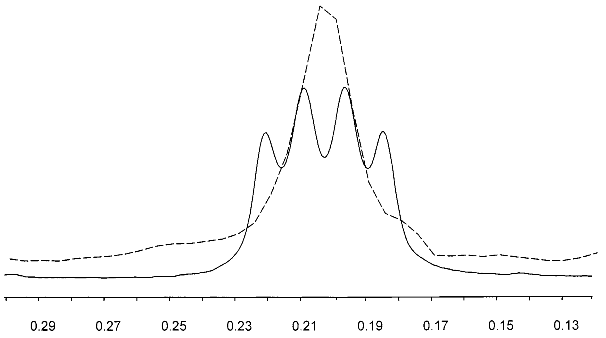
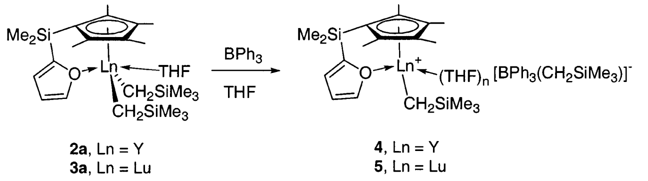


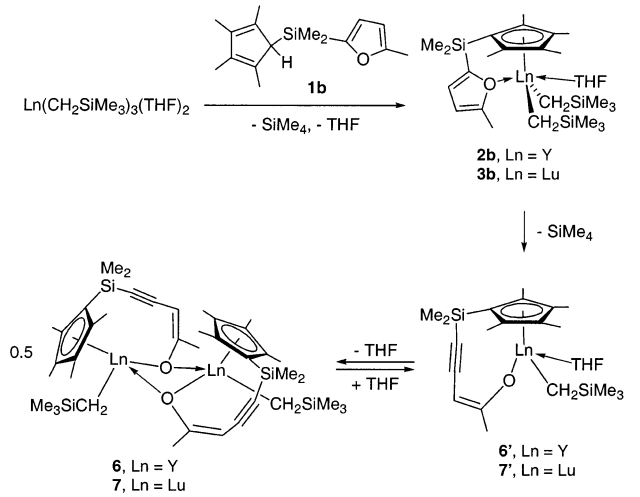
Figure 3. ^{1}H and ^{1}H{^{11}B} (dashed line) NMR spectrum of the anion $[\mathrm{BPh_3(CH_2SiMe_3)}]^-$ in the ion pair **5** for the $\mathrm{BCH_2}$ region in THF-d_8 at 25 °C.

Scheme 2



in the clean formation of the solvent-separated ion pair consisting of the mono(alkyl) cation $[\mathrm{Ln}\{\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2(C_4H_3O\text{-}2)}\}(\mathrm{CH_2SiMe_3})(\mathrm{THF})_x]^+$ (Ln = Y, **4**; Ln = Lu, **5**) and the anion $[\mathrm{BPh_3(CH_2SiMe_3)}]^-$ (Scheme 2). The NMR spectroscopic data in THF-d_8 indicate that the ion pairs formed are thermally robust. The anion, identical for both the yttrium and the lutetium derivative **4** and **5**, is characterized by a resonance at −10.3 ppm in the ^{11}B NMR spectrum and a 1:1:1:1 quartet at 0.20 ppm with $^2J_{\mathrm{BH}} = 4.7$ Hz in the ^{1}H NMR spectrum in THF-d_8. When the ^{1}H NMR spectrum was recorded under ^{11}B decoupling, the 1:1:1:1 quartet from the methylene protons of the anion collapsed to a singlet, as shown in Figure 3. The yttrium cation **4** shows signals for the alkyl group at −0.75 ppm with $^2J_{\mathrm{YH}} = 3.2$ Hz, one resonance at 0.53 ppm for the $\mathrm{SiMe_3}$ group, and two signals for the ring methyl groups at 2.02 and 2.04 ppm in the ^{1}H NMR spectrum. The methylene group of the lutetium cation **5** was recorded at −0.86 ppm. In the ^{13}C{^{1}H} NMR spectrum, the alkyl carbon of the cationic yttrium complex **4** is recorded as a doublet at 34.9 ppm with $^1J_{\mathrm{YC}} = 47.6$ Hz, whereas the corresponding signal for the bis(alkyl) **2a** is found at 32.1 ppm with $^1J_{\mathrm{YC}} = 41.2$ Hz. The lutetium analogue **5** gives rise to a singlet at 36.4 ppm. When the NMR spectroscopic data of **4** and **5** in THF-d_8 are compared with those of the lanthanide dialkyl cations with a crown ether ligand $[\mathrm{Ln(CH_2SiMe_3)_2(12\text{-}crown\text{-}4)(THF)}]^+[\mathrm{BPh_3(CH_2SiMe_3)}]^-$ (Ln = Lu, Y),[5e] the resonances of the methylene groups of **4** and **5** are shifted to lower field in the ^{1}H NMR spectrum (Ln = Y: −0.75 vs −0.86 ppm; Ln = Lu: −0.86 vs −1.12 ppm). In the ^{13}C NMR spectra a high-field shift is recorded (Ln = Y: 34.9 vs 39.8 ppm; Ln = Lu: 36.4 vs 39.5 ppm). The NMR spectroscopic features of the anion in **4** and **5** are essentially identical with those of the crown ether complexes, suggesting the presence of a noncoordinating anion.[13]

Scheme 3



When the reaction of the related 5-methylfuryl-substituted ligand **1b** with $[\mathrm{Y(CH_2SiMe_3)_3(THF)_2}]$ was monitored in cyclohexane-d_{12} at 10 °C, an unexpected reaction was discovered (Scheme 3). Within 30 min the formation of the bis(alkyl) complex $[\mathrm{Y}\{\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2(C_4H_2MeO\text{-}5)\text{-}2}\}(\mathrm{CH_2SiMe_3})_2(\mathrm{THF})]$ (**2b**), analogous to **2a**, was observed besides the new complex $[\mathrm{Y}\{\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2C{\equiv}CCH{=}CMeO)}\}(\mathrm{CH_2SiMe_3})(\mathrm{THF})]$ (**6′**) and unreacted starting materials. The diagnostic methylene protons of the alkyl group in **2b** appear as a doublet at −0.91 ppm with $^2J_{\mathrm{YH}} = 3.0$ Hz. Over a period of 2 h, the THF adduct of the yne-enolate **6′** became the main product at the expense of **2b**. The monomeric complex **6′** gradually converts into the dimer **6**, which could be isolated as colorless crystals only with difficulty from pentane. In agreement with the presence of a monomer−dimer equilibrium, the interconversion of the monomer **6′** into the dimer **6** was shown to be reversible: the monomer virtually formed exclusively when a mixture of **6** and **6′** (generated in situ from **1b** and $[\mathrm{Y(CH_2SiMe_3)_3(THF)_2}]$ in cyclohexane-d_{12} at 25 °C after 3 h) was treated with a 20-fold excess of THF. Attempts to isolate the THF adduct **6′** failed. By ^{1}H NMR spectroscopy in cyclohexane-d_{12}, the dissociation constant at 25 °C was estimated to be $K_{\mathrm{diss}} = 3.2 \pm 0.5$ L mol^{-1}. As for **6′**, the isolation of the analogous monomeric lutetium complex **7′** was not possible. Apparently, the monomer−dimer equilibrium along with the lower solubility of the dimer hampers the isolation of the monomeric THF adducts **6′** and **7′**.

The surprising structure of the dimeric yne-enolate **6** containing a ring-opened furyl ligand was revealed

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(12) (a) $[\mathrm{Lu}(\eta^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CH_2SiMe_3})\mathrm{THF}]$: Lu−C = 2.376(2) Å, see: Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194. (b) $[\mathrm{Lu}\{(\eta^5\mathrm{C_5Me_4})\mathrm{SiMe_2(C_5H_4)}\}\mathrm{CH(SiMe_3)_2}]$: Lu−C = 2.365(7) Å, see: Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558. (c) $[\mathrm{Lu}\{\eta^3\text{-}\mathrm{C_6H_3(CH_2NMe_2)_2\text{-}2,6(CH_2SiMe_3)}(\mu\text{-}\mathrm{Cl})\}]_2$: Lu−C = 2.39(3) Å, see: ref 3e.

(13) NMR spectroscopic data of the anion $[\mathrm{BPh_3(CH_2SiMe_3)}]^-$ in **4**: ^{1}H NMR (THF-d_8, 25 °C): δ 0.20 (q, $^2J_{\mathrm{BH}} = 4.7$ Hz, $\mathrm{BCH_2}$). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 167.9 (q, $^1J_{\mathrm{BC}} = 48.7$ Hz, 1-Ph). ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −10.3. **5**: ^{1}H NMR (THF-d_8, 25 °C): δ 0.20 (q, $^2J_{\mathrm{BH}} = 4.8$ Hz, $\mathrm{BCH_2}$). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 167.6 (q, $^1J_{\mathrm{BC}} = 48.6$ Hz, 1-Ph). ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −10.3. The anion was shown to be noncoordinating in the crown ether complexes $[\mathrm{Ln(CH_2SiMe_3)_2(12\text{-}crown\text{-}4)(THF)}]^+[\mathrm{BPh_3(CH_2SiMe_3)}]^-$, see ref 5e: Ln = Y: ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ 0.18 (br q, $\mathrm{BCH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ 167.5 (q, $^1J_{\mathrm{BC}} = 48.3$ Hz, 1-Ph). ^{11}B{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ −10.4. Ln = Lu: ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ 0.17 (q, $^2J_{\mathrm{BH}} = 4.7$ Hz, $\mathrm{BCH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ 167.6 (q, $^1J_{\mathrm{BC}} = 48.3$ Hz, 1-Ph). ^{11}B{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ −10.4.

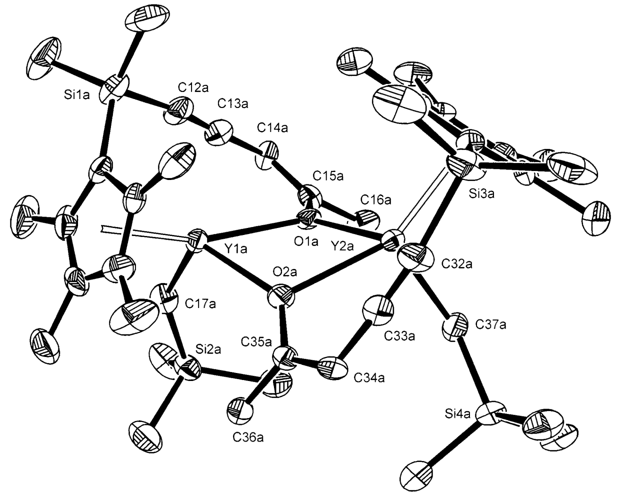
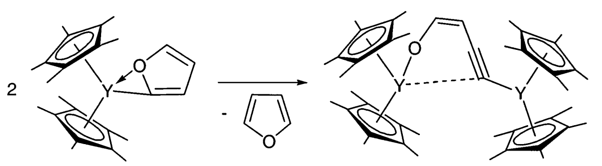


Figure 4. ORTEP diagram of the yttrium complex **6**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. One of the four independent molecules is shown. Selected bond lengths (Å) and angles (deg): Y1a−Cp_{cent}1a 2.393(5), Y1a−C17a 2.381(6), Y2a−Cp_{cent}2a 2.397(5), Y2a−C37a 2.378(5), Y1a−O1a 2.383(3), Y1a−O2a 2.272(3), Y2a−O1a 2.254(3), Y2a−O2a 2.364(3), C12a−C13a 1.226(7), C13a−C14a 1.405(7), C14a−C15a 1.333(6), C32a−C33a 1.197(6), C33a−C34a 1.423(7), C34a−C35a 1.323(6), Si1a−C12a−C13a 172.1(5), C12a−C13a−C14a 176.7(6), C13a−C14a−C15a 119.0(5), C14a−C15a−O1a 119.9(5), C14a−C15a−C16a 123.8(5), Si3a−C32a−C33a 170.2(4), C32a−C33a−C34a 176.5(5), C33a−C34a−C35a 121.0(5), C34a−C35a−O2a 120.3(5), C34a−C35a−C36a 124.3(5), Cp_{cent}1a−Y1a−Y2a−Cp_{cent}2a 84.

by an X-ray crystal structure analysis. The unit cell of **6** is shown to consist of four independent dimeric molecules (Figure 4). All further discussions of structural details refer to one of the four independent molecules. With the concomitant loss of one trimethylsilylmethyl group as tetramethylsilane from the metal center, the 5-methylfuryl group has been transformed into an yne-enolate group. The dimerization occurs through the enolate oxygen atom. Yttrium−carbon bond lengths of 2.381(6) and 2.378(5) Å for the alkyl groups are in the expected range.[6b] The cyclopentadienyl moieties are disposed in a fashion that is intermediate between the *cis* and *trans* arrangement. Dihedral angles Cp_{cent}1−Y1−Y2−Cp_{cent}2 are 84°. The slightly puckered Y_2O_2 core is somewhat distorted, featuring two short (2.272(3) and 2.254(3) Å) and two long (2.383(3) and 2.364(3) Å) yttrium−oxygen bonds. They are longer than the Y−O(enolate) distance of 2.179(2) Å in the enolate complex $[Y(\eta^5\text{-}C_5Me_5)_2(\mu\text{-OCMe}{=}\text{CHC(O)OEt})]_2$.[14a] The angles at the carbon atoms C12, C13 and C32, C33 range from 170.2(4)° to 176.7(6)°, consistent with sp-hybridization of these acetylenic carbon atoms. The corresponding bond distances C12−C13 of 1.226(7) Å and C32−C33 of 1.197(6) Å are also in agreement with the presence of triple bonds. The bond lengths C14−C15 (1.333(6) Å) as well as C34−C35 (1.323(6) Å) along with the angles at the carbon atoms C14, C15 and C34, C35 (119.0(5)−124.3(5)°) are indicative of sp^2-hybridization. The single bonds next to the triple and the double bonds C13−C14 (1.405(7) Å) and C33−C34 (1.423(7) Å) show distances within the range for those in eneynes.[14b]

Scheme 4



In agreement with the approximate C_2-symmetry in the solid state, the yttrium complex **6** appears to be a C_2-symmetric dimer in solution over a temperature range from +25 to −80 °C. At 25 °C in cyclohexane-d_{12}, the diastereotopic methylene protons of the alkyl group attached to yttrium give rise to a AB pattern at −0.86 and −0.73 ppm with $^2J_{HH} = 11.2$ Hz and $^2J_{YH} = 3.9$ Hz in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum shows a doublet at 36.9 ppm with $^1J_{YC} = 50.1$ Hz for the methylene group. In comparison with the dimeric complex **6**, the monomer **6′** exhibits higher symmetry. Due to labile THF coordination, on the NMR time scale a C_s-symmetric molecule is present. In contrast to the AB pattern observed for the dimer **6**, the methylene protons attached to yttrium give rise to a doublet at −1.20 ppm with $^2J_{YH} = 3.5$ Hz for **6′**. The resonance of the methyl group at the double bond is significantly high-field shifted in the monomer **6′** (1.67 vs 1.94 ppm). The NMR spectroscopic features of the lutetium homologue **7** in cyclohexane-d_{12} are similar to those of **6**. The observed C_2-symmetry as well as the presence of a THF-free complex is in agreement with the dimeric structure of **7**. The diagnostic methylene protons at the lutetium center give rise to AB doublets at −0.80 and −0.67 ppm with $^2J_{HH} = 11.3$ Hz in the ^{1}H NMR spectrum.

We rationalize the ring-opening process of **2b** to give **6** according to reactions proposed in Scheme 3. A crucial step is the deprotonation in the 3-position of the furyl ring, most probably facilitated by the chelate effect. There are precedents for the formation of yne-enols from furan; for example, the reaction of 2-trimethylsilylmethylfuran with *n*-butyllithium was reported to form lithium yne-enolate under ring-opening.[15] Furthermore, the bis(pentamethylcyclopentadienyl) 2-furyl yttrium complex $[Y(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}C_4H_3O)]$ was transformed by thermolysis into the crystallographically characterized dinuclear ynyl-enolate complex $[\{Y(\eta^5\text{-}C_5Me_5)_2\}_2(\mu\text{-OCH}{=}\text{CHC}{\equiv}\text{C})]$ (Scheme 4).[16] The bridging but-1-ene-3-yn-4-yl-1-olato ligand of this compound shows structural features related to those of the side chain in complex **6**. Although the ring-opening process of the bis(alkyl) complexes **2b** and **3b** to give **6** and **7** can be partially ascribed to the high oxophilicity of the rare-earth metal center, we are unable to explain at this point why the introduction of the methyl group in the 2-furyl side

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chain results in such a dramatic difference in the reactivity. We note also a similarity of this ring-opening induced by tetramethylsilane elimination to a process recently reported by Evans et al.[10b] for the allyl-functionalized analogue of **2a** and **3a**.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous trichlorides of lutetium and yttrium (ALFA or Strem) were used as received. $SiMe_2Cl_2$ was refluxed over copper turnings and distilled before use. Furan was dried over sodium and distilled before use. All other chemicals were commercially available and used after appropriate purification. $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Y, Lu) were prepared according to ref 10a. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H, 400.1 MHz, ^{13}C, 100.6 MHz; ^{11}B, 128.4 MHz). Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{11}B NMR spectra were referenced externally to a 1 M solution of $NaBH_4$ in D_2O. Elemental analyses were performed by the Microanalytical Laboratory of this department. In many cases the results were not satisfactory and the best values from repeated runs were given. Moreover the results were inconsistent from run to run and therefore not reproducible. We ascribe this difficulty observed also by other workers[17a,b] to the extreme sensitivity of the material. Metal analysis was performed by complexometric titration.[17c] The sample (20−30 mg) was dissolved in THF (2 mL) and titrated with a 0.005 M solution of EDTA using xylenol orange as indicator and 1 M ammonium acetate as buffer solution (20 mL).

$(C_5Me_4H)SiMe_2(C_4H_3O\text{-}2)$ (1a). To a solution of $C_5Me_4H_2$ (19.9 g, 163 mmol) in THF (250 mL) was added *n*-butyllithium (163 mmol of a 2.5 M hexane solution) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for a further 2 h. At −78 °C $SiMe_2Cl_2$ (21.0 g, 163 mmol) was added and the mixture was stirred overnight. After removing the solvent in vacuo, pentane (40 mL) was added to the residue. LiCl was filtered off, and all volatiles were removed in vacuo. At −78 °C, crude $(C_5Me_4H)SiMe_2Cl$ was added to 2-furyllithium, prepared by the reaction of furan (11.2 g, 163 mmol) with *n*-butyllithium (163 mmol of a 2.5 M hexane solution) in THF (200 mL) at 0 °C for 2 h, and the reaction mixture was stirred overnight. After removing the solvent in vacuo, pentane (40 mL) was added to the residue. LiCl was filtered off and the solvent was removed in vacuo, followed by distillation (70 °C, 10^{-2} mbar) to give a pale yellow oil (32.0 g, 80%). ^{1}H NMR (C_6D_6, 25 °C): δ 0.15 (s, 2 × 3 H, $SiCH_3$), 1.78 (s, 4 × 3 H, C_5CH_3), 3.07 (br s, 1 H, C_5Me_4H), 6.18 (dd, $^{3}J_{HH}$ = 3.2 Hz, 1.2 Hz, 1 H, 4-C_4H_3O), 6.49 (d, $^{3}J_{HH}$ = 3.2 Hz, 1 H, 3-C_4H_3O), 7.42 (d, $^{3}J_{HH}$ = 1.2 Hz, 1 H, 5-C_4H_3O). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ −4.7 ($SiCH_3$), 11.1, 13.7 (C_5CH_3), 54.2 (C_5Me_4 attached to $SiMe_2$), 109.5 (3-C_4H_3O), 120.2 (4-C_4H_3O), 132.6, 136.1 (C_5Me_4), 146.3 (2-C_4H_3O), 158.8 (5-C_4H_3O). EI MS *m*/*z* (%): 246 (27, M^+), 125 (100, $C_4HSiMe_2^+$). Anal. Calcd for $C_{15}H_{22}SiO$: C, 73.11; H, 9.00. Found: C, 73.32; H, 9.77.

$(C_5Me_4H)SiMe_2\{(C_4H_2MeO\text{-}5)\text{-}2\}$ (1b). Starting from $C_5Me_4H_2$ (16.7 g, 137 mmol), $SiMe_2Cl_2$ (17.6 g, 137 mmol), and 2-methylfuran (11.2 g, 137 mmol), this compound was prepared in a manner analogous to that described for the synthesis of **1a** and isolated as a yellow oil, yield 25.0 g (70%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 0.14 (s, 2 × 3 H, $SiCH_3$), 1.78, 1.83 (s, 4 × 3 H, C_5CH_3), 2.37 (s, 3 H, C_4CH_3), 3.12 (br s, 1 H, C_5Me_4H), 5.98 (d, $^{3}J_{HH}$ = 2.9 Hz, 1 H, 4-C_4H_2O), 6.49 (d, $^{3}J_{HH}$ = 2.9 Hz, 1 H, 3-C_4H_2O). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): −4.7 ($SiCH_3$), 11.1 ($C_5\mathit{C}H_3$), 13.7, 13.8 ($C_5\mathit{C}H_3$, $C_4\mathit{C}H_3$), 54.4 (C_5Me_4 attached to $SiMe_2$), 105.7 (3-C_4H_2O), 121.4 (4-C_4H_2O), 132.7, 135.9 (C_5Me_4), 156.3 (2-C_4H_2O), 156.9 (5-C_4H_2O). EI MS *m*/*z* (%): 260 (23, M^+), 178 (20, $C_5Me_4HSiMe_2^+$), 139 (100, $C_4H_2MeOSiMe_2^+$). Anal. Calcd for $C_{16}H_{24}SiO$: C, 73.79; H, 9.28. Found: C, 73.46; H, 9.84.

$[Y\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2(C_4H_3O\text{-}2)\}(CH_2SiMe_3)_2(THF)]$ (2a). $YCl_3(THF)_{3.5}$ (2.69 g, 6.0 mmol) was slurried in hexane (40 mL), and a hexane (40 mL) solution of $LiCH_2SiMe_3$ (1.73 g, 18.4 mmol) was added at −78 °C. The suspension was stirred for 3 h at 0 °C, and after filtration of LiCl, **1a** (1.40 g, 5.7 mmol) was added to the colorless solution. After it was stirred for 3 h at 0 °C and decanted from an oily byproduct, the volume was reduced in vacuo to 25 mL. After 5 days of cooling at −70 °C, colorless crystals (1.76 g, 51%) were obtained by decanting the mother liquor at −78 °C and drying in vacuo. ^{1}H NMR (C_6D_6, 25 °C): δ −0.86 (d, $^{2}J_{YH}$ = 2.9 Hz, 2 × 2 H, YCH_2), 0.25 (s, 2 × 9 H, $CH_2SiC\mathit{H}_3$), 0.55 (s, 2 × 3 H, $SiCH_3$), 1.30 (br m, 4 H, β-CH_2, THF), 1.91, 2.15 (s, 4 × 3 H, C_5CH_3), 3.67 (br m, 4 H, α-CH_2, THF), 6.16 (dd, $^{3}J_{HH}$ = 2.9 Hz, 1.5 Hz, 1 H, 4-C_4H_3O), 6.47 (d, $^{3}J_{HH}$ = 2.9 Hz, 1 H, 3-C_4H_3O), 7.98 (d, $^{3}J_{HH}$ = 1.5 Hz, 1 H, 5-C_4H_3O). ^{1}H NMR (toluene-d_8, 25 °C): δ −0.92 (d, $^{2}J_{YH}$ = 2.9 Hz, 2 × 2 H, YCH_2), 0.18 (s, 2 × 9 H, $CH_2SiC\mathit{H}_3$), 0.54 (s, 2 × 3 H, $SiCH_3$), 1.42 (br m, 4 H, β-CH_2, THF), 1.91, 2.11 (s, 4 × 3 H, C_5CH_3), 3.69 (br m, 4 H, α-CH_2, THF), 6.17 (dd, $^{3}J_{HH}$ = 3.4 Hz, 2.9 Hz, 1 H, 4-C_4H_3O), 6.47 (d, $^{3}J_{HH}$ = 3.4 Hz, 1 H, 3-C_4H_3O), 7.92 (br, 1 H, 5-C_4H_3O). ^{13}C{^{1}H} NMR (toluene-d_8, 25 °C): δ 1.2 ($SiCH_3$), 4.8 ($CH_2Si\mathit{C}H_3$), 11.5, 14.1 ($C_5\mathit{C}H_3$), 25.5 (β-CH_2, THF), 32.1 (d, $^{1}J_{YC}$ = 41.2 Hz, YCH_2), 69.6 (α-CH_2, THF), 108.3 (C_5Me_4 attached to $SiMe_2$), 110.7, 120.4 (C_4H_3O), 123.2, 126.6 (C_5Me_4), 147.5, 163.7 (C_4H_3O). ^{1}H NMR (toluene-d_8, −80° C): δ −1.08, −0.73 (br m, 2 × 2 H, YCH_2), 0.34 (s, 2 × 9 H, $CH_2SiC\mathit{H}_3$), 0.54 (s, 2 × 3 H, $SiCH_3$), 1.06 (br m, 4 H, β-CH_2, THF), 1.78, 2.14 (s, 4 × 3 H, C_5CH_3), 3.50 (br m, 4 H, α-CH_2, THF), 6.00 (br, 1 H, 4-C_4H_3O), 6.24 (br, 1 H, 3-C_4H_3O), 8.19 (br, 1 H, 5-C_4H_3O). ^{13}C{^{1}H} NMR (toluene-d_8, −80 °C): δ 0.9 ($SiCH_3$), 4.9 ($CH_2Si\mathit{C}H_3$), 11.2, 14.0 ($C_5\mathit{C}H_3$), 25.2 (β-CH_2, THF), 29.6 (d, $^{1}J_{YC}$ = 42.3 Hz, YCH_2), 70.9 (br, α-CH_2, THF), 106.9 (C_4H_3O), 122.3, 125.8 (C_5Me_4), 164.3 (5-C_4H_3O); 3 signals for the aromatic rings were not detected. Anal. Calcd for $C_{27}H_{51}Si_3O_2Y$: C, 55.83; H, 8.85; Y, 15.32. Found: C, 55.70; H, 9.01; Y, 15.11.

$[Lu\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2(C_4H_3O\text{-}2)\}(CH_2SiMe_3)_2(THF)]$ (3a). To a solution of $[Lu(CH_2SiMe_3)_3(THF)_2]$ (1.50 g, 2.60 mmol) in hexane (40 mL) was added **1a** (641 g, 2.60 mmol) at 0 °C. After the solution was stirred for 4 h at this temperature, a small amount of a colorless solid byproduct was filtered off and the volume was reduced in vacuo to 20 mL. After 10 days at −70 °C, colorless crystals (1.15 g, 66%) were obtained by decanting the solvent at −78 °C and drying in vacuo. ^{1}H NMR (C_6D_6, 25 °C): δ −0.84 (s, 2 × 2 H, $LuCH_2$), 0.28 (s, 2 × 9 H, $CH_2SiC\mathit{H}_3$), 0.59 (s, 2 × 3 H, $SiCH_3$), 1.21 (br m, 4 H, β-CH_2, THF), 1.97, 2.16 (s, 4 × 3 H, C_5CH_3), 3.64 (br m, 4 H, α-CH_2, THF), 6.15 (dd, $^{3}J_{HH}$ = 3.4 Hz, 2.5 Hz, 1 H, 4-C_4H_3O), 6.54 (d, $^{3}J_{HH}$ = 3.4 Hz, 1 H, 3-C_4H_3O), 7.58 (d, $^{3}J_{HH}$ = 2.5 Hz, 1 H, 5-C_4H_3O). ^{1}H NMR (toluene-d_8, 25 °C): δ −0.94 (s, 2 × 2 H, $LuCH_2$), 0.19 (s, 2 × 9 H, $CH_2SiC\mathit{H}_3$), 0.56 (s, 2 × 3 H, $SiCH_3$), 1.35 (br m, 4 H, β-CH_2, THF), 1.94, 2.11 (s, 4 × 3 H, C_5CH_3), 3.69 (br, 4 H, α-CH_2, THF), 6.15 (dd, $^{3}J_{HH}$ = 2.9 Hz, 1.5 Hz, 1 H, 4-C_4H_3O), 6.52 (d, $^{3}J_{HH}$ = 2.9 Hz, 1 H, 3-C_4H_3O), 7.53 (d, $^{3}J_{HH}$ = 1.5 Hz, 1 H, 5-C_4H_3O). ^{13}C{^{1}H} NMR (toluene-d_8, 25 °C): δ 0.5 ($SiCH_3$), 4.2 ($CH_2Si\mathit{C}H_3$), 11.0, 13.6 ($C_5\mathit{C}H_3$), 24.5 (β-CH_2, THF), 38.3 ($LuCH_2$), 70.3 (α-CH_2, THF), 109.1 (C_5Me_4 attached to $SiMe_2$), 109.7, 120.0 (C_4H_3O), 122.6, 125.8 (C_5Me_4), 145.9, 161.5 (C_4H_3O). ^{1}H NMR (toluene-d_8, −80 °C): δ −1.14, −0.89 (br, 2 × 2 H, $LuCH_2$), 0.33 (s, 2 × 9 H, $CH_2SiC\mathit{H}_3$), 0.54 (s, 2 × 3 H,

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SiCH$_3$), 1.05 (br m, 4 H, β-CH$_2$, THF), 1.78, 2.12 (s, 4 × 3 H, C$_5$CH$_3$), 3.47 (br m, 4 H, α-CH$_2$, THF), 6.01 (br, 1 H, 4-C$_4$H$_3$O), 6.27 (br, 1 H, 3-C$_4$H$_3$O), 8.07 (br, 1 H, 5-C$_4$H$_3$O). ^{13}C{^{1}H} NMR (toluene-d_8, −80 °C): δ 0.4, (SiCH$_3$), 4.2 (CH$_2$Si*C*H$_3$), 11.0, 13.6 (C$_5$*C*H$_3$), 24.5 (β-CH$_2$, THF), 38.3 (LuCH$_2$), 70.3 (α-CH$_2$, THF), 109.1 (C$_5$Me$_4$ attached to SiMe$_2$), 109.7, 120.0 (C$_4$H$_3$O), 122.6, 125.8 (C$_5$Me$_4$), 145.9, 161.5 (C$_4$H$_3$O). Anal. Calcd for C$_{27}$H$_{51}$Si$_3$O$_2$Lu: C, 48.63; H, 7.71; Lu, 26.24. Found: C, 45.84; H, 7.14; Lu, 25.53.

[Y{η^5:η^1-C$_5$Me$_4$SiMe$_2$(C$_4$H$_3$O-2)}(CH$_2$SiMe$_3$)(THF)$_x$]$^+$[BPh$_3$(CH$_2$SiMe$_3$)]$^-$ (4). An NMR tube was charged with a solution of **2a** (44 mg, 75 μmol) and BPh$_3$ (18 mg, 75 μmol) in THF-d_8 (0.5 mL), and spectra were recorded after 2.5 h at 25 °C. ^{1}H NMR (THF-d_8, 25 °C): δ −0.75 (d, $^2J_{YH}$ = 3.2 Hz, 2 H, YCH$_2$), −0.48 (s, 9 H, BCH$_2$SiC*H*$_3$), −0.08 (s, 9 H, YCH$_2$SiC*H*$_3$), 0.20 (q, $^2J_{BH}$ = 4.7 Hz, 2 H, BCH$_2$), 0.53 (s, 2 × 3 H, SiCH$_3$), 2.02, 2.04 (s, 4 × 3 H, C$_5$CH$_3$), 6.47 (br, 1 H, 4-C$_4$H$_3$O), 6.66 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, 4-Ph), 6.73 (d, $^3J_{HH}$ = 3.2 Hz, 1 H, 3-C$_4$H$_3$O), 6.83 (t, $^3J_{HH}$ = 7.4 Hz, 3 × 2 H, 3-Ph), 7.38 (br m, 3 × 2 H, 2-Ph), 7.66 (br, 1 H, 5-C$_4$H$_3$O). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 1.0 (SiCH$_3$), 2.8 (BCH$_2$SiCH$_3$), 4.5 (YCH$_2$Si*C*H$_3$), 12.0, 14.3 (C$_5$*C*H$_3$), 34.9 (d, YCH$_2$, $^1J_{YC}$ = 47.6 Hz), 111.4 (C$_4$H$_3$O attached to SiMe$_2$), 112.7 (C$_5$Me$_4$ attached to SiMe$_2$), 121.4 (4-Ph), 122.1 (C$_4$H$_3$O), 125.6 (3-Ph), 126.3, 130.3 (C$_5$Me$_4$), 135.7 (2-Ph), 147.2, 162.1 (C$_4$H$_3$O), 167.9 (q, $^1J_{BC}$ = 48.7 Hz, 1-Ph). ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −10.3.

[Lu{η^5:η^1-C$_5$Me$_4$SiMe$_2$(C$_4$H$_3$O)-2}(CH$_2$SiMe$_3$)(THF)$_x$]$^+$[BPh$_3$(CH$_2$SiMe$_3$)]$^-$ (5). An NMR tube charged with a solution of **3a** (50 mg, 75 μmol) and BPh$_3$ (18 mg, 75 μmol) in THF-d_8 (0.5 mL) was kept at 40 °C for 2 h and at 25 °C for 7 days. The signals of the starting material had completely disappeared and a set of signals corresponding to **5** emerged. No signals due to byproducts or decomposition products were detected. ^{1}H NMR (THF-d_8, 25 °C): δ −0.86 (s, 2 H, LuCH$_2$), −0.47 (s, 9 H, BCH$_2$SiC*H*$_3$), −0.10 (s, 9 H, LuCH$_2$SiC*H*$_3$), 0.20 (q, $^2J_{BH}$ = 4.8 Hz, 2 H, BCH$_2$), 0.54 (s, 2 × 3 H, SiCH$_3$), 2.01, 2.08 (s, 4 × 3 H, C$_5$CH$_3$), 6.47 (dd, $^3J_{HH}$ = 1.6 Hz, 3.5 Hz, 1 H, 4-C$_4$H$_3$O), 6.66 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, 4-Ph), 6.72 (d, $^3J_{HH}$ = 3.5 Hz, 1 H, 3-C$_4$H$_3$O), 6.83 (t, $^3J_{HH}$ = 7.4 Hz, 3 × 2 H, 3-Ph), 7.39 (br m, 3 × 2 H, 2-Ph), 7.65 (d, $^3J_{HH}$ = 1.6 Hz, 1 H, 5-C$_4$H$_3$O). ^{13}C{^{1}H} NMR (THF-d_8, 25 °C): δ 0.8 (SiCH$_3$), 2.8 (BCH$_2$Si*C*H$_3$), 4.5 (LuCH$_2$Si*C*H$_3$), 11.8, 14.3 (C$_5$*C*H$_3$), 36.4 (LuCH$_2$), 111.4 (C$_4$H$_3$O attached to SiMe$_2$), 113.0 (C$_5$Me$_4$ attached to SiMe$_2$), 121.4 (4-Ph), 122.2 (C$_4$H$_3$O), 125.6 (3-Ph), 125.7, 129.7 (C$_5$Me$_4$), 135.7 (2-Ph), 147.2, 162.0 (C$_4$H$_3$O), 167.6 (q, $^1J_{BC}$ = 48.6 Hz, 1-Ph). The signal of the BCH$_2$ group is obscured by one C$_5$Me$_4$ signal. ^{11}B{^{1}H} NMR (THF-d_8, 25 °C): δ −10.3.

Reaction of 1b with [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$]. In an NMR tube, [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (25 mg, 51 μmol) was dissolved in cyclohexane-d_{12} (0.5 mL). The solution was cooled to 10 °C and treated with **1b** (13 μL, 51 μmol) via syringe. At 10 °C, ^{1}H NMR spectra were recorded every 5 min over a period of 2 h. Concentration of the yttrium compounds was determined by the integrals of the well-separated YCH$_2$ signals. The integral of the solvent signal was used as internal standard to calibrate the YCH$_2$ integrals. After 25 min, the following yttrium complexes were found besides **1b**: [Y{η^5:η^1-C$_5$Me$_4$SiMe$_2${(C$_4$H$_2$-MeO-5)-2}(CH$_2$SiMe$_3$)$_2$(THF)] (**2b**) (51%), [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (36%), [Y{η^5:η^1-C$_5$Me$_4$SiMe$_2$C≡CCH=CMeO}(CH$_2$SiMe$_3$)(THF)] (**6′**) (13%), [Y{η^5:η^1-C$_5$Me$_4$SiMe$_2$C≡CCH=CMeO}(CH$_2$SiMe$_3$)]$_2$ (**6**) (0%). **2b**: ^{1}H NMR (cyclohexane-d_{12}, 10 °C): δ −0.91 (d, $^2J_{YH}$ = 3.0 Hz, 2 × 2 H, YCH$_2$), 0.46 (s, 2 × 3 H, SiCH$_3$), 2.03, 2.09 (s, 4 × 3 H, C$_5$CH$_3$), 2.28 (s, 3 H, C$_4$H$_2$CH$_3$), 5.87 (m, 1 H, 4-C$_4$H$_2$O), 6.46 (d, $^3J_{HH}$ =3.1 Hz, 1 H, 3-C$_4$H$_2$O). Signals of CH$_2$-SiC*H*$_3$ groups were obscured by signals of [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$]. **6′**: ^{1}H NMR (cyclohexane-d_{12}, 10 °C): δ −1.20 (d, $^2J_{YH}$ = 3.5 Hz, 2 H, YCH$_2$), −0.11 (s, 9 H, CH$_2$SiC*H*$_3$), 0.41 (s, 2 × 3 H, SiCH$_3$), 1.67 (s, 3 H, OCCH$_3$), 1.98 (s, 2 × 3 H, C$_5$CH$_3$), 2.01 (s, 2 × 3 H, C$_5$CH$_3$), 4.19 (s, 1 H, OC=CH). One set of THF signals is detected as broad multiplets at δ 1.86 and 3.88. After 115 min, the following product distribution was observed: **2b** (30%), [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (16%), **6′** (45%), **6** (9%). The spectroscopic data indicate quantitative formation of tetramethylsilane during the formation of **2b**, **6**, and **6′**.

Table 1. Experimental Data for the Crystal Structure Determinations of the Complexes 3a and 6

	3a	6
	Crystal Data	
formula	C$_{27}$H$_{51}$LuO$_2$Si$_3$	C$_{40}$H$_{66}$O$_2$Si$_4$Y$_2$
fw	666.92	869.12
cryst color	colorless	colorless
cryst size, mm	0.59× 0.42× 0.38	0.18 × 0.13 × 0.12
cryst syst	monoclinic	triclinic
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)
a, Å	9.4121(7)	17.948(1)
b, Å	13.583(1)	18.441(1)
c, Å	13.1981(9)	28.336(2)
α, deg	90	95.160(1)
β, deg	100.983(1)	100.853(1)
γ, deg	90	97.052(1)
V, Å^3	1656.4(2)	9079(1)
Z	2	8
ρ_{calcd}, g cm^{-3}	1.337	1.272
μ, mm^{-1}	3.108	2.679
F(000)	684	3647
	Data Collection	
2$\theta_{\max}$, deg	57	57
index ranges	h, −12 to 12; k, −18 to 18; l, −17 to 17	h, −23 to 23; k, −24 to 24; l, −37 to 36
no. of reflns measd	15 558	84 240
no. of indep reflns	7895 [R_{int} = 0.0169]	43 927 [R_{int} = 0.1011]
no. of obsd reflns [$I > 2\sigma(I)$]	7318	17 080
no. of params	338	1905
GOF	0.997	0.747
final R indices R_1, wR_2 (obsd data)	0.0244/0.0598	0.050/0.0699
final R indices R_1, wR_2 (all data)	0.0272/0.0613	0.1766/0.0909
largest e-max, e-min, e·Å^{-3}	1.013/−0.647	0.624/−0.743

[Y{η^5:η^1-C$_5$Me$_4$SiMe$_2$C≡CCH=CMeO)}(CH$_2$SiMe$_3$)]$_2$ (6). To a solution of [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (1090 mg, 2.2 mmol) in pentane (40 mL) was added **1b** (590 mg, 2.3 mmol) at 0 °C. After stirring for 3 h at this temperature, the clear, pale yellow solution was decanted from an oily residue and the volume of the solution reduced to half in vacuo. After cooling at −30 °C for 2 weeks, colorless crystals (400 mg, 35%) were obtained. ^{1}H NMR (cyclohexane-d_{12}, 25 °C): δ −0.86, −0.73 (dd, $^2J_{HH}$ = 11.2 Hz, $^2J_{YH}$ = 3.9 Hz, 2 × 2 H, YCH$_2$), −0.12 (s, 2 × 9 H, CH$_2$SiC*H*$_3$), 0.53, 0.61 (s, 4 × 3 H, SiCH$_3$), 1.91 (s, 2 × 3 H, C$_5$CH$_3$), 1.94 (s, 2 × 3 H, OCCH$_3$), 2.01, 2.12, 2.18 (s, 6 × 3 H, C$_5$CH$_3$), 4.63 (s, 2 × 1 H, OC=CH). ^{13}C{^{1}H} NMR (cyclohexane-d_{12}, 25 °C): δ 1.3, 1.8 (SiCH$_3$), 4.3 (CH$_2$Si*C*H$_3$), 11.4, 12.4, 14.6, 15.1 (C$_5$*C*H$_3$), 27.0 (OC*C*H$_3$), 36.9 (d, $^1J_{YC}$ = 50.1 Hz, YCH$_2$), 83.2 (OC=*C*), 98.7 (Si*C*≡C), 102.2 (SiC≡*C*), 117.4, 121.7, 125.7, 127.2, 127.5 (C$_5$Me$_4$), 173.3 (O*C*=C). A variable-temperature study (25 to −80 °C) in toluene-d_8 revealed no significant temperature dependence of the chemical shifts. Anal. Calcd for C$_{38}$H$_{66}$Si$_4$O$_2$Y$_2$: C, 54.01; H, 7.87. Found: C, 54.96; H, 7.81.

[Lu{η^5:η^1-C$_5$Me$_4$SiMe$_2$C≡CCH=CMeO)}(CH$_2$SiMe$_3$)]$_2$ (7). Anhydrous LuCl$_3$ (1688 mg, 6.0 mmol) was suspended in THF (30 mL) and stirred for 12 h at 40 °C. The solvent was removed in vacuo at 25 °C, and the residue was slurried in pentane (40 mL). At −78 °C, LiCH$_2$SiMe$_3$ (1715 mg, 18.0 mmol) in pentane (40 mL) was added and the suspension was stirred for 4 h at 0 °C. LiCl was filtered off at this temperature. **1b** (1560 mg, 6.0 mmol) was added to the filtrate, and the mixture was stirred for 8 h at 25 °C. After decanting from an oily residue, a clear pale yellow solution was obtained. The solvent was removed in vacuo, and the yellow oil was layered with pentane (5 mL). After standing for 10 days at 5 °C, colorless crystals precipitated (325 mg); yield: 725 mg in 2 crops (24%). ^{1}H NMR (cyclohexane-d_{12}, 25 °C): δ −0.80, −0.67 (d, $^2J_{HH}$ = 11.3 Hz, 2 × 2 H, LuCH_2), 0.27 (s, 2 × 9 H, CH_2SiCH_3), 0.45, 0.56 (s, 4 × 3 H, $SiCH_3$), 1.80 (s, 2 × 3 H, C_5CH_3), 1.93 (s, 2 × 3 H, $OCCH_3$), 1.95, 2.20, 2.26 (s, 6 × 3 H, C_5CH_3), 4.53 (s, 2 × 1 H, OC═CH). ^{13}C{^{1}H} NMR (cyclohexane-d_{12}, 25 °C): δ 1.5, 2.2 ($SiCH_3$), 5.3 (CH_2SiCH_3), 12.2, 12.9, 15.3, 15.7 (C_5CH_3), 26.8 ($OCCH_3$), 37.4 ($LuCH_2$), 84.4 (OC═C), 100.5 (SiC≡C), 102.5 (SiC≡C), 116.8, 120.7, 125.1, 127.3, 127.8 (C_5Me_4), 173.3 (OC═C). Anal. Calcd for $C_{38}H_{66}Si_4O_2Lu_2 \cdot 0.5C_5H_{12}$: C, 46.18; H, 6.89. Found: C, 46.34; H, 6.94.

Crystal Structure Analysis of 3a and 6. Relevant crystallographic data for **3a** and **6** are summarized in Table 1. Single-crystals suitable for X-ray crystal structure analysis were obtained by cooling concentrated pentane solutions of **3a** and **6** to −30 °C. Data collections were performed using ω scans on a Bruker AXS diffractometer with graphite-monochromated Mo Kα radiation at 293(2) K (**3a**) and 183(2) K (**6**). The data collection as well as the data reduction and correction for absorption was carried out using the program system SMART.[18a] The structures were solved by direct methods (SHELXS-86).[18b] From the measured reflections, all independent reflections were used, and the parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-97)[18c] and refined with anisotropic thermal parameters. The compound **3a** crystallizes in the polar space group $P2_1$, but the refinement indicated racemic twinning that was taken into account toward the end of the refinement. Hydrogen atoms were included into calculated positions except for the hydrogen atoms of the furyl group in **3a**, the olefinic hydrogen atoms in **6**, and the hydrogen atoms of the methylene groups of the CH_2SiMe_3 ligands in both compounds, which were refined with isotropic thermal parameters.

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Supporting Information Available: Tables of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for **3a** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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