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Metallocene Allyl Reactivity in the Presence of Alkenes Tethered to Cyclopentadienyl Ligands

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The reactions of the yttrium metallocene allyl complex $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, **1**, with ethylene, trimethylaluminum, and hydrogen have been examined to determine how the olefins tethered to the cyclopentadienyl ligands interact with these species that are typically present in olefin polymerizations. Complex **1** was prepared from allylmagnesium chloride and $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl$, which can be directly prepared free of solvent and alkali metal halide adducts from $YCl_3(THF)_x$ and $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]K$ in THF. **1** was characterized by NMR spectroscopy and X-ray crystallography, and the data were compared to those of three related complexes: the pentamethyl analogue, $(C_5Me_5)_2Y(C_3H_5)$, **2**, the ansa analogue, $[Me_2Si(C_5Me_4)_2]Y(C_3H_5)$, **3**, and the lutetium complex, $(C_5Me_5)_2Lu(C_3H_5)$, **4**. Although **1** shows no evidence for insertion of the tethered olefins into the $Y-(C_3H_5)$ bond, comparisons of the synthesis and variable-temperature NMR spectra of **1** with **2**−**4** suggest metal−alkene interaction. Complex **1** polymerizes ethylene and reacts with excess Al_2Me_6 to generate the allyl-free, tetramethylaluminate-bridged dimer $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y[(\mu\text{-}Me)_2AlMe_2]\}_2$, **5**. No involvement of the tethered olefins was observed in connection with this Y−C(allyl) bond breaking and Y−C(Me) bond making. The tethered olefins do become involved in the reaction chemistry of **1** in the presence of hydrogen: the tethered olefins of **1** are hydrogenated. A hydride derivative of **1** was not isolated, but **1** reacts with H_2 in diethyl ether to form the expected hydride decomposition product, the ethoxide, $\{[(C_5Me_4)SiMe_2(CH_2CH_2CH_3)]_2Y(OEt)\}_x$, **6**. Reaction of **1** with hydrogen in C_6D_6 and with deuterium in C_6H_6 shows that hydrogenation of the tethered olefin occurs before D/H exchange with arenes can occur in this system.

Introduction

Ligands containing tethered olefin functionality are attractive for elucidating metal olefin interactions, and a variety of systems have been investigated.[1−7] In the early transition metal area, olefins tethered to cyclopentadienyl ligands have been examined by Okuda[1] and Royo,[2] and olefins tethered to alkyl and alkoxide ligands have been studied by Casey[3,4] and Jordan.[5] Our recent studies of yttrium and lanthanide complexes of the alkene-substituted tetramethyl-cyclopentadienyl ligand $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ have shown that this can be a useful system to probe aspects of olefin polymerization in a metallocene environment with these metals. For example, it was shown that attachment of this ligand to an yttrium dialkyl moiety in $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]Y(CH_2SiMe_3)_2(THF)_2$ demonstrated an unusual dimetalation of the tethered $CH_2CH{=}CH_2$ substituents to form $\{[(C_5Me_4)SiMe_2(C_3H_3)]Y(L)\}_2$ (L = THF, DME),[6] which contains a trianionic cyclopentadienyl-allyl moiety. The $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ ligand was also used to probe the common competition in metallocene polymerization catalysts between coordination of anions such as $[BPh_4]^-$ and an olefin to a cationic metal center in the metallocene $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Sm\}[BPh_4]$.[7]

We report here an examination of the reactivity of the tethered olefins of this ligand with trimethylaluminum and with hydrogen, reagents that are often present in olefin polymerization systems as activators and for controlling molecular weight, respectively. These studies probe the insertion chemistry of the tethered olefin with yttrium carbon and yttrium hydrogen bonds present during olefin polymerization as well as the role of adjacent olefins during a typical Lewis acid activation step.

To examine these questions, we chose to examine a bis(cyclopentadienyl) allyl complex of the $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ ligand. Bis(pentamethylcyclopentadienyl) yttrium and lanthanide allyl complexes have been shown to be effective initiators for ethylene polymerization[8−11] and offer substantial advantages over simple alkyl or hydride precursors. The allyl complexes

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can be prepared[12] with less difficulty than alkyls or hydrides,[13−21] and they exhibit greater stability in terms of storage and handling.[12] Accordingly, the allyl complex $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, **1**, was prepared. Its synthesis, structure, and reactivity are described as well as a comparison of its structure and solution dynamics with related $(C_5Me_5)^-$ and ansa-$[Me_2Si(C_5Me_4)_2]^{2-}$ analogues.

Experimental Section

The complexes described below are extremely air and moisture sensitive. Syntheses and manipulations of these compounds were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. THF, diethyl ether, toluene, benzene, and *n*-hexane were saturated with Ar and passed through a GlassContour column.[22] Benzene-d_6 was distilled over NaK alloy and benzophenone. $(C_5Me_4H)SiMe_2(CH_2CH{=}CH_2)$,[6] $[Me_2Si(C_5Me_4)(CH_2CH{=}CH_2)]K$,[23] $(C_5Me_5)_2LnCl_2K(THF)_2$ (Ln = Y[24] and Lu[25]), $Li_2[Me_2Si(C_5Me_4)_2]$,[26] and $YCl_3(THF)_{3.5}$[27] were prepared as previously described. Anhydrous $LuCl_3$ was purchased from Strem and used without further purification. KH was purchased from Aldrich and washed with hexanes before use. Allylmagnesium chloride (2 M, in THF) and *n*-butyllithium were purchased from Aldrich and used without further purification. NMR spectra were obtained at 298 K unless otherwise specified using a Bruker 400 MHz or an Omega 500 MHz spectrometer. IR samples were prepared as thin films, and spectra were obtained using an ASI ReactIR 1000.[28] Elemental analyses were provided by Desert Analytics or Analytische Laboratorien, Lindlar, Germany.

$[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl$. In a nitrogen-containing glovebox, $(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]K$ (1.1 g, 4.25 mmol) and $YCl_3(THF)_{3.5}$ (760 mg, 1.92 mmol) were combined in a round-bottom flask, and THF (25 mL) was added. The resulting slurry was stirred for 24 h, during which time a colorless precipitate and a pale yellow solution formed. The reaction was centrifuged to remove the insoluble material, and the solvent was evaporated, leaving a pale yellow waxy solid. The solid was extracted with toluene (10 mL) and centrifuged to remove insoluble material. The toluene was removed from the pale yellow solution by exposure to vacuum, and $(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl$ (760 mg, 70%) was isolated as a colorless solid. A faint yellow color is sometimes observed due to traces amounts of the diene $(C_5Me_4H)SiMe_2(CH_2CH{=}CH_2)$; the metallocene can be separated by recrystallization from toluene. ^{1}H NMR (C_6D_6): δ 5.94 (m, 2H, $CH_2C\mathit{H}{=}CH_2$), 5.03 (d J = 16.8 Hz, 2H, $CH_2CH{=}C\mathit{H_2}$), 4.97 (d, J = 10 Hz, 2H, $CH_2CH{=}C\mathit{H_2}$), 2.31 (s, 12H, ring *Me*), 2.12 (s, 12H, ring *Me*), 1.99 (d J = 8 Hz, 4H, $C\mathit{H_2}CH{=}CH_2$), 0.57 (s, 12H, Si*Me*$_2$) ppm. ^{13}C NMR (C_6D_6): δ 136.2 (s, $CH_2\mathit{C}H{=}CH_2$) 125.5 (s, ring *C*-Me), 122.8 (s, ring *C*-Me), 112.3 (s, $CH_2CH{=}\mathit{C}H_2$), 25.9 (s, $\mathit{C}H_2CH{=}CH_2$), 14.9 (s, ring *Me*), 11.9 (s, ring *Me*), 0.00 (s, Si*Me*$_2$) ppm. Anal. Calcd for $C_{28}H_{46}ClSi_2Y$: C, 59.70; H, 8.25; 6; Y, 15.78. Found: C, 59.91; H, 8.31; Y, 15.77.

$[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, 1. Allylmagnesium chloride (0.60 mL of 2.0 M solution in THF, 1.20 mmol) was added via syringe to $(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl$ (572 mg, 1.02 mmol) in diethyl ether (20 mL) in a Schlenk flask cooled to 0 °C. The pale yellow color changed immediately to bright yellow, and a solid white precipitate formed. The reaction was warmed to room temperature and stirred for 2 h. The solvent was removed, and the remaining solids were extracted with hexanes (3 × 5 mL) to give a bright yellow solution with white insolubles. The mixtures were centrifuged and the hexanes were evaporated, leaving **1** as a bright yellow crystalline solid (415 mg, 72%). X-ray quality crystals were obtained by cooling a concentrated hexanes solution of **1** to −32 °C. ^{1}H NMR (C_6D_6): δ 7.06 (m, 1H, allyl C*H*), 5.73 (m, 2H, $CH_2C\mathit{H}{=}CH_2$), 4.92 (m, 4H, $CH_2CH{=}C\mathit{H_2}$), 3.68 (d, J = 12 Hz, allyl *anti* C*H*$_2$), 2.30 (overlapped by ring Me, allyl *syn* C*H*$_2$), 2.28 (s, 12H, ring *Me*), 1.79 (s, 12H, ring *Me*), 1.65 (d, J = 8 Hz, 4H, $C\mathit{H_2}CH{=}CH_2$), 0.21 (s, 12H, Si*Me*$_2$).^{13}C NMR (C_6D_6): δ 157.3 (s, allyl *C*H), 135.3 (s, $CH_2\mathit{C}H{=}CH_2$), 127.3 (s, ring *C*-Me), 122.3 (s, ring *C*-Me), 113.4 (s, $CH_2CH{=}\mathit{C}H_2$), 68.9 (d, J = 4 Hz, allyl *C*H$_2$), 25.6 (s, $\mathit{C}H_2CH{=}CH_2$), 15.3 (s, ring *Me*), 11.6 (s, ring *Me*), −0.2 (s, Si*Me*$_2$) ppm. IR: 3076w, 2961s, 2914s, 2860s, 1629m, 1559w, br, 1444m, 1328m, 1251s, 1220w, 1193w, 1154m, 1108w, 1023s, 988w, 953w, 930w, 892m, 834s, 807s, 672m. Anal. Calcd for $C_{31}H_{51}Si_2Y$: C, 65.45; H, 9.06; Y, 15.63. Found: C, 65.31; H, 8.99; Y, 15.55.

$(C_5Me_5)_2Y(C_3H_5)$, 2. In a nitrogen-filled glovebox, $ClMg(CH_2CHCH_2)$ (1.35 mL, 2.97 mmol) was added to a stirring slurry of $(C_5Me_5)_2YCl_2K(THF)_2$ (1.71 g, 2.48 mmol) in toluene (∼50 mL). The white slurry immediately became a yellow solution. After 1 h, the solvent was removed by rotary evaporation to yield a bright yellow solid. This material was triturated with 2% dioxanes in hexanes (75 mL) and filtered through a coarse frit to yield an orange solution. After removal of the solvent, $(C_5Me_5)_2Y(C_3H_5)(THF)$ was isolated as a yellow solid. ^{1}H NMR (C_6D_6): δ 7.04 (m, 1H, $(CH_2)_2C\mathit{H}$), 3.56 (s, br 2H, $(C\mathit{H_2})_2CH$), 2.17 (s, br 2H, $(C\mathit{H_2})_2CH$), 1.90 (s, 30H, $C_5\mathit{Me}_5$). ^{13}C NMR (C_6D_6): δ 158.0 (s, $(CH_2)_2\mathit{C}H$), 117.0 (s, C_5Me_5), 69.0 (s, $(\mathit{C}H_2)_2CH$), 11.2 (s, $C_5\mathit{Me}_5$). IR: 2910s, 2860s, 1540s, 1440s, 1378s, 1247s, 1085s, 1019s, 675s. A sublimation tube was charged with $(C_5Me_5)_2Y(C_3H_5)(THF)$ and attached to a vacuum line. The yellow powder was dried under high vacuum (1 × 10^{-5} Torr) for 24 h at 35−45 °C to remove coordinated THF. The resulting material was extracted with hexanes to yield **2** (1.12 g, 94%) upon solvent removal. X-ray quality crystals of **2** were grown from hot toluene solutions slowly cooled to −35° C. ^{1}H NMR (C_6D_6): δ 7.04 (m, $CH_2C\mathit{H}CH_2$, 1H), 3.56 (d, 2H, 15.7 Hz, $(C\mathit{H_2})_2CH$), 2.21 (d, 2H, 9.6 Hz, $(C\mathit{H_2})_2CH$), 1.93 (s, 15H, $C_5\mathit{Me}_5$), 1.85 (s, 15H, $C_5\mathit{Me}_5$) ppm. ^{13}C NMR (C_6D_6): δ 158.0 (d, 2 Hz, $(CH_2)_2\mathit{C}H$), 117.0 (s, C_5Me_5), 116.9 (s, C_5Me_5), 69.07 (d, 3.8 Hz, $(\mathit{C}H_2)_2CH_5$), 11.41 (s, $C_5\mathit{Me}_5$), 11.03 (s, $C_5\mathit{Me}_5$).

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Anal. Calcd for $YC_{23}H_{35}$: Y, 22.20; C, 68.99; H, 8.74. Found: Y, 22.15; C, 68.42; H, 8.72.

$[Me_2Si(C_5Me_4)_2]YCl_2Li(THF)_2$. In a nitrogen-filled glovebox, a 250 mL Schlenk flask was equipped with a reflux condenser and a gas inlet valve charged with $Li_2[Me_2Si(C_5Me_4)_2]$ (500 mg, 1.602 mmol) and $YCl_3(THF)_{3.5}$ (651 mg, 1.454 mmol) suspended in 150 mL of THF. The apparatus was attached to a Schlenk line, and the mixture was heated to reflux for 8 h. The solvent was removed by rotary evaporation to give a yellow solid, which was washed with hexanes, affording $Me_2Si(C_5Me_4)_2YCl_2Li(THF)_2$ (523 mg, 59%). ^1H NMR (C_6D_6): δ 3.54 (s, 8H, THF); 2.38 (s, 12H, $Me_2Si(C_5\mathit{Me}_4)_2$); 2.29 (s, 12H, $Me_2Si(C_5\mathit{Me}_4)_2$); 1.35 (s, 8H, THF); 1.05 (s, 6H, $\mathit{Me}_2Si(C_5Me_4)_2$) ppm.

$[Me_2Si(C_5Me_4)_2]Y(C_3H_5)$, 3. Allylmagnesium chloride (1.60 mL, 3.20 mmol) was added dropwise via syringe to a Schlenk flask containing $[Me_2Si(C_5Me_4)_2YCl_2Li(THF)_2]$ (1.944 g, 3.190 mmol) suspended in toluene (100 mL) cooled to −73 °C with a dry ice/2-propanol bath. The reaction mixture was allowed to warm to room temperature over the course of 12 h, and the solvent was removed by exposure to vacuum. The reaction was brought into a nitrogen-filled glovebox, and dioxane/hexane (1:10) was added. The white solid that precipitated was removed by centrifugation, the solvent was removed by exposure to vacuum, and $[Me_2Si(C_5Me_4)_2]Y(C_3H_5)(THF)$ was isolated as a yellow powder. (1.42 g, 89%). ^1H NMR (C_6D_6): δ 3.50 (s, 4H, THF), 2.10 (s, 12H, $C_5\mathit{Me}_4$), 1.79 (s, 12H, $C_5\mathit{Me}_4$), 1.26 (s, 4H, THF), 0.90 (s, 6 $Si\mathit{Me}_2$) ppm. $Me_2Si(C_5Me_4)_2Y(C_3H_5)(THF)$ was placed in a glass tube fitted with a greaseless Teflon stopcock and attached to a vacuum system at 6×10^{-5} Torr for 24 h at room temperature. The temperature was then slowly raised in 10 °C/h increments to 60° C. After 24 h, the yellow solid was brought into an argon-filled glovebox and extracted with hexane. The hexane was removed by exposure to vacuum, and **3** was isolated as a yellow powder (0.736 mg, 54%). X-ray quality crystals of **3** were grown by slow evaporation of a concentrated toluene solution. ^1H NMR (C_6D_6): δ 2.10 (s, 12H, $C_5\mathit{Me}_4$), 1.79 (s, 12H, $C_5\mathit{Me}_4$), 0.90 (s, 6H, $Si\mathit{Me}_2$) ppm. At this temperature, no resonances for the allyl ligand were observed. IR: 2957s, 2918s, 2856s, 1806w, 1559w, 1455m, 1324m, 1258s, 1092s, 1019s, 833m, 802m, 698m, 675m cm^{-1}.

$(C_5Me_5)_2Lu(C_3H_5)$, 4. As described above for **2**, $ClMg(C_3H_5)$ (2.5 mL, 5.0 mmol) was reacted with $(C_5Me_5)_2LuCl_2K(THF)_2$ (2.84 g, 4.06 mmol) in toluene (~50 mL) to form **4** (1.4 g, 71%). ^1H NMR (toluene-d_8): δ 7.35 (p, J_{HH} = 12 Hz $(CH_2)_2C\mathit{H}$, 1H), 3.73 (br s, $\Delta\nu_{1/2}$ = 97 Hz, $(C\mathit{H}_2)_2CH_2$, 2H), 1.92 (br s, $\Delta\nu_{1/2}$ = 102 Hz, $C_5\mathit{Me}_5$, $(C\mathit{H}_2)_2CH$, 32H) ppm. ^{13}C NMR (toluene-d_8): δ 162 ($(CH_2)_2\mathit{C}H$), 116 (C_5Me_5), 67.0 ($(\mathit{C}H_2)_2CH$), 11.1 (C_5Me_5) ppm. ^1H NMR (toluene-d_8, 253 K) δ 7.37 (tt, $(CH_2)_2C\mathit{H}$, 1H), 3.55 (d, J_{HH} = 15.6 Hz = *anti*-CH_2CHCH_2, 2H), 1.97 (s, $C_5\mathit{Me}_5$, 15H), 1.94 (d, J_{HH} = 9.6 Hz, *syn*-CH_2CHCH_2, 2H), 1.86 (s, C_5Me_5 15H) ppm. ^{13}C NMR (toluene-d_8): δ 162 $(CH_2)_2\mathit{C}H$), 116.2, 116.0 (C_5Me_5), 67.6 ($\mathit{C}H_2)_2CH$), 11.5, 11.0 (C_5Me_5) ppm. ^1H NMR (toluene-d_8, 380 K): δ 7.33 (p, J_{HH} = 12 Hz, $(CH_2)_2C\mathit{H}$, 1H), 2.78 (d, J_{HH} = 12 Hz, $(C\mathit{H}_2)_2CH$, 4H), 1.90 (s, C_5Me_5, 30H) ppm. Complex **4** was previously identified by hydrolysis of a mixture of organolutetium species. Two ^{13}C NMR peaks were reported that match those above.[29]

$\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(AlMe_4)\}_2$, 5. 1 (100 mg, 0.178 mmol) was dissolved in hexanes (10 mL). Excess Al_2Me_6 (0.88 mL of 2.0 M solution in hexanes, 1.78 mmol) was added, and the color gradually changed from bright yellow to yellow over a 1 h period. The solvent was removed, leaving a faint yellow waxy solid. **5** (101 mg, 96%) was isolated as a colorless solid by recrystallization from hexanes at −32 °C. Crystals suitable for X-ray diffraction were formed by layering a concentrated hexanes solution of **1** with a few drops of 2.0 M Al_2Me_6 in hexanes and chilling the resulting mixture to −32 °C for 48 h. ^1H NMR (C_6D_6): δ 5.66 (s, 2H, $CH_2C\mathit{H}{=}CH_2$), 4.87 (m, 4H, $CH_2CH{=}C\mathit{H}_2$), 2.18 (s, 12H, ring *Me*), 1.75 (s, 12H, ring *Me*), 1.65 (d *J* = 8 Hz, 4H, $C\mathit{H}_2CH{=}CH_2$), 0.31 (s, 12H, $Si\mathit{Me}_2$), −0.33 (br s, 6H, $Al\mathit{Me}_4$), −0.37 (br s, 6H, $Al\mathit{Me}_4$) ppm. ^{13}C NMR (C_6D_6): δ 135.2 (s, $CH_2\mathit{C}H{=}CH_2$), 130.1 (s, ring *C*-Me), 124.6 (s, ring *C*-Me), 114.6 (s, ring *C*-Si), 113.6 (s, $CH_2CH{=}\mathit{C}H_2$), 25.7 (s, $\mathit{C}H_2CH{=}CH_2$), 15.56 (s, ring *Me*), 11.94 (s, ring *Me*), 10.2 (br s, $\Delta\nu_{1/2}$ = 25 Hz, μ-Me_2AlMe_2), 0.39 (s, $Si\mathit{Me}_2$), −5.68 (s, μ-$Me_2Al\mathit{Me}_2$) ppm. IR: 3076 w, 2953s, 2910s, 2868s, 1629m, 1571w, br, 1444m, 1320s, 1251s, 1193m, 1150m, 1019s, 992w, 930w, 892m, 833s, br, 695m cm^{-1}.

$[(C_5Me_4)SiMe_2(CH_2CH_2CH_3)]_2Y(OEt)$, 6. 1 (87 mg, 0.153 mmol) dissolved in diethyl ether (10 mL) was placed in a round-bottom flask equipped with a high-vacuum adapter. The flask was connected to a high-vacuum line, and the solution was degassed by two freeze−pump−thaw cycles. Hydrogen at 1 atm was admitted to the flask, and in 2 min the bright yellow color faded to a pale yellow. After 10 min, the solution was colorless. The reaction was stirred for 2 h, and the solvent was removed, leaving a colorless waxy solid. The wax was extracted with hexanes and the colorless solution was evaporated, leaving **6** (69 mg, 77%) as a colorless waxy solid. ^1H NMR (C_6D_6): δ 4.28 (q, 2H, $OC\mathit{H}_2CH_3$), 2.28 (s, 12H, ring *Me*), 1.93 (s, 12H, ring *Me*), 1.35 (t, 3H, $OCH_2C\mathit{H}_3$), 1.26 (m, 4H, $SiCH_2C\mathit{H}_2CH_3$), 1.02 (t, 6H, $SiCH_2CH_2C\mathit{H}_3$), 0.73 (t, 4H, $SiC\mathit{H}_2CH_2CH_3$), 0.29 (s, 12H, $Si\mathit{Me}_2$) ppm. ^{13}C NMR (C_6D_6): δ 129.2 (ring *C*-Me), 122.3 (s, ring *C*-Me), 62.1 (s, $O\mathit{C}H_2CH_3$), 22.1 (s, $OCH_2\mathit{C}H_3$), 18.6 (s, $SiCH_2\mathit{C}H_2CH_3$), 18.3 (s, $SiCH_2CH_2\mathit{C}H_3$), 18.1 (s, $Si\mathit{C}H_2CH_2CH_3$), 14.5 (s, ring *Me*), 11.3 (s, ring *Me*), −0.10 (s, $Si\mathit{Me}_2$) ppm. GC/MS of D_2O quench of **6**: *m/z* = 223, 181, 121, 101, 73, 59.

Reaction of 1 with Ethylene. A round-bottom flask equipped with a high-vacuum adapter containing **1** (20 mg, 0.036 mmol) dissolved in *n*-hexane (10 mL) was connected to a high-vacuum line, and ethylene at 1 atm was introduced. After 20 min, the solution became viscous, and after 45 min, a white precipitate began to form. The reaction was stirred for 12 h, during which time a large amount of white solid had formed. The reaction was removed from the line, and 20 mL of methanol was added with 10 mL of 5% HCl. The resulting suspension was stirred for 1 h and then filtered, leaving 367 mg of polyethylene, mp = 139 °C.

X-ray Data Collection, Structure Solution, and Refinement. $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, 1. A yellow crystal of approximate dimensions 0.10 × 0.19 × 0.20 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[30] program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[31] and SADABS[32] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[33] program. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$, which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[34] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The absolute structure was assigned by refinement of the Flack parameter.[35] Details are given in Table 1. The crystal structures of **2**−**5** were determined similarly.

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Table 1. Experimental Data for the X-ray Diffraction Studies of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, 1, $(C_5Me_5)_2Y(C_3H_5)$, 2, $[Me_2Si(C_5Me_4)_2]Y(C_3H_5)$, 3, $(C_5Me_5)_2Lu(C_3H_5)$, 4, and $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y[(\mu\text{-}Me_2)AlMe_2]\}_2$, 5[a]

	1	2	3	4	5
formula	$C_{31}H_{51}Si_2Y$	$C_{23}H_{35}Y$	$C_{23}H_{35}SiY$	$C_{23}H_{35}Lu$	$C_{64}H_{116}Al_2Si_4Y_2$
fw	568.81	400.42	428.51	486.48	1229.71
temp (K)	163(2)	163(2)	163(2)	163(2)	171(2)
space group	$P2_12_12_1$	$P2_1/n$	$I4_1cd$	$I4$	$P2_1/n$
a (Å)	10.0582(5)	8.9218(11)	29.2318(15)	22.5779(5)	11.0875(10)
b (Å)	10.9779(6)	17.632(2)	29.2318(15)	22.5779(5)	19.7843(18)
c (Å)	28.1698(15)	13.6181(17)	28.1698(15)	8.4111(3)	15.6311(14)
β (deg)	90	90.066(2)	90	90	93.695(2)
V (Å^3)	3110.5(3)	2142.3(5)	8639.4(9)	4287.7(2)	3421.7(5)
Z	4	4	16	8	2
ρ_{calcd} (mg/m^3)	1.215	1.242	1.318	1.507	1.194
μ (mm^{-1})	1.969	2.724	2.759	4.606	1.818
refinement[b] R1 $I > 2.0\sigma(I)$	0.0426	0.0304	0.0361	0.0214	0.0531
wR2 (all data)	0.0968	0.0732	0.0965	0.0504	0.1381
goodness-of-fit on F^2	1.024	1.056	1.074	1.073	1.021

[a] Radiation: Mo Kα ($\lambda = 0.710730$ Å). Monochromator: highly oriented graphite. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; wR2 $= [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Results

Synthesis of Allyl Complexes. To examine the reactivity of the $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ ligand in a metallocene complex which mimicked an olefin polymerization system, it was necessary to make a complex of the type $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YR$ with an R group that could initiate olefin polymerization. The most common types of $(C_5R_5)_2YR$ complexes in the literature are $(C_5Me_5)_2YMe(THF)$[15] and $(C_5Me_5)_2Y[CH(SiMe_3)_2]$.[16] Since the $[CH(SiMe_3)_2]^-$ ligand is sometimes too bulky to undergo olefin insertion and since a system free of THF was desired to avoid competition with olefin coordination, $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$ was chosen as the starting material since this allyl complex can easily be made THF-free. Analogous $(C_5Me_5)_2Ln(C_3H_5)$ complexes are known to initiate polymerization of ethylene.[8–11] In fact, these allyl complexes may be the best lanthanide metallocene systems with which to start olefin polymerization studies since they are less difficult to prepare and are less prone to decomposition during storage than alkyl or hydride complexes.

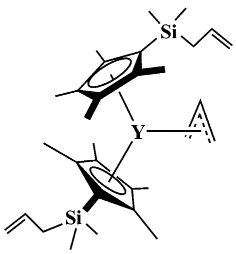
The preparation of the necessary allyl complex started with the synthesis of the chloride $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl$, according to eq 1. This synthesis is

$$[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]K + YCl_3(THF)_{3.5} \rightarrow [(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl + 2KCl \quad (1)$$

different from analogous $(C_5Me_5)^-$ reactions in that addition of MC_5Me_5 to yttrium and lanthanide trichlorides typically forms MX adducts such as $(C_5Me_5)_2LnCl_2M(solvent)_x$.[36] However, the use of the $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ ligand facilitates the formation of a product free of both KCl and THF. This difference normally might be attributed to the tethered olefin, but the ^{1}H NMR spectrum of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl$ shows no evidence for alkene coordination at room temperature.

The reaction of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl$ with allylmagnesium chloride according to eq 2 led to the formation of the desired allyl complex, $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, **1**, as a bright yellow solid in 75% yield. The ^{1}H and ^{13}C NMR spectra of **1** indicate that it is also free of THF. In contrast, the analogous $(C_5Me_5)^-$ complexes are typically isolated as THF adducts, $(C_5Me_5)_2Ln(C_3H_5)(THF)$, which require desolvation.[12,37]

$$[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl + (C_3H_5)MgCl \longrightarrow$$



$+ MgCl_2$ (2)

1

The ^{1}H and ^{13}C NMR spectra of **1** in C_6D_6 contain alkene, ring methyl, and silyl methyl proton and carbon resonances similar to those found in $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl$, $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]Y(CH_2SiMe_3)_2(THF)_2$,[6] and $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]Y(O_2CCH_2SiMe_3)_2\}_2$.[6] In the ^{1}H NMR spectrum, the terminal alkene protons display a singlet at δ 4.89 ppm and two multiplets centered at δ 4.92 and 4.93 ppm. The internal alkene proton gives a multiplet centered at δ 5.73. The allyl ligand displays a broad doublet centered at δ 3.68 for the *anti* protons with a coupling constant of 12 Hz. A peak found at δ 2.31 was assigned to the *syn* protons of the allyl group, but it is overlapped by one of the large resonances for the ring methyl protons at δ 2.28. The center proton on the allyl group was located as a multiplet centered at δ 7.06. The terminal and internal alkene carbon peaks in the ^{13}C NMR spectrum were found at δ 113.4 and 135.3, respectively. The terminal allylic carbons were located as a doublet at 68.9 (J_{YC} = 4 Hz), and a doublet at δ 157.1 (J_{YC} = 2 Hz) was assigned to the internal allylic carbon.

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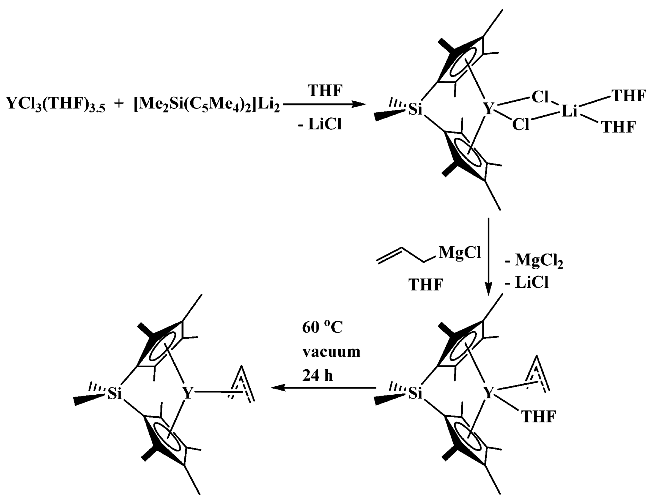
Scheme 1



3

Three related allyl complexes, $(C_5Me_5)_2Y(C_3H_5)$, **2**, $[Me_2Si(C_5Me_4)_2]Y(C_3H_5)$, **3**, and $(C_5Me_5)_2Lu(C_3H_5)$, **4**, were also synthesized and allow spectroscopic and structural comparisons to be made with **1**. Complex **4** was previously reported as a component of a mixture of decomposition products,[29] but neither synthetic nor characterization details were presented. As shown by the representative synthesis for **3** in Scheme 1, the presence of THF complicates the formation of complexes **2**−**4**. In the synthesis of each compound, **2**−**4**, the reaction of the metal trichloride with the pentamethylcyclopentadienyl ligand formed a metal halide adduct.[38] In each case, the reaction of the metal halide adduct with allylmagnesium chloride produced a THF adduct that required desolvation. The THF could be removed by placing the THF adduct under high vacuum and slowly heating to 60 °C for 24−48 h to obtain desolvated complexes.

Structure of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, 1. X-ray crystallography was used to determine if there were any long-range yttrium alkene interactions in the solid state as was found for $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Ln$ (Ln = Eu, Sm, Yb)[7] and $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Sm\}[BPh_4]$.[7] The X-ray crystal structure of **1** shows that the alkenes are oriented away from the yttrium metal center, Figure 1. The eight-coordinate bent metallocene geometry in **1** is similar to that in other yttrium and lanthanide metallocenes,[39] and the 139.7° (ring centroid)−Y−(ring centroid) angle and the 2.381 and 2.387 Å Y−C(ring centroid) distances are normal.[39] The allyl unit is bound in an η^3-mode similar to other lanthanide allyl complexes.[8] The Y−C(allyl) distances for Y(1)−C(29), Y(1)−C(30), and Y(1)−C(31) are 2.587(3), 2.613(3), and 2.585(3) Å, respectively. These are shorter than the $Y{-}C(C_5Me_4R)$ average distance of 2.675(4) Å, as expected, and are similar to the analogous 2.630(15), 2.668(18), and 2.643(18) Å distances in $(C_5Me_5)_2Sm(C_3H_5)$[8] when the 0.06 Å smaller radius of Y is considered.[40] The C(allyl)−C(allyl) distances for C(29)−C(30) and C(30)−C(31) are 1.382(5) and 1.397(5) Å. As expected, the noninteracting C(alkene)−C(alkene) distances are shorter: C(13)−C(14), 1.313(6) Å; C(27)−C(28), 1.307(7) Å.

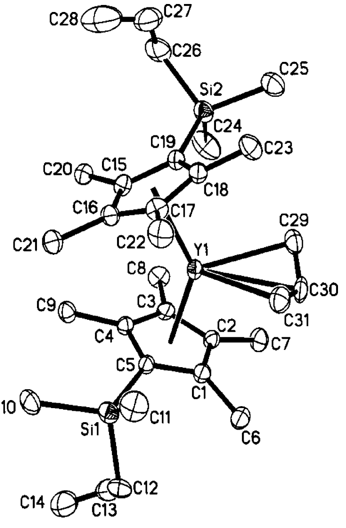


Figure 1. Thermal ellipsoid plot of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, **1**, with ellipsoids drawn at the 50% probability level.

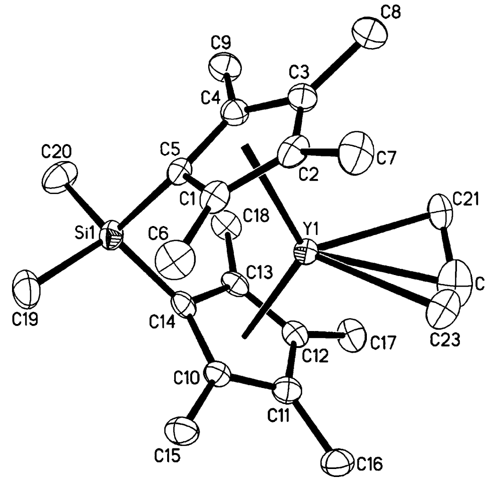


Figure 2. Thermal ellipsoid plot of $Me_2Si(C_5Me_4)_2Y(C_3H_5)$, **3**, with ellipsoids drawn at the 50% probability level.

Crystallographic data were also collected on complexes **2**, **3**, and **4**, Figures 3 and 4, respectively, for direct comparison with **1**. Table 2 summarizes the structural data for **1**−**4** and shows that the four complexes are very similar in the solid state. The Y−C(allyl) distances in **2** and **3** are indistinguishable from the distances in **1** despite the fact that the C(ring centroid)−Y−C(ring centroid) angle is only 127.1° in **3** compared to the similar 139.7° and 138.8° angles observed in **1** and **2** due to the constraint enforced by the $[Me_2Si(C_5Me_4)_2]^{2-}$ ligand.[41−45] The Lu−C(allyl) dis-

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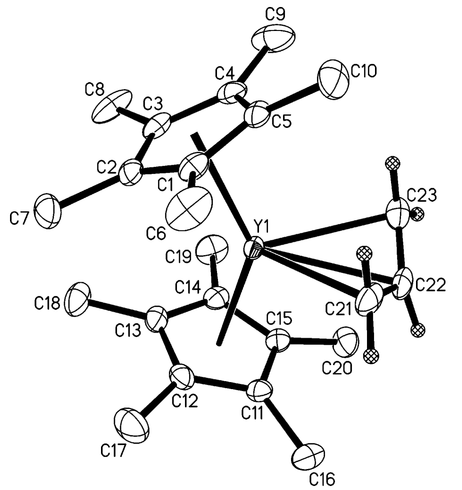
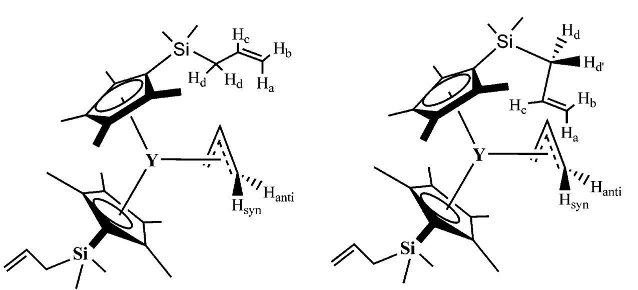


Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_2Y(C_3H_5)$, **2**, with ellipsoids drawn at the 50% probability level.

298 K 200 K



1 **1**

H_a 4.90 d J_{HH} = 4 Hz
H_b 4.87 s
H_c 5.69 m
H_d 1.62 d J_{HH} = 8 Hz
H_{syn} overlapped with C_5*Me*$_4$
H_{anti} 3.63 d J_{HH} = 12 Hz
-C=***C*** 113.4 s
-***C***=C 135.4 s

H_a 5.01 t J_{HH} = 4-8 Hz
H_b 4.97 d J_{HH} = 4 Hz
H_c 5.73 m
H_d 1.61 d J_{HH} = 8 Hz
$H_{d'}$ 1.66 d J_{HH} = 8 Hz
H_{syn} 2.26 d J_{HH} = 10 Hz
H_{anti} 3.74 d J_{HH} = 16 Hz
-C=***C*** 113.4 2 s non-coordinated
-C=***C*** 113.6 d J_{CH} = 2 Hz
-C=***C*** 111.0 d J_{CH} = 2 Hz
-***C***=C 135.3 2 s

Figure 4. ^1H and ^{13}C NMR data for **1** in toluene-d_8 (0.07 mM) at 298 and 200 K. At 298 K, the allyl group is fluxional with free rotation of the tethered alkene. At 200 K, the allyl group is static and rotation of the tethered alkene is hindered.

tances in **4** are also very close to those found in **1**−**3** considering that the ionic radius of eight-coordinate Lu(III) is 0.042 Å smaller than that of Y(III).[40]

Variable-Temperature NMR Studies. Allyl complexes **1**−**4** display fluxional behavior in toluene-d_8 due to the dynamic nature of the allyl moiety in solution. At 298 K, the cyclopentadienyl resonances in complexes **1**, **3**, and **4** are all equivalent on the NMR time scale; the motion of the allyl group is sufficiently fast to provide an averaged magnetic environment to each ring. In contrast, the $(C_5Me_5)^-$ resonance of **2** is split into two peaks at 298 K. Only at 318 K do the two cyclopentadienyl peaks have an equivalent magnetic environment.

The fluxional behavior of allyl complexes of electropositive metals has seen limited study. Some early variable-temperature analyses have been carried out by Marks and co-workers,[21] and most recently a study on the behavior of the homoleptic allyl complexes of thorium has been reported by Hanusa and co-workers.[46] A detailed study on a series of Sc-allyl compounds has been reported by Bercaw and co-workers.[47] In the scandium allyl system, evidence was reported for two mechanisms for allyl fluxionality, i.e., an η^3-C_3H_5 to η^1-C_3H_5 coordination change and a 180° rotation of the η^3-C_3H_5 moiety. It was concluded that both mechanisms can occur simultaneously.

Table 2. Comparison of Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$ 1, $(C_5Me_5)_2Y(C_3H_5)$, 2, $[Me_2Si(C_5Me_4)_2]Y(C_3H_5)$, 3, and $(C_5Me_5)_2Lu(C_3H_5)$, 4

	1	2	3	4
Y−C(centroid)	2.381	2.381	2.343	2.318
	2.387	2.362	2.330	2.301
Y−C(ring average)	2.675(4)	2.660(7)	2.632(4)	2.607(4)
C(ring centroid)−Y−C(ring centroid)	139.7	138.8	127.1	138.5
Y−C(allyl)	2.587(3)	2.582(2)	2.574(4)	2.549(5)
	2.585(3)	2.582(2)	2.586(6)	2.548(4)
	2.613(3)	2.601(2)	2.592(4)	2.545(5)
C(allyl)−C(allyl)	1.382(5)	1.392(3)	1.380(7)	1.382(8)
	1.397(5)	1.391(3)	1.384(7)	1.383(9)
C(allyl)−C(allyl)−C(allyl)	125.9(4)	125.9(2)	128.1(5)	127.7(5)

Cooling samples of **1**, **2**, **3**, and **4** in toluene-d_8 enables the measurement of coalescence temperatures of their cyclopentadienyl resonances. For **1**, coalescence of the Si*Me*$_2$ resonances occurs at 240 K. The order of coalescence for methyl resonances of the cyclopentadienyl rings is as follows: $(C_5Me_5)_2Y(C_3H_5)$, **2**, 318 K; $(C_5Me_5)_2Lu(C_3H_5)$, **4**, 283 K; $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, **1**, 257 K; $[Me_2Si(C_5Me_4)_2]Y(C_3H_5)$, **3**, 199 K.

It is reasonable that the lowest coalescence temperature occurs for the ansa system, complex **3**, since this complex has the smallest (ring centroid)−Y−(ring centroid) and the most room in the wedge for the allyl ligand to rotate. However, this trend does not apply to the Y and Lu analogues, **2** and **4**. Since Lu is slightly smaller than Y, **4** is the more crowded complex and yet it has the lower coalescence temperature. This suggests that more than one rearrangement pathway is operating in these complexes.

In the case of **2** and **4**, it is possible that increased crowding in **4** facilitates an η^3-C_3H_5 to η^1-C_3H_5 interconversion, as proposed by Bercaw et al.,[47] leading to the lower coalescence temperature. Support for this comes from the fact that a decrease in $(C_5Me_5)^-$ coalescence temperature with increased steric crowding is observed when a Lewis base, such as THF, is added to $(C_5Me_5)_2Ln(C_3H_5)$ complexes of the larger lanthanides, which have room to form base adducts. For example, although $(C_5Me_5)_2Nd(C_3H_5)$[10] and $(C_5Me_5)_2Sm(C_3H_5)$[8] display two C_5*Me*$_5$ resonances at room temperature, addition of THF causes coalescence to occur. Addition of the coordinating ligand may facilitate the rapid η^3-C_3H_5 to η^1-C_3H_5 interconversion since the additional ligand can provide extra steric and electronic saturation

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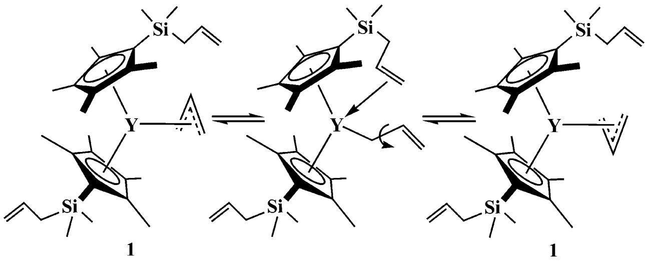
Scheme 2



needed to stabilize the η^1-alkyl intermediate necessary for rotation about the carbon−carbon single bond. A similar explanation may rationalize why the coalescence temperature for $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, **1**, is substantially lower than the 318 K value of its $(C_5Me_5)^-$ yttrium analogue, **2**. If only simple rotation of the allyl is involved, a higher temperature for **1** would be expected since the $SiMe_2(CH_2CH{=}CH_2)$ substituent is bulkier than a methyl group and could cause an increase in steric crowding. However, if the tethered olefins act like THF and coordinate the yttrium ion, the η^1-C_3H_5 intermediate might be stabilized, as shown in Scheme 2. This would explain the lower coalescence temperature of **1** compared to **2**.

The ^{1}H spectrum of **1** at 200 K revealed additional coupling that is consistent with the alkene coordination shown in Scheme 2. The ^{1}H NMR spectrum shows additional 4 Hz coupling of the terminal alkene protons changing them from a singlet and a doublet at 298 K to a doublet and a triplet at 200 K. This is consistent with J_{Y-CH} coupling of 4 Hz observed in various organoyttrium systems.[48] Furthermore, at 200 K, the $CH_2CH{=}CH_2$ protons of the $(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)$ group are split into a pair of doublets, suggesting that rotation of the tethered alkene is hindered, possibly placing the olefin in the vicinity of the yttrium. The observed increase in coupling at low temperature could be due to additional $J_{cis/trans}$ coupling from the adjacent internal alkene proton or the result of geminal J_{H-H} coupling. The ^{1}H NMR data are summarized in Figure 4.

The ^{1}H NMR evidence can be rationalized by a weak Y−C(alkene) interaction in which the coordinated olefin is in equilibrium with the free olefin. The fact that only the terminal carbon is affected by contact with the yttrium metal center at 200 K suggests that the tethered alkene approaches the metal in an unsymmetrical fashion. This is in agreement with X-ray crystal structure data obtained for the alkene coordinated complexes $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Ln$ (Ln = Eu, Sm, Yb)[7] and $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Sm[BPh_4]$,[7] in which the terminal alkenes are directed at the metals centers with shorter M−C(terminal alkene) distances compared to the M−C(internal carbon) distances. This unsymmetrical alkene binding has also been observed spectroscopically by Casey in $(C_5Me_5)_2Y[CH_2CH_2C(Me_2)$-$CH{=}CH_2]$[3,4,49] and by Jordan in $(C_5H_5)_2Zr(OCMe_2CH_2$-$CH_2CH{=}CH_2)]^+$ and $[(S,S,R)$-(EBI)$Zr(OCMe_2CH_2CH_2$-$CH{=}CH_2)]^+$ [EBI = ethylene-1,2-bis(1-indenyl)], in cases that were confirmed by X-ray crystallography.[50]

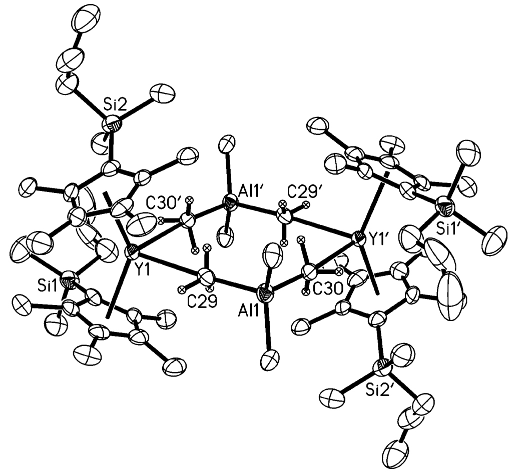


Figure 5. Thermal ellipsoid plot of $\{[(C_5Me_4)SiMe_2(CH_2$-$CH{=}CH_2)]_2Y[(\mu$-$Me_2)AlMe_2]\}_2$, **5**, with ellipsoids drawn at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y$-$[(\mu$-$Me_2)AlMe_2]\}_2$, 5[a]

Y1−Cnt1	2.383	(Cnt1)-Y1−(Cnt2)	138.5
Y1−Cnt2	2.378	C(29)−Y(1)−C(30)′	84.5(2)
Y1−C29	2.702(6)	Al(1)−C(29)−Y(1)	176.7(3)
Y1−C30′	2.703(6)	Al(1)−C(30)−Y(1)′	174.2(3)
Al1−C29	2.043(6)	C(31)−Al(1)−C(32)	111.8(3)
Al1−C30	2.054(6)	C(32)−Al(1)−C(29)	111.5(3)
Al1−C31	1.988(5)	C(31)−Al(1)−C(29)	109.8(3)
Al1−C32	1.987(5)	C(31)−Al(1)−C(30)	109.9(3)
C27−C28	1.325(10)	C(29)−Al(1)−C(30)	100.6(3)
C22−C23	1.178(11)		

[a] Cnt1 is the centroid of C(1)−C(5). Cnt2 is the centroid of C(10)−C(14).

Reactivity of 1 with CH_2CH_2. If the tethered olefin functionalities in **1** acted as substrate olefins, they might interfere with ethylene polymerization. However, complex **1** rapidly polymerizes ethylene in a reaction consistent with that observed for other $(C_5Me_5)_2Ln$-(C_3H_5) complexes.[9] Evidently, the presence of the tethered olefin ligands does not interfere with this polymerization reaction.

Reactivity of 1 with Al_2Me_6. Complex **1** was treated with Al_2Me_6 to determine how the tethered olefins would behave in the course of a typical Lewis acid activation of a metallocene alkyl initiator. Abstraction of the allyl group could form a cation that could bind the tethered olefins as observed in $\{[(C_5Me_4)SiMe_2(CH_2$-$CH{=}CH_2)]_2Sm\}[BPh_4]$.[7] Alternatively, a $[Me_3Al(C_3H_5)]^-$ unit formed by allyl abstraction could bridge to the metal. It was of interest to see if the tethered olefins would become involved in any of these metal−carbon bond-breaking or bond-making processes.

Addition of Al_2Me_6 to **1** causes the bright yellow color to fade to a pale yellow, and $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y[(\mu$-$Me_2)AlMe_2]\}_2$, **5**, was isolated in quantitative yield and definitively identified by X-ray crystallography, Figure 5, Table 3. The allyl ligand was lost as anticipated for this reaction, but a $[AlMe_4]^-$ anion was isolated instead of a $[(allyl)AlMe_3]^-$ unit, eq 3. Evidently

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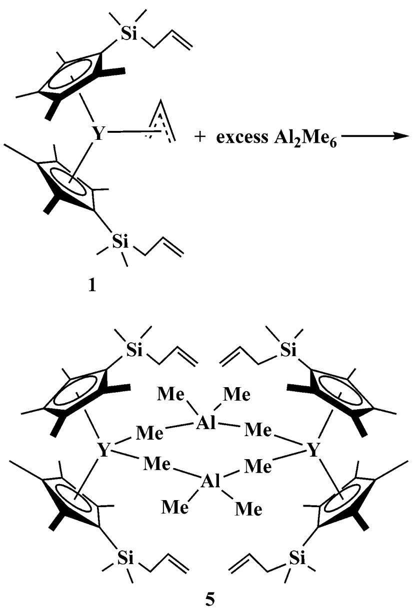
ligand redistribution occurred in which the allyl group was completely removed from yttrium.



(3)

Unlike $[(C_5Me_5)_2Y(\mu\text{-}Me_2AlMe_2)]_2$,[51,52] which exists as a monomer–dimer equilibrium in solution with the monomer form being predominant at 20 °C, the ^{1}H NMR spectrum of **5** shows only one species at room temperature. Two peaks at −0.37 and −0.33 ppm are observed for the $[AlMe_4]^-$ unit, as expected for a ligand containing bridging and nonbridging methyl groups. However, yttrium–proton coupling was not observed since the peaks overlap. The ^{13}C NMR spectrum contains two broad peaks at δ −5.68 and 10.2 ppm, which were assigned to the $[AlMe_4]^-$ unit. The resonances of the internal and terminal alkene carbons of the tethered olefins were found in their usual locations at δ 135.2 and 113.6 ppm.

Structure of $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y[(\mu\text{-}Me_2)AlMe_2]\}_2$, 5. The structure of **5** demonstrates that $[Me_4Al]^-$ ion is a stronger Lewis base for yttrium than the tethered olefins of the $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ ligands. As in **1**, the tethered olefins are oriented away from the yttrium metal ions. In contrast to complex **1**, the rings are oriented in such a way that the tethered alkene on the top ring is on the same side of the molecule as the tethered olefin of the bottom ring. The Y–C(C$_5$Me$_4$R) distances range from 2.650(5) to 2.693(5) Å with a 2.38 Å Y–ring centroid distance.

The structure of **5** is similar to that of the permethyl complexes $\{[(C_5Me_5)_2Ln]_2[(\mu\text{-}Me_2)AlMe_2]\}_2$ (Ln = Sm,[20] Y[52]). In each of these complexes, the $[AlMe_4]^-$ ligand coordinates in a $(\mu\text{-}Me_2)AlMe_2$ fashion, forming a tetrametallic eight-membered ring. The Y(1)–C(29)–Al(1) and Y(1′)–C(30)–Al(1) angles are almost linear, 176.7(3)° and 174.2(3)°, as found in $\{[(C_5Me_5)_2Ln]_2[(\mu\text{-}Me_2)AlMe_2]\}_2$: Ln = Sm, 177.8(7)° and 175.2(9)°[20] and Ln = Y, 177(1)° and 176(1)°.[52] The data for **5** were of high enough quality that the hydrogens on the $[Me_4Al]^-$ unit could be located. The Y–H(AlMe$_4$) distances average 2.60(5) Å.

The five-coordinate carbon atoms of the bridging methyl groups do not adopt a trigonal bipyramidal geometry, as observed in the neutron diffraction study of $[Nd(AlMe_4)_3]\cdot 0.5Al_2Me_6$[53] and as was predicted on the basis of the ^{1}H NMR spectrum of $\{[(C_5Me_5)_2Y]_2[(\mu\text{-}Me_2)AlMe_2]\}_2$.[52] Instead, the three hydrogen atoms point away from aluminum and toward yttrium. The three hydrogen atoms and Al form a normal tetrahedron around carbon, and the Al–C–H and H–C–H angles range from 102(3)° to 114(3)° and 106(5)° to 121(5)°, respectively. This type of Ln···H$_3$C–M geometry has previously been observed in $[(C_5Me_5)_2LuMe]_2$[54] and $(C_5Me_5)_2YbMeBeC_5Me_5$.[55] It is also found in the neutron diffraction study of LiBMe$_4$.[56]

The Y–C(μ-Me) distances for Y(1)–C(29) and Y(1)–C(30′), 2.702(6) and 2.703(6) Å, are comparable with the analogous Y–C(methyl) distances in $[(C_5Me_5)_2Y(\mu\text{-}Me_2AlMe_2)]_2$, 2.65(2) and 2.67(2) Å. However, the Y–C(Me) distances in **5** are longer than the Y–C(Me) distances of 2.553(10) and 2.537(9) Å found in the methyl-bridged complexes involving less bulky cyclopentadienyl rings, $[(C_5H_5)_2Y(\mu\text{-}Me)]_2$[57] and $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$.[58] All these Y–C($\mu$-Me) lengths are much longer than the nonbridging Y–C distances of 2.468(7), 2.44(2), and 2.427(19) Å in $(C_5Me_5)_2Y[CH(SiMe_3)_2]$,[59] $(C_5Me_5)_2Y(Me)(THF)$,[16] and $Y(CH_2SiMe_3)_3(THF)_3$,[6] respectively.

The Al–C(methyl) distances for the bridging methyls, Al(1)–C(29) and Al(1)–C(30), are 2.043(6) and 2.054(6) Å, slightly longer than the terminal methyls Al(1)–C(31) and Al(1)–C(32), which are 1.988(5) and 1.987(5) Å. The angle formed at Al for the bridging methyls, C(29)–Al(1)–C(30), is constrained slightly to 100.6(3)°, where the angle for the nonbridging methyls, C(31)–Al(1)–C(32), is close to the expected value for tetrahedral aluminum, 111.8(3)°.

Reaction of 1 with Hydrogen. Complex **1** reacts with hydrogen in diethyl ether over a 10 min period to form a colorless product, **6**, whose spectroscopic properties are consistent with $\{[(C_5Me_4)SiMe_2(CH_2CH_2CH_3)]_2Y(OEt)\}_x$. The ^{1}H and ^{13}C NMR spectra clearly indicated the disappearance of the olefinic protons of the $CH_2CH{=}CH_2$ tethered substituent of the cyclopentadienyl ligands and the appearance of new multiplets centered at δ 0.73, 0.99, and 1.29 ppm, which correspond to propyl groups. No resonance with the appropriate yttrium hydride coupling was observed to indicate the presence of an Y–H bond, and the infrared spectrum did not show a peak attributable to a yttrium hydride.[60] Instead, a quartet centered at 4.28 ppm is observed in the ^{1}H NMR spectrum. This was assigned to a $Y{-}O{-}CH_2CH_3$ moiety formed from the cleavage of diethyl ether. The $Y{-}O{-}CH_2CH_3$ peak is also observed at 1.32, but is overlapped by the alkane protons of the cyclo-

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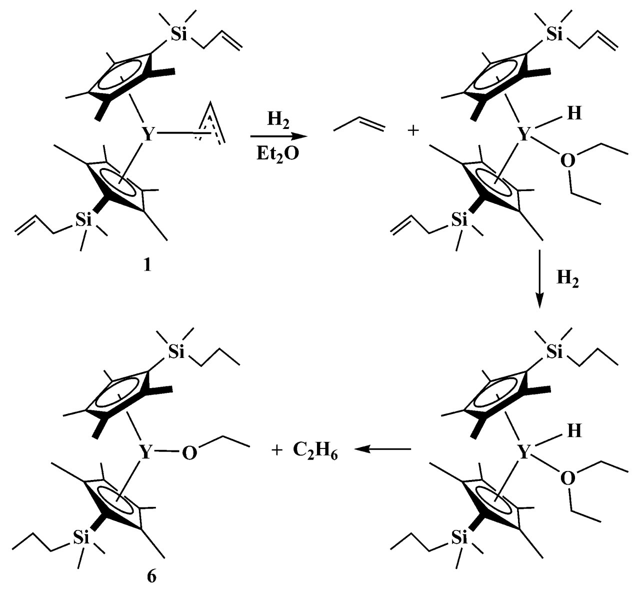
Scheme 3



pentadienyl ligand. Cleavage of Et$_2$O by $[(C_5Me_5)_2LnH]_x$ to form $[(C_5Me_5)_2Ln(OCH_2CH_3)]_x$ has previously been reported for both Y[61] and Lu.[62]

The reaction of **1** with D_2 produces a ^{1}H NMR spectrum similar to that of the hydrogen reaction, but small changes are observed in the alkane region due to the loss of proton−proton coupling. The ethoxide protons were observed at similar positions. By ^{2}H NMR spectroscopy, only two peaks were observed at δ 0.98 and 1.25 ppm that correspond to alkane deuteriums indicative of no detectable H/D scrambling. No Y−^{2}H peak was detected.

A sample of the product of **1** with hydrogen was quenched with D_2O, and the organic product was analyzed. A single peak is observed in the GC/MS trace, which was assigned to the hydrogenated alkane tethered cyclopentadiene, $(C_5Me_4D)SiMe_2(CH_2CH_2CH_3)$, with *m*/*z* of 223. The fragmentation pattern of the $(C_5Me_4D)SiMe_2(CH_2CH_2CH_3)$ contains an ion with a mass of *m*/*z* 101 corresponding to $[SiMe_2(CH_2CH_2CH_3)]^+$, consistent with hydrogenation of the tethered olefin.

On the basis of these data, it appears that **1** reacts with hydrogen to form a hydride, which hydrogenates the tethered alkanes and then reacts with diethyl ether to form an ethoxide product, Scheme 3. This is reasonable since lanthanide allyls are known to react with hydrogen to form hydrides,[9] and yttrium hydrides are known to react with cyclopentadienyl ring substituents[18,63] and to activate C−O bonds.[18,19,61−64] For example, it has been reported that addition of Et$_2$O to $[(C_5Me_5)_2YH]_2$ in C_6D_6 leads first to an H/D exchange with the solvent, C_6D_6, to form a yttrium deuteride, which makes an ether adduct, $(C_5Me_5)_2YD(Et_2O)$. After 20 min, the ether adduct is completely converted to the alkoxide product $(C_5Me_5)_2Y(OEt)$.[61] A similar reaction sequence appears to occur with **1**, Scheme 3, except that after the initial hydrogenolysis to form a yttrium hydride the tethered olefins undergo hydrogenation to form a new yttrium hydride complex containing tethered alkanes rather than olefins. This compound then goes on to cleave diethyl ether.

Discussion

Attachment of two olefin-tethered cyclopentadienyl ligands, $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$, to yttrium generates metallocene chloride and allyl complexes that, in contrast to their $(C_5Me_5)^-$ analogues, do not readily form alkali metal halide or THF adducts. The difference in the chemistry of this ligand versus $(C_5Me_5)^-$ and $[Me_2Si(C_5Me_4)_2]^{2-}$ could be attributable to the tethered olefins, but no structural or spectroscopic evidence for olefin coordination to the metal in $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2YCl$ or $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$ was observed at room temperature. However, low-temperature NMR studies of the fluxionality of the allyl ligand are consistent with interaction of the tethered alkenes in **1** with the metal such that η^3-C_3H_5 to η^1-C_3H_5 interconversions are affected.

Examination of the reactivity of $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$ in reactions typically found in olefin polymerization systems shows that the main type of involvement of the tethered olefin is in hydrogenation. In no case was a complex isolated in which the olefin had inserted into a yttrium−carbon bond. The tethered olefins do not prevent complex **1** from being a good initiator for the polymerization of ethylene. Even in reactions with the Lewis acid activator, Al_2Me_6, which involved yttrium−carbon bond breaking and bond making to form $\{[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y[(\mu\text{-}Me_2)AlMe_2]\}_2$, no olefin incorporation was observed.

However, in the presence of hydrogen, the tethered olefins appear to be rapidly hydrogenated. Deuterium labeling studies show that this tethered olefin hydrogenation occurs before subsequent reaction with the solvent. This implies that insertion of the tethered olefin into an Y−H bond is facile, as is hydrogenolysis of the resulting alkyl. If the insertion of the tethered olefin into the Y−H bond occurs during olefin polymerization (with Y−H bonds formed by β-hydrogen elimination from the growing polymer chains), the resulting intermediate is also capable of polymerizing ethylene.

Conclusion

Attachment of the $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]^-$ ligand to yttrium and subsequent formation of the metallocene allyl derivative, $[(C_5Me_4)SiMe_2(CH_2CH{=}CH_2)]_2Y(C_3H_5)$, **1**, shows that the tethered olefin ligands can influence the chemistry of this system compared to the analogous $(C_5Me_5)^-$ complex. These ligands foster the isolation of solvate-free complexes compared to $(C_5Me_5)^-$ analogues and are readily hydrogenated in the presence of hydrogen. The fact that hydrogenation of the tethered olefins by in situ generation of an yttrium hydride occurs before the reaction with diethyl ether suggests that under similar conditions hydrogenation of olefin functionalities held close to polymerization catalyst centers may be preferred over reactions with incoming substrates.

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Supporting Information Available: ^{1}H NMR spectra of **3**–**6** as well as atomic coordinates, thermal parameters, and complete bond distances and angles; listing of observed and calculated structure factor amplitudes for compounds **1**, **3**, **4**, and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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