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Ancillary Ligand Effects on Organo-f-Element Reactivity. *ansa*-Metallocenes with Bridge-Tethered Donors

Peter W. Roesky, Charlotte L. Stern, and Tobin J. Marks*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

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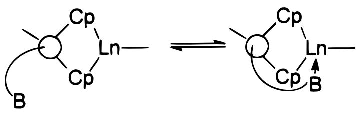
The synthesis and reactivity of *ansa*-metallocenes based upon the new ligand system $R(Me)SiCp''_2{}^{2-}$ ($Cp'' = C_5Me_4$ and $R = (CH_2)_nOMe$, $n = 3-5$) is reported. The tethered donor functionality, which is appended via varying chain lengths to the silicon bridge, is introduced to examine possible intramolecular reactivity modifications. The key step of the ligand synthesis is the hydrosilylative fusion of the donor functionality R to the silicon center. The complexes $[R(Me)SiCp''_2]LnCH(SiMe_3)_2$ (Ln = Y, Sm) were synthesized to investigate the influence of the tethered ether group on the reactivity and catalytic properties. Catalytic reactions in which the substrate is a relatively weak donor, such as in olefin hydrogenation, exhibit depressed turnover frequencies, presumably reflecting competition between the substrate and donor functionality for the empty coordination site at the metal center. In contrast, for amino−alkene hydroamination/cyclization in which a strong amine donor is the substrate, catalytic activity is significantly enhanced while diastereoselectivity is essentially unchanged. The molecular structure of the precatalyst $[MeO(CH_2)_5(Me)SiCp''_2]$-$YCH(SiMe_3)_2$ has been determined by X-ray diffraction.

Introduction

Added Lewis bases can have significant yet poorly understood effects on stoichiometric and catalytic organo-f-element reactivity patterns. Thus, while added THF accelerates both organoyttrium-catalyzed diene cyclization/silylation[1] and $(Me_5Cp)_2Th(OR)$-R' metal−carbon sigma bond hydrogenolysis processes versus rates in hydrocarbon solvents,[2] it depresses the rates of organolanthanide-mediated amino−alkene hydroamination/cyclization (while simultaneously eroding diastereoselectivity)[3] and alkene hydrogenation.[4] To better understand such Lewis base effects and to develop the means, intramolecularly, to precisely position groups of selected basicity within the metallocene "wedge"/reaction zone (for kinetic, mechanistic, and stereochemical purposes), we have begun to study the properties of *ansa*-metallocenes with Lewis base functionalities tethered to the *ansa* bridge linking group (eq 1, Cp = cyclopentadienyl-type ligand).[5] In this contribution, we



report on the design, synthesis, and implementation of the new ligand system $R(Me)SiCp''_2{}^{2-}$ (**1**), where R = $-(CH_2)_nOMe$ in organolanthanide *ansa*-metallocene chemistry.[6] This includes initial observations on the

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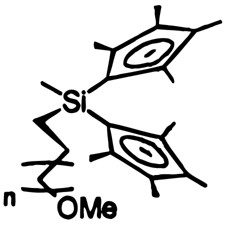

effects of the tethered base on several homogeneous catalytic transformations.

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line or interfaced to a high-vacuum (10^{-5} Torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a high-capacity recirculator (≤1 ppm O_2). Argon (Matheson, prepurified) and dihydrogen (Linde) were purified by passage through MnO/SiO_2 oxygen-removal columns[7] and Davison 4A molecular sieve columns. Ether solvents (tetrahydrofuran, diethyl ether, and 1,2-dimethoxyethane) were pre-

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dried over KOH and distilled under nitrogen from sodium benzophenone ketyl. Hydrocarbon solvents (toluene, pentane, and heptane) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored *in vacuo* over Na/K alloy in resealable bulbs. Deuterated solvents were obtained from Cambridge Isotope Laboratories (all 99 atom % D) and were degassed, dried, and stored *in vacuo* over Na/K alloy in resealable bulbs. $K[CH(SiMe_3)_2]$,[8] $Na(C_5Me_4H)$ $(NaCp'')$,[9] $Me_2SiCp''_2Li_2$,[9] allylmethyl ether,[10] and 4-pentenyl-1-methyl ether,[11] 2-methyl-1-aminopent-4-ene,[12] and 2-aminohex-5-ene[13] were prepared by literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded on either a Varian Gemini 300 or a Varian VXR 300 (FT, 300 MHz, ^1H; 75 MHz, ^{13}C) instrument. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. NMR experiments on air-sensitive samples were conducted in Teflon-valve-sealed tubes (J. Young). Analytical gas chromatography was performed on a Varian model 3700 gas chromatograph with FID detectors and a Hewlett-Packard 3390A digital recorder/integrator using a 0.125 in. i.d. column with 3.8% w/w SE-30 liquid phase on Chromosorb W support. Elemental analyses were performed by Oneida Research Service, Inc., Whitesboro, NY.

General Synthesis of Dichloro(methoxyalkyl)methylsilanes. To 94 mmol of 3-methoxy-1-alkene was added 20 mg of H_2PtCl_6. At 0 °C, 94 mmol of dichloromethylsilane was added dropwise to the stirring solution. The mixture was carefully warmed to room temperature and then heated at reflux overnight. The color of the reaction mixture changed from light yellow to deep red during the course of reaction. Finally, the volatile components were removed from the reaction mixture at 30 Torr. The liquid which remained was then purified by vacuum distillation.

Dichloro(3-methoxy-1-propyl)methylsilane. Bp: 74 °C/29 Torr. Yield: 2.77 g (16%). ^1H NMR (300 MHz $CDCl_3$, 25 °C): δ 3.39 (t, 2H, $^3J(H,H) = 6.3$ Hz, CH_2O), 3.33 (s, 3H, CH_3O), 1.81−1.72 (m, 2H, CH_2CH_2O), 1.20−1.45 (m, 2H, $SiCH_2$), 0.76 (s, 3H, $SiCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 73.7 (CH_2O), 58.4 (CH_3O), 22.7 (CH_2CH_2O), 18.2 (CH_2Si), 5.2 (CH_3Si).

Dichloro(5-methoxy-1-pentyl)methylsilane. Bp: 89 °C/19 Torr. Yield: 2.2 g (10%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.38 (t, 2H, $^3J(H,H) = 6.6$ Hz, CH_2O), 3.33 (s, 3H, CH_3O), 1.65−1.37 (m, 6H, $(CH_2)_3CH_2O$), 1.14−1.09 (m, 2H, $SiCH_2$), 0.77 (s, 3H, $SiCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 72.5 (CH_2O), 58.5 (CH_3O), 29.0 (CH_2CH_2O), 28.9 ($CH_2CH_2CH_2O$), 22.3 (CH_2CH_2Si), 21.5 (CH_2Si), 5.1 (CH_3Si).

General Synthesis of Dilithium Bis(1,2,3,4-tetramethylcyclopentadienyl)(methoxyalkyl)]methylsilanes (1). To a solution of 21.5 mmol of NaCp″ in 30 mL of THF at −78 °C was slowly added with stirring 9.7 mmol of the corresponding dichloro(methoxyalkyl)methylsilane dissolved in 25 mL of THF. The mixture was then warmed to room temperature and finally refluxed overnight. Next, the solvent was removed *in vacuo*, and the residue was extracted with pentane (3 × 25 mL). The extracts were combined, and the solvent was removed *in vacuo*. A yellow oil remained which was dissolved in THF and cooled to −78 °C. Next, 25 mmol of *n*-BuLi in hexane was added with stirring. The mixture was then warmed to room temperature and stirred for 24 h. During this time, the color of the solution changed from yellow to orange. Next, the solvent was removed *in vacuo*, and the remaining solid was stirred in pentane for 1 day. The pentane was filtered off, and the white residue was washed with pentane (4 × 20 mL) and dried *in vacuo*.

Dilithium Bis(2,3,4,5-tetramethylcyclopentadienyl)(3-methoxy-1-propyl)methylsilane (1a). Yield: 66%. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 3.28 (t, 2H, $^3J(H,H) = 7.1$ Hz, CH_2O), 3.19 (s, 3H, CH_3O), 2.05 (s, 12H, CH_3Cp''), 1.91 (s, 12H, CH_3Cp''), 1.61−1.50 (m, 2H, CH_2CH_2O), 1.04−0.95 (m, 2H, $SiCH_2$), 0.42 (s, 3H, $SiCH_3$). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 116.7 (Cp″), 111.0 (Cp″), 104.5 (Cp″), 77.9 (CH_2O), 58.3 (CH_3O), 26.3 (CH_2CH_2O), 17.0 (CH_2Si), 14.7 (CH_3Cp''), 11.6 (CH_3Cp'), 3.9 (CH_3Si).

Dilithium Bis(2,3,4,5-tetramethylcyclopentadienyl)(5-methoxy-1-pentyl)methylsilane (1b). Yield: 80%. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 3.25 (t, 2H, $^3J(H,H) = 6.45$ Hz, CH_2O), 3.20 (s, 3H, CH_3O), 2.04 (s, 12H, CH_3Cp''), 1.90 (s, 12H, CH_3Cp''), 1.61−1.50 (m, 2H, CH_2CH_2O), 1.40−1.25 (m, 4H, $(CH_2)_2CH_2CH_2O$), 1.06−0.98 (m, 2H, $SiCH_2$), 0.42 (s, 3H, $SiCH_3$). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 116.6 (Cp″), 110.9 (Cp″), 104.8 (Cp″), 73.9 (CH_2O), 58.5 (CH_3O), 31.9 (CH_2CH_2O), 30.6 ($CH_2CH_2CH_2O$), 26.0 (CH_2CH_2Si), 21.7 (CH_2Si), 14.7 (CH_3Cp''), 11.7 (CH_3Cp''), 4.1 (CH_3Si).

General Synthesis of $[MeO(CH_2)_n(Me)Si(\eta^5\text{-}C_5Me_4)_2]Ln(\mu\text{-}Cl)_2Li(OEt_2)$ Complexes (2). Onto a mixture of $LnCl_3$ and **1** at −78 °C was condensed 20 mL of THF. The mixture was then stirred for 18 h at room temperature. The solvent was evaporated *in vacuo*, and ether was condensed onto the mixture. This procedure was repeated twice. Finally, the solution was filtered, concentrated, and cooled to −78 °C to afford crystalline product. Additional crystalline product could be recovered by repeatedly concentrating and cooling the mother liquor.

$[MeO(CH_2)_3(Me)Si(\eta^5\text{-}C_5Me_4)_2]Y(\mu\text{-}Cl)_2Li(OEt_2)$ (2a). Yield: 52%. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 3.44−3.35 (m, 6H, Et_2O, CH_2O), 3.28 (s, 3H, CH_3O), 1.99 (s, 6H, CH_3Cp''), 1.98 (s, 6H, CH_3Cp''), 1.87 (s, 12H, CH_3Cp''), 1.80−1.70 (m, 2H, CH_2CH_2O), 1.38−1.32 (m, 2H, $SiCH_2$), 1.12 (t, 6H, Et_2O), 0.82 (s, 3H, $SiCH_3$). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 125.3 (Cp″), 125.2 (Cp′), 120.7 (Cp″), 120.1 (Cp′), 100.3 (Cp′), 76.7 (CH_2O), 66.3 (Et_2O), 58.4 (CH_3O), 25.9 (CH_2CH_2O), 16.4 (CH_2Si), 15.7 (Et_2O), 15.0 (CH_3Cp'), 12.3 (CH_3Cp''), 2.1 (CH_3Si). Anal. Calcd for $C_{27}H_{46}Cl_2LiO_2SiY$: C, 54.28; H, 7.75. Found: C, 54.84; H, 8.03.

$[MeO(CH_2)_5(Me)Si(\eta^5\text{-}C_5Me_4)_2]Y(\mu\text{-}Cl)_2Li(OEt_2)$ (2b). Yield: 81%. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 3.38 (q, 4H, Et_2O), 3.33 (t, 2H, $^3J(H,H) = 4.77$ Hz, CH_2O), 3.24 (s, 3H, CH_3O), 2.00 (s, 12H, CH_3Cp''), 1.86 (s, 12H, CH_3Cp''), 1.68−1.48 (m, 6H, $(CH_2)_3CH_2O$), 1.12 (t, 6H, Et_2O), 1.06−0.98 (m, 2H, $SiCH_2$), 0.81 (s, 3H, $SiCH_3$). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 125.2 (Cp″), 125.1 (Cp′), 120.6 (Cp″), 120.0 (Cp″), 100.4 (Cp″), 73.5 (CH_2O), 66.3 (Et_2O), 58.5 (CH_3O), 31.5 (CH_2CH_2O), 30.6 ($CH_2CH_2CH_2O$), 25.8 (CH_2CH_2Si), 20.6 (CH_2Si), 15.7 (Et_2O), 15.0 (CH_3Cp''), 12.3 (CH_3Cp''), 2.1 (CH_3Si).

$[MeO(CH_2)_3(Me)Si(\eta^5\text{-}C_5Me_4)_2]Sm(\mu\text{-}Cl)_2Li(OEt_2)$ (2c). Yield: 36%. ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 3.43−3.37 (m, 6H, Et_2O, CH_2O), 3.27 (s, 3H, CH_3O), 2.55 (s, 6H, CH_3Cp''), 2.51 (s, 6H, CH_3Cp''), 2.20−2.10 (m, 2H, CH_2CH_2O), 1.25−1.16 (m, 2H, $SiCH_2$), 1.12 (t, 6H, Et_2O), 0.74 (s, 3H, $SiCH_3$), −0.73 (s, 12H, CH_3Cp''). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ 124.6 (Cp′), 124.5 (Cp″), 116.3 (Cp″), 115.7 (Cp″), 90.2 (Cp″), 76.7 (CH_2O), 66.3 (Et_2O), 58.4 (CH_3O), 25.8 (CH_2CH_2O), 19.0 (CH_3Cp''), 19.0 (CH_3Cp''), 18.6 (CH_2Si), 17.5 (CH_3Cp''), 17.5 (CH_3Cp''), 15.7 (Et_2O), 4.4 (CH_3Si).

$[MeO(CH_2)_5(Me)Si(\eta^5\text{-}C_5Me_4)_2]Sm(\mu\text{-}Cl)_2Li(OEt_2)$ (2d). This compound could not be obtained in analytically pure form. Therefore, the crude product was used without further purification as the starting material for the synthesis of hydrocarbyl **3d**, which could be obtained analytically pure.

General Synthesis of $[(MeO(CH_2)_n)MeSi(\eta^5\text{-}C_5Me_4)_2]LnCH(SiMe_3)_2$ Complexes (3). Onto an equimolar mixture of $KCH[Si(Me)_3)]_2$ and **2** was condensed at −78 °C 20 mL of toluene. The mixture was then stirred for 18 h at room temperature. The solvent was evaporated *in vacuo*, and

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pentane was condensed onto the mixture. Finally, the solution was filtered, concentrated, and slowly cooled to −78 °C to yield crystalline product. Additional crystalline product could be obtained by repeatedly concentrating and cooling the mother liquor.

[MeO(CH$_2$)$_3$(Me)Si(η^5-C$_5$Me$_4$)$_2$]YCH(SiMe$_3$)$_2$ (3a). Yield: 53%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 3.40 (t, 2H, ^3J(H,H) = 6.10 Hz, CH_2O), 3.20 (s, 3H, CH_3O), 2.08 (s, 3H, CH_3Cp″), 2.00 (s, 3H, CH_3Cp″), 1.95 (s, 6H, CH_3Cp″), 1.94 (s, 6H, CH_3Cp″), 1.86 (s, 3H, CH_3Cp″), 1.85 (s, 3H, CH_3Cp″), 1.79−1.70 (m, 2H, CH_2CH$_2$O), 1.65−1.55 (m, 2H, SiCH_2), 0.97 (s, 3H, SiCH_3), 0.08 (s, 18H, Si(CH_3)$_3$),−0.54 (d, 1H, ^2J(Y,H) = 1.71 Hz, YC*H*Si). ^{13}C NMR (75 MHz, toluene-d_8, 25 °C): δ 127.1 (Cp″), 126.3 (Cp″), 122.5 (Cp″), 122.1 (Cp″), 107.4 (Cp″), 105.4 (Cp″), 75.4 (*C*H$_2$O), 58.0 (*C*H$_3$O), 27.7 (d, ^1J(Y,C) = 31.5 Hz, Y*C*HSi), 24.18 (*C*H$_2$CH$_2$O), 20.8 (*C*H$_2$Si), 15.1 (*C*H$_3$Cp″), 14.1 (*C*H$_3$Cp″), 14.1 (*C*H$_3$Cp″), 12.5 (*C*H$_3$Cp″), 11.9 (*C*H$_3$Cp″), 11.6 (*C*H$_3$Cp″), 11.9 (*C*H$_3$Cp″), 3.7 (Si(*C*H$_3$)$_3$), 3.6 (Si(*C*H$_3$)$_3$), 0.9 (*C*H$_3$Si). Anal. Calcd for $C_{30}H_{55}OSi_3Y$: C, 59.57; H, 9.16. Found: C, 58.98; H, 9.54.

[MeO(CH$_2$)$_5$(Me)Si(η^5-C$_5$Me$_4$)$_2$]YCH(SiMe$_3$)$_2$ (3b). Yield: 66%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): 3.27 (t, 2H, ^3J(H,H) = 4.77 Hz, CH_2O), 3.15 (s, 3H, CH_3O), 1.98 (s, 3H, CH_3Cp″), 1.97 (s, 3H, CH_3Cp″), 1.97 (s, 6H, CH_3Cp″), 1.96 (s, 6H, CH_3Cp″), 1.86 (s, 6H, CH_3Cp″), 1.70−1.59 (m, 6H, (CH_2)$_3$-CH$_2$O), 1.57−1.48 (m, 2H, SiCH_2), 0.99 (s, 3H, SiCH_3), 0.09 (s, 9H, Si(CH_3)$_3$), 0.08 (s, 9H, Si(CH_3)$_3$), −0.53 (d, 1H, ^2J(Y,H) = 1.8 Hz), YC*H*Si). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 127.1 (Cp″), 127.0 (Cp″), 126.6 (Cp″), 126.6 (Cp″), 122.8 (Cp″), 122.6 (Cp″), 122.2 (Cp″), 122.3 (Cp″), 107.8 (Cp″), 105.8 (Cp″), 72.9 (*C*H$_2$O), 58.3 (*C*H$_3$O), 30.8 (*C*H$_2$CH$_2$O), 30.0 (*C*H$_2$CH$_2$CH$_2$O), 27.7 (d, ^{1}J(Y,C) = 30.7 Hz, Y*C*HSi), 23.9 (*C*H$_2$CH$_2$Si), 19.3 (*C*H$_2$Si), 14.5 (*C*H$_3$Cp″), 14.3 (*C*H$_3$Cp″), 12.8 (*C*H$_3$Cp″), 12.2 (*C*H$_3$Cp″), 12.0 (*C*H$_3$Cp″), 11.6 (*C*H$_3$Cp″), 11.3 (*C*H$_3$Cp″), 11.0 (*C*H$_3$Cp″), 4.0 (Si(*C*H$_3$)$_3$), 3.9 (Si(*C*H$_3$)$_3$), 1.3 (*C*H$_3$Si). Anal. Calcd for $C_{32}H_{59}OSi_3Y$: C, 60.72; H, 9.39. Found: C, 61.30; H, 9.30.

[MeO(CH$_2$)$_3$(Me)Si(η^5-C$_5$Me$_4$)$_2$]SmCH(SiMe$_3$)$_2$ (3c). Yield: 27%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 20.6 (br, 1H, SmC*H*Si), 3.97 (t, 2H, ^3J(H,H) = 5.88 Hz, CH_2O), 3.90−3.75 (m, 2H, CH_2CH$_2$O), 3.38 (s, 3H, CH_3O), 3.03 −2.99 (m, 2H, SiCH_2), 2.55 (s, 3H, SiCH_3), 2.54 (s, 3H, CH_3Cp″), 2.49 (s, 3H, CH_3Cp′), 2.44 (s, 3H, CH_3Cp″), 2.40 (s, 3H, CH_3Cp″), −3.96 (s, 3H, CH_3Cp″), −3.99 (s, 3H, CH_3Cp″), −4.25 (s, 3H, CH_3-Cp″), −4.29 (s, 3H, CH_3Cp″), −5.40 (s, 9H, Si(CH_3)$_3$), −5.50 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 136.3 (Cp′), 136.0 (Cp″), 129.4 (Cp″), 129.2 (Cp″), 126.9 (Cp″), 126.6 (Cp″), 119.6 (Cp″), 118.7 (Cp″), 117.9 (Cp″), 117.2 (Cp″), 76.3 (*C*H$_2$O), 58.0 (*C*H$_3$O), 25.4 (*C*H$_2$CH$_2$O), 22.9 (*C*H$_3$Cp″), 22.8 (*C*H$_3$Cp″), 22.4 (*C*H$_3$Cp″), 22.3 (*C*H$_3$Cp″), 20.8 (*C*H$_2$Si), 16.8 (*C*H$_3$Cp″), 16.7 (*C*H$_3$Cp″), 16.5 (*C*H$_3$Cp″), 16.4 (*C*H$_3$Cp″), 6.7 (*C*H$_3$Si), −4.7 (Si(*C*H$_3$)$_3$), −5.0 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{30}H_{55}OSi_3Sm$: C, 54.07; H, 8.32. Found: C, 53.87; H, 8.19.

[MeO(CH$_2$)$_5$(Me)Si(η^5-C$_5$Me$_4$)$_2$]SmCH(SiMe$_3$)$_2$ (3d). Yield: 23%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 20.7 (br, 1H, SmC*H*Si), 3.53 (t, 2H, CH_2O), 3.26 (s, 3H, CH_3O), 3.13 (m, 2H, CH_2CH$_2$O), 3.93−2.90 (m, 2H, SiCH_2), 2.58 (s, 3H, SiCH_3), 2.55 (s, 3H, CH_3Cp″), 2.51 (s, 3H, CH_3Cp″), 2.44 (s, 3H, CH_3Cp″), 2.42 (s, 3H, CH_3Cp″), 2.20−1.80 (m, 6H, (CH_2)$_3$CH$_2$O), −3.93 (s, 3H, CH_3Cp″), −4.02 (s, 3H, CH_3Cp″), −4.22 (s, 3H, CH_3-Cp″), −4.32 (s, 3H, CH_3Cp″), −5.35 (s, 9H, Si(CH_3)$_3$), −5.53 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 136.3 (Cp″), 136.1 (Cp″), 135.6 (Cp″), 133.7 (Cp″), 133.3 (Cp″), 129.4 (Cp″), 119.8 (Cp″), 118.9 (Cp″), 118.1 (Cp″), 117.2 (Cp″), 73.1 (*C*H$_2$O), 58.5 (*C*H$_3$O), 31.5 (*C*H$_2$CH$_2$O), 30.5 (*C*H$_2$CH$_2$CH$_2$O), 25.0 (*C*H$_2$CH$_2$O), 24.7 (*C*H$_3$Cp′), 24.4 (*C*H$_3$Cp″), 22.9 (*C*H$_3$Cp″), 22.7 (*C*H$_3$Cp″), 22.3 (*C*H$_2$Si), 15.1 (*C*H$_3$Cp″), 15.0 (*C*H$_3$Cp″), 14.3 (*C*H$_3$Cp″), 14.2 (*C*H$_3$Cp″), 6.8 (*C*H$_3$Si), −4.7 (Si(*C*H$_3$)$_3$), −5.0 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{32}H_{59}OSi_3Sm$: C, 55.35; H, 8.56. Found: C, 55.38; H, 8.39.

[Me$_2$Si(η^5-C$_5$Me$_4$)$_2$]YCH(SiMe$_3$)$_2$ (4). Onto a mixture of 613 mg (2.86 mmol) of YCl_3 and 892 mg (3.04 mmol) of Me$_2$SiCp″$_2$Li$_2$ at −78 °C was condensed 20 mL of THF. The mixture was then stirred for 18 h at room temperature. The solvent was evaporated *in vacuo*, and ether was condensed onto the residue. This procedure was repeated twice. Finally, the solution was filtered and the solvent removed. To the residue was added 216 mg (1.30 mmol) of LiCH[Si(Me)$_3$)]$_2$, and then 20 mL of toluene was condensed in at −78 °C. The mixture was stirred for 18 h at room temperature. The solvent was evaporated *in vacuo*, and pentane was condensed onto the residue. The solution was then filtered, concentrated, and slowly cooled to −78 °C to afford crystalline product. Repeated concentration and cooling of the mother liquor afforded additional crystalline product. Yield: 430 mg (27%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.95 (s, 12H, CH_3Cp′), 1.94 (s, 6H, CH_3Cp″), 1.85 (s, 6H, CH_3Cp″), 0.91 (s, 6H, SiCH_3), 0.07 (s, 18H, Si(CH_3)$_3$), −0.54 (d, 1H, ^2J(Y,H) = 1.71 Hz, YC*H*Si). Anal. Calcd for $C_{27}H_{49}OSi_3Y$: C, 59.30; H, 9.03. Found: C, 59.26; H, 9.05.

Table 1. Crystallographic Details for [MeO(CH$_2$)$_5$(Me)SiCp″$_2$]YCH[Si(Me)$_3$)]$_2$ (3b)

formula	$C_{32}H_{59}YOSi_3$
fw	632.98
cryst color, habit	colorless, plates
crystal dimens (mm)	0.51 × 0.25 × 0.05
cryst syst	triclinic
a, Å	9.574(4)
b, Å	11.43(2)
c, Å	16.046(9)
α, deg	90.56(8)
β, deg	101.13(4)
γ, deg	95.81(8)
V, Å^3	1713(2)
space group	$P\bar{1}$ (No. 2)
Z	2
d(calcd), g/cm^3	1.227 g/ cm^3
diffractometer	Enraf-Nonius CAD 4
temperature, °C	−120
radiation	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega-\theta$
intensity (unique, R_i)	5373
intensities > 3.00 $\sigma(I)$	2473
R	0.102
R_w for $w = 1/s^2(F_0)$	0.094

X-ray Crystallographic Study of [MeO(CH$_2$)$_5$(Me)Si(η^5-C$_5$Me$_4$)$_2$]YCH(SiMe$_3$)$_2$ (3b). Crystals of $C_{32}H_{59}OSi_3Y$ (**3b**) were grown by slow evaporation of a heptane solution. A suitable crystal was covered in dry, degassed Paratone N oil (Exxon) and mounted on a glass fiber. The crystal was transferred directly to the −120 °C cold stream of an Enraf-Nonius CAD4 diffractometer. Subsequent computations were carried out on a microVax 3600 computer.

Crystal data collection parameters are listed in Table 1. Lattice parameters were determined for 25 angle reflections set in the range 18.0° < 2θ < 29.8°. Systematic absences and successful refinement of the proposed structure showed **3b** to crystallize in the space group $P\bar{1}$ (No. 2). Intensities of 3 standard reflections were measured every 1.5 h of X-ray exposure and showed no significant variations. No decay correction was applied. An analytical absorption correction was applied to **3b,** which resulted in transmission factors ranging from 0.54 to 0.97. The structure was solved by direct methods and expanded using Fourier techniques.[14] The silicon and yttrium atoms were refined anisotropically, while the rest of the non-hydrogen atoms were refined isotropically. Hydrogen atoms were included in fixed positions but not refined, except for those on the restrained C39, C40, O1 atoms. Due to the apparent high thermal motion in the pendant donor chain, the C38, C39, C40, and O1 positions were restrained.

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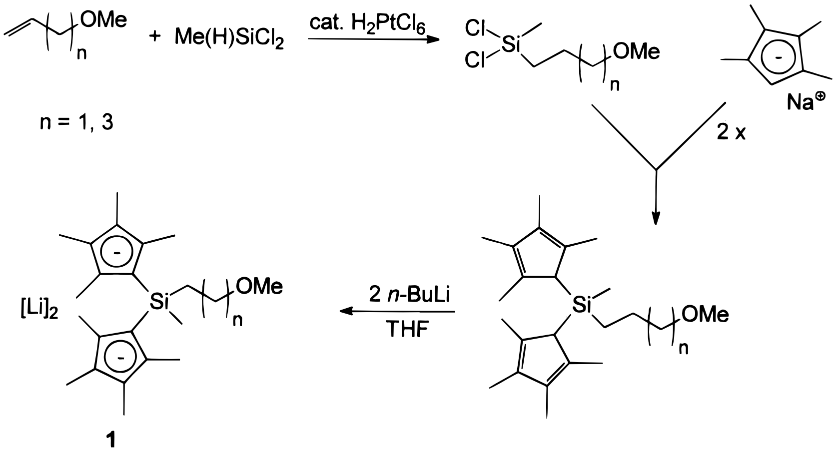
(14) ORIENT: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

Scheme 1



The final cycle of full-matrix least-squares refinement[15] was based on 2473 observed reflections ($I > 3.0\sigma(I)$) and 170 variable parameters and converged (largest parameter shift was 0.07 times its esd) with unweighted and weighted agreement factors of $R = 0.102$ and $R_w = 0.094$. The standard deviation of an observation of unit weight was 3.17. The weighting scheme was based on counting statistics. Plots of $\sum\omega(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks in the final difference Fourier map were 1.57 and −1.26 $e^-/Å^3$, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[16] Anomalous dispersion effects were included in F_{calc};[17] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[18] The values from the mass attenuation coefficients are those of Creagh and Hubble.[19] All calculations were performed using the TEXAN[20] crystallographic software package of Molecular Structure Corp.

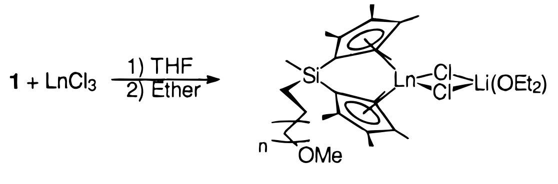
Catalytic Hydrogenation and Hydroamination Experiments. These experiments were performed according to the procedures described in refs 3 and 4.

Results and Discussion

The design and synthesis of ligand system $R(Me)SiCp''_2{}^{2-}$ ($Cp'' = C_5Me_4$ and $R = (CH_2)_nOMe$, $n = 3-5$) as dilithio derivatives (**1**) will be presented first, followed by the synthesis and characterization of lanthanide chloro and hydrocarbyl complexes of this ligand. The structural aspects of the donor side arm disposition in the solid state as well as in solution will be discussed for the hydrocarbyls, which are the precatalysts for olefin hydrogenation and amino−olefin hydroamination/cyclization. Finally, the homogeneous catalytic activity of the new complexes will be compared to that of the analogous but donor-unfunctionalized $Me_2SiCp''_2LnR$ system.

Ligand Design and Synthesis. The length of the hydrocarbon tether necessary for coordination to the lanthanide center was estimated using metrical parameters for several $Me_2SiCp''_2LnR$ complexes[6,8,21] taken from the CSD database[22] and implemented using PLUTO software.[23] Depending upon the assumed details of the coordination configuration, a C_3-C_5 tether length was judged to be optimum. The synthesis of ligand system **1** as dilithio derivatives is shown in Scheme 1. The key step of the synthesis is the attachment of the $MeO(CH_2)_n-$ side chain to the silicon atom. This is achieved by hydrosilyation of the corresponding methyl−alkenyl ether with dichloromethylsilane in the presence of H_2PtCl_6 as the catalyst (Speier reaction). The synthesis is generally applicable to various carbon tether lengths. The resulting silanes, $MeO(CH_2)_nSi(Me)Cl_2$, are then reacted with 2 equiv of NaCp″ to obtain the neutral ligand, which can then be cleanly converted to the dilithium salts of **1** by reaction with an excess of *n*-BuLi.

Organolanthanide Chloro Complexes. Transmetalation of **1** with a slight excess of anhydrous yttrium or samarium trichloride in THF (eq 2), followed by workup in diethyl ether, yields the corresponding lanthanide chloro complexes **2** as pure crystalline solids in reasonable yields. These complexes tend to lose ether rather easily, which may result from substitution of the bound ether by the pendant methoxy group of the side



(2)

	2a	2b	2c	2d
Ln	Y	Y	Sm	Sm
n	1	3	1	3

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[15] DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

[16] Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; The Kynoch Press, Birmingham, England, 1974; Vol. IV, Table 2.2A.

[17] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

[18] Creagh, D. C.; McAuley, W. J. *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 4.2.6.8, p 219.

[19] Creagh, D. C.; Hubbel, J. H. *International Tables for X-ray Crystallography*; Wilson, J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 4.2.6.8., p 200.

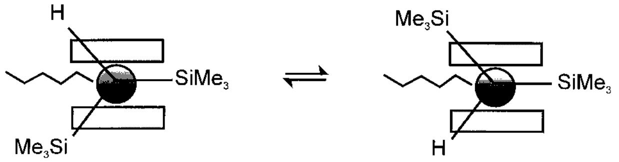
[20] Swepston, P. N. teXsan: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1987, 1992.

[21] (a) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110. (b) Marsh, R. E.; Schaefer, W. P.; Coughlin, E. B.; Bercaw, J. E. *Acta Crystallogr., Sect. C* **1992**, *48*, 1773−1776. (c) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558−9575. (d) Conticello, V. P.; Brard, L.; Giardello, M. A.; Tsuji, Y.; Sabat, M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 2761−2762.

[22] Cambridge Structure Database, Cambridge Crystallographic Data Centre, Cambridge U.K., 1994−1997.

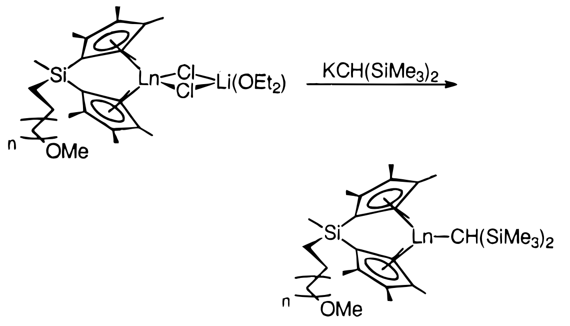
[23] *PLUTO*; Cambridge Crystallographic Data Centre: Cambridge, U.K., 1994−1997.

Scheme 2



arm. In the ^{1}H NMR spectra of complexes **2**, magnetic nonequivalence of the methyl Cp″ Me signals is observed which is doubtless due to the asymmetric substitution of the silicon atom of the *ansa*-metallocene bridge. Nevertheless, the maximum number of four resonances can rarely be resolved at 300 MHz. In contrast, the inequivalence of all five ring carbon Cp resonances is readily observed in the ^{13}C NMR spectra.

Synthesis of Organolanthanide Hydrocarbyls. Alkylation of chloro complexes **2** with 1 equiv of KCH(SiMe$_3$)$_2$ in toluene followed by extraction with pentane affords alkyls **3** (eq 3). Yttrium complexes **3a,b** can be obtained in good yield, whereas the yields of samarium complexes **3c,d** are somewhat lower. Using LiCH(SiMe$_3$)$_2$ instead of the more reactive potassium reagent decreases the yields further. Recrystallization of **3** from pentane affords analytically and spectroscopically pure compounds (see Experimental Section for details).



(3)

	3a	3b	3c	3d
Ln	Y	Y	Sm	Sm
n	1	3	1	3

In regard to the solution phase structures of **3**, the ^{1}H NMR spectra of these complexes exhibit departures from idealized C_s symmetry at room temperature, which are consistent with restricted Ln$-$CH(SiMe$_3$)$_2$ rotation (e.g., Scheme 2; observed previously in Me$_2$Cp″$_2$LnCH(SiMe$_3$)$_2$ complexes[6,21a,24]). Although ^{1}H NMR resolution of eight Cp″ Me signals and two SiMe$_3$ signals is only partial in diamagnetic complexes **3a** and **3b**, the greater chemical shift dispersion in paramagnetic **3c** and **3d** (+20.7 to -5.5 ppm) clearly reveals the lower symmetry. NOE and T_1 NMR experiments were also carried out on complexes **3** in order to probe the proximity of the methoxy group to the lanthanide center. ^{1}H NOEs were first measured for diamgnetic **3a** and **3b** by irradiation of the CH_3O- and the CH_2O resonances as well as the Y$-$CH and the Cp″CH_3 resonances. No obvious CH_3O$-$ and CH_2O intensity enhancements were observed when the Y$-$CH and the Cp″CH_3 resonances were irradiated and vice versa. Since the presence of the oxygen atom in the pendant base side chains may introduce other relaxation mechanisms and consequent ambiguity in the NOE results,[25] spin$-$lattice relaxation time experiments were performed on paramagnetic Sm(III) complex **3c**. Static or transitory Sm···O interactions should result in efficient electron-nuclear dipolar relaxation ($\sim 1/r^6$)[26] of the CH_3O$-$ and $-$CH$_2$O$-$ spin systems. The T_1 results depicted in structure **3c** (in s) indicate an *increase* in T_1 along the pendant chain as the OMe group is approached, suggesting that coordination of the pendant base is negligible in solution in the presence of the sterically encumbered $-$CH(SiMe$_3$)$_2$ group. This result is consistent with solid state diffraction results (see below).

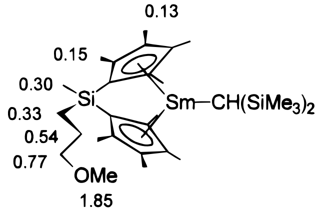
Table 2. Selected Bond Lengths (Å) and Angles (deg) for [MeO(CH$_2$)$_5$(Me)SiCp″$_2$]YCH[Si(Me)$_3$)]$_2$ (3b)[a]

Y−C(1)	2.54(1)	Y−C(14)	2.60(1)
Y−C(2)	2.66(1)	Y−C(19)	2.43(1)
Y−C(3)	2.73(1)	Y−Cg1	2.366(2)
Y−C(4)	2.705(9)	Y−Cg2	2.366(1)
Y−C(5)	2.61(1)	Si(1)−C(1)	1.899(9)
Y−C(10)	2.544(9)	Si(1)−C(10)	1.85(1)
Y−C(11)	2.626(9)	Si(1)−C(34)	1.89(1)
Y−C(12)	2.783(9)	Si(1)−C(35)	1.89(1)
Y−C(13)	2.73(1)		

Cg(1)−Y−Cg2	124.58(6)	Y−C(4)−C(8)	124.5(7)
C1−Si(1)−C(10)	98.2(4)	Y−C(5)−C(9)	118.8(6)
C34−Si(1)−C(35)	105.1(5)	Y−C(11)−C(15)	119.8(6)
Y−C(19)−Si(2)	127.1(6)	Y−C(12)−C(16)	128.2(6)
Y−C(19)−Si(3)	101.6(5)	Y−C(13)−C(17)	124.8(6)
Y−C(2)−C(6)	120.7(7)	Y−C(14)−C(18)	121.4(6)
Y−C(3)−C7	127.0(7)		

[a] Cg = ring centroid.

3c



Attempts to isolate hydrides such as [(MeO(CH$_2$)$_5$)MeSiCp″$_2$YH]$_n$ were not successful. Exposing complex **3** in hexane to 1.0 atm of hydrogen results in the immediate precipitation of an insoluble product. Most probably oligomeric/polymeric species are formed in this reaction.

Molecular Structure of [MeO(CH$_2$)$_5$(Me)SiCp″$_2$]YCH(SiMe$_3$)$_2$ (3b). The molecular structure and side arm disposition in **3** were probed further by single-crystal X-ray diffraction. Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. Although some orientational disorder of the methoxy group limits the precision of the structure determination, significant conclusions can still be drawn with regard to the solid state geometry of **3b**. As seen in Figure 1, there is neither intermolecular nor intramolecular coordination of the methoxy group to the metal center. It is likely that the steric bulk of the $-$CH(SiMe$_3$)$_2$ group hinders such donor$-$metal interactions. While no crystal structure data are available for the comparable molecule Me$_2$-

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(24) Haar, C. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1996**, *15*, 1765−1784.

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(26) (a) Bertini, I.; Luchinat, C. *NMR of Paramagnetic Molecules in Biological Systems*; Benjamin: Menlo Park, CA, 1986; Chapters 2, 3, 10. (b) Fischer, R. D. in ref 6f, Chapter 8.

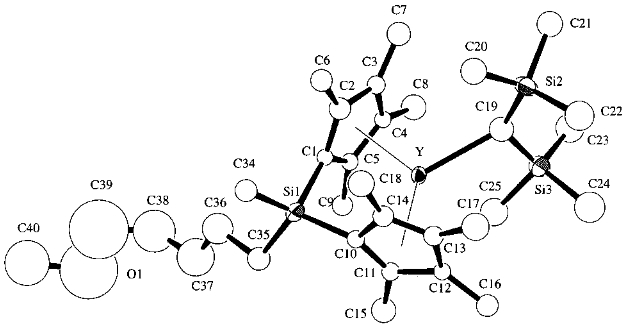
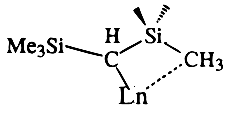


Figure 1. Perspective ORTEP view of the molecular structure of $[MeO(CH_2)_5(Me)Si(C_5Me_4)_2]YCH[Si(Me)_3)]_2$ (**3b**). Thermal ellipsoids are drawn to encompass 50% probability.

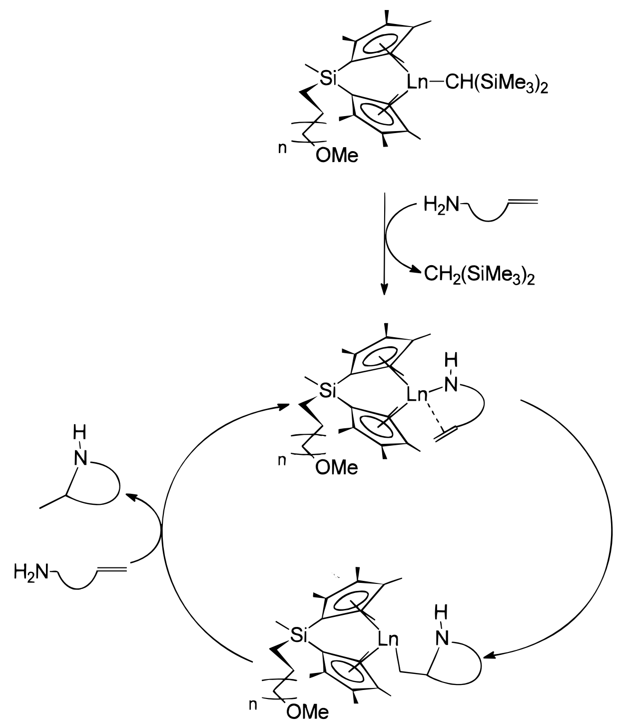
$SiCp''_2YCH(SiMe_3)_2$ (**4**), the present metrical parameters for **3b** (Table 2) exhibit distinct structural similarities to chiral organoyttrium metallocenes such as (*R*)-Me_2SiCp''[(+)neo-menthylCp]$YCH(SiMe_3)_2$ (**5**).[24b] Thus, the Y−$CH(SiMe_3)_2$ coordination in both compounds is similar: the Y−C(σ) distances (2.43(1) Å in **3a** and 2.41(1) Å in **5**, respectively) as well as the Cg1−Y−Cg2 angle (124.58(6)° in **3b** and 123.9° in **5**, respectively). While the C(1)−Si(1)−C(10) angle in **3b** is slightly smaller (by 5.7°) than that in **5**, the −CH($SiMe_3)_2$ ligation in both complexes involves a highly unsymmetrical Y−hydrocarbyl interaction (**A**). This type of $LnLMe_3Si$−C structure has been well-studied both experimentally[6,8,21,24] as well as theoretically;[27] it reflects both the electron richness of the Si−CH_3 fragment as well as the pronounced electrophilicity of the lanthanide center.

A



Homogeneous Catalytic Chemistry. The influence of the tethered Lewis base on lanthanocene catalytic activity and selectivity was probed via comparisons under identical reaction conditions of complex **3b** and $Me_2SiCp''_2YCH(SiMe_3)_2$ (**4**) in two mechanistically well-characterized model processes: 1-hexene hydrogenation[4] and amino−alkene hydroamination/cyclization.[3] Catalytic rate measurements and product characterization procedures were as described previously.[3,4,24]

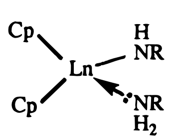
Scheme 3



At 25 °C in toluene solution (100:1 substrate:catalyst ratio; [catalyst] ≈ 1 mM), the turnover frequency (N_t) for **4**-mediated 1-hexene hydrogenation is 11 100 h^{-1}. As discussed previously, 1-hexene insertion into the Ln−H bond in such systems is both exothermic and operationally irreversible, while product-releasing Ln−alkyl hydrogenolysis is turnover-limiting (velocity ≈ $[substrate]^0[Ln]^1[H_2]^1$) with an appreciable k_{H_2}/k_{D_2} kinetic isotope effect. In contrast to the high activity exhibited by complex **4**, under the same conditions, N_t for 1-hexene hydrogenation mediated by base-tethered **3b** is 200 h^{-1}, a decrease in rate by a factor of 55. Although the kinetics for the latter transformation were not characterized in detail, the H_2 uptake plots indicate a rate law which is zero-order in substrate with constant H_2 uptake to ~90% conversion, at which point leveling-off is observed. Within the mechanistic scenario established for lanthanocene-mediated olefin hydrogenation,[3b,4b] the present consequences of the tethered Lewis base appear to be coordination which either competes with olefin activation (the rate law would then tend toward first-order behavior in [olefin], which would be most evident at higher conversions/lower [olefin]), or H_2 activation (blocking the activation site and/or diminishing the electrophilicity of the lanthanide center). These results are consistent with earlier THF effects concerned with $(Me_5C)_2Ln$-catalyzed olefin hydrogenation.[4b] Thus, for $(Me_2SiCp''_2NdH)_2$ + 1-hexene under the same conditions as the present, equimolar THF depresses the hydrogenation N_t by a factor of 16.

The effect of the tethered Lewis base was also examined for **3b**/**4**-mediated amino−olefin hydroamination/cyclization. For typical lanthanocenes, the turnover-limiting step in this process has been identified as intramolecular insertion of the alkenyl functionality into the Ln−amide bond, which is followed by rapid Ln−alkyl protonolysis (Scheme 3).[3c] The resting state of the catalyst is an amine−amido complex (**B**), and catalytic turnover is competitively inhibited by primary alkylamines[3c] and, in some cases, by product.[3b] In the case of substrates such as 2-amino-5-hexene cyclization (eq 4), turnover frequency and diastereoselection are a sensitive function of the lanthanide ionic radius, ancil-

B



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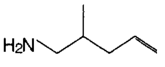
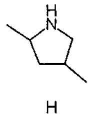
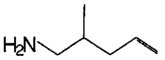
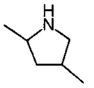
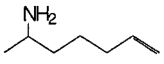
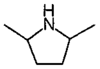
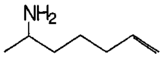
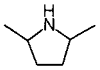
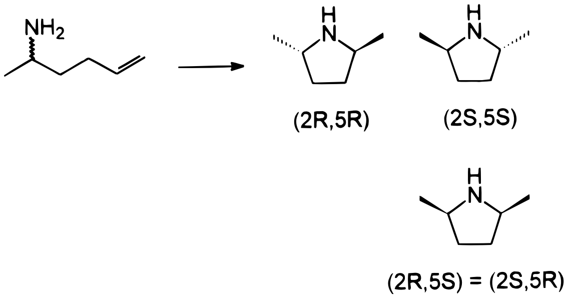
(27) (a) Di Bella, S.; Lanza, G.; Fragala, I. L.; Marks, T. J. *Organometallics* **1996**, *15*, 205−208. (b) Di Bella, S.; Gulino, A.; Lanza, G.; Fragala, I. L.; Stern, D.; Marks, T. J. *Organometallics* **1994**, *13*, 3810−3815. (c) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108−112. (d) Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 3195−3206. (e) Bursten, B. E.; Fang, A. *Inorg. Chim. Acta* **1985**, *110*, 153−160.

Table 3. Catalytic Hydroamination/Cyclization Results

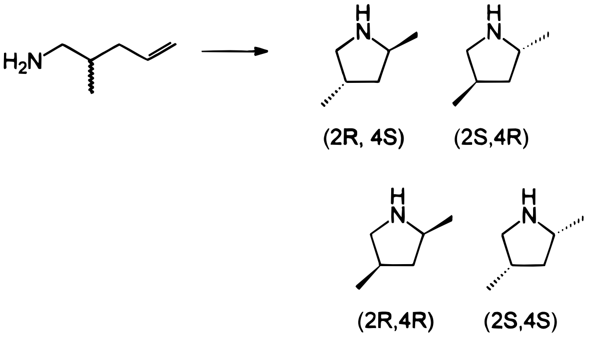
Entry	Substrate	Product	Precatalyst	$N_t(h^{-1})^{a}$	Product isomer ratio
1			**3b**	118	1:1
2			4	24	1:1
3			**3b**	12	1:2
4			4	6.0	1:7

[a] Temperature: 60 °C.

lary ligation, temperature, and medium. For example, at 25 °C in toluene-d_8 $(Me_5Cp)_2Nd$-mediated cyclization affords a 5:1 *trans*:*cis* product which is increased to ≥50:1 in the presence of 3.0 equiv of *n*-propylamine,[3c] increased to ≥100:1 with chiral catalysts,[3b] and decreased to 2:1 in neat THF-d_8.[3c] For the corresponding 2,2-dimethyl-1-aminopent-4-ene cyclization, the turnover frequency in neat THF-d_8 is a factor of 5.3 less than in toluene-d_8. In marked contrast to the selectivity effects observed in the transformation in eq 4, the cyclization of 2-methyl-1-aminopent-4-ene (eq 5) is rather insensitive to ancillary ligation.[3c] In the present study (Table 3), it is found that the tethered Lewis base effects a 2-fold increase in the turnover frequency for eq 4 versus complex **4** and a ~5-fold increase for eq 5 versus complex **4**. Interestingly, however, little influence of the appended ether is exerted on product diastereoselection, with the *trans*:*cis* ratio declining from 1.0:2.0 to 1.0:1.7 for eq 4 and with negligible effect on product composition for eq 5. The mechanism by which the tethered Lewis base functionality enhances the rate of cyclization while marginally affecting diastereoselectivity is not immediately obvious, however an attractive hypothesis is that it intramolecularly stabilizes a polar transition state for olefin insertion (e.g., **C**).

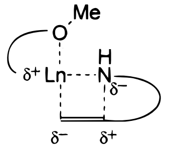


(4)



(5)

C



Conclusions

Lanthanide complexes of the new chelating ligand $[MeO(CH_2)_n(Me)SiCp''_2]^{2-}$ are the first examples of *ansa*-metallocenes with a donor functionality attached to the ligand bridging juncture. The donor functionality has been found to exert a strong influence on the catalytic activity of these complexes. For catalytic conversions of weakly donating substrates, the activity is decreased. Apparently, one or more of the substrates cannot compete with the methoxy group of the ligand for the vacant coordination site on the metal center, resulting in a decreased activity in comparison to unfunctionalized systems. In contrast, catalytic hydroaminations exhibit increased activity. Here, the substrates have a higher Lewis base strength so that the methoxy group apparently does not block the metal center but rather may alter the polarity of the medium in proximity to the metal center.

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Supporting Information Available: Text giving full details of the data collection, data reduction, and structure solution and refinement and tables of experimental details, positional and thermal parameters, bond lengths, bond angles, and torsion angles (33 pages). Ordering information is given on any current masthead page. Further details of the crystal structure investigation are also available from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-406687.

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