Enantiomerically Pure Organolanthanides for Asymmetric Catalysis. Synthesis, Structures, and Catalytic Properties of Complexes Having Pseudo-*meso*-$Me_2Si(\eta^5-C_5H_3R)(\eta^5-C_5H_3R^*)$ Ancillary Ligation

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

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

Received May 27, 1997[⊗]

As established by NMR, circular dichroism, and X-ray diffraction, organolanthanides of the new chelating ligand $Me_2Si(^tBuCp)[(+)$-*neo*-Men-Cp$]^{2-}$ (Men = menthyl; Cp = η^5-C_5H_3) preferentially adopt a single chiral configuration of the asymmetric metal−ligand template. Metallocene dichloro complexes (R,S)-$Me_2Si(^tBuCp)[(+)$-*neo*-Men-Cp$]Ln(\mu-Cl_2)Li(OEt_2)_2$ (Ln = Y, Lu) are synthesized by alkylation of the corresponding lanthanide trichlorides with the ligand dilithium salt and are isolated isomerically pure by crystallization from diethyl ether. Alkylation of the (R,S)-epimers with $MCH(SiMe_3)_2$ (M = Li, K) proceeds with retention of configuration at the lanthanide center, affording chiral hydrocarbyl complexes in high yield. Reaction of the Lu−hydrocarbyl with hydrogen affords diastereomerically pure {(R,S)-$Me_2Si(^tBuCp)[(+)$-*neo*-Men-Cp$]LuH\}_2$, an active catalyst for asymmetric olefin hydrogenation. X-ray diffraction reveals a pseudo-C_2-symmetric dimer with a pseudo-*meso* Cp ring substituent arrangement. The two $Me_2Si(^tBu$-Cp$)[(+)$-*neo*-Men-Cp$]LuH$ fragments are slightly twisted with respect to each other. These hydrocarbyls are effective precatalysts for asymmetric hydrogenation of unfunctionalized olefins. The ee values obtained for deuteration of 1-pentene (up to 63%) are the highest reported to date for this reaction, and in all reactions, the (R)-product enantiomer is favored. These results together with those obtained using other chiral organolanthanides provide better insight into lanthanocene stereochemical preferences and chirality transfer mechanisms.

Introduction

In the recent years, intense research efforts have focused on the synthesis and properties of chiral metallocene catalysts of group 4 metals.[1] In sharp contrast, far less is known about the corresponding chiral metallocenes of the lanthanides,[2] despite the interesting catalytic activity of organolanthanides in a variety of alkene and alkyne transformations including hydrogenation,[3] polymerization,[4] hydroamination,[5] hydrosilylation,[6] hydroboration,[7] and reductive or silylative cyclization of α,ω-dienes.[8]

The first approach to enantiomerically pure organolanthanides for asymmetric catalysis involved the introduction of the $Me_2SiCp''(CpR^*)$ ligand ($Cp'' = \eta^5$-C_5Me_4; R* = (+)-neomenthyl, (−)-menthyl, (+)-phenylmenthyl)[9] (Scheme 1) for the diastereoselective synthesis of C_1-symmetric catalysts capable of effecting moderate to high (up to 96% ee) enantioselectivities in the catalytic hydrogenation[10] and hydrosilylation[6a] of styrenic olefins as well as in the hydroamination/

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

[1] Reviews, see: (a) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *27*, 144−187. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. (c) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (d) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29. (e) Kaminsky, W. *Catal. Today* **1994**, *479*, 1−29.

[2] For recent reviews of organolanthanide chemistry, see: (a) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II* Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, 1995; Vol. 4, pp 11−812, and references therein. (b) Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466−2488. (c) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865−986 and references therein. (d) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283−362 and references therein. (e) Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79−94. (f) Schumann, H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalá, I., Eds.; D. Reidel: Dordrecht, The Netherlands, 1985; Chapter 1. (g) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131−177.

[3] (a) Molander, G. A.; Hoberg, J. O. *J. Org. Chem.* **1992**, *57*, 3266−3268. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111−8118. (c) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401−1403.

[4] (a) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495−2502. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110. (c) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337−339. (d) Watson, P. L.; Roe, D. C *J. Am. Chem. Soc.* **1982**, *104*, 6471−6473.

[5] (a) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295−9306. (b) Li, Y.; Marks, T. J. *Organometallics* **1996**, *15*, 3770−3772. (c) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 707−708. (d) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294. (e) Gagné, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716−1718. (f) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108−4109.

[6] (a) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am Chem. Soc.* **1995**, *117*, 7157−7168. (b) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347−6351. (c) Sakakura, T.; Lautenschlager, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40−41. (d) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564−8566.

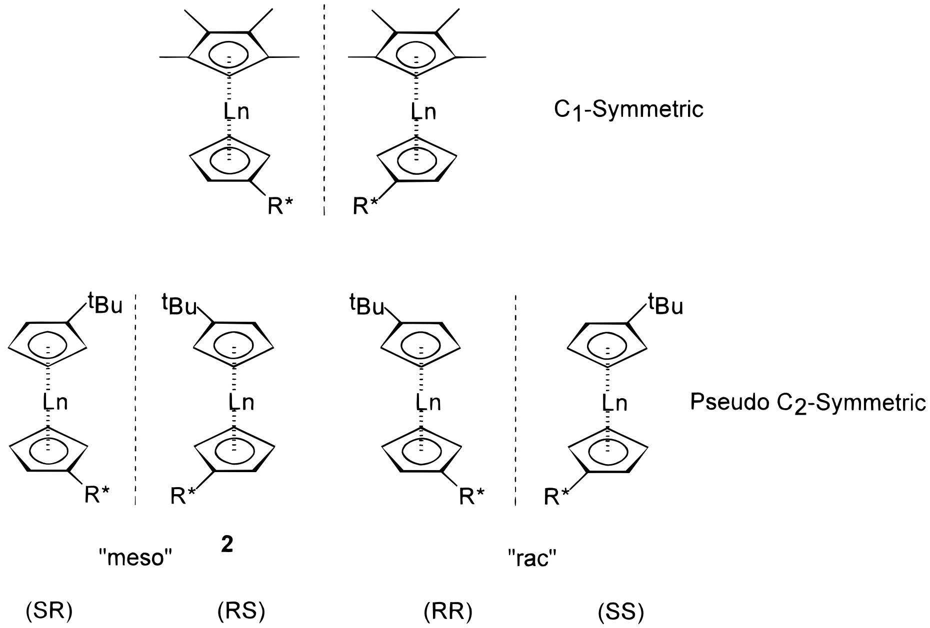
[7] (a) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal.* **1995**, *95*, 121−128. (b) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220−9221.

[8] (a) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415−4416. (b) Molander, G. A.; Hoberg, J. O. *J. Am. Chem. Soc.* **1992**, *114*, 3123−3125.

[9] Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212−10240.

S0276-7333(97)00434-2 CCC: $14.00

Scheme 1



cyclization of a variety of amino−olefins.[10,11] The enantiopure auxiliaries (R*) provide lateral and transverse substrate steric discrimination and ensure that the resulting organolanthanides are diastereomeric, hence potentially separable. Herein, we report on the properties of a second generation of asymmetric organolanthanide catalysts employing a new type of potentially pseudo-C_2-symmetric ligation of the general formula (R,S)-$Me_2Si[(^tBuCp)(R^*Cp)]LnR$ (Ln = Lu, Y; R = $CH(SiMe_3)_2$; R* = (+)-neomenthyl ((+)-*neo*-Men)). These catalysts are obtained selectively as one of the four possible diastereomers shown in Scheme 1. This report describes the synthesis and characterization of such complexes, the crystal structure of the dimeric hydride derivative $\{$(R,S)-$Me_2Si(^tBuCp)$[(+)-*neo*-Men-Cp]LuH$\}_2$, and the use of these complexes as precatalysts for asymmetric olefin hydrogenation.

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, 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[12] and Davison 4A molecular sieve columns. Ether solvents (tetrahydrofuran and diethyl ether) were predried over KOH and distilled under nitrogen from sodium benzophenone ketyl. The 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. Heptane and diethyl ether (Aldrich, HPLC grade) for circular dichroism spectroscopy were degassed, dried over Na/K alloy, and vacuum transferred immediately before sample preparation.

The prochiral olefin 2-phenyl-1-butene (prepared from propiophenone *via* Wittig reaction with (methylene)triphenylphosphorane[13]) and 1-pentene (Aldrich) were degassed, dried over Na/K alloy for 0.5 h, and vacuum transferred prior to use. Styrene (Aldrich, Gold Label) was washed with base, distilled twice from CaH_2, and vacuum transferred from CaH_2 immediately prior to use. Sodium (+)-neomenthylcyclopentadienide (Na[(+)-*neo*-Men-Cp]),[9] $Me_2Si(^tBuCp)Cl$,[14] $Li[CH(SiMe_3)_2]$,[15] and $K[CH(SiMe_3)_2]$[9] 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). Optical rotations were measured at 25 °C with an Optical Activity, Ltd., AA-100 polarimeter (±0.001°) using 0.50 (2-phenylbutane) and 0.10 dm (neat hydrocarbon products) quartz cells. Concentrations reported with the specific rotations are in units of $g \cdot (100\ cm^2)^{-1}$. 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 a 3.8% w/w SE-30 liquid phase on Chromosorb W support. Circular dichroism spectra were recorded on a Jasco J-500 spectrometer equipped with a Jasco DP-500/AT software package (version 1.2). Air-sensitive samples were prepared in 1.00 or 10.0 mm path length cylindrical quartz cuvettes (Hellma Cells) modified with Teflon needle valves. Solvent blanks were recorded under identical conditions, and the base line was subtracted from the experimental spectrum. Molecular ellipticities [θ] are reported relative to absorption maxima

---

[10] Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241−10254.

[11] For complementary approaches to enantiomerically pure C_2-symmetric yttrium and lanthanide complexes, see: (a) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. J.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045−1053. (b) Ihara, E.; Nodono, M.; Yasuda, H.; Kanehisa, N.; Kai, Y. *Macromol. Chem. Phys.* **1996**, *197*, 1909−1917. (c) Kanehisa, N.; Hashimoto, H.; Yamagashira, M.; Kai, Y.; Nodono, M.; Ihara, E.; Yasuda, H. *Abstracts of Papers*, 42nd Symposium on Organometallic Chemistry, Hiroshima, Japan, October 1995; PA 119.

[12] Moeseler, R.; Horvath, B.; Lindenau, D.; Horvath, E. G.; Krauss, H. L. *Z. Naturforsch., B* **1976**, *31B*, 892−893.

[13] (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863−927. (b) Meacker, A. *Org. React.* **1965**, *14*, 270−490.

[14] Okuda, J. *Chem. Ber.* **1989**, *122*, 1075−1077.

[15] Cowley, A. H.; Kemp, R. A. *Synth. React. Inorg. Met.−Org. Chem.* **1981**, *11*, 591−595.

in units of deg·cm^2·dmol^{-1}. Elemental analyses were performed by Oneida Research Service, Inc., Whitesboro, New York.

Hydrogenation/deuteration experiments were performed according to the procedure in ref 16. The products of the catalytic conversions were characterized by ^{1}H NMR and GC/MS.

$Li_2Me_2Si(^tBuCp)$[(+)-*neo*-Men-Cp]THF (1). To a solution of 5.00 g (22.1 mmol) of Na[neomenthylC_5H_4] in 100 mL of THF was added 4.80 g (22.1 mmol) of $Me_2Si(^tBuCp)Cl$. The mixture was stirred overnight. Subsequently, the solvent was evaporated and the residue was extracted with pentane. Next, 28 mL of a 1.6 M (44.2 mmol) ^{n}BuLi solution in hexane was added to the pentane extract. The mixture was stirred overnight, and the solution was then concentrated until it formed a gel. Next, 10 mL of THF was added. A white precipitate formed, which was collected by filtration and washed with pentane, giving **1** as a white solid. Yield: 7.3 g (70%). ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ 6.28 (m, 4H, Cp), 6.15 (m, 2H, Cp), 4.02 (m, 4H, THF), 3.58 (br m, 1H, neomenthyl), 2.43 (br m, 1H, neomenthyl), 2.30−1.30 (m, 8H, neomenthyl), 2.18 (m, 4H, THF), 1.62 (s, 9H, ^{t}Bu), 1.29 (d, 3H, $J = 6.4$ Hz, neomenthyl), 1.19 (d, 3H, $J = 6.4$ Hz, neomenthyl), 1.10 (d, 3H, $J = 6.4$ Hz, neomenthyl), 0.65 (s, 6H, $SiMe_2$).

(*R*,*S*)-$Me_2Si(^tBuCp)$[(+)-*neo*-Men-Cp]Y(μ-Cl_2)Li(OEt_2) (2a). Onto a mixture of 1.76 g (4.29 mmol) of $YCl_3(THF)_3$ and 2.00 g (4.29 mmol) of **1** at −78 °C was condensed 20 mL of ether. The mixture was stirred for 12 h at room temperature. The solution was then filtered and concentrated, and the product crystallized at −78 °C. The product was then recrystallized a second time from ether. The mother liquor was concentrated, and additional product was recovered by crystallization. Yield: 1.97 g (74%). ^{1}H NMR (400 MHz, ether-d_{10}, 25 °C): δ 6.11 (dd, 1H, $J = 2.4$ Hz, Cp), 6.00 (dd, 1H, $J = 2.4$ Hz, Cp), 5.96 (dd, 1H, $J = 2.4$ Hz, Cp), 5.95 (dd, 1H, $J = 2.4$ Hz, Cp), 5.78 (dd, 1H, $J = 2.4$ Hz, Cp), 5.77 (dd, 1H, $J = 2.4$ Hz, Cp), 3.39 (q, 4H, ether), 3.20 (m, 1H, neomenthyl), 2.29 (m, 1H, neomenthyl), 1.93 (m, 1H, neomenthyl), 1.82 (m, 1H, neomenthyl), 1.49 (m, 1H, neomenthyl), 1.20−0.89 (m, 5H, neomenthyl), 1.22 (s, 9H, ^{t}Bu), 1.12 (t, 6H, ether), 0.86 (d, 3H, $J = 6.4$ Hz, neomenthyl), 0.85 (d, 3H, $J = 6.4$ Hz, neomenthyl), 0.70 (s, 3H, $SiMe_2$), 0.56 (d, 3H, $J = 6.8$ Hz, neomenthyl), 0.50 (s, 3H, $SiMe_2$). ^{13}C NMR (75 MHz, ether-d_{10}, 25 °C): δ 149.5, 140.5, 120.4, 119.2, 118.7, 116.7, 114.0, 113.1, 111.3, 108.7, 66.3, 50.6, 41.9, 38.4, 36.7, 33.2, 31.8, 29.8, 29.4, 24.7, 23.5, 23.0, 20.8, 15.6, −2.2, −5.7. CD (ether, 25 °C), λ_{max} ([θ]): 300 (4530), 258 (13 830), 241sh (3400) nm. Anal. Calcd for $C_{30}H_{50}Cl_2LiOSiY$: C, 57.97; H, 8.11. Found: C, 58.20; H, 8.27.

(*R*,*S*)-$Me_2Si(^tBuCp)$[(+)-*neo*-Men-Cp]Lu(μ-Cl_2)Li(OEt_2)$_2$ (2b). The procedure given above for the yttrium analog was used with 1.21 g (4.29 mmol) of $LuCl_3$ and 2.00 g (4.29 mmol) of **1** in ether. The total yield of **2b** was 2.15 g (71%), isolated as colorless crystals. ^{1}H NMR (400 MHz, ether-d_{10}, 25 °C): δ 6.06 (dd, 1H, $J = 2.9$ Hz, Cp), 5.95 (dd, 1H, $J = 2.9$ Hz, Cp), 5.90 (dd, 1H, $J = 2.9$ Hz, Cp), 5.86 (dd, 1H, $J = 2.9$ Hz, Cp), 5.72 (dd, 2H, $J = 3.2$ Hz, Cp), 3.39 (q, 8H, ether), 3.21 (m, 1H, neomenthyl), 2.28 (m, 1H, neomenthyl), 1.99 (m, 1H, neomenthyl), 1.82 (m, 1H, neomenthyl), 1.45 (m, 1H, neomenthyl), 1.22 (s, 9H, ^{t}Bu), 1.20−0.88 (m, 5H, neomenthyl), 1.12 (t, 12H, ether), 0.86 (d, 6H, $J = 6.5$ Hz, neomenthyl), 0.69 (s, 3H, $SiMe_2$), 0.56 (d, 3H, $J = 6.9$ Hz, neomenthyl), 0.49 (s, 3H, $SiMe_2$). ^{13}C NMR (75 MHz, ether-d_{10}, 25 °C): δ 148.8, 139.9, 118.6, 118.2, 115.6, 113.0, 111.9, 111.8, 110.3, 107.3, 66.3, 50.5, 41.4, 38.4, 36.6, 33.2, 31.7, 29.7, 29.5, 24.5, 23.4, 22.9, 20.6, 15.6, −2.1, −6.0. CD (ether, 25 °C), λ_{max} ([θ]): 292 (5150), 251 (12 510), 231 (3630) nm. Anal. Calcd for $C_{34}H_{60}Cl_2LiLuO_2Si$: C, 52.23, H, 7.74. Found: C, 52.26; H, 7.76.

(*R*,*S*)-$Me_2Si(^tBuCp)$[(+)-*neo*-Men-Cp]YCH($SiMe_3$)$_2$ (3a). To a mixture of 0.53 g (0.86 mmol) of **2a** and 0.17 g (0.86 mmol) of $KCH(SiMe_3)_2$ was added 10 mL of toluene at room temperature. The mixture was stirred for 24 h, the solvent was evaporated in vacuum, and 10 mL of pentane was condensed in. Solvent removal and pentane condensation was repeated three times. Finally, the KCl byproduct was filtered off, and the solvent was evaporated from the filtrate *in vacuo*. Yield: 248 mg (46%). ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 6.72 (br, 1H, Cp), 6.65 (br, 1H, Cp), 6.53 (br, 1H, Cp), 6.47 (br, 1H, Cp), 6.33 (br, 1H, Cp), 6.29 (br, 1H, Cp), 6.28 (br, 1H, Cp), 6.24 (br, 2H, Cp), 6.17 (br, 1H, Cp), 6.03 (br, 2H, Cp), 3.06 (br, 1H, neomenthyl), 3.00 (br, 1H, neomenthyl), 1.96 (br, 2H, neomenthyl), 1.82 (br, 2H, neomenthyl), 1.44 (br, 4H, neomenthyl), 1.29−0.77 (m, 10H, neomenthyl), 1.10 (s, 9H, ^{t}Bu), 1.09 (s, 9H, ^{t}Bu), 0.90 (m, 12H, neomenthyl), 0.72 (s, 3H, $SiMe_2$), 0.71 (s, 3H, $SiMe_2$), 0.56 (d, 3H, $J = 5.8$ Hz, neomenthyl), 0.55 (s, 3H, $SiMe_2$), 0.54 (d, 3H, $J = 5.8$ Hz, neomenthyl), 0.53 (s, 3H, $SiMe_2$), 0.28 (m, 20H, $SiMe_3$ and $CH(SiMe_3)_2$), 0.10 (m, 18H, $SiMe_2$). ^{13}C NMR (75 MHz, benzene-d_6, 25 °C): δ 147.8, 147.4, 138.6, 138.3, 119.7, 119.3, 119.0, 118.9, 118.8, 118.6, 115.9, 115.8, 114.8, 114.1, 112.3, 112.0, 111.9, 111.6, 110.6, 109.2, 50.0, 49.8, 42.1, 41.8, 38.8, 38.5, 36.4, 36.1, 33.0, 32.9, 32.2, 32.2, 32.1, 32.1, 30.0, 29.8 (d, ^1J(Y,C) = 19.8 Hz), 29.6, 28.7, 28.5, 24.0, 23.9, 23.1, 23.0, 5.6, 5.5, 3.3, 3.3, 2.9, 2.6, −1.7, −1.9, −5.6, −5.5. CD (*n*-heptane, 25 °C), λ_{max} ([θ]): 314 (2720), 266 (16 920) nm. Anal. Calcd for $C_{33}H_{59}Si_3Y$: C, 63.01; H, 9.46. Found: C, 63.03; H, 9.56.

(*R*,*S*)-$Me_2Si(^tBuCp)$[(+)-*neo*-Men-Cp]LuCH($SiMe_3$)$_2$ (3b). To 0.33 g (0.43 mmol) of **2b** in toluene, a solution of 0.070 g (0.43 mmol) of $LiCH(SiMe_3)_2$ in 10 mL of toluene was added dropwise with stirring over 2 h at room temperature. The product was worked up as described for **3a**. Yield: 190 mg (63%). ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 6.60 (dd, 1H, Cp), 6.55 (dd, 2H, Cp), 6.51 (dd, 1H, Cp), 6.33 (dd, 1H, Cp), 6.25 (dd, 1H, Cp), 6.19 (dd, 1H, Cp), 6.15 (dd, 2H, Cp), 6.10 (dd, 1H, Cp), 5.92 (dd, 2H, Cp), 3.02 (br, 1H, neomenthyl), 2.97 (br, 1H, neomenthyl), 2.02 (br, 2H, neomenthyl), 1.84 (br, 2H, neomenthyl), 1.60−0.80 (m, 14H, neomenthyl), 1.12 (s, 9H, ^{t}Bu), 1.10 (s, 9H, ^{t}Bu), 0.94 (d, 3H, $J = 5.9$ Hz, neomenthyl), 0.93 (d, 3H, $J = 5.9$ Hz, neomenthyl), 0.92 (d, 3H, $J = 5.9$ Hz, neomenthyl), 0.91 (d, 3H, $J = 5.9$ Hz, neomenthyl), 0.73 (s, 3H, $SiMe_2$), 0.72 (s, 3H, $SiMe_2$), 0.57 (d, 3H, $J = 6.5$ Hz, neomenthyl), 0.54 (d, 3H, $J = 6.5$ Hz, neomenthyl), 0.53 (s, 3H, $SiMe_2$), 0.52 (s, 3H, $SiMe_2$), 0.31 (s, 9H, $SiMe_3$), 0.29 (s, 9H, $SiMe_3$), 0.27 (s, 1H, $CH(SiMe_3)_2$), 0.26 (s, 1H, $CH(SiMe_3)_2$), 0.17 (s, 9 H, $SiMe_3$), 0.13 (s, 9H, $SiMe_3$). ^{13}C NMR (75 MHz, benzene-d_6, 25 °C): δ 147.4, 147.0, 138.2, 137.9, 119.2, 118.8, 118.6, 118.5, 118.4, 118.2, 115.5, 115.4, 114.4, 113.7, 111.9, 111.6, 111.5, 111.2, 110.2, 108.8, 49.5, 49.4, 41.7, 41.3, 38.4, 38.0, 36.0, 35.7, 32.5, 32.4, 31.8, 31.7, 29.6, 29.4, 29.2, 29.1, 28.3, 28.1, 23.6, 23.5, 23.4, 22.7, 22.6, 5.3, 5.2, 5.1, 2.9, 2.8, 2.2, −2.1, −2.3, −6.0, −6.1. CD (*n*-heptane, 25 °C), λ_{max} ([θ]): 322 (−5510), 272 (18 240), 240 (53 030) nm. Anal. Calcd for $C_{33}H_{59}LuSi_3$: C, 55.43; H, 8.32. Found: C, 55.55; H, 8.15.

{(*R*,*S*)-$Me_2Si(^tBuCp)$[(+)-*neo*-Men-Cp]LuH}$_2$ (4). Onto 0.50 g (0.70 mmol) of **3b** at −78 °C was condensed 20 mL of pentane. The apparatus was then back-filled with hydrogen, and the solution was allowed to warm to room temperature with stirring. The solution was stirred for 3 days, during which time the apparatus was back-filled with hydrogen several times. The filtrate was then concentrated *in vacuo* until crystallization occurred at room temperature. Yield: 243 mg (62%). ^{1}H NMR (300 MHz, benzene-d_6, 25 °C): δ 7.23 (dd, 1H, Cp), 7.18 (dd, 1H, Cp), 6.89 (s, 1H, Lu−H), (dd, 1H, Cp), 6.30 (dd, 1H, Cp), 5.55 (m, 2H, Cp), 3.80 (m, 1H, neomenthyl), 1.85 (m, 1H, neomenthyl), 1.32 (s, 9H, ^{t}Bu), 1.80−0.88 (m, 8H, neomenthyl), 0.81 (d, 6H, neomenthyl), 0.75 (s, 3H, $SiMe_2$), 0.73 (d, 3H, neomenthyl), 0.34 (s, 3H, $SiMe_2$). ^{13}C NMR (75 MHz, benzene-d_6, 25 °C): δ 148.5, 119.3, 118.0, 114.2, 113.9, 113.7, 113.6, 112.3, 112.0, 110.6, 48.9, 42.9, 38.3, 36.0, 32.5, 32.3, 30.4, 28.5, 25.0, 23.6, 22.3, 21.6, −2.5, −6.4. CD (*n*-heptane, 25 °C), λ_{max} ([θ]): 309 (1.820), 259 (13 780) nm.

---

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

Anal. Calcd for $C_{26}H_{41}LuSi$: C, 56.10; H, 7.42. Found: C, 56.21; H, 7.52.

Catalytic Enantioselective Olefin Hydrogenation. Kinetic studies were performed in the all glass, metal, and Teflon grease-free, constant-volume, pseudo-constant-pressure, gas-uptake apparatus described previously.[16] In a typical experiment, the oven-dried, jacketed reactor was attached to the vacuum line while still hot, evacuated/back-filled with argon 5−7 times, and finally evacuated continuously for at least 1 h (ultimate vacuum attainable, $2-4 \times 10^{-6}$ Torr). The burets were then back-filled with argon and sealed, and the entire reaction vessel was transported into the glovebox. The burets were then filled with freshly-prepared, volumetric solutions of precatalyst (2−20 mM) and olefin in *n*-heptane (0.950 or 1.90 M). The burets were tightly sealed, and the entire apparatus was quickly transported outside to the vacuum line. The reaction volume was evacuated/back-filled with argon (more efficient displacement of air and moisture) until the ultimate vacuum was $<2 \times 10^{-6}$ Torr. The apparatus was subsequently evacuated/back-filled with H_2 repetitively, usually 5−6 times, to ensure complete removal of argon. On the ultimate evacuation cycle, the pressure was recorded from a mercury manometer. The entire system was then filled with H_2 and adjusted to the desired pressure. A thermostated (±0.2 °C) water circulating system was connected to the reactor jacket and actuated. After all components had attained thermal equilibrium and equilibrium with the reactor atmosphere, a measured volume of olefin solution (1.00 mL) was titrated into the reactor. Stirring (vortex agitation) was then initiated to equilibrate the atmosphere with solvent vapor, and a final pressure reading was recorded from the manometer. A measured aliquot of the catalyst solution (1.00 mL) was quickly transferred to the reaction vessel, and the change in H_2 pressure recorded as a function of time using the previously described electronic manometer.[16] Conditions were adjusted such that for all lanthanide (∼1−10 mM) and olefin (∼0.5−2 M) concentrations, the overall drop in H_2 pressure was always less than 2% (usually <1%) of its initial value (180−700 Torr). The instantaneous reaction rate (ν) at a particular substrate concentration (C) was estimated at a number of points over at least a 10-fold range of C by fitting the data on a small segment of the uptake curve (essentially the instantaneous slope) *via* least-squares analysis to eq 1 where $C_1 = C + x$ and $C_2 = C - x$ are the olefin concentrations at the start and end of the assay, respectively. The interval of each assay (i.e., $2x$) was always less than $0.3C_1$ and usually $\sim 0.05C_1$. The turnover frequency (N_t) was, thus, estimated for a given catalyst concentration and hydrogen pressure by eq 2, where $[Ln]_T$ is the total concentration of the catalyst precursor.

$$C_1 - C_2 = \nu t \qquad (1)$$

$$N_t\,(s^{-1}) = \nu/[Ln]_T \qquad (2)$$

X-ray Cystallographic Study of {(*R*,*S*)-Me$_2$Si(^{t}BuCp)-[(+)-*neo*-Men-Cp]LuH}$_2$ (4). A yellow, transparent columnar crystal of **4** was mounted on a glass fiber using dried and degassed oil (Paratone-N, Exxon). The crystal was transferred directly to the −120 °C cold stream of an Enraf-Nonius CAD4 diffractometer. The crystal, data collection, and refinement parameters are collected in Table 1. An empirical absorption correction using the program DIFABS[17] was applied. The data were corrected for Lorentz and polarization effects.

Table 1. Crystallographic Details for {(*R*,*S*)-Me$_2$Si(^{t}BuCp)[(+)-*neo*-Men-Cp]LuH}$_2$ (4)

formula	$C_{52}H_{82}Si_2Lu_2$
fw	1113.17
cryst color, habit	transparent columnar
cryst dimens, mm	0.45 × 0.11 × 0.09
cryst syst	primitive orthorhombic
a, Å	10.536(4)
b, Å	13.340 (3)
c, Å	36.820(9)
V, Å^3	5175(2)
space group	$P2_12_12_1$ (No. 19)
Z	4
d(calcd), g/cm^3	1.40
diffractometer	CAD4
temp, °C	−120
transm factors range	0.75−1.15
radiation	Mo Kα = 0.710 69 Å, graphite monochromator
scan type	$\omega-\theta$
intensities (unique, R_i)	4099
intensities > 3.00 $\sigma(I)$	2978
R	0.061
R_w for $w = 1/s^2(F_0)$	0.079

The structure was solved using standard Fourier techniques.[18] Carbon atoms were refined isotropically, and the remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions and refined except the ones on C8−C12 and on Lu. The Cp ring atoms C8−C12 were modeled as a rigid group owing to some disorder. The final peaks in the difference Fourier map near the end of the refinement were located close to C23, a result of the disorder. The final cycle of full-matrix least-squares refinement was based on 2978 observed reflections ($I > 3.00\sigma(I)$) and 232 variable parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.03 and −1.61 e$^-$/Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[19] Anomalous dispersion effects were included in F_{calc};[20] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[21] The values from the mass attenuation coefficients are those of Creagh and Hubble.[22] All calculations were performed using the TeXsan[23] crystallographic software package of Molecular Structure Corp.

Results and Discussion

The straightforward synthesis of the chiral chelating ligand Me$_2$Si(^{t}BuCp)(R*Cp)Li$_2$·THF (**1**) is shown in Scheme 2. In a one-pot reaction starting from 6,6′-dimethylfulvene, methyllithium, and dimethyldichlorosilane, the desired product Me$_2$Si(^{t}BuCp)Cl is obtained, which is then alkylated with Na[(+)-*neo*-Men-Cp] to afford the neutral ligand in good yield. Reaction with ^{n}BuLi then affords the dilithium salt **1** as a colorless crystalline solid. The synthesis of the organolanthanide chlorides (*R*,*S*)-Me$_2$Si(^{t}BuCp)(R*Cp)Ln(μ-Cl$_2$)Li(OEt$_2$)$_2$ (Ln = Y, Lu) (**2**; Scheme 3) was performed by transmetalation of **1** with anhydrous lutetium or yttrium trichloride. ^{1}H NMR spectra of **2** indicate that the products isolated by simple crystallization are diastereomerically pure. Thus, one of the four possible diastereomers shown in Scheme 1 can be *selectively*

---

[17] DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166. An empirical absorption correction program.

[18] DIRDIF92: Beurskens, 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.

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

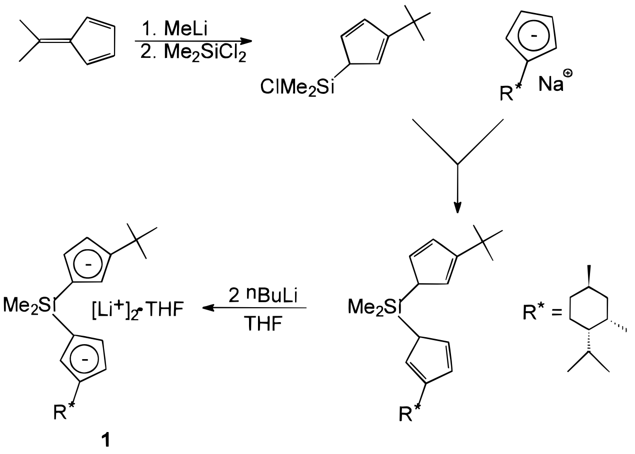
[20] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

[21] Creagh, D. C.; McAuley, W. J. *International Tables of Crystallography;* Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, Table 4.2.6.8, pp 219−222.

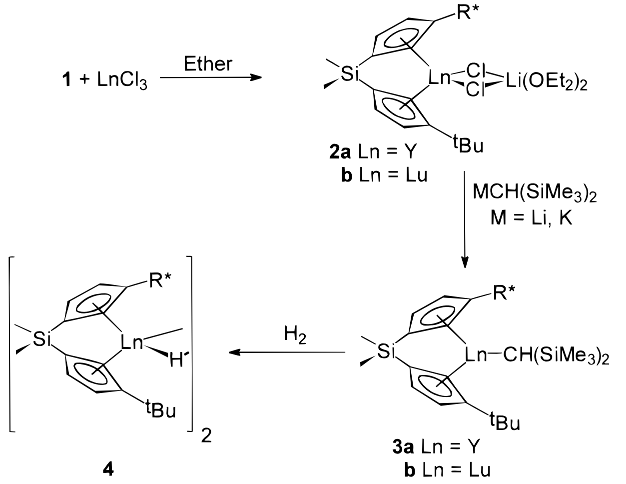
[22] Creagh, D. C.; Hubbel, J. H. *International Tables of Crystallography;* Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Table 4.2.6.8, pp 206.

[23] TeXan: *Crystal Structure Analysis Package*; Molecular Structure Corp.; The Woodlands, TX, 1985, 1992.

Scheme 2



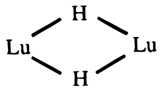
Scheme 3



isolated. Nevertheless, the NMR observation of epimerization[9] upon dissolution of **2** in THF suggests that the other pseudo-*meso* and -*rac* configurations do not differ greatly in free energy and are kinetically accessible. The absolute configurations of the isolated diastereomers of **2** were determined by circular dichroism (CD) spectroscopy and NMR experiments. The CD spectra show a positive Cotton effect (see Experimental Section for data), which indicates an (*S*)-configuration of the (+)-*neo*-Men-Cp ring.[24] Furthermore, NOE experiments indicate a pseudo-*meso* disposition (Scheme 1) of the *ansa*-dicyclopentadienyl ligand substituents. These results are consistent with the single-crystal X-ray diffraction data on the hydride derivative [(*R,S*)-Me$_2$Si(^{t}BuCp)(R*Cp)LuH]$_2$ (see below).

Alkylation of **2** with 1 equiv of MCH(SiMe$_3$)$_2$ (M = K for **3a**; Li for **3b**) in toluene affords the alkyl derivatives Me$_2$Si(^{t}BuCp)(R*Cp)LnCH(SiMe$_3$)$_2$ (**3**; Scheme 3). To suppress epimerization during the course of the reaction, the lithium alkylation reagent must be slowly added to the organolanthanide chloride. The CD spectrum of complex **3** shows that alkylation proceeds with complete retention of the R*CpLn fragment configuration. As a result of the hindered rotation of the $-$CH(SiMe$_3$)$_2$ group about the σ Ln$-$C bond axis, two different rotamers can be observed in the ^{1}H and ^{13}C NMR spectra at room temperature (suggested structures are shown in Scheme 4). At higher temperatures, the signals of the two rotamers begin to broaden and coalesce; however, complete coalescence cannot be observed in toluene. Similar ground state structures and dynamic structural interconversions have been observed in analogous organolanthanides.[9,16]

Solutions of complex **3b** in hydrocarbon solvents undergo rapid hydrogenolytic cleavage of the hydrocarbyl group to afford the hydrido complex [(*R,S*)-Me$_2$Si(^{t}BuCp)(R*Cp)LuH]$_2$ (**4**; Scheme 3), the active species for the asymmetric hydrogenation catalysis. This is the first *diastereomerically pure chiral lanthanide hydride* complex which has been characterized by NMR spectroscopy and by single-crystal X-ray diffraction. The crystal structure of **4** (Figure 1) shows that this compound is a pseudo-C_2-symmetric dimer.[4a,b,9] The coordination geometry features an unusual pseudo-*meso* arrangement of the substituents on the Cp rings as well as an (*S*)-configuration of the (+)-*neo*-Men-Cp ring, consistent with the positive Cotton effect observed in the CD spectrum of **4** (see Experimental Section for data). The two Me$_2$Si(^{t}BuCp)(R*Cp)LuH fragments are slightly twisted with respect to each other, and the torsional angle between planes [Cg1$-$Lu(1)$-$Cg2] and [Cg3$-$Lu(2)$-$Cg4] is 6.6(2)°. Although the Lu$-$H atom positions could not be located precisely in this structure determination, data from several analogous achiral structures[2,25] argues for a Lu(μ-H)$_2$Lu geometry. This



symmetry is consistent with the ^{1}H NMR data, which exhibit six Cp ring resonances, as expected for a single diastereomer, and a hydride signal at δ 6.89 (2H), in the range observed for achiral organolutetium hydrides.[2,25]

The internal Me$_2$Si(^{t}BuCp)(R*Cp)Lu metrical parameters of complex **4** (Table 2) are unexceptional for an organolutetium metallocene (cf., Me$_2$Si(Me$_3$SiCp)[($-$)-menthylCp]Lu(μ-Cl)$_2$Li(OEt$_2$)$_2$[16] and Me$_2$Si(Cp″)(R*Cp)-Lu(μ-Cl)$_2$Li(OEt$_2$)$_2$[10]). The same is true for the Cp centroid$-$Lu$-$Cp centroid angles ($\angle$Cg1$-$Lu(1)$-$Cg2 = 124.36(6)° and $\angle$Cg3$-$Lu(2)$-$Cg4 = 121.40(7)°). However, the disposition of the ring substituents and of the LuH$_2$ fragments with respect to the ring substituents is unusual. Thus, as previously observed for Me$_2$Si(Me$_3$SiCp)[($-$)-menthylCp]Lu(μ-Cl)$_2$Li(OEt$_2$)$_2$ (**5**),[16] the present structure involves a pseudo-*meso* arrangement of ring substituents rather than what would appear a priori to be a sterically somewhat less-encumbered[26] pseudo C_2-symmetric one (Scheme 1). Also, analogously to the case of Me$_2$Si(Me$_3$SiCp)[($-$)-menthylCp]Lu(μ-Cl)$_2$Li(OEt$_2$)$_2$, the present Me$_2$Si$-$Lu$-$Lu$-$SiMe$_2$ vector is bent substantially from linearity, with $\angle$Si(1)$-$Lu(1)$-$Lu(2) = 148.9(2)° and $\angle$Si(2)$-$Lu(2)$-$Lu(2) = 156.1(2)° in **4**. A distortion of this magnitude which orients the Lu$-$X

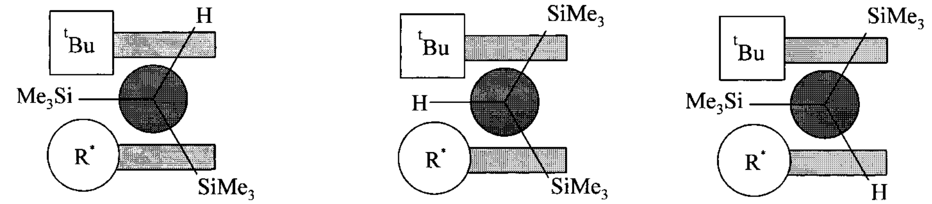
---

[24] Previous work has established a direct correlation between the sign of the Cotton effect and the attachment mode of the R*Cp moiety in Me$_2$SiCp″(R*Cp)Ln(μ-Cl$_2$)Li(OEt$_2$)$_2$ complexes (R* = (+)-neomenthyl).[9]

[25] Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558$-$9575.

[26] Examination of non-hydrogen atom nonbonded contacts reveals that all intramonomer ^{t}Bu⋯neomenthyl distances in **4** are >3.60 Å but that several of the corresponding intermonomer distances are in the range 3.4$-$3.6 Å.

Scheme 4



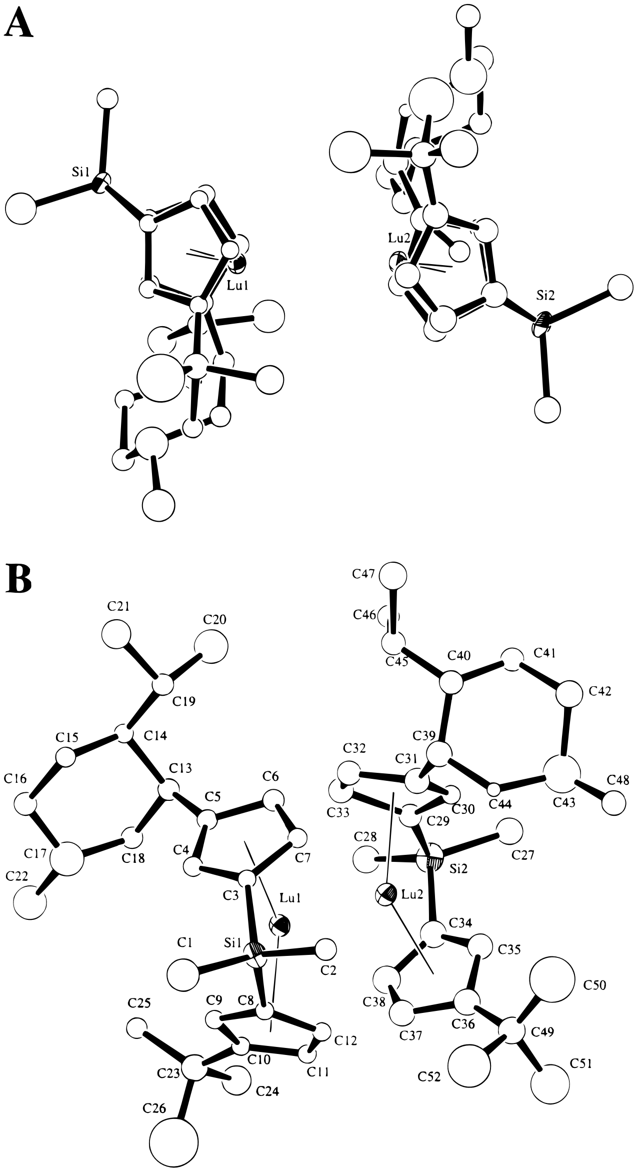


Figure 1. Perspective ORTEP view of the molecular structure of (*R*,*S*)-{Me$_2$Si(^{t}BuCp)[(+)-*neo*-Men-Cp]LuH}$_2$, **4**. (A) View parallel to the Me−Si−Me planes. (B) View parallel to the ring centroid−Lu−ring centroid planes. Thermal ellipsoids are drawn to encompass 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in {(*R*,*S*)-Me$_2$Si(^{t}BuCp)[(+)-*neo*-Men-Cp]LuH}$_2$ (4)[a]

Lu(1)−C(3)	2.53(3)	Lu(2)−C(29)	2.46(3)
Lu(1)−C(4)	2.56(3)	Lu(2)−C(30)	2.53(3)
Lu(1)−C(5)	2.68(3)	Lu(2)−C(31)	2.52(3)
Lu(1)−C(6)	2.68(3)	Lu(2)−C(32)	2.64(3)
Lu(1)−C(7)	2.56(3)	Lu(2)−C(33)	2.64(3)
Lu(1)−C(8)	2.47(2)	Lu(2)−C(34)	2.53(3)
Lu(1)−C(9)	2.50(2)	Lu(2)−C(35)	2.53(3)
Lu(1)−C(10)	2.66(2)	Lu(2)−C(36)	2.66(2)
Lu(1)−C(11)	2.73(2)	Lu(2)−C(37)	2.59(3)
Lu(1)−C(12)	2.62(2)	Lu(2)−C(38)	2.54(3)
Cg1−Lu(1)	2.304(1)	Cg3−Lu(2)	2.226(1)
Cg2−Lu(1)	2.316(1)	Cg4−Lu(2)	2.305(1)
C(3)−Si(1)−C(8)	94(1)	C(29)−Si(2)−C(34)	92(1)
C(3)−Lu(1)−C(8)	67.9(8)	C(29)−Lu(2)−C(34)	61(1)
Lu(1)−C(3)−Si(1)	98(1)	Lu(2)−C(29)−Si(2)	106(2)
Lu(1)−C(8)−Si(1)	98.0(8)	Lu(2)−C(34)−Si(2)	99(1)
Cg1−Lu(1)−Cg2	124.35(6)	Cg3−Lu(2)−Cg4	121.40(7)

[a] Cg, ring centroid

σ-bonded network *away* from the Cp ring substituents has not, to our knowledge, been previously observed in lanthanocene molecular structures.[2] This possibility of “swivelling” the σ ligand system with respect to the π ligand system represents a heretofore unappreciated flexibility in lanthanocene ligation geometry which must be taken into account in ligand design and in analyzing chirality transfer. This mode of relieving what might otherwise be substantial α ligand to π ligand nonbonded repulsions[16] may also account for the stabilization of pseudo-*meso* geometries in what are now two different chiral ancillary ligand systems (**4** and **5**).

The efficacy of the present chiral complexes **3** as precatalysts for asymmetric olefin hydrogenation and deuteration was assayed using the unfunctionalized olefins 2-phenyl-1-butene,[27] styrene,[28] and 1-pentene.[29] These unfunctionalized olefins are typically difficult substrates to hydrogenate/deuterate with substantial enantioselectivity and at appreciable rates.[6c,30] A constant pressure (pseudo-zero-order in H$_2$ pressure), vortex-mixed batch reactor was employed using procedures described previously.[16] The rate of substrate consumption is constant with time (zero-order behavior) through approximately 90% conversion and then gradually begins to deviate from linearity. The ee values and the turnover frequencies measured are shown in Table 3. Catalysts derived from complexes **3a** and **3b** exhibit high catalytic activities (e.g., for 2-phenylbutene, N_t (**3a**) = 1210 h^{-1} at 25 °C, 1.0 atm H$_2$ pressure). The high ee's obtained for deuteration of 1-pentene (up to 63%) are, to our knowledge, the highest reported to date for this reaction.[16,29c] In all reactions, the (*R*)-product enantiomer is favored, indicating that the pro-(*R*) activation of the olefin face by the metal hydride is favored. In the frontal pro-(*R*) approach of the olefin, the largest substituent (L) of the olefin would be

---

(27) (a) Lardicci, L.; Menicagli, R.; Salvadori, P. *Gazz. Chim. Ital.* **1968**, *98*, 738−759. (b) Bonner, W. A.; Greenlee, T. W. *J. Am. Chem. Soc.* **1959**, *81*, 3336−3341.

(28) Elsenbaumer, R. L.; Mosher, H. S. *J. Org. Chem.* **1979**, *44*, 600−604.

(29) (a) Streitwieser, A.; Granger, M. R. *J. Org. Chem.* **1967**, *32*, 1528−1529. (b) Streitwieser, A.; Schwager, I.; Verbit, L.; Rabitz, H. *J. Org. Chem.* **1967**, *32*, 1532−1534. (c) Pino, P.; Galimberti, M. *J. Organomet. Chem.* **1989**, *370*, 1−7.

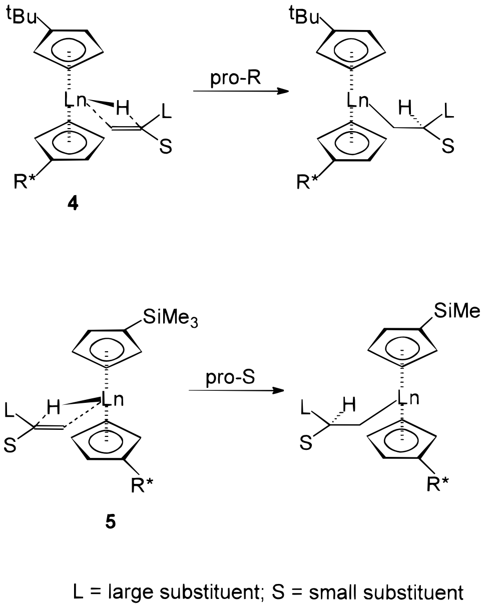
(30) (a) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911−4914. (b) Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883−892. (c) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501−1505.

Table 3. Product Enantiomeric Excesses (ee) and Catalytic Turnover Frequencies for Olefin Hydrogenation and Deuteration using Complexes 3a and 3b as Precatalysts[a]

substrate	Ln	*T* (°C)	ee (%)[c]	$N_t[h^{-1}]$[e]
2-phenylbutene	Y	22	26	1210
styrene[b]	Y	22	3	
styrene[b]	Lu	22	6	730
1-pentene[b]	Y	0	55[d]	
1-pentene[b]	Y	−15	61[d]	
1-pentene[b]	Lu	0	59[d]	280
1-pentene[b]	Lu	−5	63[d]	

[a] Conditions: substrate/[catalyst] = (100−1000)/1; P_{H_2} or P_{D_2} = 750 Torr; rapid stirring; 100% conversion by GC/MS and ^{1}H NMR. [b] Deuterium experiment. [c] Absolute configuration, *R*, measured after vacuum transfer of the products. [d] Traces of oligomeric products also found. [e] Turnover frequencies measured at 25 °C.

Scheme 5



oriented *syn* to the ^{t}Bu substituent and *anti* to the bulkier (+)-neomenthyl group (Scheme 5). Interestingly, and in complete agreement with this model, the corresponding (*S*,*R*)-$Me_2Si(Me_3SiCp)$[(−)-menthylCp]-LnCH$(SiMe_3)_2$ precatalysts (**5**) convert the same olefins into the (*S*)-enantiomeric products (Scheme 5).[16] However, while chirality transfer to 1-pentene for **4**-based catalysts is more efficient than that for **5**-based catalysts (55% ee versus 30% ee for 0 °C, Ln = Lu), the opposite trend holds for styrenic olefins (2-phenylbutene, 45% ee versus 26% ee at 22 °C, Ln = Lu; styrene, 10% ee versus 6% ee at 22 °C, Ln = Lu).

Conclusions

The results of this study offer an interesting contrast to the other known classes of diastereomerically pure asymmetric organolanthanide catalysts based upon chiral ring substituents, C_1-symmetric $Me_2SiCp''(CpR^*)$-Ln−R and potentially C_2-symmetric $Me_2Si(Me_3SiCp)$-[(−)-menthylCp]Ln−R. The former ligand structure (Scheme 1) is by design locked into a single C_1-symmetric metal−ligand template. In contrast, the latter, as in the present ligand system, can potentially populate either pseudo-C_2-symmetric or "*meso*" configurations (Scheme 1). Interestingly, for *both* $Me_2Si(Me_3SiCp)$-[(−)-menthylCp]LnR and the present $Me_2(^tBuCp)$[(+)-*neo*-Men-Cp]LnR metal−ligand pairs, pseudo-*meso* structures ((*S*,*R*)- and (*R*,*S*)-configurations, respectively) are isolated preferentially. This *meso* metal−ligand template offers relatively high (perhaps suprisingly so) enantioselectivties when employed in asymmetric reduction of unfunctionalized olefins, underscoring both the potential of organolanthanides in asymmetric catalysis and the considerable conformational flexibility of these metal−ligand bonding configurations.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-961889) and the Deutsche Forschungsgemeinschaft (postdoctoral fellowships for P.W.R. and U.D.) for generous support of this research. We thank Professor Paul Loach for access to his CD spectrometer.

Supporting Information Available: Text giving the details of data collection, data, and structure solution and refinement, tables of experimental details, bond lengths, bond angles, torsion angles, and positional and thermal parameters, and ORTEP diagram (43 pages). Ordering information is given on any current masthead page.

OM970434B