Menthyl-Functionalized Chiral Nonracemic Bis(indenyl) Complexes of Zirconium, Iron, Nickel, and Ruthenium

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Optically active complexes of Zr, Fe, Ni, and Ru containing the chiral, menthyl-substituted indenyl ligands (−)-3-menthyl-4,7-dimethylindene and (−)-2-menthylindene are described. Metathetic reaction of the chiral main-group-metal salts of these indenyl systems with the appropriate starting materials of Zr, Fe, and Ni yielded the complexes (*pR*)(*pR*)-/(*pR*)(*pS*)-(1-menthyl-4,7-dimethylindenyl)$_2$ZrCl$_2$ (**4a**/**4b**), (*pR*)-/(*pS*)-(cyclopentadienyl)(1-menthyl-4,7-dimethylindenyl)ZrCl$_2$ (**5a**/**5b**), (*pR*)(*pR*)-/(*pR*)(*pS*)-/(*pS*)(*pS*)-(1-menthyl-4,7-dimethylindenyl)$_2$Fe (**6a**/**6b**/**6c**), (*pR*)(*pR*)-/(*pR*)(*pS*)-/(*pS*)(*pS*)-(1-menthyl-4,7-dimethylindenyl)$_2$Ni (**7a**/**7b**/**7c**), (+)-(2-menthylindenyl)$_2$Fe (**8**), and (−)-(2-menthylindenyl)$_2$Ni (**9**). Ru(acac)$_3$ reacts with (−)-(2-menthylindenyl)lithium (**3**), yielding (−)-(2-menthylindenyl)$_2$Ru (**10**). Depending on the reaction conditions, compounds **4**−**7** were formed as mixtures of diastereomers with respect to the planar chirality of the indenyl ring system. The apparent diasteromeric excess varied between 13 and 50% de. The Fe, Ni, and Ru complexes were purified by chromatography via dried alumina under nitrogen. The structures of **4b** and **8** were determined by single-crystal X-ray diffractometry.

Introduction

Chiral indenyl complexes of the group 4 metals are very important catalysts for olefin polymerization, stereoselective hydrogenations, carboaluminations, polymerizations,[1] or other carbon−carbon[2] and carbon−hydrogen[3] bond formations. Late-transition-metal complexes have been shown to be active catalysts for hydrogenations, hydroformylations, isomerizations, or cycloadditions,[4] but chiral indenyl complexes of these metals have been only barely exploited. The most widely applied chiral metallocenes are conformationally constrained *ansa*-metallocenes such as 1′,2′-ethylbis(tetrahydroindenyl)zirconium dichloride,[5] which are always formed as mixtures of stereoisomers and must be separated before application.[6]

As part of our investigations to find new nonracemic chiral metallocenes,[6−9] this paper describes the synthe-

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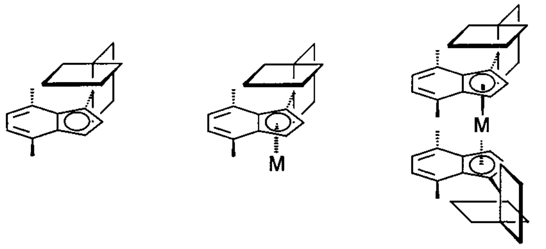
Chart 1



sis and characterization of some new stereomerically pure bis(indenyl)metal complexes of zirconium, iron, ruthenium, and nickel containing (−)-3-menthyl-4,7-dimethylindene and (−)-2-menthylindene bonded to the transition metal. We have demonstrated that metathetic reactions of the alkali-metal salts of chiral menthyl-substituted indenyl ligands, such as (−)-3-menthyl-4,7-dimethylindene, (−)-4,7-diisopropyl-3-menthylindene, and (+)-3-neomenthylindene with [RhCl(COD)]$_2$, [IrCl(COD)]$_2$, CoCl$_2$(dppe), and Mo(CO)$_6$ provide a convenient entry into chiral nonracemic mono(indenyl) transition-metal complexes.[10] In order for the 4,7-dialkyl-1-menthylindenyl ligands to favor the formation of one specific diastereomeric transition-metal complex, the chiral auxiliary should direct metalation to only one ligand face. As illustrated for mono(indenyl)- and bis(indenyl)-metal complexes in Chart 1, the 7-alkyl substituent is used to orient the 1-menthyl moiety in such a way that its isopropyl group blocks one diastereotopic face, resulting in diastereoselective metalation.[9] Metalations of the 2-menthylindenyl ligand can provide only a single stereoisomer.

Experimental Section

All operations involving organometallic compounds were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques in dry, oxygen-free solvents. Melting points were measured in sealed capillaries with a Büchi 510 melting point determination apparatus and are uncorrected. Optical rotations were determined on a Schmidt+Haensch Polartronic-D polarimeter. The NMR spectra were recorded on a Bruker ARX 200 (^{1}H, 200 MHz; ^{13}C, 50.32 MHz) or ARX 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the deuterated solvents. The IR spectra were recorded on a Nicolet Magna System 750 spectrometer. Mass spectra (EI, 70 eV) were obtained using a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities in percent are given in parentheses. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. (−)-(1-Menthyl-4,7-dimethylindenyl)lithium (**1**), (−)-(1-menthyl-4,7-dimethylindenyl)potassium (**2**), (−)-(2-menthylindenyl)lithium (**3**),[9] CpZrCl$_3$(DME),[11] FeCl$_2$(THF)$_{1.15}$,[12] and NiCl$_2$(DME)[13] were prepared according to published procedures. Zirconium tetrachloride was used as purchased.

Dichlorobis(η^5-1-menthyl-4,7-dimethylindenyl)zirconium(IV) (4a/4b). Method A. To a suspension of zirconium tetrachloride (0.79 g, 3.39 mmol) in toluene (40 mL) was added (−)-(η^5-1-menthyl-4,7-dimethylindenyl)lithium (**1**; 2.17 g, 7.52 mmol) at −78 °C. The mixture was stirred for 3 h, warmed to 25 °C over 8 h, and stirred for an additional 10 h. The suspension was filtered with a d4-frit, and the residue was extracted with toluene (10 mL). The solvent was removed under vacuum (10^{-2} mbar), leaving a yellow solid as a mixture of the (*pR*)(*pR*)- and (*pR*)(*pS*)-diastereomers **4a** and **4b** in the ratio 0.8:1. The crude product was suspended in *n*-pentane (10 mL) and the suspension filtered with a d4-frit. The residue of the filtration was recrystallized from dichloromethane (10 mL) at −78 °C, giving 0.81 g (33%) of yellow crystals of the (*pR*)(*pS*) diastereomer **4b**, while recrystallization of the filtrate from dichloromethane (10 mL) at −78 °C gave 0.62 g (25%) of yellow crystals of the (*pR*)(*pR*) diastereomer **4a**.

Method B. In analogy to method A, a solution of zirconium tetrachloride (0.38 g, 1.63 mmol) in toluene (15 mL) was treated at −78 °C with (−)-(1-menthyl-4,7-dimethylindenyl)potassium (**2**; 1.04 g, 3.24 mmol). The workup gave 1.02 g (87%) of a yellow solid as a mixture of the (*pR*)(*pR*) and (*pR*)(*pS*) diastereomers **4a** and **4b** in the ratio 0.9:1.

***(pR)(pR)* Diastereomer 4a.** ^{1}H NMR (dichloromethane-d_2, 400 MHz): δ 6.87 (m, 2H, H^{5}), 6.78 (m, 2H, H^{6}), 6.70 (d, ^{3}J = 3.2 Hz, 2H, H^{2}), 6.37 (d, ^{3}J = 3.2 Hz, 2H, H^{3}), 3.21 (m, 2H, H$^{3'}$), 2.72 (s, 6H, H^{11}), 2.47 (m, 2H, H$^{2'}$), 2.31 (m, 2H, H$^{8'}$), 2.30 (s, 6H, H^{10}), 1.88 (m, 2H, H$^{6'}$), 1.73 (m, 2H, H$^{5'}$), 1.55 (m, 2H, H$^{1'}$), 1.29 (m, 2H, H$^{2'}$), 1.25 (m, 2H, H$^{5'}$), 1.19 (m, 2H, H$^{4'}$), 1.10 (m, 2H, H$^{6'}$), 1.04 (d, ^{3}J = 6.5 Hz, 6H, H$^{7'}$), 0.61 (d, ^{3}J = 6.7 Hz, 6H, H$^{9'/10'}$), 0.54 (d, ^{3}J = 6.5 Hz, 6H, H$^{9'/10'}$). ^{13}C{^{1}H} NMR (dichloromethane-d_2, 100.64 MHz): δ 139.41, 134.19, 133.32, 132.98 (C^{4,7,8,9}), 127.66 (C^{6}), 127.42 (C^{5}), 127.19 (C^{1}), 116.06 (C^{2}), 95.88 (C^{3}), 54.62 (C$^{4'}$), 45.51 (C$^{2'}$), 41.03 (C$^{3'}$), 35.80 (C$^{6'}$), 33.93 (C$^{1'}$), 27.29 (C$^{8'}$), 25.99 (C$^{5'}$), 22.66 (C$^{7'}$), 22.52 (C$^{9'/10'}$), 21.96 (C^{11}), 19.59 (C^{10}), 16.63 (C$^{9'/10'}$).

***(pR)(pS)* Diastereomer 4b.** The first signal set is as follows (^{1}H/^{13}C pairs are correlated). ^{1}H NMR (dichloromethane-d_2, 400 MHz): δ 6.89 (m, 1H, H$^{5/6}$), 6.86 (m, 1H, H$^{5/6}$), 6.56 (d, ^{3}J = 3.3 Hz, 1H, H^{2}), 5.36 (s br, 1H, H^{3}), 3.34 (m, 1H, H$^{3'}$), 2.72 (s, 3H, H$^{10/11}$), 2.63 (s, 3H, H$^{10/11}$), 2.55 (m, 1H, H$^{2'}$), 1.87 (m, 1H, H$^{6'}$), 1.81 (m, 1H, H$^{5'}$), 1.53 (m, 1H, H$^{1'}$), 1.52 (m, 1H, H$^{4'}$), 1.39 (m, 1H, H$^{2'}$), 1.32 (m, 1H, H$^{5'}$), 1.15 (d, ^{3}J = 6.8 Hz, 3H, H$^{9'/10'}$), 0.96 (d, ^{3}J = 6.4 Hz, 3H, H$^{7'}$), 0.90 (m, 1H, H$^{6'}$), 0.71 (m, 1H, H$^{8'}$), 0.58 (d, ^{3}J = 6.8 Hz, 3H, H$^{9'/10'}$). ^{13}C{^{1}H} NMR (dichloromethane-d_2, 100.64 MHz): δ 134.78, 134.42, 133.23, 133.20 (C^{4,7,8,9}), 125.34 (C^{1}), 125.33, 125.04 (C^{5,6}), 122.85 (C^{2}), 96.89 (C^{3}), 45.52 (C$^{4'}$), 43.90 (C$^{2'}$), 41.45 (C$^{3'}$), 35.83 (C$^{6'}$), 33.05 (C$^{1'}$), 27.20 (C$^{8'}$), 25.46 (C$^{5'}$), 22.80 (C$^{7'}$), 22.49 (C$^{9'/10'}$), 21.89 (C$^{10/11}$), 20.79 (C$^{10/11}$), 17.10 (C$^{9'/10'}$). The second signal set is as follows (^{1}H/^{13}C pairs are correlated). ^{1}H NMR (dichloromethane-d_2, 400 MHz): δ 6.99 (m, 1H, H$^{5/6}$), 6.88 (m, 1H, H$^{5/6}$), 6.49 (d, ^{3}J = 3.3 Hz, 1H, H^{2}), 4.89 (s br, 1H, H^{3}), 3.19 (m, 1H, H$^{3'}$), 2.46 (s br, 3H, H$^{10/11}$), 2.02 (s br, 3H, H$^{10/11}$), 1.78 (m, 1H, H$^{6'}$), 1.67 (m, 1H, H$^{5'}$), 1.52 (m, 1H, H$^{2'}$), 1.51 (m, 1H, H$^{1'}$), 1.18 (m, 1H, H$^{5'}$), 1.13 (m, 1H, H$^{4'}$), 0.88 (m, 1H, H$^{6'}$), 0.81 (d, ^{3}J = 6.5 Hz, 3H, H$^{9'/10'}$), 0.75 (d, ^{3}J = 6.5 Hz, 3H, H$^{7'}$), 0.68 (m, 1H, H$^{8'}$), 0.53 (d, ^{3}J = 6.5 Hz, 3H, H$^{9'/10'}$), 0.42 (m, 1H, H$^{2'}$). ^{13}C{^{1}H} NMR (dichloromethane-d_2, 100.64 MHz): δ 134.55, 134.32, 134.06, 133.41 (C^{4,7,8,9}), 129.37 (C^{1}), 127.04, 126.52 (C^{5,6}), 120.96 (C^{2}), 97.15 (C^{3}), 54.74 (C$^{4'}$), 47.95 (C$^{2'}$), 41.27 (C$^{3'}$), 35.36 (C$^{6'}$), 33.74 (C$^{1'}$), 27.28 (C$^{8'}$), 26.25 (C$^{5'}$), 22.77 (C$^{9'/10'}$), 22.48 (C$^{7'}$), 19.12 (C$^{10/11}$), 18.79 (C$^{10/11}$), 17.92 (C$^{9'/10'}$).

***(pR)(pR)* and *(pR)(pS)* Diastereomers 4a and 4b in the Ratio 1:1.2.** Mp: 231 °C dec. $[\alpha]_{\mathrm{D}}^{25} = -91.8°$ (*c* 0.7, *n*-hexane). IR (CsI; cm^{-1}): $\bar{\nu}$ 3096 (w), 3018 (m), 2955 (s), 2928 (s), 2868

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(m), 2859 (m), 2730 (w), 1850 (w), 1700 (m), 1646 (w), 1606 (m), 1491 (m), 1459 (s), 1384 (m), 1377 (m), 1367 (m), 1346 (m), 1301 (w), 1252 (m), 1176 (w), 1149 (w), 1106 (m), 1084 (w), 1067 (m), 1035 (w), 1009 (w), 992 (w), 824 (s), 787 (s), 656 (m), 321 (m), 304 (m). MS (191 °C; *m/z* (%)): 722 (20) $[M]^+$, 687 (3) $[(C_{21}H_{29})_2ClZr]^+$, 583 (2) $[(C_{11}H_{10})(C_{21}H_{29})Cl_2Zr]^+$, 441 (97) $[(C_{21}H_{29})Cl_2Zr]^+$, 371 (3) $[(C_{21}H_{29})Zr]^+$, 158 (100) $[C_{12}H_{14}]^+$. Anal. Calcd for $C_{42}H_{58}Cl_2Zr$ (mol wt 725.04): C, 69.58; H, 8.06. Found: C, 69.24; H, 7.69.

Dichloro(η^5-cyclopentadienyl)(η^5-1-menthyl-4,7-dimethylindenyl)zirconium(IV) (5a/5b). To a suspension of trichloro(η^5-cyclopentadienyl)zirconium(IV)(DME) (0.26 g, 0.74 mmol) in THF (20 mL) was added **2** (0.18 g, 0.56 mmol) at −78 °C. The mixture was stirred for 3 h, warmed to 25 °C over 8 h, and stirred for an additional 10 h. The suspension was filtered with a d4-frit, and the residue was extracted with THF (10 mL). The solvent was removed under vacuum (10^{-2} mbar), leaving a yellow solid as a mixture of the (*pR*) and (*pS*) diastereomers **5a** and **5b** in the ratio 1:1.3. The crude product was suspended in *n*-pentane (15 mL) and filtered with a d4-frit. The residue of the filtration was recrystallized from dichloromethane (10 mL) at −78 °C, giving 0.62 g (25%) of yellow crystals of the (*pR*) and (*pS*) diastereomers **5a** and **5b** in the ratio 1:2.7.

Diastereomer 5a. ^{1}H NMR (dichloromethane-d_2, 200 MHz): δ 6.91−6.70 (m, 2H, $H^{5,6}$), 6.49 (d, ^3J = 3.2 Hz, 1H, $H^{2/3}$), 6.36 (s, 5H, $C_5\mathit{H}_5$), 6.23 (d, ^3J = 3.2 Hz, 1H, $H^{2/3}$), 3.41−0.45 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 2.82 (s, 3H, $H^{10/11}$), 2.27 (s, 3H, $H^{10/11}$), 1.00 (d, ^3J = 6.4 Hz, 3H, $H^{7'/9'/10'}$), 0.90 (d, ^3J = 7.0 Hz, 3H, $H^{7'/9'/10'}$), 0.88 (d, ^3J = 6.5 Hz, 3H, $H^{7'/9'/10'}$). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 50.32 MHz): δ 133.57, 133.23, 133.02, 129.97, 120.81 ($C^{1,4,7,8,9}$), 127.66, 126.97 ($C^{5,6}$), 116.90 ($\mathit{C}^{2/3}$), 116.22 (C_5H_5), 96.34 ($\mathit{C}^{2/3}$), 46.24, 40.86, 33.69, 27.33 ($C^{1',3',4',8'}$), 44.86, 35.61, 26.04 ($C^{2',5',6'}$), 22.60, 22.15, 21.68, 19.24, 16.88 ($C^{7',9',10,10',11}$).

Diastereomer 5b. ^{1}H NMR (dichloromethane-d_2, 200 MHz): δ 6.90−6.69 (m, 2H, $H^{5,6}$), 6.47 (d, ^3J = 3.3 Hz, 1H, $H^{2/3}$), 6.31 (s, 5H, $C_5\mathit{H}_5$), 6.29 (d, ^3J = 3.3 Hz, 1H, $H^{2/3}$), 3.39−0.55 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 2.73 (s, 3H, $H^{10/11}$), 2.21 (s, 3H, $H^{10/11}$), 1.10 (d, ^3J = 7.0 Hz, 3H, $H^{7'/9'/10'}$), 0.83 (d, ^3J = 6.6 Hz, 3H, $H^{7'/9'/10'}$), 0.77 (d, ^3J = 6.5 Hz, 3H, $H^{7'/9'/10'}$). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 50.32 MHz): δ 138.30, 135.90, 134.00, 133.38, 124.20 ($C^{1,4,7,8,9}$), 127.30, 126.75 ($C^{5,6}$), 116.03 (C_5H_5), 112.73, 94.49 ($C^{2,3}$), 48.24, 35.26, 25.36 ($C^{2',5',6'}$), 45.26, 41.86, 33.05, 28.06 ($C^{1',3',4',8'}$), 22.50, 22.27, 21.04, 18.89, 17.67 ($C^{7',9',10,10',11}$).

Diastereomers 5a and 5b in the Ratio 1:2.7. Mp: 148 °C dec. $[\alpha]_D^{25} = -63.2°$ (*c* 0.2, diethyl ether). IR (CsI; cm^{-1}): $\bar{\nu}$ 3108 (m), 2959 (s), 2947 (s), 2927 (m), 2867 (m), 2844 (w), 1653 (m), 1623 (m), 1617 (m), 1492 (m), 1463 (m), 1454 (m), 1441 (m), 1391 (w), 1377 (w), 1369 (w), 1257 (m), 1247 (m), 1139 (w), 1107 (w), 1072 (w), 1069 (w), 1019 (m), 851 (s), 819 (s), 656 (m), 652 (m), 516 (m), 328 (m), 313 (m), 303 (m), 278 (m), 254 (m). MS (204 °C; *m/z* (%)): 506 (6) $[M]^+$, 471 (2) $[(C_{21}H_{29})(C_5H_5)ClZr]^+$, 421 (2) $[(C_{20}H_{26})(C_5H_5)Zr]^+$, 121 (100) $[C_9H_{13}]^+$. Anal. Calcd for $C_{26}H_{34}Cl_2Zr$ (mol wt 508.68): C, 61.39; H, 6.74. Found: C, 60.91; H, 6.33.

Bis(η^5-1-menthyl-4,7-dimethylindenyl)iron(II) (6a/6b/6c). To a solution of $FeCl_2(THF)_{1.5}$ (0.54 g, 2.58 mmol) in THF (20 mL) was added **1** (1.25 g, 4.33 mmol) at −78 °C. The mixture was stirred for 2 h, warmed to 25 °C over 8 h, and stirred for an additional 10 h. The solvent was removed under vacuum (10^{-2} mbar), leaving a black solid which was suspended in *n*-hexane (10 mL) and filtered with a d4-frit. The residue was extracted twice with *n*-hexane (10 mL). The solvent was removed under vacuum (10^{-2} mbar), leaving a black solid as a mixture of the (*pR*)(*pR*), (*pR*)(*pS*), and (*pS*)(*pS*) diastereomers **6a**, **6b**, and **6c** in the ratio 4.8:1.8:1. The solid was suspended in *n*-hexane (2 mL) and the suspension fractionally chromatographed under nitrogen with alumina. Elution with *n*-hexane gave colorless and finally black solutions. The solvent of the black fractions was removed under vacuum (10^{-2} mbar), yielding solids which were recrystallized from *n*-pentane at −28 °C, giving 1.80 g (49%) of black crystals of the diastereomers **6a**, **6b**, and **6c** in the ratio (*pR*)(*pR*):(*pR*)(*pS*):(*pS*)(*pS*) = 4.8:1.8:1.

(*pR*)(*pR*) Diastereomer 6a. ^{1}H NMR (benzene-d_6, 200 MHz): δ 6.53 (m, 1H, $H^{5/6}$), 6.37 (m, 1H, $H^{5/6}$), 4.98 (d, ^3J = 2.5 Hz, 1H, H^2), 4.36 (d, ^3J = 2.5 Hz, 1H, H^3), 3.25−0.60 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 2.60 (s, 3H, $H^{10/11}$), 1.81 (s, 3H, $H^{10/11}$), 1.18 (d, ^3J = 6.2 Hz, 3H, $H^{7'}$), 0.55 (d, ^3J = 6.9 Hz, 3H, $H^{9'/10'}$), 0.46 (d, ^3J = 6.8 Hz, 3H, $H^{9'/10'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.32 MHz): δ 132.80, 127.80 ($C^{4,7}$), 123.61, 120.73 ($C^{5,6}$), 89.77, 88.75, 84.09 ($C^{1,8,9}$), 68.90, 60.91 ($C^{2,3}$), 52.09, 38.93, 34.35, 26.95 ($C^{1',3',4',8'}$), 47.13, 35.47, 25.66 ($C^{2',5',6'}$), 23.14, 22.59, 22.03, 19.35, 16.13 ($C^{7',9',10,10',11}$).

(*pR*)(*pR*), (*pR*)(*pS*), and (*pS*)(*pS*) Diastereomers 6a, 6b, and 6c in the Ratio 4.8:1.8:1. Mp: 81 °C. $[\alpha]_D^{25} = -46.6°$ (*c* 0.1, diethyl ether). IR (CsI; cm^{-1}): $\bar{\nu}$ 3026 (w), 2953 (s), 2927 (s), 2867 (s), 1737 (m), 1698 (m), 1679 (m), 1650 (w), 1608 (m), 1556 (w), 1483 (m), 1463 (s), 1405 (w), 1383 (m), 1375 (m), 1367 (m), 1345 (m), 1327 (w), 1275 (m), 1251 (m), 1093 (m), 1062 (m), 915 (m), 810 (s), 594 (m), 580 (m), 458 (m), 303 (m). MS (136 °C; *m/z* (%)): 618 (100) $[M]^+$, 603 (1) $[(C_{20}H_{26})(C_{21}H_{29})Fe]^+$, 575 (1) $[(C_{18}H_{22})(C_{21}H_{29})Fe]^+$, 479 (4) $[(C_{11}H_{10})(C_{21}H_{29})Fe]^+$, 309 (1) $[M]^{2+}$, 198 (2) $[(C_{11}H_{10})Fe]^+$. Anal. Calcd for $C_{42}H_{58}Fe$ (mol wt 618.77): C, 81.53; H, 9.45. Found: C, 81.09; H, 9.36. Mol wt (cryoscopy in benzene; *m/z*): 602.

Bis(η^5-1-menthyl-4,7-dimethylindenyl)nickel(II) (7a/7b/7c). In analogy with the synthesis of **6**, a solution of $NiCl_2(DME)$ (0.26 g, 1.18 mmol) in THF (20 mL) was treated at −78 °C with **1** (0.75 g, 2.60 mmol). The workup gave a violet solid as a mixture of the (*pR*)(*pR*), (*pR*)(*pS*), and (*pS*)(*pS*) diastereomers **7a**, **7b**, and **7c** in the ratio 5.9:4.0:1. Fractional chromatography under nitrogen with alumina gave 0.69 g (47%) of a violet oil as a mixture of the diastereomers **7a**, **7b**, and **7c** in the ratio (*pR*)(*pR*):(*pR*)(*pS*):(*pS*)(*pS*) = 5.9:4.0:1.

(*pR*)(*pR*) Diastereomer 7a. ^{1}H NMR (benzene-d_6, 200 MHz): δ 5.88 (m, 2H, $H^{5,6}$), 5.56 (s br, 1H, H^2), 5.42 (s br, 1H, H^3), 3.03−0.59 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 2.38 (s, 3H, $H^{10/11}$), 1.97 (s, 3H, $H^{10/11}$), 0.99 (d, ^3J = 6.1 Hz, 3H, $H^{7'}$), 0.86 (d, ^3J = 6.6 Hz, 3H, $H^{9'/10'}$), 0.70 (d, ^3J = 6.6 Hz, 3H, $H^{9'/10'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.32 MHz): δ 129.29, 127.41 ($C^{5,6}$), 124.66, 123.71, 123.38, 122.93, 121.64 ($C^{1,4,7,8,9}$), 104.57 (C^2), 64.48 (C^3), 55.52, 45.05, 34.56, 28.30 ($C^{1',3',4',8'}$), 53.26, 35.52, 26.17 ($C^{2',5',6'}$), 23.46, 22.75, 21.08, 18.22, 17.06 ($C^{7',9',10,10',11}$).

(*pR*)(*pR*), (*pR*)(*pS*), and (*pS*)(*pS*) Diastereomers 7a, 7b, and 7c in the Ratio 5.9:4.0:1. $[\alpha]_D^{25} = +38.3°$ (*c* 0.2, diethyl ether). IR (CsI; cm^{-1}): $\bar{\nu}$ 3012 (m), 2952 (s), 2918 (s), 2868 (s), 2730 (w), 1868 (w), 1834 (w), 1700 (s), 1589 (m), 1566 (m), 1491 (s), 1456 (s), 1383 (s), 1368 (s), 1345 (m), 1333 (m), 1291 (m), 1280 (m), 1259 (m), 1211 (m), 1177 (m), 1139 (m), 1047 (m), 1031 (m), 992 (m), 981 (m), 933 (m), 922 (m), 916 (m), 901 (m), 874 (m), 841 (m), 802 (s), 787 (m), 775 (m), 770 (m), 640 (m), 533 (m), 491 (m), 457 (m), 303 (m). MS (149 °C; *m/z* (%)): 620 (43) $[M]^+$, 577 (1) $[(C_{18}H_{22})(C_{21}H_{29})Ni]^+$, 562 (6) $[(C_{18}H_{22})(C_{20}H_{26})Ni]^+$, 310 (2) $[M]^{2+}$, 200 (1) $[(C_{11}H_{10})Ni]^+$, 158 (100) $[C_{12}H_{14}]^+$. Anal. Calcd for $C_{42}H_{58}Ni$ (mol wt 621.61): C, 81.15; H, 9.40. Found: C, 81.63; H, 9.81.

(+)-Bis(η^5-2-menthylindenyl)iron(II) (8). In analogy with the synthesis of **6**, a solution of $FeCl_2(THF)_{1.5}$ (0.49 g, 2.34 mmol) in THF (20 mL) was treated at 0 °C with (−)-(2-menthylindenyl)lithium (**3**; 1.12 g, 4.30 mmol). The workup and fractional chromatography under nitrogen with alumina gave a black solid. Recrystallization from *n*-pentane gave 1.05 g (90%) of black crystals of **8**. Mp: 147 °C. $[\alpha]_D^{25} = +31.8°$ (*c* 0.1, diethyl ether). ^{1}H NMR (benzene-d_6, 200 MHz): δ 7.37 (m, 2H, H^4), 6.90 (m, 2H, H^5), 6.88 (m, 2H, H^6), 6.65 (m, 2H, H^7), 4.39 (d, ^4J = 0.6 Hz, 2H, H^3), 4.33 (d, ^4J = 0.6 Hz, 2H, H^1), 3.13 (m, 2H, $H^{2'}$), 2.12 (m, 2H, $H^{3'}$), 1.80 (m, 2H, $H^{6'}$), 1.64 (m, 2H, $H^{1'}$), 1.60 (m, 2H, $H^{5'}$), 1.48 (m, 2H, $H^{2'}$), 1.47 (m, 2H, $H^{8'}$), 1.22 (d, ^3J = 6.2 Hz, 6H, $H^{7'}$), 1.02 (m, 2H, $H^{5'}$), 0.93 (m, 2H, H$^{6'}$), 0.75 (d, $^3J = 6.8$ Hz, 6H, H$^{9'/10'}$), 0.74 (m, 2H, H$^{4'}$), 0.57 (d, $^3J = 6.9$ Hz, 6H, H$^{9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 129.19 (C^4), 125.70 (C^7), 123.34 (C^5), 122.74 (C^6), 95.88 (C^2), 85.88, 85.82 (C^{8,9}), 65.06, 59.63 (C^{1,3}), 50.62 (C$^{4'}$), 43.23 (C$^{2'}$), 39.61 (C$^{3'}$), 35.68 (C$^{6'}$), 33.97 (C$^{1'}$), 26.89 (C$^{8'}$), 25.17 (C$^{5'}$), 23.27 (C$^{7'}$), 21.51, 15.60 (C$^{9',10'}$). IR (CsI; cm^{-1}): $\bar{\nu}$ 3076 (w), 3057 (m), 3007 (m), 2957 (s), 2946 (s), 2938 (s), 2924 (s), 2874 (s), 2848 (s), 1714 (m), 1610 (m), 1457 (m), 1384 (m), 1369 (m), 1346 (m), 1295 (w), 1176 (w), 1078 (w), 999 (w), 921 (m), 834 (m), 749 (m), 738 (s), 716 (m), 576 (m), 461 (m), 203 (w). MS (40 °C; *m*/*z* (%)): 562 (100) [M]$^+$, 547 (1) [($C_{18}H_{22}$)($C_{19}H_{25}$)Fe]$^+$, 519 (6) [($C_{16}H_{18}$)($C_{19}H_{25}$)Fe]$^+$, 423 (3) [(C_9H_6)($C_{19}H_{25}$)Fe]$^+$, 309 (2) [($C_{19}H_{25}$)Fe]$^+$. Anal. Calcd for $C_{38}H_{50}Fe$ (mol wt 562.65): C, 81.12; H, 8.96. Found: C, 81.59; H, 8.47.

(−)-Bis(η^5-2-menthylindenyl)nickel(II) (9). In analogy with the synthesis of **6**, a suspension of NiCl$_2$(DME) (0.38 g, 1.73 mmol) in THF (25 mL) was treated at 0 °C with **3** (0.86 g, 3.30 mmol). The workup and fractional chromatography under nitrogen with alumina gave a red solid. Recrystallization from *n*-pentane at −78 °C gave 0.53 g (57%) red crystals of **9**. Mp: 140 °C dec. $[\alpha]_D^{25} = -276.8°$ (*c* 0.5, benzene). ^{1}H NMR (benzene-d_6, 200 MHz): δ 7.33−6.33 (m, 8H, H^{4,5,6,7}), 5.23 (d, $^4J = 1.6$ Hz, 2H, H$^{1/3}$), 4.88 (d, $^4J = 1.6$ Hz, 2H, H$^{1/3}$), 2.37−0.70 (m, 20H, H$^{1',2',3',4',5',6',8'}$), 1.00 (d, $^3J = 6.3$ Hz, 6H, H$^{7'/9'/10'}$), 0.92 (d, $^3J = 6.9$ Hz, 6H, H$^{7'/9'/10'}$), 0.82 (d, $^3J = 6.6$ Hz, 6H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 135.20, 133.82, 133.76 (C^{2,8,9}), 123.75, 123.39 (C^{4,7}), 116.35, 116.06 (C^{5,6}), 68.29, 63.98 (C^{1,3}), 51.38, 42.11, 32.77, 27.82 (C$^{1',3',4',8'}$), 40.59, 35.34, 24.92 (C$^{2',5',6'}$), 22.25, 21.38, 15.61 (C$^{7',9',10'}$). IR (CsI; cm^{-1}): $\bar{\nu}$ 3069 (m), 2956 (s), 2933 (s), 2914 (s), 2867 (s), 2855 (s), 2844 (s), 2031 (m), 1964 (m), 1713 (m), 1606 (w), 1459 (s), 1444 (m), 1431 (m), 1384 (m), 1370 (m), 1346 (m), 1331 (m), 1320 (m), 1298 (w), 1249 (w), 1226 (m), 1134 (w), 1119 (w), 1079 (w), 1015 (m), 999 (w), 966 (m), 955 (m), 920 (s), 873 (m), 858 (m), 846 (m), 747 (s), 744 (s), 716 (m), 703 (m), 689 (m), 452 (m), 429 (m), 395 (m). MS (46 °C; *m*/*z* (%)): 564 (100) [M]$^+$, 506 (2) [($C_{16}H_{18}$)($C_{18}H_{22}$)Ni]$^+$, 425 (1) [(C_9H_6)($C_{19}H_{25}$)Ni]$^+$, 382 (3) [(C_9H_6)($C_{16}H_{18}$)Ni]$^+$, 311 (8) [($C_{19}H_{25}$)Ni]$^+$. Anal. Calcd for $C_{38}H_{50}Ni$ (mol wt 565.51) C, 80.71; H, 8.91. Found: C, 81.16; H, 9.26. Mol wt (cryoscopy in benzene; *m*/*z*): 593.

(−)-Bis(η^5-2-menthylindenyl)ruthenium(II) (10). To a red solution of tris(acetylacetonato)ruthenium(III) (0.26 g, 0.65 mmol) in benzene (25 mL) was added **3** (0.55 g, 2.11 mmol) at 0 °C. The brown suspension was heated for 40 h to 80 °C. The solvent was removed under vacuum (10^{-2} mbar), leaving a black solid which was suspended in *n*-hexane (3 mL) and fractionally chromatographed under nitrogen with alumina. Elution with *n*-hexane and finally with diethyl ether gave colorless and then orange solutions. The solvents of the orange fractions were removed under vacuum (10^{-2} mbar), yielding a yellow solid. Recrystallization from warm *n*-pentane (5 mL) gave 0.28 g (70%) of orange crystals of **10**. Mp: 67 °C. $[\alpha]_D^{25} = -111.1°$ (*c* 0.1, diethyl ether). ^{1}H NMR (benzene-d_6, 200 MHz): δ 7.20−6.60 (m, 8H, H^{4,5,6,7}), 5.12 (s, 2H, H$^{1/3}$), 4.65 (s, 2H, H$^{1/3}$), 2.79−0.68 (m, 20H, H$^{1',2',3',4',5',6',8'}$), 1.16 (d, $^3J = 6.4$ Hz, 3H, H$^{7'/9'/10'}$), 1.05 (d, $^3J = 6.9$ Hz, 3H, H$^{7'/9'/10'}$), 0.95 (d, $^3J = 6.9$ Hz, 3H, H$^{7'/9'/10'}$), 0.90 (d, $^3J = 6.4$ Hz, 3H, H$^{7'/9'/10'}$), 0.72 (d, $^3J = 6.9$ Hz, 3H, H$^{7'/9'/10'}$), 0.27 (d, $^3J = 6.8$ Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 125.99, 121.63, 121.03, 120.32 (C^{4,5,6,7}), 99.54, 90.61, 88.32 (C^{2,8,9}), 68.19, 63.86 (C^{1,3}), 50.75, 40.59, 34.15, 27.47 (C$^{1',3',4',8'}$), 43.98, 35.66, 25.27 (C$^{2',5',6'}$), 23.12, 21.61, 15.66 (C$^{7',9',10'}$). IR (CsI; cm^{-1}): $\bar{\nu}$ 3053 (w), 3017 (m), 2956 (s), 2919 (s), 2869 (m), 2848 (m), 1611 (m), 1518 (m), 1463 (s), 1385 (m), 1368 (m), 1345 (w), 1005 (w), 982 (w), 903 (w), 843 (w), 764 (m), 760 (m), 753 (m), 732 (m), 727 (m), 722 (m), 572 (w), 491 (w), 418 (w), 350 (w). MS (128 °C; *m*/*z* (%)): 608 (100) [M]$^+$, 593 (2) [($C_{18}H_{22}$)($C_{19}H_{25}$)Ru]$^+$, 565 (14) [($C_{16}H_{18}$)($C_{19}H_{25}$)Ru]$^+$, 469 (10) [(C_9H_6)($C_{19}H_{25}$)Ru]$^+$, 355 (1) [($C_{19}H_{25}$)Ru]$^+$. Anal. Calcd for $C_{38}H_{50}Ru$ (mol wt 607.88): C, 75.08; H, 8.29. Found: C, 75.52; H, 8.23.

Table 1

	4b	**8**
empirical formula	$C_{42}H_{58}Cl_2Zr$	$C_{38}H_{50}Fe$
fw	725.04	562.65
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a (Å), α (deg)	11.7782(2), 90	9.9996(2), 90
b (Å), β (deg)	17.7250(2), 90	10.8994(2), 90
c (Å), γ (deg)	18.2727(1), 90	29.3406(7), 90
V (Å^3)	3814.77(8)	3197.82(12)
Z	4	4
D(calcd) (g/cm^3)	1.262	1.169
μ(Mo Kα) (mm^{-1})	0.456	0.495
F(000)	1536	1216
cryst size (mm^3)	0.85 × 0.52 × 0.48	0.22 × 0.18 × 0.08
θ_{min}, θ_{max} (deg)	1.60, 27.50	1.39, 26.50
index ranges	$-12 \le h \le 15$	$-12 \le h \le 11$
	$-23 \le k \le 21$	$-13 \le k \le 11$
	$-23 \le l \le 23$	$-36 \le l \le 34$
no. of rflns collected	29 161	22 627
no. of indep rflns	8721 (R_{int} = 0.0377)	6619 (R_{int} = 0.1175)
max, min transmissn	0.8492, 0.7172	0.9705, 0.6329
no. of data, restraints, params	8721, 0, 416	6619, 0, 358
GOF on F^2	1.061	1.025
R indices ($I > 2\sigma(I)$)	R1 = 0.0239	R1 = 0.0655
	wR2 = 0.0552	wR2 = 0.1048
R indices (all data)	R1 = 0.0272	R1 = 0.1241
	wR2 = 0.0571	wR2 = 0.1225
abs structure param	−0.04(2)	−0.01(2)
residual electron density (e/Å^3)	max 0.273	max 0.447
	min −0.360	min −0.619

X-ray Structure Determination. The crystal data and details of data collection are given in Table 1. Data were collected on a Siemens SMART CCD diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.710\,73$ Å) with area detector by use of ω scans at 173 K for **4b** and **8**. The structures were solved by direct methods using SHELXS-97[14] and refined on F^2 using all reflections with SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. The idealized methyl groups were allowed to rotate about their C−C bond. Absolute structure parameters were determined according to Flack[16] with SHELX-97. SADABS[17] was used to perform area-detector scaling and absorption corrections. The maximum and minimum transmission factors and the resulting crystallographic data are summarized in Table 1. The geometrical aspects of the structures were analyzed by using the PLATON program.[18]

Results and Discussion

Metallocenes with Diastereotopic Indenyl Ligands. Substituted unbridged planar chiral[19] indenyl ligands having enantiotopic faces tend to give upon metalation three stereoisomeric bis(indenyl)metal complexes (pR)(pR), (pR)(pS), and (pS)(pS) in the statistical ratio 1:2:1. If indenyl ligands with chiral substituents are used, the metalation ratio for these diastereotopic

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[14] Sheldrick, G. M. SHELXS-97: Program for the Solution of Crystal Structures; Universität Göttingen, Göttingen, Germany, 1997.

[15] Sheldrick, G. M. SHELXL-97: Program for the Refinement of Crystal Structures; Universität Göttingen, Göttingen, Germany, 1997.

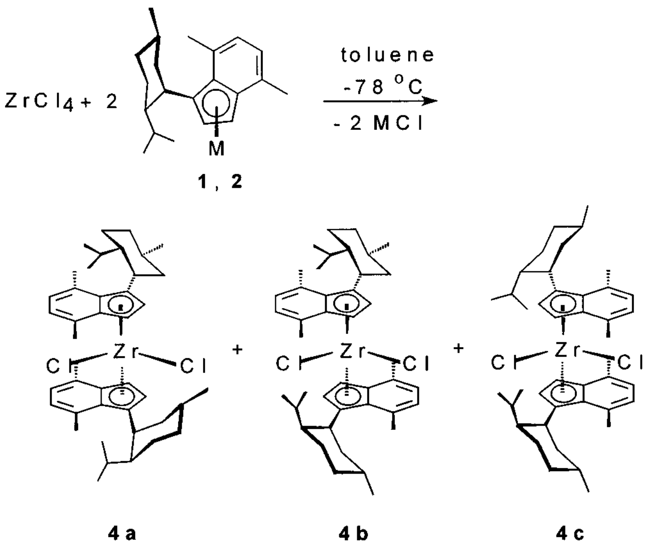
[16] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

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

[18] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

[19] (a) Schlögl, K. *Fortschr. Chem. Forsch.* **1966**, *6*, 479. (b) Schlögl, K. *Top. Stereochem.* **1967**, *1*, 39.

Scheme 1



ligands no longer tends to be statistically determined but is strongly influenced by steric interactions, as illustrated in Scheme 1, where the 4′-isopropyl group of the menthyl moiety is more sterically demanding than the corresponding 1′-methyl group. The metathetic reaction of 2 equiv of the lithium (**1**) or sodium (**2**) salts of (−)-3-menthyl-4,7-dimethylindene with $ZrCl_4$ in toluene at −78 °C gave the (*pR*)(*pR*)- and (*pR*)(*pS*)-bis(1-menthyl-4,7-dimethylindenyl)zirconium dichloride complexes **4a** and **4b** in 58−87% isolated yield without any trace of the (*pS*)(*pS*) diastereomer **4c**.

The compounds **4a**, **4b**, and **4c** were formed in the ratio 0.8:1:0 when the lithium salt **1** is used, where as the potassium salt **2** gives the products in the ratio 0.9:1:0. The corresponding metalation ratios are therefore (*pR*):(*pS*) = 2.6:1 and (*pR*):(*pS*) = 2.8:1, giving rise to apparent diastereoselectivities of 44% and 47%. Given this selectivity, the (*pS*)(*pS*) diastereomer **4c** should be formed in about 7% yield. Since this isomer was not observed, its formation could be disfavored by additional ligand−ligand interactions beyond the ligand−metal interactions assumed for the ratios above. It is particularly noteworthy that even though the lithium salt **1** itself can be synthesized almost quantitively in the (*pR*) configuration, the following reaction is surprisingly much less selective. In the course of the metathesis, the diastereotopic faces of the indenyl moiety are therefore not well energetically discriminated by the menthyl functionality. The apparent diastereoselectivities in the syntheses of **4** depend only slightly on the main-group cation of the (−)-3-menthyl-4,7-dimethylindene ligand. They do not vary as much as in the synthesis of (*pR*)- and (*pS*)-(−)-(η^4-cycloocta-1,5-diene)(η^5-1-menthyl-4,7-dimethylindenyl)rhodium(I), where the (*pR*) complex is formed with +39% de when the lithium salt **1** is used, whereas the potassium salt **2** gives the (*pS*) complex with 50% de.[10] The similar complex bis(4,7-dimethyl-3-neomenthylindenyl)zirconium dichloride could be synthesized with an increased apparent diastereoselectivity of 97%.[20]

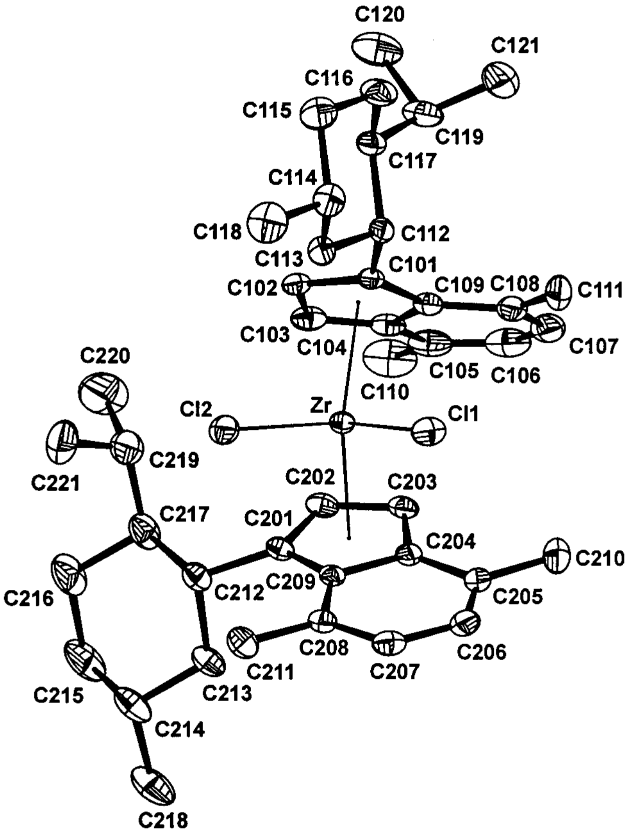


Figure 1. ORTEP plot[25] of the molecular structure and numbering scheme of **4b**, with 50% probability thermal ellipsoids. For clarity, all hydrogens are removed. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:[25] Zr−Cg(1) = 2.2492(8), Zr−Cg(2) = 2.2517(7), Zr−Cl(1) = 2.4305(5), Zr−Cl(2) = 2.4200(4), C(101)−C(102) = 1.406(2), C(102)−C(103) = 1.413(2), C(103)−C(104) = 1.424(3), C(104)−C(109) = 1.443(2), C(101)−C(109) = 1.456(2), C(201)−C(202) = 1.407(2), C(202)−C(203) = 1.421(3), C(203)−C(204) = 1.427(2), C(204)−C(209) = 1.436(2), C(201)−C(209) = 1.452(2); Cg(1)−Zr−Cg(2) = 129.84(3), Cg(1)−Zr−Cl(1) = 109.75(2), Cg(1)−Zr−Cl(2) = 105.76(2), Cl(1)−Zr−Cl(2) = 94.244(17), Cg(2)−Zr−Cl(1) = 104.65(2), Cg(2)−Zr−Cl(2) = 106.90(2).

The air- and moisture-sensitive mixtures of **4a** and **4b** and their solutions do not allow separation by GC, HPLC, or column chromatography (using SiO_2 or reversed-phase C_{18}-modified SiO_2). Repeatedly washing of the crude mixture with small amounts of *n*-pentane results in the less soluble (*pR*)(*pS*) diastereomer **4b**, forming a solid residue, and the (*pR*)(*pR*) diastereomer **4a** remaining in solution. Recrystallization of both from dichloromethane yields the diastereomerically pure compounds **4b** and **4a**.

Crystals of **4b** suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from dichloromethane. The solid-state structure was determined by X-ray diffraction methods. **4b** crystallizes in the space group $P2_12_12_1$ with four superimposable molecules in the unit cell. The monomeric, solvent-free complex is diastereomerically pure and shows the desired three stereocenters of the menthyl moiety. The zirconium atom is coordinated pseudo-tetrahedrally by the centroids of the five-membered indenyl rings and the two chlorine atoms (Figure 1). The indenyl ligands differ by the Zr metal being attached either on the prochiral (*pR*) or on the (*pS*) side. It is particularly

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[20] Knickmeier, M.; Erker, G.; Fox, T. *J. Am. Chem. Soc.* **1996**, *118*, 9623.

noteworthy that regardless of the (*pR*) or (*pS*) metalation the terpene moiety adopts similar conformations (+anticlinal and +synclinal) with the menthyl moiety being more or less perpendicular to the indenyl plane with the protons at C(112) and C(212) pointing toward C(111) and C(211), respectively. No rotation of approximately 180° is observed for the energetically disfavored (*pS*) metalated ligand to lower the steric constraint, as the menthyl group is sterically too hindered by the methyl group C(211) to perform this motion. The bond lengths of Zr to the centroids of the five-membered rings are slightly longer than in (*pR*)-(*pR*)-(+)-dichlorobis(η^5-neoisomenthylindenyl)zirconium(IV) (2.243 Å) and in (*pS*)(*pS*)-(−)-dichlorobis(η^5-neomenthylindenyl)zirconium(IV) (2.238 Å),[21] because of the steric hindrance of both isopropyl groups of the indenyl ligands. The average bond lengths Zr−Cl (2.43 Å in **4b** compared to 2.43 and 2.42 Å, respectively) as well as the angles Cg(1)−Zr−Cg(2) (129.8° in **4b** compared to 130.3 and 129.5°, respectively) and Cl(1)−Zr−Cl(2) (94.2° in **4b** compared to 96.7 and 91.6°, respectively) are in agreement with those in the other two compounds. The main axes of the indenyl systems show a rotation angle of 102.5°. The bent angle[22] between the two indenyl planes is 54.9°. The five-membered rings of the indenyl systems are not equally bound to the zirconium atom but resemble an unsymmetrical η^5-coordination. For example, the bond lengths of the carbon atoms C(101), C(102), and C(103) to the metal are the shortest ones in the case of the (*pR*)-indenyl ligand, while in the (*pS*)-metalated ligand the atoms C(202), C(203), and C(204) show the shortest bond lengths. The steric interactions between the menthyl and the metal moieties give rise to slip distortions[23] Δ of 0.063 and 0.079 Å as well as ring slippages RS[23] of 0.098 and 0.210 Å for the (*pR*) and the (*pS*) ligand. The tendency for slight η^3-coordination which is higher for the (*pS*) metalated ligand accounts for the nonplanar cyclopentadienyl rings and therefore to hinge angles HA as well as fold angles FA.[24] The values for the HA and FA are 3.4 and 8.8° for the (*pR*) ligand and are 2.5 and 5.2° for the (*pS*) ligand.

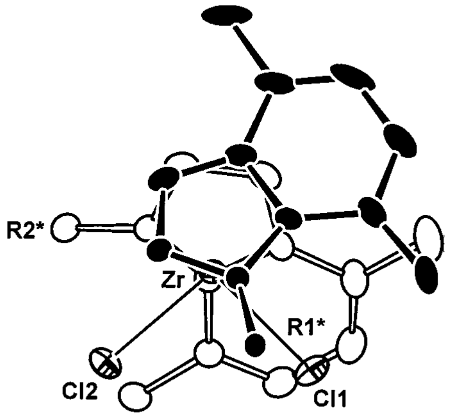
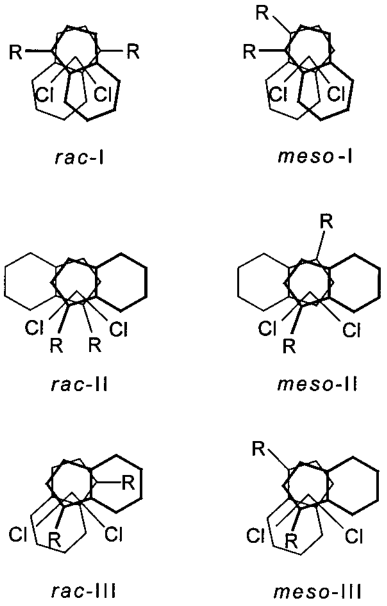


Figure 2. Conformation of **4b** in the solid state (R1* = R2* = menthyl). Thermal ellipsoids are shown with 50% probability.

Chart 2. Torsional Isomers of Bis(1-hydrocarbylindenyl)zirconium(IV) Dichloride Compounds



This first molecular structure of a *meso*-like menthyl-substituted metallocene proves that the chiral auxiliary menthyl itself is not able to allow a high diastereoselectivity with regard to the metalation of the planar chiral indenyl moiety, as the ligands are metalated on the sterically free and the sterically hindered side as well. This is due to the insufficient steric demand of the menthyl's isopropyl group. In contrast to the literature, the formation of the mixture is independent from the conformational rigidity along the C(101)−C(112) and C(201)−C(212) axes,[20,27] which would more or less interconvert the sterically free and hindered sides. The solid-state conformation of **4b** is shown in Figure 2. Both chlorine atoms show interactions with the two menthyl moieties so that interesting catalytical properties can be expected.[28] Comparison with the torsional isomers of other hydrocarbylindenyl ligands depicted in Chart 2, whose arrangements are derived from conformational analysis,[29] NMR spectroscopy, and X-ray diffraction analyses,[20] shows that **4b** gives rise to a new minimum structure which shows similarities to the *meso*-III isomer.

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[21] Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590.

[22] Bent angle = angle between the least-squares ring planes defined by C(101), C(102), C(103), C(104), C(109) and C(201), C(202), C(203), C(204), C(209).

[23] Slip distortion Δ = difference in the average metal to carbon distances: 0.5(M−C(*x*04) + M−C(*x*09)) − 0.5(M−C(*x*01) + M−C(*x*03)); ring slippage RS = distance from the normal of the least-squares ring plane defined by C(*x*01), C(*x*02), C(*x*03), C(*x*08), C(*x*09) to the metal atom and the centroid of the five-membered ring. Kakkar, A.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198*, 219.

[24] Hinge angle = angle between normals to the least-squares planes defined by C(*x*01), C(*x*02), C(*x*03) and C(*x*01), C(*x*09), C(*x*04), C(*x*03); fold angle = angle between normals to the least-squares planes defined by C(*x*01), C(*x*02), C(*x*03) and C(*x*04), C(*x*05), C(*x*06), C(*x*07), C(*x*08), C(*x*09). Kakkar, A.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198*, 219.

[25] Zsolnai, L.; Pritzkow, H. ZORTEP: ORTEP Program for PC; Universität Heidelberg, Heidelberg, Germany, 1994.

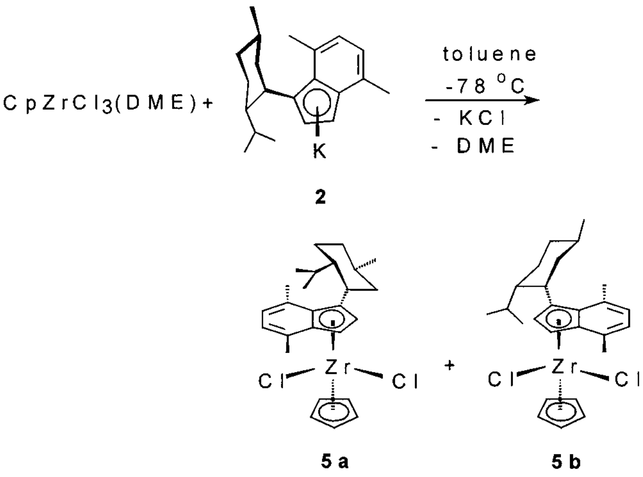
[26] C(g) defines the centroid of the ring atoms C(*x*01), C(*x*02), C(*x*03), C(*x*04), C(*x*09).

[27] Knickmeier, M. Dissertation, Universität Münster, Münster, Germany, 1995.

[28] Raubenheimer, H. G.; Halterman, R. L.; Stenzel, O.; Dechert, S.; Schumann, H. Manuscript in preparation.

[29] Krüger, C.; Lutz, F.; Nolte, M.; Erker, G.; Aulbach, M. *J. Organomet. Chem.* **1993**, *452*, 79.

Scheme 2



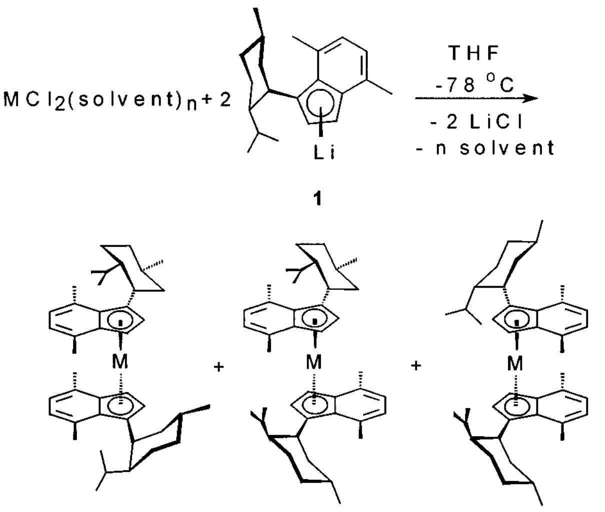
The indenyl–Zr bond in **4** can be opened and closed reversibly, which was proven by heating a 1:4 mixture of the diastereomers **4a** and **4b** in THF to 65 °C over 5 h and slow cooling to room temperature within 3 h. After three additional heating and cooling cycles the ratio changed to **4a**:**4b** = 1:2, with the thermodynamical more stable (*pR*)(*pR*) diastereomer being enriched. **4a** and **4b** are soluble in polar solvents such as THF, pyridine, and diethyl ether as well as in aromatic solvents such as toluene and nonpolar solvents such as *n*-hexane. ^{1}H NMR measurements at low temperatures, as well as ^{13}C{^{1}H} NMR, ^{1}H,^{1}H COSY, ^{1}H,^{13}C correlated, and COLOC measurements were performed to assign the ^{1}H,^{13}C signal pairs to the complicated NMR spectra. The (*pR*)(*pR*) diastereomer shows sharp signals, while the (*pR*)(*pS*) diastereomer, which consists of two signal sets for the diastereotopic indenyl protons, already gives rise to broadened signals due to slow conversions of the torsional isomers depicted in Chart 2 on the NMR time scale.

Cyclopentadienylzirconium trichloride reacts with (−)-(1-menthyl-4,7-dimethylindenyl)potassium (**2**) in toluene at −78 °C with formation of a yellow crystalline air-, light-, and moisture-sensitive product consisting of the (*pR*) and (*pS*) diastereomers **5a** and **5b** in the ratio 1:1.3 with an apparent diastereomeric excess of 13% (Scheme 2).

The iron complex of (−)-3-menthyl-4,7-dimethylindene was synthesized in a metathetic reaction similar to the synthesis of **4** using 2 equiv of the lithium salt **1** and FeCl$_2$(THF)$_{1.15}$ in THF at −78 °C (Scheme 3).

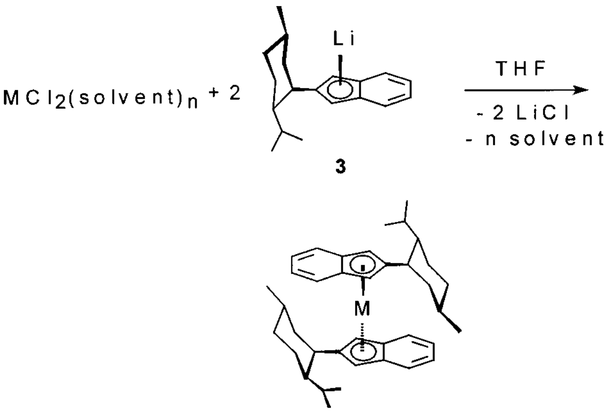
The (*pR*)(*pR*)-, (*pR*)(*pS*)-, and (*pS*)(*pS*)-bis(η^5-1-menthyl-4,7-dimethylindenyl)iron(II) compounds **6a**, **6b**, and **6c** were formed in the ratio 4.8:1.8:1 in 49% yield as black moisture- and air-sensitive solids. In contrast to the zirconocenes **4a**/**4b**, the energetically least favorable (*pS*)(*pS*) diastereomer of **6** is formed also, even though the overall apparent diastereomeric excess is, at 50%, slightly higher than in the synthesis of **4**. The separation of the diastereomers by fractional crystallization was not possible.

Scheme 3



6a, b, c: M = Fe (n = 1.15, solvent = THF)
7a, b, c: M = Ni (n = 1, solvent = DME)

Scheme 4



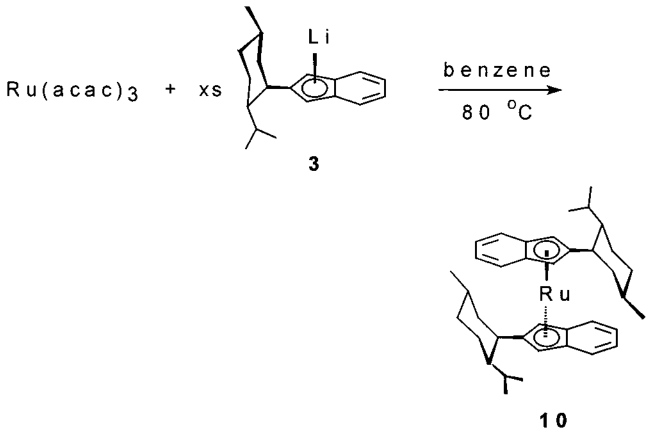
8: M = Fe (n = 1.15, solvent = THF)
9: M = Ni (n = 1, solvent = DME)

The nickel complex **7** of (−)-3-menthyl-4,7-dimethylindene was synthesized in a similiar metathetic reaction (Scheme 3). All three possible diastereomers were formed in 47% yield in the ratio (*pR*)(*pR*):(*pR*)(*pS*):(*pS*)(*pS*) = 5.9:4.0:1 with an apparent diastereomeric excess of 45%. In both of these last two cases, more of the (*pR*)(*pS*) and (*pS*)(*pS*) isomers were formed, given expectations based on the 45–50% facial selectivity. Again, direct ligand–ligand interactions could explain these deviations from ideal behavior.

Metallocenes with Homotopic Indenyl Ligands. Using indenyl ligands with homotopic faces which are substituted by a chiral organic group should avoid the formation of different diastereomers during the metalation. This was proved by the reaction of (−)-2-menthylindenyllithium (**3**)[8] with FeCl$_2$(THF)$_{1.15}$ in THF at 0 °C, which resulted in the formation of the iron complex **8** in 90% yield (Scheme 4). After recrystallization from *n*-pentane black crystals of **8** were obtained. The analogous metathetic reaction of **3** with NiCl$_2$(DME) in THF at 0 °C and recrystallization from *n*-pentane gives the nickel complex **9** as red crystals in 57% yield (Scheme 4).

In contrast, the analogous ruthenium compound cannot be synthesized via metathetic methods at low temperature but can in general be obtained by reaction of alkali-metal salts of cyclopentadienyl systems with compounds such as Ru$_3$(CO)$_{12}$, Ru(acac)$_3$, [RuCl$_2$(COD)]$_x$,

Scheme 5



and [RuCl$_2$(p-cymol)]$_2$ between 80 and 180 °C.[30] This excludes the use of ligands with diastereotopic faces which require kinetically controlled reaction conditions. Ligands with homotopic faces do not need to fulfill this requirement. Ru(acac)$_3$ reacts smoothly with 3 equiv of **3** in benzene at 80 °C, forming orange crystals of (−)-bis(η^5-2-menthylindenyl)ruthenium(II) (**10**) in 70% yield (Scheme 5).

The mass spectra of **8**, **9**, and **10** give the molecular ion as the peak of highest mass and highest intensity. The ^{1}H as well as the ^{13}C NMR spectra show only one signal set for both indenyl systems, proving either a symmetrical, fixed arrangement of both indenyls or a fast rotation of them around the indenyl−metal axes.

The molecular structure of **8** (Figure 3) shows the iron atom coordinated linearly by the centroids of the five-membered indenyl rings. The indenyl planes are almost parallel to each other, giving rise to a bent angle[22] of 2.1°. The terpene moieties adopt in both ligands a +synclinal arrangement to the indenyl plane, with each of the isopropyl groups pointing away from the metal. The average bond lengths of both five-membered-ring centroids to the metal are 2.07 Å. These lengths correlate with the bond lengths of 2.07 Å in bis(η^5-heptamethylindenyl)iron(II), which are 0.01 Å longer than the bond lengths in bis(η^5-indenyl)iron(II).[31] The main axes of the indenyl systems form a rotation angle of 134°, which is probably due to intramolecular steric interactions of the terpene units with the indenyl ligands, as the sterically less constrained bis(η^5-indenyl)iron(II) complex shows a rotation angle of only 9.1°. In bis(η^5-heptamethylindenyl)iron(II) an increased angle of 151.3° is found, which was attributed to orbital effects.[32] The five-membered rings of the indenyl systems are not equally bound but resemble an unsymmetrical η^5-coordination with slip distortions of 0.065 and 0.051 Å as well as ring slippages toward the C(102) and the C(202) atom of 0.052 and 0.058 Å, respectively. The tendency to a slight η^3- coordination accounts for HA values of 4.9 and 2.5° as well as FA values of 6.0 and 4.1°. For the bis(η^5-heptamethylindenyl)iron(II) and bis(η^5-indenyl)iron(II) complexes lower values of Δ = 0.030 and 0.043 Å, HA = 2.5 and 2.2°, and FA = 4.4 and 0.8° are found, which are probably due to packing effects.

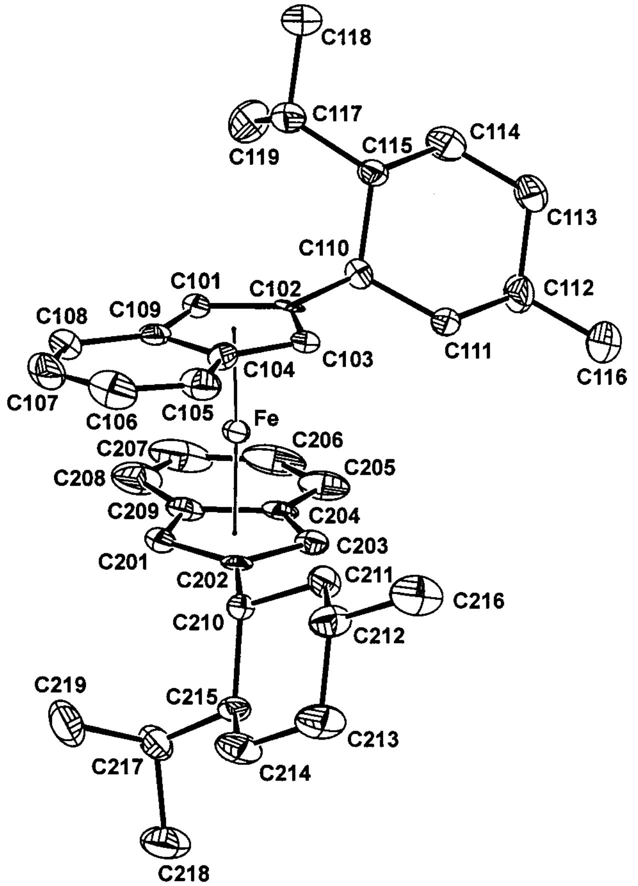


Figure 3. ORTEP plot[25] of the molecular structure and numbering scheme of **8**, with 50% probability thermal ellipsoids. For clarity, all hydrogens are removed. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:[25] Fe−Cg(1) = 1.676(2), Fe−Cg(2) = 1.675(2), C(101)−C(102) = 1.442(6), C(102)−C(103) = 1.424(6), C(103)−C(104) = 1.437(6), C(104)−C(109) = 1.445(7), C(101)−C(109) = 1.433(7), C(201)−C(202) = 1.418(7), C(202)−C(203) = 1.443(7), C(203)−C(204) = 1.437(7), C(204)−C(209) = 1.455(7), C(201)−C(209) = 1.419(7); Cg(1)−Fe−Cg(2) = 177.78(11).

Conclusion

Novel chiral nonracemic transition-metal complexes of Zr, Fe, and Ni containing optically active, menthyl-substituted indenyl ligands were prepared by metathetic reactions of chiral main-group-metal salts of (−)-3-menthyl-4,7-dimethylindene and (−)-2-menthylindene and ZrCl$_4$, CpZrCl$_3$(DME), FeCl$_2$(THF)$_{1.15}$, and NiCl$_2$-(DME). Ru(acac)$_3$ is reduced by excess (−)-(2-menthylindenyl)lithium, yielding (−)-(2-menthylindenyl)$_2$Ru. Depending on the reaction conditions, compounds with diastereotopic indenyl ligands were formed as mixtures of diastereomers with apparent diastereomerical excesses of 13−50% with regard to the planar chirality of the indenyl ring system. Compounds with homotopic indenyl ligands were obtained as stereomerically pure complexes. X-ray diffraction analyses of **4b** and **8** showed the monomeric, free of solvent, diastereomerically pure compounds with the indenyl moiety being η^2

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[30] Stenz, S. Dissertation, Technische Universität Berlin, Berlin, Germany, 1999.

[31] Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777.

[32] Crossley, N. S.; Green, J. C.; Nagy, A.; Stringer, G. *J. Chem. Soc., Dalton Trans.* **1989**, 2139.

$+ \eta^3$ coordinated. **4b** is the first molecular structure of a *meso*-like menthyl-substituted metallocene. It proves that the chiral auxiliary menthyl is not able to allow a high diastereoselectivity with regard to the planar chirality of the indenyl moiety, independently from the conformational rigidity along the indenyl−menthyl axis.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, the Deutschen Forschungsgemeinschaft (Graduate College “Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren”), the Technical University of Berlin (Erwin-Stephan-Scholarship), and the Partnership between the Technical University of Berlin and the University of Oklahoma.

Supporting Information Available: Full details of the X-ray structures of complexes **4b** and **8**, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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