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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 $(pR)(pR)-/(pR)(pS)-(1-menthyl-4,7-dimethylindenyl)_2Tcl_2$ (**4a**/**4b**), $(pR)-/(pS)-(cyclopentadienyl)(1-menthyl-4,7-dimethylindenyl)_2Tcl_2$ (**5a**/**5b**), $(pR)(pR)-/(pR)(pS)-((pS)(pS)-(1-menthyl-4,7-dimethylindenyl)_2Fe ($ **6a**/**6b**/**6c** $), <math>(pR)(pR)-/(pR)(pS)-/(pS)(pS)-(1-menthyl-4,7-dimethylindenyl)_2Fe ($ **6a**/**6b**/**6c** $), <math>(pR)(pR)-/(pR)(pS)-((pS)(pS)-(1-menthyl)_4,7-dimethylindenyl)_2Fe ($ **6a**/**6b**/**6c** $), <math>(pR)(pR)-/(pR)(pS)-((pS)(pS)-(1-menthyl)_4,7-dimethylindenyl)_2Fe ($ **6a**/**6b**/**6c** $), <math>(pR)(pR)-/(pR)(pS)-/(pS)(pS)-(1-menthyl)_2Ni ($ **9** $). Ru(acac)_3 reacts with (–)-(2-menthylindenyl)_2Fe ($ **8** $), and (–)-(2-menthylindenyl)_2Ni ($ **9** $). Ru(acac)_3 reacts with (–)-(2-menthylindenyl)]thium ($ **3** $), yielding (–)-(2-menthylindenyl)_2Ru ($ **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–carbon² and carbon– hydrogen³ 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-4,7dimethylindene and (-)-2-menthylindene bonded to the transition metal. We have demonstrated that metathetic reactions of the alkali-metal salts of chiral menthylsubstituted indenyl ligands, such as (-)-3-menthyl-4,7dimethylindene, (-)-4,7-diisopropyl-3-menthylindene, and (+)-3-neomenthylindene with [RhCl(COD)]₂, [IrCl-(COD)₂, CoCl₂(dppe), and Mo(CO)₆ provide a convenient entry into chiral nonracemic mono(indenyl) transitionmetal 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 (1H, 200 MHz; 13C, 50.32 MHz) or ARX 400 (1H, 400 MHz; 13C, 100.64 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm relative to the ¹H and ¹³C 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 CpZrCl₃-(DME),¹¹ FeCl₂(THF)_{1.15},¹² and NiCl₂(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 (-)- $(\eta^{5}$ -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.** ¹H NMR (dichloromethaned₂, 400 MHz): δ 6.87 (m, 2H, H⁵), 6.78 (m, 2H, H⁶), 6.70 (d, ³J = 3.2 Hz, 2H, H²), 6.37 (d, ³J = 3.2 Hz, 2H, H³), 3.21 (m, 2H, H³), 2.72 (s, 6H, H¹¹), 2.47 (m, 2H, H²), 2.31 (m, 2H, H⁸), 2.30 (s, 6H, H¹⁰), 1.88 (m, 2H, H⁶), 1.73 (m, 2H, H⁵), 1.55 (m, 2H, H¹), 1.29 (m, 2H, H²), 1.25 (m, 2H, H⁵), 1.19 (m, 2H, H⁴), 1.10 (m, 2H, H⁶), 1.04 (d, ³J = 6.5 Hz, 6H, H⁷), 0.61 (d, ³J = 6.7 Hz, 6H, H^{9'/10'}), 0.54 (d, ³J = 6.5 Hz, 6H, H^{9'/10'}). ¹³C{¹H} NMR (dichloromethane-*d*₂, 100.64 MHz): δ 139.41, 134.19, 133.32, 132.98 (C^{4.7,8.9}), 127.66 (C⁶), 127.42 (C⁵), 127.19 (C¹), 116.06 (C²), 95.88 (C³), 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 (C¹¹), 19.59 (C¹⁰), 16.63 (C^{9'/10'}).

(pR)(pS) Diastereomer 4b. The first signal set is as follows (1H/13C pairs are correlated). 1H 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, H²), 5.36 (s br, 1H, H³), 3.34 (m, 1H, H³), 2.72 (s, 3H, H^{10/11}), 2.63 (s, 3H, H^{10/11}), 2.55 (m, 1H, H²), 1.87 (m, 1H, H⁶), 1.81 (m, 1H, H⁵), 1.53 (m, 1H, H¹), 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, H⁸), 0.58 (d, ${}^{3}J$ = 6.8 Hz, 3H, H^{9/10}). ${}^{13}C{}^{1}H$ NMR (dichloromethane-d₂, 100.64 MHz): δ 134.78, 134.42, 133.23, 133.20 (C4,7,8,9), 125.34 (C1), 125.33, 125.04 (C5,6), 122.85 (C2), 96.89 (C³), 45.52 (C⁴), 43.90 (C²), 41.45 (C³), 35.83 (C⁶), 33.05 (C1'), 27.20 (C8'), 25.46 (C5'), 22.80 (C7'), 22.49 (C9'/10'), 21.89 $(C^{10/11})$, 20.79 $(C^{10/11})$, 17.10 $(C^{9'/10'})$. The second signal set is as follows (1H/13C pairs are correlated). 1H 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, H²), 4.89 (s br, 1H, H³), 3.19 (m, 1H, H³), 2.46 (s br, 3H, H^{10/11}), 2.02 (s br, 3H, H^{10/11}), 1.78 (m, 1H, H⁶), 1.67 (m, 1H, H⁵), 1.52 (m, 1H, H²), 1.51 (m, 1H, H¹), 1.18 (m, 1H, H⁵), 1.13 (m, 1H, H⁴), 0.88 (m, 1H, H⁶), 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, H⁸), 0.53 (d, ${}^{3}J = 6.5$ Hz, 3H, H^{9'/10'}), 0.42 (m, 1H, H^{2'}). ${}^{13}C$ -{¹H} NMR (dichloromethane- d_2 , 100.64 MHz): δ 134.55, 134.32, 134.06, 133.41 (C4,7,8,9), 129.37 (C1), 127.04, 126.52 (C^{5,6}), 120.96 (C²), 97.15 (C³), 54.74 (C⁴), 47.95 (C²), 41.27 (C³), 35.36 (C⁶), 33.74 (C¹), 27.28 (C⁸), 26.25 (C⁵), 22.77 (C^{9/10}), 22.48 (C⁷), 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. $[\alpha]_D^{25} = -91.8^{\circ}$ (*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) [(C₂₁H₂₉)₂ClZr]⁺, 583 (2) [(C₁₁H₁₀)(C₂₁H₂₉)Cl₂Zr]⁺, 441 (97) [(C₂₁H₂₉)Cl₂Zr]⁺, 371 (3) [(C₂₁H₂₉)Zr]⁺, 158 (100) [C₁₂H₁₄]⁺. Anal. Calcd for C₄₂H₅₈Cl₂Zr (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. ¹H NMR (dichloromethane- d_2 , 200 MHz): δ 6.91–6.70 (m, 2H, H^{5.6}), 6.49 (d, ${}^{3}J$ = 3.2 Hz, 1H, H^{2/3}), 6.36 (s, 5H, C₅ H_5), 6.23 (d, ${}^{3}J$ = 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, ${}^{3}J$ = 6.4 Hz, 3H, H^{7′,9′,10}), 0.90 (d, ${}^{3}J$ = 7.0 Hz, 3H, H^{7′,9′,10′}), 0.88 (d, ${}^{3}J$ = 6.5 Hz, 3H, H^{7′,9′,10′}). ¹³C{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 (C^{2/3}), 116.22 (C₅H₅), 96.34 (C^{2′,5′,6′}), 22.60, 22.15, 21.68, 19.24, 16.88 (C^{7′,9′,10,10′,11}).

Diastereomer 5b. ¹H NMR (dichloromethane- d_2 , 200 MHz): δ 6.90–6.69 (m, 2H, H^{5.6}), 6.47 (d, ${}^{3}J$ = 3.3 Hz, 1H, H^{2/3}), 6.31 (s, 5H, C₅*H*₅), 6.29 (d, ${}^{3}J$ = 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, ${}^{3}J$ = 7.0 Hz, 3H, H^{7′,9′,10}), 0.83 (d, ${}^{3}J$ = 6.6 Hz, 3H, H^{7′,9′,10′}), 0.77 (d, ${}^{3}J$ = 6.5 Hz, 3H, H^{7′,9′,10′}). ¹³C{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_5 H₅), 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/,11}).

Diastereomers 5a and 5b in the Ratio 1:2.7. Mp: 148 °C dec. $[\alpha]_D^{25} = -63.2^\circ$ (*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) [(C₂₁H₂₉)-(C₅H₅)ClZr]⁺, 421 (2) [(C₂₀H₂₆)(C₅H₅)Zr]⁺, 121 (100) [C₉H₁₃]⁺. Anal. Calcd for C₂₆H₃₄Cl₂Zr (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 FeCl₂(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.** ¹H 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, H²), 4.36 (d, ³J = 2.5 Hz, 1H, H³), 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, H⁷), 0.55 (d, ³J = 6.9 Hz, 3H, H^{9'/10'}), 0.46 (d, ³J = 6.8 Hz, 3H, H^{9'/10}). ¹³C{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. $[\alpha]_D^{25} = -46.6^{\circ}$ (*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) [(C₂₀H₂₆)(C₂₁H₂₉)-Fe]⁺, 575 (1) [(C₁₈H₂₂)(C₂₁H₂₉)Fe]⁺, 479 (4) [(C₁₁H₁₀)(C₂₁H₂₉)-Fe]⁺, 309 (1) [M]²⁺, 198 (2) [(C₁₁H₁₀)Fe]⁺. Anal. Calcd for C₄₂H₅₈Fe (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 NiCl₂-(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*):(*pS*)(*pS*) = 5.9:4.0:1.

(*pR*)(*pR*) **Diastereomer 7a.** ¹H NMR (benzene-*d*₆, 200 MHz): δ 5.88 (m, 2H, H^{5,6}), 5.56 (s br, 1H, H²), 5.42 (s br, 1H, H³), 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, ³*J* = 6.1 Hz, 3H, H⁷), 0.86 (d, ³*J* = 6.6 Hz, 3H, H^{9'/10'}), 0.70 (d, ³*J* = 6.6 Hz, 3H, H^{9'/10'}). ¹³C{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 (C²), 64.48 (C³), 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. $[\alpha]_D^{25} = +38.3^{\circ}$ (*c* 0.2, diethyl ether). IR (CsI; cm⁻¹): \bar{v} 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) [(C₁₈H₂₂)(C₂₁H₂₉)Ni]⁺, 562 (6) [(C₁₈H₂₂)-(C₂₀H₂₆)Ni]⁺, 310 (2) [M]²⁺, 200 (1) [(C₁₁H₁₀)Ni]⁺, 158 (100) [C₁₂H₁₄]⁺. Anal. Calcd for C₄₂H₅₈Ni (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 FeCl₂(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. [α]_D²⁵ = +31.8° (*c* 0.1, diethyl ether). ¹H NMR (benzene-*d*₆, 200 MHz): δ 7.37 (m, 2H, H⁴), 6.90 (m, 2H, H⁵), 6.88 (m, 2H, H⁶), 6.65 (m, 2H, H⁷), 4.39 (d, ⁴*J* = 0.6 Hz, 2H, H³), 4.33 (d, ⁴*J* = 0.6 Hz, 2H, H¹), 3.13 (m, 2H, H²), 2.12 (m, 2H, H³), 1.80 (m, 2H, H⁶), 1.64 (m, 2H, H¹), 1.60 (m, 2H, H⁵), 1.48 (m, 2H, H²), 1.47 (m, 2H, H⁸), 1.22 (d, ³*J* = 6.2 Hz, 6H, H⁷), 1.02 (m, 2H, H⁵), 0.93 (m,

2H, H⁶), 0.75 (d, ${}^{3}J = 6.8$ Hz, 6H, H^{9'/10}), 0.74 (m, 2H, H⁴), 0.57 (d, ${}^{3}J = 6.9$ Hz, 6H, H^{9'/10}). ${}^{13}C{}^{1}H$ NMR (benzene-*d*₆, 50.32 MHz): δ 129.19 (C⁴), 125.70 (C⁷), 123.34 (C⁵), 122.74 (C⁶), 95.88 (C²), 85.88, 85.82 (C^{8,9}), 65.06, 59.63 (C^{1.3}), 50.62 (C⁴), 43.23 (C²), 39.61 (C³), 35.68 (C⁶), 33.97 (C¹), 26.89 (C⁸), 25.17 (C⁵), 23.27 (C⁷), 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) [(C₁₈H₂₂)-(C₁₉H₂₅)Fe]⁺, 519 (6) [(C₁₆H₁₈)(C₁₉H₂₅)Fe]⁺, 423 (3) [(C₉H₆)-(C₁₉H₂₅)Fe]⁺, 309 (2) [(C₁₉H₂₅)Fe]⁺. Anal. Calcd for C₃₈H₅₀Fe (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 NiCl₂(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. $[\alpha]_D^{25} = -276.8^\circ$ (*c* 0.5, benzene). ¹H NMR (benzene- d_6 , 200 MHz): δ 7.33–6.33 (m, 8H, H^{4,5,6,7}), 5.23 (d, ${}^{4}J = 1.6$ Hz, 2H, H^{1/3}), 4.88 (d, ${}^{4}J = 1.6$ Hz, 2H, H^{1/3}), 2.37-0.70 (m, 20H, $H^{1',2',3',4',5',6',8'}$), 1.00 (d, ${}^{3}J = 6.3$ Hz, 6H, $H^{7'/9'/10'}$), 0.92 (d, ${}^{3}J = 6.9$ Hz, 6H, $H^{7'/9'/10'}$), 0.82 (d, ${}^{3}J = 6.6$ Hz, 6H, $H^{7/9/10'}$). ¹³C{¹H} 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{v} 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) [(C16H18)(C18H22)Ni]+, 425 (1) [(C9H6)(C19H25)Ni]+, 382 (3) [(C₉H₆)(C₁₆H₁₈)Ni]⁺, 311 (8) [(C₁₉H₂₅)Ni]⁺. Anal. Calcd for C₃₈H₅₀Ni (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 $(\eta^{5}$ -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). ¹H NMR (benzene-d₆, 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, ${}^{3}J = 6.4$ Hz, 3H, $H^{7/9'/10'}$), 1.05 (d, ${}^{3}J = 6.9$ Hz, 3H, $H^{7'/9'/10'}$), 0.95 (d, ${}^{3}J$ = 6.9 Hz, 3H, $H^{7/9'/10'}$), 0.90 (d, ${}^{3}J$ = 6.4 Hz, 3H, $H^{7'/9'/10'}$), 0.72 (d, ${}^{3}J = 6.9$ Hz, 3H, H^{7'/9'/10'}), 0.27 (d, ${}^{3}J = 6.8$ Hz, 3H, H^{7'/9'/10'}). ¹³C{¹H} 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 (C1,3), 50.75, 40.59, 34.15, 27.47 (C1',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{v} 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) [(C₁₈H₂₂)(C₁₉H₂₅)Ru]⁺, 565 (14) $[(C_{16}H_{18})(C_{19}H_{25})Ru]^+$, 469 (10) $[(C_{9}H_{6})(C_{19}H_{25})Ru]^+$, 355 (1) [(C₁₉H₂₅)Ru]⁺. Anal. Calcd for C₃₈H₅₀Ru (mol wt 607.88): C, 75.08; H, 8.29. Found: C, 75.52; H, 8.23.

Table 1

	4b	8	
empirical formula	C42H58Cl2Zr	C ₃₈ H ₅₀ Fe	
fw	725.04	562.65	
cryst syst	orthorhombic	orthorhombic	
space group	P212121 (No. 19)	P212121 (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 K α) (mm ⁻¹)	0.456	0.495	
F(000)	1536	1216	
cryst size (mm ³)	$0.85 \times 0.52 \times 0.48$	$0.22\times0.18\times0.08$	
$\theta_{\min}, \theta_{\max}$ (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	$8721 (R_{int} = 0.0377)$	$6619 (R_{int} = 0.1175)$	
may min transmissn	0.0377)	0.1175	
no of data restraints	8721 0 416	6619 0 358	
params	0721, 0, 110	0010, 0, 000	
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	
(0,11)	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 (graphitemonochromated Mo K α radiation, $\lambda = 0.71073$ 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-9714 and refined on F² using all reflections with SHELXL-97.¹⁵ All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å². The idealized methyl groups were allowed to rotate about their C-C bond. Absolute structure parameters were determined according to Flack¹⁶ with SHELX-97. SADABS¹⁷ was used to perform areadetector 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 chiral¹⁹ 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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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 ZrCl₄ in toluene at -78 °C gave the (*pR*)(*pR*)- and (*pR*)(*pS*)-bis(1menthyl-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)-(-)- $(\eta^4$ -cycloocta-1,5-diene)(\eta^5-1-menthyl-4,7dimethylindenyl)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

The air- and moisture-sensitive mixtures of **4a** and **4b** and their solutions do not allow separation by GC,



Figure 1. ORTEP plot²⁵ 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).

HPLC, or column chromatography (using SiO₂ or reversed-phase C_{18} -modified SiO₂). 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

⁽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 indenvl 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 angle²² 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 distortions²³ Δ of 0.063 and 0.079 Å as well as ring slippages RS23 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.

This first molecular structure of a *meso*-like menthylsubstituted 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

(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(x04) + M-C(x09)) - 0.5(M-C(x01) + M-C(x03)); ring slippage RS = distance from the normal of the least-squares ring plane defined by C(x01), C(x02), C(x03), C(x08), C(x09) 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(x01), C(x02), C(x03) and C(x01), C(x09), C(x04), C(x03); fold angle = angle between normals to the least-squares planes defined by C(x01), C(x02), C(x03) and C(x04), C(x05), C(x06), C(x07), C(x08), C(x09), Kakkar, A.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198*, 219.



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





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.

⁽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(x01), C(x02), C(x03), C(x04), C(x09).

⁽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.

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



The indenvl-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. ¹H NMR measurements at low temperatures, as well as ¹³C{¹H} NMR, ¹H, ¹H COSY, ¹H, ¹³C correlated, and COLOC measurements were performed to assign the ¹H,¹³C 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 FeCl₂(THF)_{1.15} in THF at -78 °C (Scheme 3).

The (pR)(pR)-, (pR)(pS)-, and (pS)(pS)-bis $(\eta^5$ -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.

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







Scheme 4



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

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 FeCl₂(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 NiCl₂(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 Ru₃(CO)₁₂, Ru(acac)₃, [RuCl₂(COD)]₃,





and [RuCl₂(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 ¹H as well as the ¹³C NMR spectra show only one signal set for both indenyl systems, proving either a symmetrical, fixed arrangement of both indenvls 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 fivemembered indenyl rings. The indenyl planes are almost parallel to each other, giving rise to a bent angle²² 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 $bis(\eta^{5}-indenyl)iron(II)$.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 $\Delta =$



Figure 3. ORTEP plot²⁵ 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).

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.

Conclusion

Novel chiral nonracemic transition-metal complexes of Zr, Fe, and Ni containing optically active, menthylsubstituted indenyl ligands were prepared by metathetic reactions of chiral main-group-metal salts of (-)-3menthyl-4,7-dimethylindene and (-)-2-menthylindene and ZrCl₄, CpZrCl₃(DME), FeCl₂(THF)_{1.15}, and NiCl₂-(DME). Ru(acac)₃ is reduced by excess (-)-(2-menthylindenyl)lithium, yielding (-)-(2-menthylindenyl)₂Ru. 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 indenvel moiety being η^2

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⁽³¹⁾ Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; (32) Crossley, N. S.; Green, J. C.; Nagy, A.; Stringer, G. J. Chem.

Soc., Dalton Trans. 1989, 2139.

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+ η^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.

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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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