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Menthyl-Functionalized Chiral Nonracemic Monoindenyl Complexes of Rhodium, Iridium, Cobalt, and Molybdenum

Herbert Schumann,* Oleg Stenzel, Sebastian Dechert, and Frank Girgsdies

Institut für Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135,
D-10623 Berlin, Germany

Ronald L. Halterman*

Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval,
Norman, Oklahoma 73019

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Optically active complexes of Rh, Ir, Co, and Mo containing the chiral, menthyl-substituted indenyl ligands (−)-3-menthyl-4,7-dimethylindene, (−)-4,7-diisopropyl-3-menthylindene, and (+)-3-neomenthylindene are described. Metathetic reaction of the chiral main group metal salts of these indenyl systems with the appropriate starting materials of Rh and Ir yielded the complexes (−)-(*pR*)/(*pS*)-(1-menthyl-4,7-dimethylindenyl)Rh(COD) (**7a/b**), (*pR*)/(*pS*)-(1-menthyl-4,7-diisopropylindenyl)Rh(COD) (**8a/b**), (+)-(*pR*)/(*pS*)-(1-neomenthylindenyl)Rh(COD) (**9a/b**), (*pR*)/(*pS*)-(1-menthyl-4,7-dimethylindenyl)Rh(C_2H_4)$_2$ (**10a/b**), (*pR*)/(*pS*)-(1-menthyl-4,7-dimethylindenyl)Rh(CO)$_2$ (**11a/b**), (*pR*)/(*pS*)-(1-menthyl-4,7-dimethylindenyl)Rh(CO)(PPh$_3$) (**12a/b**), (*pR*)/(*pS*)-(1-menthyl-4,7-dimethylindenyl)Rh(CO)(PPh$_2$CH$_2$CH$_2$Si(OCH$_3$)$_3$) (**13a/b**), and (−)-(*pR*)/(*pS*)-(1-menthyl-4,7-dimethylindenyl)Ir(COD) (**14a/b**). CoCl$_2$(dppe) reacts with (−)-(1-menthyl-4,7-dimethylindenyl)lithium (**1**), yielding (*pR*)/(*pS*)-(1-menthyl-4,7-dimethylindenyl)Co(dppe) (**15a/b**). Li[(*pR*)/(*pS*)-(1-menthyl-4,7-dimethylindenyl)Mo(CO)$_3$] (**16a/b**), formed by transmetalation of Mo(CO)$_6$, is oxidized by I$_2$, yielding (*pR*)/(*pS*)-(1-menthyl-4,7-dimethylindenyl)Mo(CO)$_3$I (**17a/b**). Depending on the reaction conditions, all compounds were formed as mixtures of diastereomers with respect to the planar chirality of the indenyl ring system. The diasteromeric excess varied between 9% and 71% de. Diastereomerically pure compounds were obtained after chromatography by dried alumina under nitrogen. The structures of **7a**, **7b**, **9a**, **9b**, and **14a** were determined by single-crystal X-ray diffractometry.

Introduction

Chiral bis(indenyl) complexes of the group 4 metals and of the lanthanides have attracted a great deal of interest in synthetic chemistry because of their ability to selectively catalyze reactions such as hydrogenations, carboaluminations, or polymerizations.[1] Due to the lack of general, efficient synthetic methods to prepare enantiomerically pure complexes, most of the commonly used compounds are only available in racemic form and thus not suitable for enantioselective applications.[2] Furthermore, the corresponding complexes of late transition metals are only barely exploited even though late-transition-metal complexes have been shown to be active catalysts for a multitude of organic transformations such as hydrogenations, hydroformylations, isomerizations, or cycloadditions.[3] They even found application in large-scale industrial processes.[4] Especially rhodium complexes with phosphine, sulfide, or cyclopentadiene systems containing chiral substituents have been widely applied as asymmetric catalysts.[5] To improve the scope of and enantiomeric excess in such catalytic processes, we developed a new facile synthetic method to prepare conformationally well-defined, enantiomerically pure 3-menthylindenes followed by diastereoselective metalation to form chiral main group metal complexes.[6a] The

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* To whom correspondence should be addressed. E-mail: schumann@chem.tu-berlin.de (H.S.), rlhalterman@chemdept.chem.ou.edu (R.L.H.).

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preparation and characterization of chiral bis(indenyl)metal complexes of 3-menthyl-4,7-dimethylindene are described in ref 6b. In this paper we describe how these menthylindenyl ligands can be used to synthesize diastereomerically pure monoindenyl transition-metal complexes of rhodium, iridium, cobalt, and molybdenum. Their utilization as hydrogenation and hydroformylation catalysts will be reported in an additional paper.[7] Similar bis(2-menthylindenyl)zirconium dichlorides which gave decent asymmetric induction in the stereoselective polymerization of propylene were recently reported by us.[8]

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; ^{31}P, 80.94 MHz) or ARX 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz; ^{103}Rh, 12.60 MHz) spectrometer at ambient temperature. Chemical shifts are reported in parts per million relative to the ^{1}H and ^{13}C residue of the deuterated solvents. Chemical shifts for ^{31}P and ^{103}Rh measurements are given relative to phosphoric acid in D_2O and hexachlororhodate in D_2O. IR spectra were recorded on a Nicolet Magna System 750 spectrometer and are listed in the Supporting Information along with the mass spectra (EI, 70 eV), obtained by using a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. All compounds apart from the lithium salts **16a** and **16b** show the molecular ion. Relative intensities (%) 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**),[6a] (+)-(4,7-diisopropyl-1-menthylindenyl)lithium (**2**),[6a] (1-neomenthylindenyl)lithium (**3**),[6a] (1-menthyl-4,7-dimethylindenyl)sodium(THF) (**4**),[6a] (−)-(1-menthyl-4,7-dimethylindenyl)potassium (**5**),[6a] tri-*n*-butyl(η^1-1-(3-menthyl-4,7-dimethylindenyl))stannane (**6**),[6a] (2-trimethoxysilylethyl)diphenylphosphine,[9] di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I),[10] tetracarbonyldi-μ-chlorodirhodium(I),[11] and di-μ-chlorobis(η^4-cycloocta-1,5-diene)diiridium(I)[12] were prepared according to published procedures. Dichloro(1,2-bis(diphenylphosphino)ethane)cobalt(II) and molybdenum hexacarbonyl(0) were used as purchased.

(−)-(η^4-Cycloocta-1,5-diene)(η^5-1-menthyl-4,7-dimethylindenyl)rhodium(I) (7a/b). Method A (General Procedure). To a solution of di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (1.05 g, 2.13 mmol) in diethyl ether (30 mL) was added (−)-(η^5-1-menthyl-4,7-dimethylindenyl)lithium (**1**) (1.20 g, 4.16 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 an orange solid which was suspended in *n*-hexane (10 mL) and filtrated with a d4-frit. The residue was extracted twice with *n*-hexane (10 mL). The solvent was removed under vacuum (10^{-2} mbar), leaving 2.00 g (98%) of an orange solid as a mixture of the (*pR*)- and (*pS*)-diastereomers **7a** and **7b** in the ratio 2.3:1. The solid was suspended in *n*-hexane (2 mL) and fractionally chromatographed under nitrogen with alumina. Elution with *n*-hexane gave colorless and finally yellow solutions. The solvents of the yellow fractions were removed under vacuum (10^{-2} mbar), yielding yellow solids. Recrystallization from warm *n*-pentane (5 mL) gave 0.83 g (40%) of yellow crystals of the (*pR*)-diastereomer **7a** and 0.43 g (21%) of the (*pS*)-diastereomer **7b**.

Method B. To a solution of (−)-sparteine (0.15 mL, 0.65 mmol) in diethyl ether (5 mL) was added *n*-butyllithium (0.40 mL, 0.64 mmol of a 1.6 M solution in *n*-hexane) at −78 °C. After the resulting solution was stirred for 1 h, (−)-3-menthyl-4,7-dimethylindene (0.16 g, 0.57 mmol) in diethyl ether (5 mL) was added. After the yellow suspension was stirred for 5 h, di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (0.12 g, 0.24 mmol) was added. The workup in analogy to method A gave 0.21 g (88%) of an orange oil as a mixture of **7a** and **7b** in the ratio 2.2:1.

Method C. In analogy to method A, a solution of di-μ-chlorobis-(η^4-cycloocta-1,5-diene)dirhodium(I) (0.12 g, 0.24 mmol) and tri-*n*-butyl(η^1-1-(3-menthyl-4,7-dimethylindenyl))stannane (**6**) (0.28 g, 0.49 mmol) as a mixture of **6a** and **6b** in the ratio 1:1 in diethyl ether (5 mL) gave after workup 0.19 g (79%) of an orange oil as a mixture of **7a** and **7b** in the ratio 2.1:1.

Method D. To a solution of **1** (0.60 g, 2.08 mmol) in diethyl ether (20 mL) was added 12-crown-4 (0.42 g, 2.38 mmol) at room temperature. After the resulting solution was stirred for 1 h and cooled to −78 °C, di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (0.53 g, 1.07 mmol) was added. The workup in analogy to method A gave 0.95 g (93%) of an orange oil as a mixture of **7a** and **7b** in the ratio 1.4:1.

Method E. In analogy to method A, a solution of di-μ-chlorobis-(η^4-cycloocta-1,5-diene)dirhodium(I) (0.05 g, 0.10 mmol) and (1-menthyl-4,7-dimethylindenyl)sodium(THF) (**4**) (0.18 g, 0.48 mmol) in THF (5 mL) gave after workup 0.07 g (70%) of an orange oil as a mixture of **7a** and **7b** in the ratio 1:2.0.

Method F. In analogy to method A, a solution of di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (0.81 g, 1.64 mmol) and (−)-(1-menthyl-4,7-dimethylindenyl)potassium (**5**) (1.01 g, 3.15 mmol) in diethyl ether (30 mL) gave after workup 1.38 g (89%) of an orange oil as a mixture of **7a** and **7b** in the ratio 1:3.0.

(*pR*)-Diastereomer 7a. Mp 140 °C. $[\alpha]_D^{25}$ −75.1° (*c* 0.8, diethyl ether). ^{1}H NMR (benzene-d_6, 400 MHz): δ 6.75 (m, 1H, H^6), 6.68 (m, 1H, H^5), 5.71 (m, 1H, H^2), 5.02 (d, $^3J = 2.9$ Hz, 1H, H^3), 3.87 (m, 2H, C*H*(COD)), 3.60 (m, 2H, C*H*(COD)), 2.95 (m, 1H, $H^{3'}$), 2.47 (s, 3H, H^{11}), 2.31 (s, 3H, H^{10}), 2.30 (m, 1H, $H^{2'}$), 2.00, 1.89 (m, 4H, CH_2(COD)), 1.84, 1.61 (m, 4H, CH_2-

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(COD)), 1.76 (m, 1H, H$^{6'}$), 1.63 (m, 1H, H$^{5'}$), 1.42 (m, 1H, H$^{1'}$), 1.36 (m, 1H, H$^{8'}$), 1.35 (m, 1H, H$^{2'}$), 1.20 (m, 1H, H$^{4'}$), 1.03 (m, 1H, H$^{5'}$), 0.97 (d, ^3J = 6.5 Hz, 3H, H$^{7'}$), 0.95 (m, 1H, H$^{6'}$), 0.67 (d, ^3J = 7.0 Hz, 3H, H$^{9'/10'}$), 0.57 (d, ^3J = 6.9 Hz, 3H, H$^{9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 100.64 MHz): δ 127.26, 126.96 (C^{4,7}), 124.50 (C^6), 121.28 (C^5), 110.56 (d, $^1J_{CRh}$ = 3.2 Hz, C$^{1/8/9}$), 108.08 (d, $^1J_{CRh}$ = 2.1 Hz, C$^{1/8/9}$), 108.00 (d, $^1J_{CRh}$ = 3.7 Hz, C$^{1/8/9}$), 91.41 (d, $^1J_{CRh}$ = 4.3 Hz, C^2), 73.55 (d, $^1J_{CRh}$ = 4.7 Hz, C^3), 68.09 (d, $^1J_{CRh}$ = 13.8 Hz, *C*H(COD)), 66.88 (d, $^1J_{CRh}$ = 14.0 Hz, *C*H(COD)), 53.07 (C$^{4'}$), 45.70 (C$^{2'}$), 39.38 (C$^{3'}$), 35.48 (C$^{6'}$), 34.00 (C$^{1'}$), 32.87 (*C*H$_2$(COD)), 30.80 (*C*H$_2$(COD)), 27.07 (C$^{8'}$), 25.79 (C$^{5'}$), 22.77 (C$^{7'}$), 22.34 (C$^{9'/10'}$), 21.72 (C^{11}), 18.98 (C^{10}), 16.45 (C$^{9'/10'}$). ^{103}Rh NMR (chloroform-d_1:diethyl ether = 1:3, 12.60 MHz): δ −151.25. Anal. Calcd for $C_{29}H_{41}Rh$ (mol wt 492.55): C, 70.72; H, 8.39. Found: C, 70.56; H, 8.21. Mol wt cryosc in benzene: 465.

(*pS*)-Diastereomer 7b. Mp 99 °C. $[\alpha]_D^{25}$ −70.2° (*c* 0.6, diethyl ether). ^{1}H NMR (benzene-d_6, 400 MHz): δ 6.77 (d, ^3J = 6.9 Hz, 1H, H^6), 6.67 (d, ^3J = 6.9 Hz, 1H, H^5), 5.49 (m, 1H, H^2), 4.67 (d, ^3J = 2.8 Hz, 1H, H^3), 4.16 (m, 2H, C*H*(COD)), 3.50 (m, 2H, C*H*(COD)), 2.79 (m, 1H, H$^{3'}$), 2.35 (s, 3H, H^{10}), 2.29 (s, 3H, H^{11}), 2.00 (m, 1H, H$^{2'}$), 1.95, 1.86 (m, 4H, C*H*$_2$(COD)), 1.77, 1.67 (m, 4H, C*H*$_2$(COD)), 1.74 (m, 1H, H$^{5'}$), 1.55 (m, 1H, H$^{4'}$), 1.41 (m, 1H, H$^{6'}$), 1.37 (m, 1H, H$^{8'}$), 1.35 (m, 1H, H$^{1'}$), 1.18 (m, 1H, H$^{5'}$), 1.17 (d, ^3J = 7.0 Hz, 3H, H$^{9'/10'}$), 1.01 (d, ^3J = 6.8 Hz, 3H, H$^{7'}$), 0.81 (m, 1H, H$^{6'}$), 0.73 (d, ^3J = 6.5 Hz, 3H, H$^{9/10'}$), 0.61 (m, 1H, H$^{2'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 100.64 MHz): δ 128.53, 125.96 (C^{4,7}), 125.16 (C^6), 120.10 (C^5), 111.36 (d, $^1J_{CRh}$ = 3.2 Hz, C$^{1/8/9}$), 108.30 (d, $^1J_{CRh}$ = 3.6 Hz, C$^{1/8/9}$), 106.07 (d, $^1J_{CRh}$ = 2.6 Hz, C$^{1/8/9}$), 90.67 (d, $^1J_{CRh}$ = 4.2 Hz, C^2), 71.62 (d, $^1J_{CRh}$ = 4.9 Hz, C^3), 71.46 (d, $^1J_{CRh}$ = 13.6 Hz, *C*H(COD)), 64.47 (d, $^1J_{CRh}$ = 14.1 Hz, *C*H(COD)), 48.13 (C$^{2'}$), 45.71 (C$^{4'}$), 38.90 (C$^{3'}$), 35.32 (C$^{6'}$), 32.88 (C$^{1'}$), 32.52 (*C*H$_2$(COD)), 31.20 (*C*H$_2$(COD)), 27.13 (C$^{8'}$), 25.31 (C$^{5'}$), 22.77 (C$^{9'/10'}$), 22.30 (C$^{9'/10'}$), 21.02 (C^{11}), 19.01 (C^{10}), 17.76 (C$^{7'}$). ^{103}Rh NMR (chloroform-d_1:diethyl ether = 1:3, 12.60 MHz): δ −129.50. Anal. Calcd for $C_{29}H_{41}Rh$ (mol wt 492.55): C, 70.72; H, 8.39. Found: C, 70.64; H, 8.60.

(η^4-Cycloocta-1,5-diene)(η^5-4,7-diisopropyl-1-menthylindenyl)rhodium(I) (8a/b). Reaction in analogy to **7** of di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (0.08 g, 0.16 mmol) with (+)-(1-menthyl-4,7-diisopropylindenyl)lithium (**2**) (0.10 g, 0.29 mmol) in diethyl ether (15 mL) gave after workup and chromatography 0.12 g (75%) of an orange oil as a mixture of **8a** and **8b** in the ratio 2.2:1. $[\alpha]_D^{25}$ −35.9° (*c* 0.9, diethyl ether). Anal. Calcd for $C_{33}H_{49}Rh$ (mol wt 548.66): C, 72.24; H, 9.00. Found: C, 72.67; H, 9.43.

(*pR*)-Diastereomer 8a. ^{1}H NMR (benzene-d_6, 200 MHz): δ 6.99 (d, ^3J = 1.6 Hz, 1H, H$^{5/6}$), 6.81 (d, ^3J = 1.6 Hz, 1H, H$^{5/6}$), 5.75 (m, 1H, H^2), 4.89 (d, ^3J = 2.8 Hz, 1H, H^3), 3.96 (m, 2H, C*H*(COD)), 3.61 (sept, ^3J = 6.9 Hz, 1H, H$^{10/13}$), 3.14 (m, 1H, H$^{3\_}$), 2.89 (m, 2H, C*H*(COD)), 2.87 (sept, ^3J = 6.9 Hz, 1H, H$^{10/13}$), 2.23−0.89 (m, 9H, H$^{1',2',4',5',6',8'}$), 1.73 (m, 4H, C*H*$_2$(COD)), 1.61 (m, 4H, C*H*$_2$(COD)), 1.39−1.28 (m, 12H, H^{11,12,14,15}), 0.95 (d, ^3J = 6.9 Hz, 3H, H$^{7'/9'/10'}$), 0.91 (d, ^3J = 7.0 Hz, 3H, H$^{7'/9'/10'}$), 0.71 (d, ^3J = 7.1 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 143.15, 141.33 (C^{4,7}), 119.90, 113.99 (C^{5,6}), 112.03 (d, $^1J_{CRh}$ = 3.0 Hz, C$^{1/8/9}$), 107.66 (d, $^1J_{CRh}$ = 2.1 Hz, C$^{1/8/9}$), 106.32 (d, $^1J_{CRh}$ = 3.5 Hz, C$^{1/8/9}$), 92.26 (d, $^1J_{CRh}$ = 4.6 Hz, C^2), 74.74 (d, $^1J_{CRh}$ = 4.9 Hz, C^3), 68.54 (d, $^1J_{CRh}$ = 14.2 Hz, *C*H(COD)), 67.05 (d, $^1J_{CRh}$ = 13.6 Hz, *C*H(COD)), 51.65, 40.60, 34.68, 33.29, 26.91, 24.64 (C$^{1',3',4',8',10,13}$), 38.34, 30.19 (*C*H$_2$(COD)), 46.71, 35.64, 26.03 (C$^{2',5',6'}$), 23.56, 23.22, 22.92, 22.57, 22.36, 20.00, 16.79 (C$^{7',9',10',11,12,14,15}$).

(*pS*)-Diastereomer 8b. ^{1}H NMR (benzene-d_6, 200 MHz): δ 7.24 (d, ^3J = 1.6 Hz, 1H, H$^{5/6}$), 7.04 (d, ^3J = 1.6 Hz, 1H, H$^{5/6}$), 5.50 (m, 1H, H^2), 4.58 (d, ^3J = 2.8 Hz, 1H, H^3), 3.97 (m, 2H, C*H*(COD)), 3.77 (sept, ^3J = 6.9 Hz, 1H, H$^{10/13}$), 3.13 (m, 1H, H$^{3\_}$), 2.90 (m, 2H, C*H*(COD)), 2.81 (sept, ^3J = 6.9 Hz, 1H, H$^{10/13}$), 2.33−0.89 (m, 9H, H$^{1',2',4',5',6',8'}$), 1.75 (m, 4H, C*H*$_2$(COD)), 1.68 (m, 4H, C*H*$_2$(COD)), 1.41−1.26 (m, 12H, H^{11,12,14,15}), 0.90 (d, ^3J = 6.9 Hz, 3H, H$^{7'/9'/10'}$), 0.77 (d, ^3J = 6.9 Hz, 3H, H$^{7'/9'/10'}$), 0.58 (d, ^3J = 6.9 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 140.91, 139.52 (C^{4,7}), 120.57, 115.78 (C^{5,6}), 112.17 (d, $^1J_{CRh}$ = 3.0 Hz, C$^{1/8/9}$), 107.14 (d, $^1J_{CRh}$ = 3.5 Hz, C$^{1/8/9}$), 106.43 (d, $^1J_{CRh}$ = 2.1 Hz, C$^{1/8/9}$), 91.41 (d, $^1J_{CRh}$ = 4.1 Hz, C^2), 72.91 (d, $^1J_{CRh}$ = 5.2 Hz, C^3), 70.03 (d, $^1J_{CRh}$ = 13.9 Hz, *C*H(COD)), 65.70 (d, $^1J_{CRh}$ = 13.9 Hz, *C*H(COD)), 46.14, 43.99, 40.04, 34.61, 25.71, 24.48 (C$^{1',3',4',8',10,13}$), 37.56, 30.11 (*C*H$_2$(COD)), 48.39, 35.89, 25.17 (C$^{2',5',6'}$), 23.42, 23.38, 22.86, 22.61, 22.38, 17.86, 15.66 (C$^{7',9',10',11,12,14,15}$).

(+)-(η^4-Cycloocta-1,5-diene)(η^5-1-neomenthylindenyl)rhodium(I) (9a/b). Reaction in analogy to **7** of di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (0.92 g, 1.87 mmol) and (1-neomenthylindenyl)lithium (**3**) (0.96 g, 3.69 mmol) in diethyl ether (20 mL) gave after workup 0.96 g (3.69 mmol) of an orange solid (0.96 g, 3.69 mmol) of **9a** and **9b** in the ratio 1:1.5. Chromatography and recrystallization from warm *n*-pentane (5 mL) gave 0.31 g (18%) of yellow crystals of **9a** and 0.49 g (29%) of **9b**.

(*pR*)-Diastereomer 9a. Mp 130 °C. $[\alpha]_D^{25}$ +71.3° (*c* 0.6, diethyl ether). ^{1}H NMR (benzene-d_6, 200 MHz): δ 7.32−6.90 (m, 4H, H^{4,5,6,7}), 5.78 (m, 1H, H^2), 4.63 (d, ^3J = 2.7 Hz, 1H, H^3), 3.86 (m, 2H, C*H*(COD)), 3.61 (m, 2H, C*H*(COD)), 3.23 (m, 1H, H$^{3\_}$), 2.90−0.80 (m, 9H, H$^{1',2',4',5',6',8'}$), 2.00−1.60 (m, 8H, C*H*$_2$(COD)), 1.08 (d, ^3J = 6.6 Hz, 3H, H$^{7'/9'/10'}$), 1.05 (d, ^3J = 7.2 Hz, 3H, H$^{7\_/9\_/10\_}$), 0.67 (d, ^3J = 6.3 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 122.82, 121.37, 120.88, 119.30 (C^{4,5,6,7}), 110.86 (d, $^1J_{CRh}$ = 3.0 Hz, C$^{8/9}$), 110.09 (d, $^1J_{CRh}$ = 2.4 Hz, C$^{8/9}$), 101.50 (d, $^1J_{CRh}$ = 3.5 Hz, C^1), 95.15 (d, $^1J_{CRh}$ = 4.4 Hz, C^2), 72.56 (d, $^1J_{CRh}$ = 5.2 Hz, C^3), 70.11 (d, $^1J_{CRh}$ = 13.7 Hz, *C*H(COD)), 68.20 (d, $^1J_{CRh}$ = 14.0 Hz, *C*H(COD)), 49.12, 35.23, 28.13, 27.02 (C$^{1',3',4',8'}$), 40.62, 35.30, 25.70 (C$^{2',5',6'}$), 32.33, 31.19 (*C*H$_2$(COD)), 25.12, 22.11, 21.16 (C$^{7',9',10'}$). ^{103}Rh NMR (chloroform-d_1:diethyl ether = 1:3, 12.60 MHz): δ −127.62. Anal. Calcd for $C_{27}H_{37}Rh$ (mol wt 464.50): C, 69.82; H, 8.03. Found: C, 69.40; H, 7.54.

(*pS*)-Diastereomer 9b. Mp 82 °C. $[\alpha]_D^{25}$ +103.1° (*c* 0.2, diethyl ether). ^{1}H NMR (benzene-d_6, 200 MHz): δ 7.31−6.91 (m, 4H, H^{4,5,6,7}), 5.84 (m, 1H, H^2), 4.69 (d, ^3J = 2.8 Hz, 1H, H^3), 3.85 (m, 2H, C*H*(COD)), 3.76 (m, 2H, C*H*(COD)), 3.11 (m, 1H, H$^{3'}$), 2.12−0.60 (m, 9H, H$^{1',2',4',5',6',8'}$), 2.00−1.50 (m, 8H, C*H*$_2$(COD)), 1.07 (d, ^3J = 6.5 Hz, 3H, H$^{7'/9'/10'}$), 0.61 (d, ^3J = 6.5 Hz, 3H, H$^{7'/9'/10'}$), 0.55 (d, ^3J = 6.6 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 122.54, 121.72, 120.69, 118.59 (C^{4,5,6,7}), 112.31 (d, $^1J_{CRh}$ = 2.2 Hz, C$^{8/9}$), 110.68 (d, $^1J_{CRh}$ = 2.8 Hz, C$^{8/9}$), 102.55 (d, $^1J_{CRh}$ = 3.7 Hz, C^1), 93.82 (d, $^1J_{CRh}$ = 4.6 Hz, C^2), 73.31 (d, $^1J_{CRh}$ = 5.0 Hz, C^3), 68.84 (d, $^1J_{CRh}$ = 13.7 Hz, *C*H(COD)), 68.41 (d, $^1J_{CRh}$ = 13.9 Hz, *C*H(COD)), 47.11, 33.84, 28.45, 28.01 (C$^{1',3',4',8'}$), 39.43, 35.23, 24.42 (C$^{2',5',6'}$), 32.40, 31.10 (*C*H$_2$(COD)), 23.31, 21.95, 20.59 (C$^{7',9',10'}$). ^{103}Rh NMR (chloroform-d_1:diethyl ether = 1:3, 12.60 MHz): δ −137.23. Anal. Calcd for $C_{27}H_{37}Rh$ (mol wt 464.50): C, 69.82; H, 8.03. Found: C, 69.79; H, 7.57.

Bis(η^2-ethylene)(η^5-1-menthyl-4,7-dimethylindenyl)rhodium(I) (10a/b). Reaction in analogy to **7** of di-μ-chlorotetrakis(η^2-ethylene)dirhodium(I) (0.39 g, 1.00 mmol) and **1** (0.43 g, 1.50 mmol) in diethyl ether (25 mL) gave after workup and chromatography 0.51 g (78%) of an orange oil as a mixture of **10a** and **10b** in the ratio 2.0:1. $[\alpha]_D^{25}$ −123.6° (*c* 1.1, diethyl ether). Anal. Calcd for $C_{25}H_{37}Rh$ (mol wt 440.48): C, 68.17; H, 8.47. Found: C, 68.53; H, 8.76.

(*pR*)-Diastereomer 10a. ^{1}H NMR (benzene-d_6, 200 MHz): δ 6.80−6.60 (m, 2H, H^{5,6}), 5.55 (m, 1H, H^2), 4.83 (d, ^3J = 2.8 Hz, 1H, H^3), 4.00−0.60 (m, 10H, H$^{1',2',3',4',5',6',8'}$), 2.51 (s, 3H, H$^{10/11}$), 2.18 (s, 3H, H$^{10/11}$), 1.92 (m, 8H, C$_2$*H*$_4$), 0.87 (d, ^3J = 6.7 Hz, 3H, H$^{7'/9'/10'}$), 0.63 (d, ^3J = 6.1 Hz, 3H, H$^{7'/9'/10'}$), 0.60 (d, ^3J = 7.3 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 129.00, 128.59 (C^{4,7}), 125.63, 121.59 (C^{5,6}), 109.59 (d, $^1J_{CRh}$ = 3.4 Hz, C$^{8/9}$), 109.15 (d, $^1J_{CRh}$ = 3.8 Hz, C$^{8/9}$), 107.60 (d, $^1J_{CRh}$ = 2.8 Hz, C^1), 90.67 (d, $^1J_{CRh}$ = 4.7 Hz, C^2), 75.70 (d, $^1J_{CRh}$ = 4.8 Hz, C^3), 53.72, 39.36, 33.98, 27.10 (C$^{1',3',4',8'}$), 44.91, 35.55, 25.97 (C$^{2',5',6'}$), 43.54 (d, $^1J_{\mathrm{CRh}}$ = 12.5 Hz, $C_2\mathrm{H}_4$), 22.83, 22.54 (C^{10,11}), 21.78, 18.88, 16.69 (C$^{7',9',10'}$).

(*pS*)-Diastereomer 10b. ^{1}H NMR (benzene-d_6, 200 MHz): δ 6.80−6.60 (m, 2H, H^{5,6}), 5.40 (m, 1H, H^2), 4.60 (d, ^3J = 2.8 Hz, 1H, H^3), 4.00−0.60 (m, 10H, H$^{1',2',3',4',5',6',8'}$), 2.35 (s, 3H, H$^{10/11}$), 2.28 (s, 3H, H$^{10/11}$), 1.95 (m, 8H, C_2H_4), 1.08 (d, ^3J = 7.1 Hz, 3H, H$^{7'/9'/10'}$), 0.95 (d, ^3J = 6.8 Hz, 3H, H$^{7'/9'/10'}$), 0.80 (d, ^3J = 6.5 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 129.07, 129.06 (C^{4,7}), 125.76, 120.65 (C^{5,6}), 110.52 (d, $^1J_{\mathrm{CRh}}$ = 3.4 Hz, C$^{8/9}$), 109.04 (d, $^1J_{\mathrm{CRh}}$ = 3.6 Hz, C$^{8/9}$), 104.42 (d, $^1J_{\mathrm{CRh}}$ = 2.9 Hz, C^1), 90.21 (d, $^1J_{\mathrm{CRh}}$ = 4.3 Hz, C^2), 74.78 (d, $^1J_{\mathrm{CRh}}$ = 4.9 Hz, C^3), 48.14, 35.35, 25.29 (C$^{2',5',6'}$), 46.06, 38.98, 32.93, 26.64 (C$^{1',3',4',8'}$), 43.38 (d, $^2J_{\mathrm{CRh}}$ = 13.4 Hz, $C_2\mathrm{H}_4$), 22.71, 22.42 (C^{10,11}), 20.94, 18.89, 18.44 (C$^{7',9',10'}$).

Dicarbonyl(η^5-1-menthyl-4,7-dimethylindenyl)rhodium(I) (11a/b). Reaction in analogy to **7** of tetracarbonyldi-μ-chlorodirhodium(I) (0.64 g, 1.65 mmol) and **5** (1.17 g, 3.65 mmol) in diethyl ether (30 mL) gave after workup, chromatography, and recrystallization from warm *n*-pentane (5 mL) 1.09 g (75%) of an orange oil as a mixture of the (*pR*)- and (*pS*)-diastereomers **11a/11b** in the ratio 1:1.5. $[\alpha]_{\mathrm{D}}^{25}$ −280.5° (*c* 3.7, diethyl ether). Anal. Calcd for $\mathrm{C}_{23}\mathrm{H}_{29}\mathrm{O}_2\mathrm{Rh}$ (mol wt 440.39): C, 62.73; H, 6.64. Found: C, 62.99; H, 6.46.

Diastereomer 11a. ^{1}H NMR (chloroform-d_1, 200 MHz): δ 6.80 (m, 2H, H^{5,6}), 5.89 (m, 1H, H^2), 5.63 (d, ^3J = 3.2 Hz, 1H, H^3), 3.14 (m, 1H, H$^{3'}$), 2.60−0.70 (m, 9H, H$^{1',2',4',5',6',8'}$), 2.56 (s, 3H, H$^{10/11}$), 2.38 (s, 3H, H$^{10/11}$), 1.00 (d, ^3J = 6.4 Hz, 3H, H$^{7'/9'/10'}$), 0.77 (d, ^3J = 6.9 Hz, 3H, H$^{7'/9'/10'}$), 0.64 (d, ^3J = 6.9 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (chloroform-d_1, 50.32 MHz): δ 190.39 (d, $^1J_{\mathrm{CRh}}$ = 86.2 Hz, *C*O), 127.49 (C$^{5/6}$), 125.99, 125.47 (C^{4,7}), 124.52 (C$^{5/6}$), 114.83 (d, $^1J_{\mathrm{CRh}}$ = 2.8 Hz, C$^{8/9}$), 113.31 (d, $^1J_{\mathrm{CRh}}$ = 3.2 Hz, C$^{8/9}$), 111.20 (d, $^1J_{\mathrm{CRh}}$ = 1.9 Hz, C^1), 94.70 (d, $^1J_{\mathrm{CRh}}$ = 5.7 Hz, C^2), 70.35 (d, $^1J_{\mathrm{CRh}}$ = 4.0 Hz, C^3), 52.03, 34.86, 25.00 (C$^{2',5',6'}$), 51.20, 37.38, 34.19, 27.27 (C$^{1',3',4',8'}$), 22.42, 21.91, 20.77, 17.97, 16.23 (C$^{7',9',10,10',11'}$).

Diastereomer 11b. ^{1}H NMR (chloroform-d_1, 200 MHz): δ 6.81 (m, 2H, H^{5,6}), 5.73 (m, 1H, H^2), 5.68 (d, ^3J = 3.1 Hz, 1H, H^3), 2.99 (m, 1H, H$^{3'}$), 2.60−0.70 (m, 9H, H$^{1',2',4',5',6',8'}$), 2.51 (s, 3H, H$^{10/11}$), 2.36 (s, 3H, H$^{10/11}$), 0.99 (d, ^3J = 7.0 Hz, 3H, H$^{7'/9'/10'}$), 0.89 (d, ^3J = 6.8 Hz, 3H, H$^{7'/9'/10'}$), 0.82 (d, ^3J = 6.5 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (chloroform-d_1, 50.32 MHz): δ 190.01 (d, $^1J_{\mathrm{CRh}}$ = 86.6 Hz, *C*O), 127.31 (C$^{5/6}$), 125.80, 125.42 (C^{4,7}), 124.32 (C$^{5/6}$), 116.66 (d, $^1J_{\mathrm{CRh}}$ = 2.4 Hz, C$^{8/9}$), 113.49 (d, $^1J_{\mathrm{CRh}}$ = 3.3 Hz, C$^{8/9}$), 106.35 (d, $^1J_{\mathrm{CRh}}$ = 3.3 Hz, C^1), 94.15 (d, $^1J_{\mathrm{CRh}}$ = 5.7 Hz, C^2), 71.27 (d, $^1J_{\mathrm{CRh}}$ = 3.8 Hz, C^3), 47.80, 34.90, 24.42 (C$^{2',5',6'}$), 45.05, 38.82, 33.01, 26.17 (C$^{1',3',4',8'}$), 22.41, 21.58, 20.32, 18.01, 15.94 (C$^{7',9',10,10',11'}$).

Diastereomers 11a and 11b in the Ratio 1:1.5. ^{103}Rh NMR (chloroform-d_1:diethyl ether = 1:3, 12.60 MHz): δ −683.32 (1Rh), −722.36 (0.67Rh).

Carbonyl(η^5-1-menthyl-4,7-dimethylindenyl)(triphenylphosphine)rhodium (I) (12a/b). The diastereomers **11a/11b** in the ratio 1:1.5 (0.21 g, 0.48 mmol) were dissolved in *n*-hexane (16 mL) and treated with triphenylphosphine (0.20 g, 0.76 mmol) at room temperature. The solution was heated under gas evolution for 18 h to 60 °C. The suspension was filtered with a d4-frit and extracted with *n*-hexane (10 mL). The solvent was removed under a vacuum (10^{-2} mbar), leaving an orange solid (0.31 g, 97%) as a mixture of the (*pR*)- and (*pS*)-diastereomers **12a/12b** in the ratio 1.9:1. Mp 67 °C. $[\alpha]_{\mathrm{D}}^{25}$ −19.2° (*c* 0.5, diethyl ether). Anal. Calcd for $\mathrm{C}_{40}\mathrm{H}_{44}\mathrm{OPRh}$ (mol wt 674.67): C, 71.21; H, 6.57. Found: C, 70.82; H, 6.19.

Diastereomer 12a. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.60−7.30 (m, 15H, C*H*(phenyl)), 6.93 (d, ^3J = 6.9 Hz, 1H, H$^{5/6}$), 6.80 (d, ^3J = 6.9 Hz, 1H, H$^{5/6}$), 5.97 (m, 1H, H^2), 4.80 (m, 1H, H^3), 4.30−0.80 (m, 10H, H$^{1',2',3',4',5',6',8'}$), 2.68 (s, 3H, H$^{10/11}$), 1.80 (s, 3H, H$^{10/11}$), 1.13 (d, ^3J = 7.0 Hz, 3H, H$^{7'/9'/10'}$), 1.12 (d, ^3J = 7.0 Hz, 3H, H$^{7'/9'/10'}$), 0.77 (d, ^3J = 6.4 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 195.54 (dd, $^1J_{\mathrm{CRh}}$ = 88.6 Hz, $^2J_{CP}$ = 22.2 Hz, *C*O), 136.79 (dd, $^1J_{\mathrm{CP}}$ = 44.1 Hz, $^2J_{\mathrm{CRh}}$ = 1.4 Hz, *C*$^{\mathrm{q}}$(phenyl)), 133.58 (d, $^2J_{\mathrm{CP}}$ = 12.8 Hz, *C*H$^{\mathrm{ortho}}$(phenyl)), 129.74 (*C*H$^{\mathrm{para}}$(phenyl)), 128.08 (d, $^3J_{\mathrm{CP}}$ = 10.4 Hz, *C*H$^{\mathrm{meta}}$-(phenyl)), 125.76, 121.08 (C^{5,6}), 116.53, 109.78 (C^{4,7}), 102.10 (d, $^1J_{\mathrm{CRh}}$ = 3.5 Hz, C$^{8/9}$), 101.84 (d, $^1J_{\mathrm{CRh}}$ = 3.5 Hz, C$^{8/9}$), 94.69 (d, $^1J_{\mathrm{CRh}}$ = 2.5 Hz, C^2), 94.20 (d, $^1J_{\mathrm{CRh}}$ = 2.5 Hz, C^1), 79.19 (d, $^1J_{\mathrm{CRh}}$ = 3.3 Hz, C^3), 51.08, 34.89, 24.59 (C$^{2',5',6'}$), 45.22, 39.05, 32.68, 26.41 (C$^{1',3',4',8'}$), 22.37, 21.59, 20.58, 17.51, 16.06 (C$^{7',9',10,10',11}$). ^{31}P{^{1}H} NMR (pyridine-d_5, 80.94 MHz): δ 49.35 (d, $^1J_{\mathrm{PRh}}$ = 209.5 Hz).

Diastereomer 12b. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.60−7.30 (m, 15H, C*H*(phenyl)), 6.92 (m, 2H, H^{5,6}), 6.31 (m, 1H, H^2), 4.80 (m, 1H, H^3), 3.30−0.80 (m, 10H, H$^{1',2',3',4',5',6',8'}$), 2.77 (s, 3H, H$^{10/11}$), 1.64 (s, 3H, H$^{10/11}$), 0.96 (d, ^3J = 6.5 Hz, 3H, H$^{7'/9'/10'}$), 0.70 (d, ^3J = 6.9 Hz, 3H, H$^{7'/9'/10'}$), 0.64 (d, ^3J = 6.8 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 193.82 (dd, $^1J_{\mathrm{CRh}}$ = 88.3 Hz, $^2J_{\mathrm{CP}}$ = 22.5 Hz, *C*O), 137.66 (dd, $^1J_{\mathrm{CP}}$ = 43.3 Hz, $^2J_{\mathrm{CRh}}$ = 1.4 Hz, *C*$^{\mathrm{q}}$(phenyl)), 133.64 (d, $^2J_{\mathrm{CP}}$ = 12.8 Hz, *C*H$^{\mathrm{ortho}}$(phenyl)), 129.75 (*C*H$^{\mathrm{para}}$(phenyl)), 128.04 (d, $^3J_{\mathrm{CP}}$ = 10.4 Hz, *C*H$^{\mathrm{meta}}$(phenyl)), 125.75, 122.06 (C^{5,6}), 115.93, 113.05 (C^{4,7}), 107.90 (d, $^1J_{\mathrm{CRh}}$ = 3.8 Hz, C$^{8/9}$), 107.63 (d, $^1J_{\mathrm{CRh}}$ = 3.8 Hz, C$^{8/9}$), 93.69 (d, $^1J_{\mathrm{CRh}}$ = 3.0 Hz, C^1), 93.59 (d, $^1J_{\mathrm{CRh}}$ = 3.0 Hz, C^2), 77.50 (d, $^1J_{\mathrm{CRh}}$ = 3.5 Hz, C^3), 51.54, 38.04, 34.15, 27.23 (C$^{1',3',4',8'}$), 47.78, 34.96, 25.27 (C$^{2',5',6'}$), 22.48, 21.88, 21.07, 17.59, 16.24 (C$^{7',9',10,10',11}$). ^{31}P{^{1}H} NMR (pyridine-d_5, 80.94 MHz): δ 47.68 (d, $^1J_{\mathrm{PRh}}$ = 204.9 Hz).

Carbonyl(η^5-1-menthyl-4,7-dimethylindenyl)(η^1-(2-trimethoxysilylethyl)diphenylphosphino)rhodium(I) (13a/b). In analogy to **12**, a 1:1.5 mixture of **11a/11b** (0.21 g, 0.48 mmol) was dissolved in *n*-hexane (10 mL) and treated with (2-trimethoxysilylethyl)diphenylphosphine (0.16 g, 0.48 mmol). The solution was heated under gas evolution for 18 h to 60 °C. The solvent was removed under a vacuum (10^{-2} mbar), leaving 0.35 g (97%) of a brown solid as a mixture of the (*pR*)- and (*pS*)-diastereomers **13a/13b** in the ratio 2.0:1. Anal. Calcd for $\mathrm{C}_{39}\mathrm{H}_{52}\mathrm{O}_4\mathrm{PRhSi}$ (mol wt 746.81): C, 62.72; H, 7.02. Found: C, 62.47; H, 6.84.

Diastereomer 13a. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.70−7.30 (m, 10H, C*H*(phenyl)), 6.85 (m, 1H, H$^{5/6}$), 6.76 (m, 1H, H$^{5/6}$), 5.96 (m, 1H, H^2), 4.84 (m, 1H, H^3), 4.30−0.80 (m, 14H, H$^{1',2',3',4',5',6',8'}$, PCH_2, SiCH_2), 3.56 (s, 9H, OCH_3), 2.67 (s, 3H, H$^{10/11}$), 1.92 (s, 3H, H$^{10/11}$), 1.27 (d, ^3J = 7.0 Hz, 3H, H$^{7'/9'/10'}$), 1.15 (d, ^3J = 7.0 Hz, 3H, H$^{7'/9'/10'}$), 0.78 (d, ^3J = 6.4 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 194.00 (dd, $^1J_{\mathrm{CRh}}$ = 77.9 Hz, $^2J_{\mathrm{CP}}$ = 23.2 Hz, *C*O), 138.93 (dd, $^1J_{\mathrm{CP}}$ = 40.6 Hz, $^2J_{\mathrm{CRh}}$ = 1.4 Hz, *C*$^{\mathrm{q}}$(phenyl)), 137.54 (dd, $^1J_{\mathrm{CP}}$ = 40.5 Hz, $^2J_{\mathrm{CRh}}$ = 1.4 Hz, *C*$^{\mathrm{q}}$(phenyl′)), 132.80 (d, $^2J_{\mathrm{CP}}$ =11.7 Hz, *C*H$^{\mathrm{ortho}}$-(phenyl)), 130.15 (d, $^3J_{\mathrm{CP}}$ = 2.5 Hz, *C*H$^{\mathrm{para}}$(phenyl)), 128.55 (d, $^3J_{\mathrm{CP}}$ = 9.8 Hz, *C*H$^{\mathrm{meta}}$(phenyl)), 125.93, 121.36 (C^{5,6}), 116.83, 110.23 (C^{4,7}), 102.89 (d, $^1J_{\mathrm{CRh}}$ = 3.8 Hz, C$^{8/9}$), 102.64 (d, $^1J_{\mathrm{CRh}}$ = 3.5 Hz, C$^{8/9}$), 93.98 (d, $^1J_{\mathrm{CRh}}$ = 2.7 Hz, C^1), 93.88 (d, $^1J_{\mathrm{CRh}}$ = 2.7 Hz, C^2), 77.42 (d, $^1J_{\mathrm{CRh}}$ = 3.5 Hz, C^3), 51.64, 39.42, 33.08, 27.28 (C$^{1',3',4',8'}$), 50.58 (O*C*H$_3$), 48.29, 35.33, 25.00 (C$^{2',5',6'}$), 27.01 (d, $^1J_{CP}$ = 26.4 Hz, P*C*H$_2$), 23.19, 22.27, 21.37, 18.47, 17.01 (C$^{7',9',10,10',11}$), 5.16 (Si*C*H$_2$). ^{31}P{^{1}H} NMR (pyridine-d_5, 80.94 MHz): δ 49.99 (d, $^1J_{\mathrm{PRh}}$ = 207.1 Hz).

Diastereomer 13b. ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.70−7.30 (m, 10H, C*H*(phenyl)), 6.89 (m, 1H, H$^{5/6}$), 6.72 (m, 1H, H$^{5/6}$), 6.27 (m, 1H, H^2), 4.85 (m, 1H, H^3), 3.54 (s, 9H, OCH_3), 3.30−0.80 (m, 14H, H$^{1',2',3',4',5',6',8'}$, PCH_2, SiCH_2), 2.76 (s, 3H, H$^{10/11}$), 1.79 (s, 3H, H$^{10/11}$), 0.81 (d, ^3J = 7.0 Hz, 3H, H$^{7'/9'/10'}$), 0.70 (d, ^3J = 6.9 Hz, 3H, H$^{7'/9'/10'}$), 0.64 (d, ^3J = 6.8 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 195.58 (dd, $^1J_{\mathrm{CRh}}$ = 88.8 Hz, $^2J_{\mathrm{CP}}$ = 22.9 Hz, *C*O), 138.37 (dd, $^1J_{\mathrm{CP}}$ = 40.1 Hz, $^2J_{\mathrm{CRh}}$ = 1.4 Hz, *C*$^{\mathrm{q}}$(phenyl)), 136.65 (dd, $^1J_{\mathrm{CP}}$ = 40.0 Hz, $^2J_{\mathrm{CRh}}$ = 1.4 Hz, *C*$^{\mathrm{q}}$(phenyl′)), 133.25 (d, $^2J_{\mathrm{CP}}$ =12.0 Hz, *C*H$^{\mathrm{ortho}}$-(phenyl)), 130.01 (d, $^3J_{\mathrm{CP}}$ = 2.5 Hz, *C*H$^{\mathrm{para}}$(phenyl)), 128.50 (d, $^3J_{\mathrm{CP}}$ = 10.1 Hz, *C*H$^{\mathrm{meta}}$(phenyl)), 125.83, 122.32 (C^{5,6}), 115.71, 113.57 (C^{4,7}), 108.54 (d, $^1J_{\mathrm{CRh}}$ = 3.5 Hz, C$^{8/9}$), 108.28 (d, $^1J_{\mathrm{CRh}}$ = 3.5 Hz, C$^{8/9}$), 94.86 (d, $^1J_{\mathrm{CRh}}$ = 2.5 Hz, C^1), 94.80 (d, $^1J_{\mathrm{CRh}}$ = 2.5 Hz, C^2), 76.05 (d, $^1J_{\mathrm{CRh}}$ = 3.5 Hz, C^3), 51.70, 38.38, 34.58, 26.84 (C$^{1',3',4',8'}$), 50.57 (O*C*H$_3$), 48.39, 34.81, 25.65 (C$^{2',5',6'}$), 27.28 (d, $^1J_{CP}$ = 25.0 Hz, P*C*H$_2$), 22.86, 22.24, 21.47, 18.13, 16.43

($C^{7',9',10,10',11}$), 5.15 (SiCH_2). $^{31}P\{^1H\}$ NMR (pyridine-d_5, 80.94 MHz): δ 48.90 (d, $^1J_{PRh}$ = 202.5 Hz).

(−)-(η^4-Cycloocta-1,5-diene)(η^5-1-menthyl-4,7-dimethylindenyl)iridium(I) (14a/b). Method A. Reaction in analogy to **7** of di-μ-chlorobis(η^4-cycloocta-1,5-diene)diiridium(I) (0.68 g, 1.01 mmol) with **1** (0.60 g, 2.08 mmol) in diethyl ether (25 mL) gave after workup an orange oil (0.98 g, 83%) as a mixture of **14a** and **14b** in the ratio 2.2:1. Chromatography and recrystallization from *n*-pentane gave yellow crystals of the (*pR*)-diastereomer **14a** (0.51 g, 43%) and a yellow oil of the (*pS*)-diastereomer **14b** (0.19 g, 16%).

Method B. Reaction in analogy to **7** of di-μ-chlorobis(η^4-cycloocta-1,5-diene)diiridium(I) (0.70 g, 1.04 mmol) and **5** (0.61 g, 1.90 mmol) in diethyl ether (20 mL) gave after workup 0.83 g (75%) of an orange solid as a mixture of **14a** and **14b** in the ratio 1.2:1.

(*pR*)-Diastereomer 14a. Mp 154 °C. $[\alpha]_D^{25}$ −177.5° (*c* 0.5, diethyl ether). ^1H NMR (benzene-d_6, 400 MHz): δ 6.55 (m, 2H, $H^{5,6}$), 5.28 (d, ^3J = 2.7 Hz, 1H, $H^{2/3}$), 5.17 (d, ^3J = 2.7 Hz, 1H, $H^{2/3}$), 3.77 (m, 2H, C*H*(COD)), 3.46 (m, 2H, C*H*(COD)), 2.93 (m, 1H, $H^{3'}$), 2.45 (s, 3H, $H^{10/11}$), 2.40−0.87 (m, 9H, $H^{1',2',4',5',6',8'}$), 2.19 (s, 3H, $H^{10/11}$), 1.97 (m, 4H, CH_2(COD)), 1.61 (m, 4H, CH_2-(COD)), 1.03 (d, ^3J = 6.4 Hz, 3H, $H^{7'/9'/10'}$), 0.68 (d, ^3J = 7.0 Hz, 3H, $H^{7'/9'/10'}$), 0.59 (d, ^3J = 6.9 Hz, 3H, $H^{7'/9'/10'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.64 MHz): δ 128.79, 128.69 ($C^{4,7}$), 124.87, 121.67 ($C^{5,6}$), 105.88, 102.93, 102.65 ($C^{1,8,9}$), 83.66 (C^2), 70.74 (C^3), 52.46, 38.89, 34.16, 27.51 ($C^{1',3',4',8'}$), 51.81, 49.54 (*C*H-(COD)), 47.09, 34.45, 25.76 ($C^{2',5',6'}$), 34.45, 32.85 (*C*H_2(COD)), 22.72, 22.15, 21.69, 18.68, 16.28 ($C^{7',9',10,10',11}$). Anal. Calcd for $C_{29}H_{41}Ir$ (mol wt 581.86): C, 59.86; H, 7.10. Found: C, 59.48; H, 6.86. Mol wt cryosc in benzene: 553.

(*pS*)-Diastereomer 14b. Mp 146 °C. $[\alpha]_D^{25}$ −68.5° (*c* 0.5, diethyl ether). ^1H NMR (benzene-d_6, 400 MHz): δ 6.61 (m, 2H, $H^{5,6}$), 5.34 (d, ^3J = 2.6 Hz, 1H, $H^{2/3}$), 4.87 (d, ^3J = 2.6 Hz, 1H, $H^{2/3}$), 4.07 (m, 2H, C*H*(COD)), 3.36 (m, 2H, C*H*(COD)), 2.79 (m, 1H, $H^{3'}$), 2.57−0.58 (m, 9H, $H^{1',2',4',5',6',8'}$), 2.32 (s, 3H, $H^{10/11}$), 2.27 (s, 3H, $H^{10/11}$), 1.87 (m, 4H, CH_2(COD)), 1.35 (m, 4H, CH_2-(COD)), 0.98 (d, ^3J = 6.9 Hz, 3H, $H^{7'/9'/10'}$), 0.88 (d, ^3J = 6.9 Hz, 3H, $H^{7'/9'/10'}$), 0.73 (d, ^3J = 6.7 Hz, 3H, $H^{7'/9'/10'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.64 MHz): δ 128.11, 127.88 ($C^{4,7}$), 125.50, 120.25 ($C^{5,6}$), 105.27, 103.97, 101.27 ($C^{1,8,9}$), 84.48 (C^2), 68.63 (C^3), 54.16, 47.38 (*C*H(COD)), 51.92, 38.15, 34.36, 27.12 ($C^{1',3',4',8'}$), 48.51, 35.18, 25.26 ($C^{2',5',6'}$), 34.04, 32.80 (*C*H_2(COD)), 22.60, 22.58, 22.18, 18.86, 15.58 ($C^{7',9',10,10',11}$). Anal. Calcd for $C_{29}H_{41}Ir$ (mol wt 581.86): C, 59.86; H, 7.10. Found: C, 59.91; H, 7.43.

(η^5-1-Menthyl-4,7-dimethylindenyl)(η^2-1,2-bis(diphenylphosphino)ethane)cobalt(I) (15a/b). Reaction in analogy to **7** of dichloro(1,2-bis(diphenylphosphino)ethane)cobalt(II) (0.50 g, 0.95 mmol) and **1** (0.55 g, 1.91 mmol) in diethyl ether (30 mL) gave after workup and chromatography with diethyl ether and recrystallization from *n*-pentane at −78 °C 0.23 g (33%) of a brown powder of the (*pR*)- and (*pS*)-diastereomers **15a/15b** in the ratio 6.0:1. Mp 109 °C dec. $[\alpha]_D^{25}$ −61.5° (*c* 0.1, diethyl ether). Anal. Calcd for $C_{47}H_{53}CoP_2$ (mol wt 738.82): C, 76.41; H, 7.23. Found: C, 75.99; H, 7.61.

Diastereomer 15a. ^1H NMR (benzene-d_6, 400 MHz): δ 7.73−6.90 (m, 20H, C*H*(phenyl)), 6.72 (m, 2H, $H^{5,6}$), 5.20 (d, ^3J = 2.7 Hz, 1H, H^2), 4.39 (d, ^3J = 2.7 Hz, 1H, H^3), 2.95−0.57 (m, 14H, $H^{1',2',3',4',5',6',8'}$, PCH_2), 2.13 (s, 3H, $H^{10/11}$), 1.76 (s, 3H, $H^{10/11}$), 0.88 (d, ^3J = 6.5 Hz, 3H, $H^{7'/9'/10'}$), 0.65 (d, ^3J = 6.7 Hz, 3H, $H^{7'/9'/10'}$), 0.59 (d, ^3J = 7.0 Hz, 3H, $H^{7'/9'/10'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.64 MHz): δ 140.03−138.42 (m, C^q(phenyl)), 133.09−127.20 (m, *C*H(phenyl)), 125.14, 119.22 ($C^{5/6}$), 116.85, 116.61, 116.37, 116.11, 98.80 ($C^{1,4,7,8,9}$), 85.18 (C^2), 64.99 (C^3), 54.23, 38.81, 33.44, 26.59 ($C^{1',3',4',8'}$), 46.59, 36.40, 26.24 ($C^{2',5',6'}$), 35.56 (d, $^1J_{PC}$ = 23.4 Hz, P*C*H_2), 30.71 (d, $^1J_{PC}$ = 25.0 Hz, P*C*H_2), 22.98, 22.59, 21.21, 18.12, 17.19 ($C^{7',9',10,10',11}$).

Diastereomers 15a and 15b in the Ratio 6.0:1. $^{31}P\{^1H\}$ NMR (benzene-d_6, 80.94 MHz): δ 83.40 (1P), 72.44 (0.17P).

Lithium Tricarbonyl(η^5-1-menthyl-4,7-dimethylindenyl)molybdate(0)(THF)$_2$ (16a/b). To a solution of **1** (1.40 g, 4.85 mmol) in THF (50 mL) was added $Mo(CO)_6$ (1.20 g, 4.55 mmol) at −78 °C. The mixture was stirred for 3 h, warmed to 25 °C over 8 h, stirred for an additional 10 h, and heated for 24 h to 65 °C. The solvent was removed under vacuum (10^{-2} mbar), leaving an orange solid as a mixture of the (*pR*)- and (*pS*)-diastereomers **16a/16b** (2.64 g, 95%) in the ratio 2.4:1. Mp 56 °C. $[\alpha]_D^{25}$ −61.9° (*c* 1.9, diethyl ether). Anal. Calcd for $C_{32}H_{45}LiMoO_5$ (mol wt 612.58): C, 62.74; H, 7.40. Found: C, 63.07; H, 6.92.

Diastereomer 16a. ^1H NMR (pyridine-d_5, 200 MHz): δ 6.64 (m, 2H, $H^{5,6}$), 5.95 (d, ^3J = 3.1 Hz, 1H, $H^{2/3}$), 5.80 (d, ^3J = 3.1 Hz, 1H, $H^{2/3}$), 3.74 (m, 8H, THF), 3.44−0.81 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 2.96 (s, 3H, $H^{10/11}$), 2.56 (s, 3H, $H^{10/11}$), 1.81 (m, 8H, THF), 1.02 (d, ^3J = 5.7 Hz, 3H, H^{7-}), 0.77 (d, ^3J = 7.1 Hz, 3H, $H^{9'/10'}$), 0.72 (d, ^3J = 6.9 Hz, 3H, $H^{9'/10'}$). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 50.32 MHz): δ 236.77 (*C*O), 129.71, 129.39 ($C^{4,7}$), 121.98, 119.00 ($C^{5,6}$), 110.88, 110.61, 108.18 ($C^{1,8,9}$), 94.04 (C^2), 72.35 (C^3), 67.56 (THF), 52.24, 35.35, 24.62 ($C^{2',5',6'}$), 51.70, 38.44, 34.32, 27.16 ($C^{1',3',4',8'}$), 25.47 (THF), 22.66, 21.90, 21.86, 18.69, 16.01 ($C^{7',9',10,10',11}$).

Diastereomer 16b. ^1H NMR (pyridine-d_5, 200 MHz): δ 6.58 (m, 2H, $H^{5,6}$), 5.88 (d, ^3J = 3.0 Hz, 1H, $H^{2/3}$), 5.80 (d, ^3J = 3.0 Hz, 1H, $H^{2/3}$), 3.97−0.80 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 3.74 (m, 8H, THF), 2.92 (s, 3H, $H^{10/11}$), 2.59 (s, 3H, $H^{10/11}$), 1.81 (m, 8H, THF), 1.36 (d, ^3J = 6.7 Hz, 3H, $H^{7'/9'/10'}$), 1.22 (d, ^3J = 7.0 Hz, 3H, $H^{7'/9'/10'}$), 0.83 (d, ^3J = 6.2 Hz, 3H, $H^{7'/9'/10'}$). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 50.32 MHz): δ 236.01 (*C*O), 130.22, 129.17 ($C^{4,7}$), 121.26, 119.61 ($C^{5,6}$), 114.54, 108.03, 103.70 ($C^{1,8,9}$), 94.00 (C^2), 70.83 (C^3), 67.56 (THF), 49.80, 35.35, 24.54 ($C^{2',5',6'}$), 45.15, 39.53, 32.74, 26.23 ($C^{1',3',4',8'}$), 25.47 (THF), 22.50, 21.97, 21.37, 18.70, 16.33 ($C^{7',9',10,10',11}$).

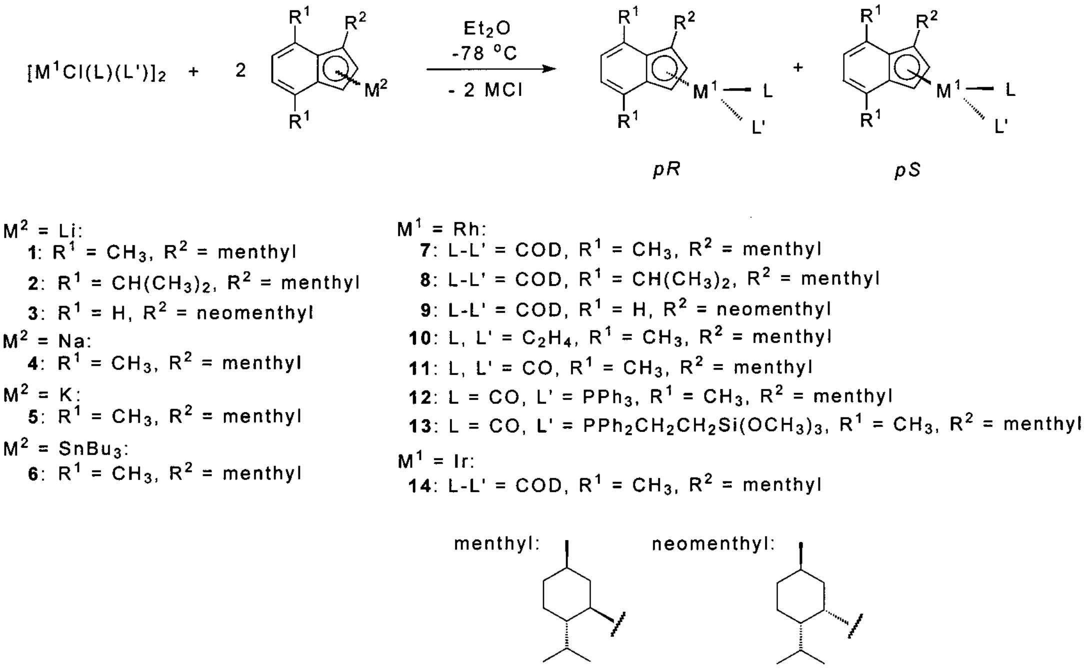
Tricarbonyliodo(η^5-1-menthyl-4,7-dimethylindenyl)molybdenum(II) (17a/b). A solution of lithium tricarbonyl(η^5-1-menthyl-4,7-dimethylindenyl)molybdate(0)(THF)$_2$ (2.50 g, 4.08 mmol) as a mixture of **16a/16b** in the ratio 2.4:1 in THF (50 mL) was treated with iodine (1.01 g, 3.98 mmol) at 0 °C. Under heat evolution a red solution formed which was stirred for 24 h at room temperature. The analogous workup to **7** and chromatography with *n*-hexane:diethyl ether = 1:1 gave red crystals (0.99 g, 52%) as a mixture of the (*pR*)- and (*pS*)-diastereomers **17a/17b** in the ratio 2.0:1. Mp 41 °C. $[\alpha]_D^{25}$ +33.1° (*c* 0.1, diethyl ether). Anal. Calcd for $C_{24}H_{29}IMoO_3$ (mol wt 588.33): C, 49.00; H, 4.97. Found: C, 49.23; H, 4.92.

Diastereomer 17a. ^1H NMR (benzene-d_6, 400 MHz): δ 6.45 (m, 2H, $H^{5,6}$), 4.99 (d, ^3J = 2.8 Hz, 1H, $H^{2/3}$), 4.54 (d, ^3J = 2.8 Hz, 1H, $H^{2/3}$), 3.07−0.51 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 2.41 (s, 3H, $H^{10/11}$), 1.90 (s, 3H, $H^{10/11}$), 1.02 (d, ^3J = 6.5 Hz, 3H, $H^{7'}$), 0.67 (d, ^3J = 6.9 Hz, 3H, $H^{9'/10'}$), 0.48 (d, ^3J = 6.9 Hz, 3H, $H^{9'/10'}$). $^{13}C\{^1H\}$ NMR (chloroform-d_1, 100.64 MHz): δ 239.17, 222.39, 219.37 (*C*O), 133.88, 132.97 ($C^{4,7}$), 131.26, 126.38 ($C^{5,6}$), 119.56, 118.29, 110.38 ($C^{1,8,9}$), 88.90 (C^2), 75.78 (C^3), 51.67, 37.86, 34.00, 27.16 ($C^{1',3',4',8'}$), 50.56, 34.69, 25.17 ($C^{2',5',6'}$), 22.49, 22.46, 22.01, 18.06, 16.03 ($C^{7',9',10,10',11}$).

Diastereomer 17b. ^1H NMR (benzene-d_6, 400 MHz): δ 6.60 (m, 2H, $H^{5,6}$), 5.26 (d, ^3J = 2.9 Hz, 1H, $H^{2/3}$), 4.93 (d, ^3J = 2.9 Hz, 1H, $H^{2/3}$), 3.08−0.50 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 2.35 (s, 3H, $H^{10/11}$), 2.01 (s, 3H, $H^{10/11}$), 1.12 (d, ^3J = 6.7 Hz, 3H, $H^{7'}$), 1.00 (d, ^3J = 7.1 Hz, 3H, $H^{9'/10'}$), 0.67 (d, ^3J = 7.0 Hz, 3H, $H^{9'/10'}$). $^{13}C\{^1H\}$ NMR (chloroform-d_1, 100.64 MHz): δ 237.10, 220.99, 219.98 (*C*O), 133.18, 133.13 ($C^{4,7}$), 129.93, 125.37 ($C^{5,6}$), 128.00, 119.46, 114.12 ($C^{1,8,9}$), 91.64 (C^2), 79.74 (C^3), 49.11, 35.27, 24.53 ($C^{2',5',6'}$), 45.73, 40.37, 32.88, 26.84 ($C^{1',3',4',8'}$), 21.96, 21.77, 21.70, 18.16, 15.81 ($C^{7',9',10,10',11}$).

X-ray Structure Determination. The crystal data and details of data collection for **7a** and **7b** are given in Table 1 and the data for **9a, 9b,** and **14** in the Supporting Information. Data were collected on a Siemens SMART CCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å) with an area detector by use of ω scans at 173 K for **7a**, **9a**,

Scheme 1



M^2 = Li:
1: $R^1 = CH_3$, R^2 = menthyl
2: $R^1 = CH(CH_3)_2$, R^2 = menthyl
3: R^1 = H, R^2 = neomenthyl
M^2 = Na:
4: $R^1 = CH_3$, R^2 = menthyl
M^2 = K:
5: $R^1 = CH_3$, R^2 = menthyl
$M^2 = SnBu_3$:
6: $R^1 = CH_3$, R^2 = menthyl

M^1 = Rh:
7: L-L' = COD, $R^1 = CH_3$, R^2 = menthyl
8: L-L' = COD, $R^1 = CH(CH_3)_2$, R^2 = menthyl
9: L-L' = COD, R^1 = H, R^2 = neomenthyl
10: L, L' = C_2H_4, $R^1 = CH_3$, R^2 = menthyl
11: L, L' = CO, $R^1 = CH_3$, R^2 = menthyl
12: L = CO, L' = PPh_3, $R^1 = CH_3$, R^2 = menthyl
13: L = CO, L' = $PPh_2CH_2CH_2Si(OCH_3)_3$, $R^1 = CH_3$, R^2 = menthyl
M^1 = Ir:
14: L-L' = COD, $R^1 = CH_3$, R^2 = menthyl

Table 1. Crystal Data and Structure Refinement for 7a and 7b

	7a	7b
empirical formula	$C_{29}H_{41}Rh$	$C_{29}H_{41}Rh$
fw	492.53	492.53
temp (K)	173(2)	293(2)
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a (Å), α (deg)	9.176(1), 90	8.3734(1), 90
b (Å), β (deg)	12.735(2), 90	16.7604(17), 90
c (Å), γ (deg)	20.898(2), 90	18.3275(9), 90
vol (Å^3)	2442.0(5)	2572.1(3)
Z	4	4
D(calcd) (g/cm^3)	1.340	1.272
μ(Mo Kα) (mm^{-1})	0.712	0.676
F(000)	1040	1040
cryst size (mm^3)	0.40 × 0.30 × 0.20	0.52 × 0.28 × 0.20
θ_{min}, θ_{max} (deg)	1.87, 27.49	1.65, 26.49
index ranges	$-11 \le h \le +11$ $-16 \le k \le +16$ $-20 \le l \le +27$	$-10 \le h \le +7$ $-20 \le k \le +20$ $-23 \le l \le +14$
no. of reflns collected	15538	8724
no. of independent reflns	5595 [$R_{int} = 0.0489$]	5276 [$R_{int} = 0.0360$]
max, min transmissn	0.8541, 0.5132	0.9038, 0.5331
no. of data, restraints, params	5595, 0, 276	5276, 0, 276
GOF on F^2	1.012	1.000
R indices [$I > 2\sigma(I)$]	R1 = 0.0291 wR2 = 0.0610	R1 = 0.0365 wR2 = 0.0698
R indices (all data)	R1 = 0.0352 wR2 = 0.0627	R1 = 0.0508 wR2 = 0.0744
abs structure param	−0.03(3)	0.00(4)
residual electron density (e/Å^3)	max 0.461 min −0.615	max 0.449 min −0.502

9b, and **14a** and at room temperature for **7b**. The structures were solved by direct methods using SHELXS-97[13] and refined on F^2 using all reflections with SHELXL-97.[14] 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[15] with SHELX-97. SADABS[16] was used to perform area-detector scaling and absorption corrections. The maximum and minimum transmission factors and the resulting crystallographic data for **7a** and **7b** are summarized in Table 1. The geometrical aspects of the structures were analyzed by using the PLATON program.[17]

Results and Discussion

Rhodium and Iridium Complexes. The metathetic reactions of 1 equiv of the main group metal salts **1**−**6** with the appropriate binuclear rhodium complex [$L_2Rh(\mu\text{-}Cl)_2RhL_2$], (L = COD, C_2H_4, or CO) in diethyl ether at −78 °C gave the corresponding indenyl complexes of rhodium in 47−98% isolated yield (Scheme 1).

Chiral indenyl ligands having diastereotopic π-faces can form two diastereomeric indenylmetal complexes in various ratios. As shown for the formation of the diastereomerically pure lithium salt **1**,[6a] the different steric demands of the menthyl group in 3-menthyl-4,7-dimethylindene (4′-isopropyl group vs 1′-methyl group) favored the formation of only one diastereomer. Reacting [RhCl(COD)]$_2$ with **1**, we therefore anticipated the formation of only **7a** due to the bulky Rh(COD) moiety being situated on the less hindered (pR)-side[18] of the indenyl plane (method A). However, a mixture of both diastereomers was formed as demonstrated by two sets of signals in the ^{1}H and ^{13}C NMR spectra (diastereoselectivity: 39%).

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(17) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C-34.

(18) The planar chirality in the indenylmetal complex is assigned pR or pS on the basis of the Cahn−Ingold−Prelog configuration of the 1-position where the metal is treated as being individually bonded to all five of the $^1/_4$-atoms. For nomenclature see: (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (b) Schlögl, K. *Top. Stereochem.* **1967**, *1*, 39. (c) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem.* **1966**, *78*, 414. (d) Schlögl, K. *Fortschr. Chem. Forsch.* **1966**, *6*, 479. (e) Also see: Halterman, R. L. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 455 and 461−462.

Using 1 equiv of (−)-sparteine as an additional chiral auxiliary for the asymmetric complexation[19] of lithium salt **1** did not increase the diastereoselectivity of the metathesis (method B). Substitution of the hard, η^5-bound lithium salt **1** by the corresponding soft, η^1-bound tributyltin derivative **6** (as a 1:1 mixture of diastereomers) also did not change the diastereoselectivity (method C). In contrast the sodium salt **4** (method E) or the potassium salt **5** (method F) inverted the diastereoselectivity to −33% or −50%, respectively, forming the thermodynamically less favorable (*pS*)-diastereomer in excess. The addition of crown ethers to the alkali-metal salt **1** leads to the "naked" anion and resulted in a relatively low metalation diastereoselectivity of 17%—still in favor of the (*pR*)-isomer (method D). Thus, the salt composition and coordination strongly influenced the composition of the diastereomeric mixture. With respect to the similar electronegativity values of Li (0.97), Na (1.01), and K (0.91),[20] an explanation for this varying reactivity pattern can be drawn from their different ionic radii (Li = 0.68 Å, Na = 0.97 Å, K = 1.33 Å),[21] leading to a higher tendency of larger cations to form oligomeric units.[22,23] That favors one of the following reaction mechanisms or a combination of them: (i) frontal attack, the (*pR*)-configurated indenyl alkali-metal salt produces the (*pR*)-configurated indenyl rhodium complex; (ii) backside attack, the (*pR*)-configurated indenyl alkali-metal salt forms the (*pS*)-configurated indenylrhodium complex; (iii) stepwise transmetalation, the decoordinated indenyl anion generates a sterically controlled mixture of (*pR*)- and (*pS*)-configurated indenylrhodium complexes; (iv) previous oxidative addition, the electrophilic rhodium atom precoordinates the diene system in the six-membered ring of the indenyl system followed by a concerted reductive elimination and metathesis, yielding a 1:1 mixture of the (*pR*)- and (*pS*)-configurated indenylrhodium complexes due to the limited chiral induction of the terpene at the six-membered ring.

The oily mixtures of the two rhodium diastereomers **7a** and **7b** could not be separated by recrystallization, but chromatographic separation in an inert atmosphere with dried aluminum oxide and *n*-hexane as eluent resulted in the isolation of diastereomerically pure compounds after crystallization from *n*-pentane. The contact of even traces of oxygen during chromatography led to immediate decomposition of the complexes under dimerization of the indenyl ligand to 1,1′-bis(3-menthyl-4,7-dimethylindene). In contrast to their solutions, pure crystalline compounds **7**−**14** are stable to air and moisture. They are soluble in polar solvents such as THF, pyridine, or diethyl ether as well as in aromatic solvents such as toluene and unpolar solvents such as *n*-hexane. The high thermal stability of **7a** and **7b** can be shown by mass spectrometry as the molecular ions form the peaks of highest intensity.

As the diastereoselectivity of the metalation of 3-menthyl-4,7-dimethylindene did not allow the separatation of the diastereomers by simple crystallization, the chemistry of the substituted compound 4,7-diisopropyl-3-menthylindene was exploited. Metathesis of (+)-(4,7-diisopropyl-1-menthylindenyl)lithium (**2**) with [RhCl(COD)]$_2$ gave again a mixture of the (*pR*)- and (*pS*)-diastereomers of (COD)(η^5-4,7-diisopropyl-1-menthylindenyl)rhodium(I), **8a** and **8b**. A diastereoselectivity of 38% was detected, showing that the exchange of the methyl groups attached to the indene unit by the sterically more demanding isopropyl groups had no effect on the diastereoselectivity of the metalation.

Similar mixtures of (*pR*)- and (*pS*)-diastereomers are formed by reacting lithium salt **1** with [RhCl(C$_2$H$_4$)$_2$]$_2$, or sodium salt **5** with [RhCl(CO)$_2$]$_2$. Rhodium complexes **10a/10b** and **11a/11b** were formed with a diastereoselectivity of 33% and 20%, respectively. With no solid-state structures available, it could not be determined whether the (*pR*)- or (*pS*)-diastereomer was formed in excess.

One of the two carbonyl ligands of **11** could be displaced by equimolar amounts of triphenylphosphine or (2-trimethoxysilylethyl)diphenylphosphine in boiling *n*-hexane, yielding mixtures of (*pR*)- and (*pS*)-diastereomers **12a/12b** and **13a/13b**, respectively. They are solids but cannot be separated by crystallization, too.

An even lower diastereoselectivity of 20% is found in the metathesis of (1-neomenthylindenyl)lithium (**3**), an indenyl derivative without substituents in positions 4 and 7, with [RhCl(COD)]$_2$ yielding a mixture of the (*pR*)- and (*pS*)-diastereomeres **9a** and **9b**. The diastereomerically pure compounds were obtained after chromatography and crystallization from *n*-pentane.

[IrCl(COD)]$_2$ reacts with **1** or **5**, yielding **14a** and **14b** in 75−83% yield. Using the lithium salt **1**, a diastereoselectivity of 38% was achieved whereas the potassium salt **5** generates a diastereoselectivity of only 9%, forming again the (*pR*)-diastereomer in excess. Iridium as the heavier homologue of rhodium therefore does not affect the diastereoselectivity of the metalation to a large extent. The diastereomers **14a** and **14b** were separated by chromatography under inert atmosphere and crystallization.

Crystals of **7a**, **7b**, **9a**, **9b**, and **14a** suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from *n*-pentane. The solid-state structures were determined by X-ray diffraction methods. The menthylindenyl and neomenthylindenyl complexes **7a**, **7b**, **9b**, and **14a** crystallize in the same orthorhombic space group, $P2_12_12_1$, with four superimposable molecules in the unit cell, while the unit cell of the monoclinic **9a** ($P2_1$) consists of two molecules. The iridium complex **14a** is isostructural to the rhodium complex **7a**. The solid-state structures of these molecules are shown in Figures 1−5.

All five complexes are monomeric, free of solvent, and diastereomerically pure and cleary show the characteristic three stereocenters of the menthyl or neomenthyl moiety. In all cases the transition metals of the formal oxidation state +1 are coordinated trigonal planar by the centroids of the cyclopentadienyl systems and the

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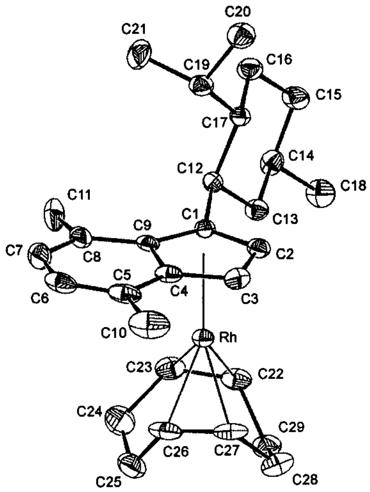

Figure 1. ORTEP plot[24] of the molecular structure and numbering scheme of **7a**, with 50% probability thermal ellipsoids. For clarity, all hydrogens are removed. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations:[25] Rh−Cg 1.9394(13), Rh−C(22) 2.119(3), Rh−C(23) 2.125(3), Rh−C(26) 2.131(3), Rh−C(27) 2.134(3), C(1)−C(2) 1.434(4), C(2)−C(3) 1.393(4), C(3)−C(4) 1.437(4), C(4)−C(9) 1.449(3), C(1)−C(9) 1.458(4), C(22)−C(23) 1.406(4), C(26)−C(27) 1.383(5); Cg−Rh−C(22) 138.71(10), Cg−Rh−C(23) 132.98(8), Cg−Rh−C(26) 132.55(8), Cg−Rh−C(27) 129.34(8), C(22)−Rh−C(23) 38.71(12), C(26)−Rh−C(27) 37.84(13), C(22)−Rh−C(27) 81.05(11), C(23)−Rh−C(26) 80.85(12).

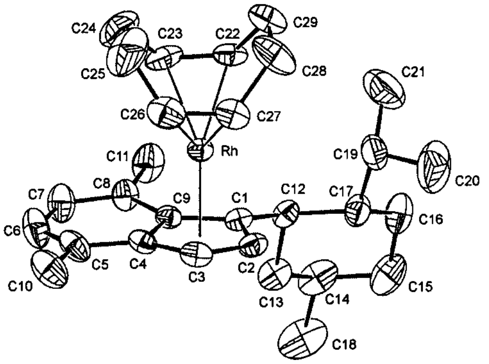

Figure 2. ORTEP plot[24] of the molecular structure and numbering scheme of **7b**, with 40% probability thermal ellipsoids. For clarity, all hydrogens are removed. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations:[25] Rh−Cg 1.9327(17), Rh−C(22) 2.142(4), Rh−C(23) 2.143(4), Rh−C(26) 2.122(4), Rh−C(27) 2.110(4), C(1)−C(2) 1.410(5), C(2)−C(3) 1.404(5), C(3)−C(4) 1.442(6), C(4)−C(9) 1.441(5), C(1)−C(9) 1.466(5), C(22)−C(23) 1.382(7), C(26)−C(27) 1.387(6); Cg−Rh−C(22) 135.44(12), Cg−Rh−C(23) 132.02(14), Cg−Rh−C(26) 132.96(15), Cg−Rh−C(27) 132.73(13), C(22)−Rh−C(23) 37.62(18), C(26)−Rh−C(27) 38.26(18), C(22)−Rh−C(27) 81.48(17), C(23)−Rh−C(26) 81.05(19).

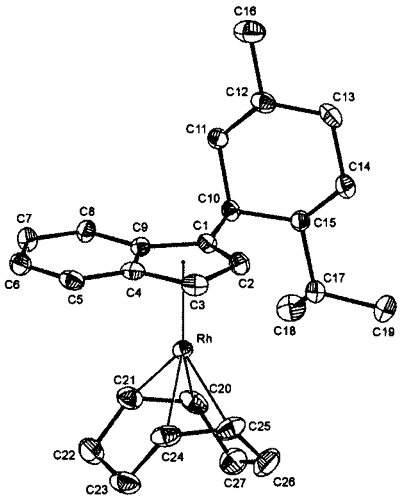

Figure 3. ORTEP plot[24] of the molecular structure and numbering scheme of **9a**, with 50% probability thermal ellipsoids. For clarity, all hydrogens are removed. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations:[25] Rh−Cg 1.9377(11), Rh−C(20) 2.149(3), Rh−C(21) 2.140(3), Rh−C(24) 2.125(2), Rh−C(25) 2.101(2), C(1)−C(2) 1.404(3), C(2)−C(3) 1.436(4), C(3)−C(4) 1.440(4), C(4)−C(9) 1.441(3), C(1)−C(9) 1.461(3), C(20)−C(21) 1.403(5), C(24)−C(25) 1.409(4); Cg−Rh−C(20) 138.22(10), Cg−Rh−C(21) 131.85(8), Cg−Rh−C(24) 132.21(15), Cg−Rh−C(25) 130.07(14), C(20)−Rh−C(21) 38.20(12), C(24)−Rh−C(25) 38.95(10), C(20)−Rh−C(25) 81.63(17), C(21)−Rh−C(24) 81.08(16).

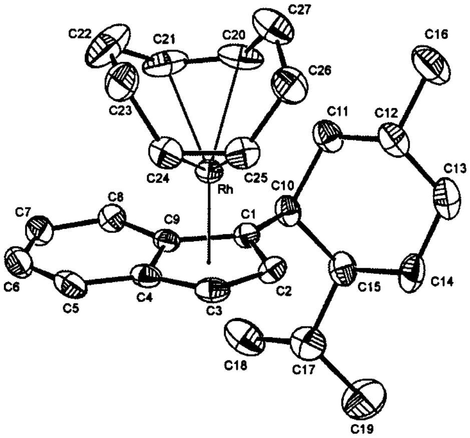

Figure 4. ORTEP plot[24] of the molecular structure and numbering scheme of **9b**, with 50% probability thermal ellipsoids. For clarity, all hydrogens are removed. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations:[25] Rh−Cg 1.9511(10), Rh−C(20) 2.158(3), Rh−C(21) 2.137(2), Rh−C(24) 2.117(2), Rh−C(25) 2.111(2), C(1)−C(2) 1.416(3), C(2)−C(3) 1.423(3), C(3)−C(4) 1.442(3), C(4)−C(9) 1.435(3), C(1)−C(9) 1.473(3), C(20)−C(21) 1.397(5), C(24)−C(25) 1.404(3); Cg−Rh−C(20) 141.21(8), Cg−Rh−C(21) 133.99(8), Cg−Rh−C(24) 127.93(9), Cg−Rh−C(25) 129.22(9), C(20)−Rh−C(21) 37.96(13), C(24)−Rh−C(25) 38.77(9), C(20)−Rh−C(25) 80.79(11), C(21)−Rh−C(24) 81.64(12).

diene systems of the COD ligands. The pairs of diastereomers differ by the arrangement of the M(COD) unit being attached to one of the two prochiral (*pR*)- and (*pS*)-sides of the indenyl moiety. It is particularly noteworthy that regardless of the (*pR*)- or (*pS*)-metalation the terpene moiety adopts similar conformations (**7a**, **9b**, **14a**, +anticlinal; **7b**, **9a**, antiperiplanar), with the menthyl moiety being more or less perpendicular to the indenyl plane and the proton at C(12) always pointing toward C(11) or the proton at C(10) pointing toward C(8), respectively. Because of the different steric interactions between the Rh(COD) and the menthyl/neomenthyl moiety, the corresponding dihedral angles differ by 31° (**7a** vs **7b**) and 52° (**9a** vs **9b**), respectively. This conformation was found to be energetically more favorable.[22] As no rotation by approximately 180° is observable, the rhodium−isopropyl interaction has to be

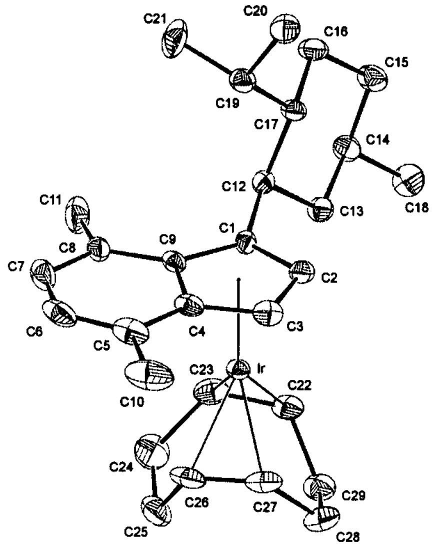

Figure 5. ORTEP plot[24] of the molecular structure and numbering scheme of **14a**, with 50% probability thermal ellipsoids. For clarity, all hydrogens are removed. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations:[25] Ir−Cg 1.9272(17), Ir−C(22) 2.108(4), Ir−C(23) 2.112(4), Ir−C(26) 2.130(4), Ir−C(27) 2.119(4), C(1)−C(2) 1.436(5), C(2)−C(3) 1.409(6), C(3)−C(4) 1.431(6), C(4)−C(9) 1.444(5), C(1)−C(9) 1.468(5), C(22)−C(23) 1.425(6), C(26)−C(27) 1.413(7); Cg−Ir−C(22) 138.71(13), Cg−Ir−C(23) 133.15(13), Cg−Ir−C(26) 132.61(11), Cg−Ir−C(27) 129.33(12), C(22)−Ir−C(23) 39.46(18), C(26)−Ir−C(27) 38.86(19), C(22)−Ir−C(27) 80.48(15), C(23)−Ir−C(26) 80.11(18).

smaller than the interaction of the terpene moiety with the methyl group C(11) in the case of **7a/7b**. The latter is strong enough to prevent successfully the rotation of 180° along the C(1)−C(12) axis. Nevertheless, two diastereomers are formed, demonstrating that the steric demand of the isopropyl group of the menthyl moiety is shielding the (*pS*)-space around the indenyl system only unefficiently. The structures of **7a/7b** prove that the menthyl group itself is not able to force a high diastereoselectivity with regard to the metalation of the planar chiral indenyl moiety. In contradiction to the literature the formation of the mixture is independent from the conformational rigidity along the C(1)−C(12) axis.[26] It has to be pointed out that in case of the lithium salt **1** exclusively one diastereomer is formed, while the chirality transfer in the following metathesis gives rise to an only unselective transmetalation. The steric demand of the isopropyl group might be enhanced by a substitution pattern realized in (−)-8-phenylmenthol. While the increase in stereoselectivity using this derivative in catalysis was already mentioned,[27] the empirical observation can be explained by our results for the first time.

The average bonding distances of rhodium to the five-membered indenyl rings are 2.29 Å (**7a**), 2.28 Å (**7b**), 2.29 Å (**9a**), and 2.30 Å (**9b**); the average bond lengths of rhodium to the diene systems of the COD units are 2.13 Å for all four complexes. These distances are in close accordance with the bond lengths given for (COD)(η^5-indenyl)rhodium (2.28 and 2.13 Å) and (COD)(η^5-heptamethylindenyl)rhodium (2.28 and 2.12 Å).[28] The bent angles defined by the center of the COD−olefin bonds and the rhodium atoms of 86.7° (**7a**), 86.4° (**7b**), 87.2° (**9a**), and 87.1° (**9b**) are only insignificantly smaller than the literature value of 87.6°.[28] The five-membered ring of the indenyl system is not equally bound to Rh but resembles an unsymmetrical η^5-coordination. The bond lengths of the carbon atoms C(1), C(2), and C(3) to the metal are typically 0.07 Å shorter than the bond lengths to the bridging atoms C(4) and C(9). An exception occurs for **7b** as the C(1)−Rh distance is, at 2.32 Å, one of the longest bonds because of the sterical interaction between the menthyl and the Rh(COD) unit, generating an unsymmetrical shift toward C(3). In general slip distortions (Δ)[29] and ring slippages (RS)[29] toward the C(2) atoms are found. The values for Δ and RS are 0.083 and 0.087 Å in **7a**, 0.063 and 0.120 Å in **7b**, 0.066 and 0.163 Å in **9a**, and 0.099 and 0.200 Å in **9b**. The tendency to a slight η^3-coordination accounts for the uneven cyclopentadienyl ring and therefore for hinge angles (HA)[30] as well as fold angles (FA).[30] The values for HA and FA are 5.3° and 5.3° in **7a**, 5.9° and 6.0° in **7b**, 5.8° and 4.4° in **9a**, and 6.0° and 4.6° in **9b**. The values are in the expected range for distorted η^5-coordinations as they were found in (COD)(η^5-indenyl)rhodium[31] (Δ = 0.152 Å, HA = 8.9°, FA = 7.4°), bis(ethylene)(η^5-indenyl)rhodium(I)[32] (Δ = 0.161 Å, HA = 8.1°, FA = 7.4°), bis(trimethylphosphine)(η^5-indenyl)rhodium(I)[32] (Δ = 0.201 Å, HA = 8.4°, FA = 7.9°), and do not show the characteristics of η^3-coordinations as they are found in tris(dimethylphenylphosphine)(η^3-indenyl)rhodium(I)[33] (Δ = 0.79 Å, HA = 25°, FA = 28°). Such distortions can further be detected by the differences in the C−C bond lengths in the five-membered indenyl rings. The maximum variations of 0.07 Å (**7a**), 0.15 Å (**7b**), 0.06 Å (**9a**), and 0.06 Å (**9b**) are higher than can be accounted for by the influence of the condensed six-membered ring alone. Compound **7b** shows a much higher trend toward the η^2+η^3-coordination than **7a**, as the latter is the thermodynamically more stable, sterically less strained diastereomer. In general the trend toward η^3-coordination is not strongly shown, as the substitution patterns favor a distortion not only toward C(2) but toward (C3) as well. In an accompanying paper

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(25) Cg defines the centroid of the ring atoms C(1), C(2), C(3), C(4), and C(9).

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(30) Hinge angle = angle between normals to the least-squares planes defined by C(1), C(2), C(3) and C(1), C(9), C(4), C(3). Fold angle = angle between normals to the least-squares planes defined by C(1), C(2), C(3) and C(4), C(5), C(6), C(7), C(8), C(9). Kakkar, A.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198*, 219.

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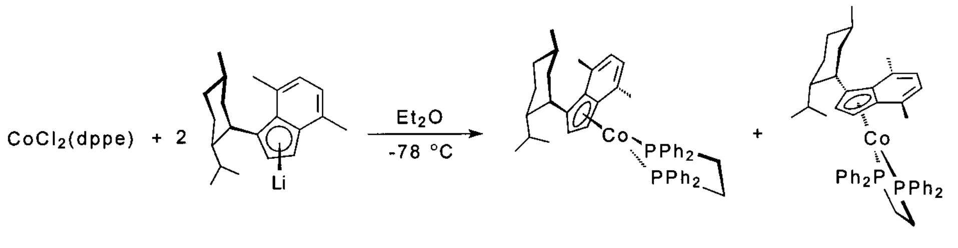
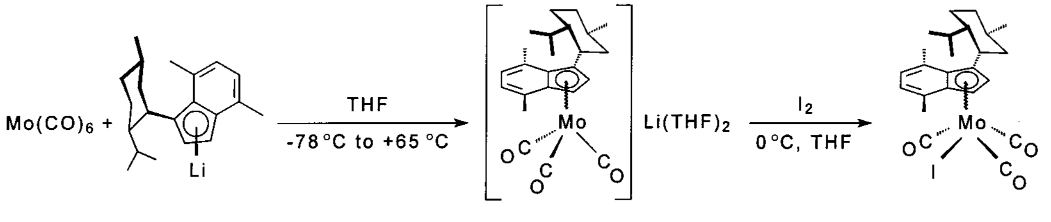
Scheme 2



1 **15a** **15b**

Scheme 3



1 **16a/b** **17a/b**

we describe that the distortions are much higher for the symmetrically substituted bis(2-menthylindenyl)metal complexes.[6b] The structure parameters for **7a, 7b, 9a,** and **9b** are compiled in the Supporting Information.

The parallel alignment of the diene systems of the COD ligand to the longitudinal axis of indene is due to an orbital control as the HOMO of the indenyl unit can best be stabilized at a rotation angle (RA) of 0°.[32,34,35] In our cases the values for RA = 19.4° (**7a**), 22.7° (**7b**), 21.1° (**9a**), and 14.1° (**9b**) are bigger than the theoretical value because of the unsymmetrical substitution pattern of the indenyl ring, a sterical interaction with the menthyl moiety, and probably packing effects. The ionic compound (−)-(η^5-1-menthyl-4,7-dimethylindenyl)lithium, which crystallizes in the same space group as **7a, 7b**, and **9b,** shows an increased rotation angle of 59° because of a lack of orbital control.[6a]

^{13}C NMR chemical shift values of the bridging carbon atoms C(4) and C(9) have been found to be indicative of the extent of ring slippages in rhodium complexes.[31] Following this theory the slippage from η^5- to η^3-coordination should lead to a stronger deshielding of the less coordinated atoms and therefore to a low-field shift. The chemical shifts of the rhodium compounds investigated by X-ray diffraction vary only between 108.6 and 111.5 ppm, and therefore, this theory can be confirmed, as **7a**, **7b**, **9a**, and **9b** show a distorted η^5-coordination. A similar distorted η^5-coordinated molecular structure can be presumed for the other complexes described in this paper, as they show chemical shifts of the bridging atoms varying between 102.0 and 115.1 ppm.

The iridium complex **14a** shows bond lengths which are in close accordance with the bond lengths given for the rhodium complexes as a consequence of the lanthanide contraction causing similar ionic radii for Rh and Ir.[36] The Ir−C distances correspond to previously published data.[37−39] While the bent angle is only insignificantly smaller than the values given earlier, the C−C bond lengths of the diene systems of COD are 0.03 Å longer than in **7a** and 0.08 Å longer than in free COD.[40] This is a sign of a stronger back-bonding of the metal into antibonding orbitals of COD, which results in a stronger ligand−metal bond. **14a** shows a significantly weaker tendency toward a η^2+η^3-coordination than the analogous rhodium complex **7a**, as besides possible packing effects the stronger back-bonding of iridium to the neutral ligand increases the Lewis acidity of the metal and therefore the η^5-coordination is favored.

Cobalt and Molybdenum Complexes. The cobalt complexes **15** were synthesized in a metathetic reaction under reduction of the metal center by adding 2 equiv of **1** to CoCl$_2$(dppe) in diethyl ether at −78 °C (Scheme 2). Chromatography under inert atmosphere with dried alumina in diethyl ether followed by crystallization from *n*-pentane at −78 °C gives the product as a brown powder in 33% yield. This complex consists of the (*pR*)- and (*pS*)-diastereomers in the ratio 6.0:1. This diastereoselectivity of 71% is the highest achieved in our studies by using the ligand 3-menthyl-4,7-dimethylindene. This is probably due to the higher sterical demand of the dppe ligand in comparison to COD, giving rise to an increased unfavorable interaction and therefore a more selective metalation. Diastereomeric cobalt complexes **15a** and **15b** are air and moisture sensitive, but they form the molecular ions as the peaks of highest intensity in the mass spectra.

As shown in Scheme 3 the molybdenum complexes **16** were synthesized in a transmetalation reaction by adding 1 equiv of **1** to Mo(CO)$_6$ in THF at −78 °C. The intermediates **16a/16b** were obtained in 30% yield with a diastereoselectivity of 41% by warming the reaction

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mixture to room temperature. Heating the reaction mixture for 24 h to 65 °C gives almost quantitative conversion without affecting the diastereomeric excess. Evaporation of the solvent gives the (*pR*)- and (*pS*)-diastereomers in the ratio 2.4:1 as an orange, extremely air and moisture sensitive solid. It could not be determined which diastereomer was formed in excess. The characteristic CO resonances of **16a** and **16b** can be detected in the ^{13}C NMR at 236.8 und 236.0 ppm and are low field shifted with regard to the similar rhodium(I) complex **11** by 46 ppm.

Oxidation of the mixture of the anionic molybdenum tricarbonyl complexes **16a/16b** with 1 equiv of iodine in THF results in the formation of iodomolybdenum tricarbonyls **17**. Chromatography under inert atmosphere and crystallization from warm *n*-pentane yields 52% of red crystals of the (*pR*)- and (*pS*)-diastereomers **17a/17b** in the ratio 2.0:1.

NMR Spectra. All described transition-metal complexes exhibited C_1 symmetry in their solution NMR spectra, and each diastereomeric compound gave only one set of signals at room temperature without unusual peak broadening. This is consistent with the menthyl group not rotating along the $C^{1}-C^{3'}$ axis as this would lead to a new rotamer in which all atoms are in a new chemical environment with potentially different chemical shifts. In addition the used ligands COD, CO, C_2H_4, phosphines, and iodide do not seem to rotate around the indenyl−rhodium axis on the NMR time scale as was found for similar complexes.[41] The COD signals show no broadening but give complicated coupling patterns as all of their 12 protons are chemically inequivalent. In the ^{13}C NMR spectra only four of the eight chemically inequivalent carbon atoms of COD are detected. This gives rise to an empirically low induction of the chiral indenyl ligand on the COD moiety or to a rotating COD ligand on the ^{13}C NMR time scale. ^{13}C NMR measurements at different temperatures to differentiate between the two possibilities were not performed.

The assignment of the ^{1}H and ^{13}C signals was based on ^{1}H,^{1}H COSY and ^{1}H,^{13}C correlated spectra as well as two-dimensional NOE experiments. In rhodium compound **9** the protons H^{4-7} form a complicated multiplet whereas the protons $H^{5,6}$ of the further complexes form more or less well resolved doublets between 7.32 and 6.45 ppm which show no coupling to the methyl substituents. The two protons attached to the five-membered ring of the indenyl system show a characteristic AX coupling pattern with coupling constants $^{3}J = 2.6-3.2$ Hz. The proton H^2 shows a long-range coupling $^{4}J = 1.6$ Hz with $H^{3'}$. In comparison to the indenyl main group complexes their chemical shifts are approximately 2 ppm high field shifted. The resonances of the three methyl groups of the menthyl moiety appear between 0.48 and 1.36 ppm with coupling constants $^{3}J = 5.7-7.3$ Hz. The further proton signals of the menthyl unit show complicated coupling patterns between 4.30 and 0.50 ppm.

Characteristic $^{1}J_{CRh}$ coupling constants varying between 1.9 and 5.7 Hz for the five-membered indenyl ring and from 12.5 to 86.6 Hz for the neutral ligands could be determined. Higher coupling constants correlate to higher electron density; therefore, the bridging atoms C^8 and C^9 are only weakly bonded in comparison to the atoms C^1 to C^3, which show the 2-fold value. This is consistent with the η^3-coordination found in the solid-state structure. The higher *J* values of the neutral ligands are due to the shorter bond lengths in comparison to the indenyl−rhodium bond.

Decoupled ^{103}Rh NMR spectra of **7a**, **7b**, **9a**, **9b**, **11a**, and **11b** in Et_2O/D_2O (3:1) show chemical shifts between −127.6 and −722.4 ppm relative to hexachlororhodate in D_2O with typical half-widths of $\nu_{1/2} = 20$ Hz. The high-field shift grows with higher alkylation of the indenyl ligand and stronger σ-donor bonds to the metal due to the increase in electron density.[42]

Conclusion

Metathetic reactions of $[RhCl(L)(L')]_2$, $[IrCl(COD)]_2$, $CoCl_2$(dppe), and $Mo(CO)_6$ with chiral, menthyl-functionalized nonracemic indenyl salts provide a convenient entry into chiral nonracemic transition-metal complexes of rhodium, iridium, cobalt, and molybdenum. X-ray diffraction analyses of the monomeric, diastereomerically pure complexes **7a**, **7b**, **9a**, **9b**, and **14a** confirm the enantiomeric purity of the stereogenic centers in the ligands and the indenyl moiety being $\eta^2+\eta^3$-coordinated. The structures prove for the first time that neither the chiral auxiliary menthyl nor neomenthyl is able to allow a high diastereoselectivity in regard to the planar chirality of the indenyl moiety independently from the conformational rigidity along the indenyl−menthyl axis. The reaction conditions strongly influence the composition of the diastereomeric mixture, and the diastereomeric excesses can be varied between 9% and 71% de, with the (*pR*)- or the (*pS*)-diastereomer being preferably formed.

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Supporting Information Available: Full details of the X-ray structures of complexes **7a**, **7b**, **9a**, **9b**, and **14a** including complete tables of crystal data, atomic coordinates, bond lengths, bond angles, and positional and anisotropic thermal parameters as well as additional analytical data of compounds **7**−**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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