Synthesis, Structure, and Catalytic Activity of Some New Chiral 2-Menthylindenyl and 2-Menthyl-4,7-dimethylindenyl Rhodium Complexes

Herbert Schumann,*[a] Oleg Stenzel,[a] Sebastian Dechert,[a] Frank Girgsdies,[a] Jochanan Blum,[b] Dmitri Gelman,[b] and Ronald L. Halterman[c]

Dedicated to Prof. Dr. Rudolf Taube on the occasion of his 70th birthday

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Optically active rhodium complexes containing the chiral, menthyl-substituted indenyl ligands (–)-2-menthyl-4,7-dimethylindene and (–)-2-menthylindene are described. Metathesis reactions of the chiral lithium salts of these indenyl systems with the appropriate starting materials yielded the complexes (–)-(2-menthyl-4,7-dimethylindenyl)$Rh(CO)_2$ (**2**), (–)-(2-menthyl-4,7-dimethylindenyl)Rh(dppe) (**3**), (+)-(2-menthylindenyl)Rh(dppe) (**5**), (–)-(2-menthylindenyl)$Rh(PMe_3)_2$ (**6**), and (–)-(2-menthylindenyl)Rh(nbd) (**8**). All compounds obtained were diastereomerically pure. The structures of **2**, **3**, and **6** were determined by single crystal X-ray diffractometry. Complexes **3** as well as (–)-bis(η^2-ethylene)(η^5-2-menthyl-4,7-dimethylindenyl)rhodium(I) (**9**), (–)-(cycloocta-1,5-diene)(η^5-1-menthyl-4,7-dimethylindenyl)rhodium(I) (**10**), (–)-(cycloocta-1,5-diene)(η^5-2-menthyl-4,7-dimethylindenyl)rhodium(I) (**11**), and (–)-(cycloocta-1,5-diene)(η^5-2-menthylindenyl)rhodium(I) (**12**) were found to be active as double bond hydrogenation catalysts. Two of them proved to induce asymmetry up to 18% *ee*. These complexes also promote the hydroformylation of olefins yielding both linear and branched aldehydes in varying ratios but hardly transfer chirality.

Introduction

Rhodium catalysts are widely used in organic synthesis and some are currently used in large-scale industrial processes.[1] Combining the high reactivity of rhodium with chiral phosphane, sulfide, or cyclopentadienyl ligands containing chiral substituents led to their wide application as asymmetric catalysts.[2,3] Over the last few years we have exploited the use of the inexpensive commercially available chiral compound menthol in combination with dinuclear rhodium complexes to prepare chiral catalysts. Using a menthyl-substituted phosphane as a chiral ligand in the complex $[(R^*Ph_2P)(CO)Rh(\mu\text{-}Cl)(\mu\text{-}SR)Rh(CO)(PPh_2R^*)]$ [R* = (+)-neomenthyl; R = *t*Bu, $CH_2CH_2Si(OEt)_3$] asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate could be performed. An optical purity of up to 97% *ee* at low conversions was achieved, but it dropped gradually when the reduction advanced.[4] Using a menthyl-substituted thiolato group as a chiral bridging ligand in (+)-*cis*-$[tBu_3P(CO)Rh(\mu\text{-}Cl)(\mu\text{-}SR^*)Rh(CO)PtBu_3]$ [R* = (+)-neomenthyl], an optical purity of up to 50% *ee* was obtained in moderate yields.[5] Our newly developed synthesis of conformationally well-defined, enantiomerically pure 3-menthylindenyl[6] and 2-menthylindenyl ligands[7] and their transition metal complexes,[8,9] enable us to describe in this paper a third example for exploiting the menthyl-derived chirality in catalysis.

[a] Institut für Chemie der Technischen Universität,
Straße des 17. Juni 135, 10623 Berlin, Germany,
Fax: (internat.) + 49-(0)30/3142-2168
E-mail: schumann@chem.tu-berlin.de
[b] Department of Organic Chemistry, Hebrew University,
Jerusalem 91904, Israel
Fax: (internat.) + 972-2/651-3832
E-mail: jblum@chem.ch.huji.ac.il
[c] Department of Chemistry and Biochemistry, University of Oklahoma,
620 Parrington Oval, Norman, OK 73019, USA
Fax: (internat.) + 1-405/325-6111
E-mail: rHalterman@ou.edu

Results and Discussion

Rhodium Complexes

The metathesis reaction of two equivalents of the lithium salt **1** with the binuclear rhodium complex $[(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$, in diethyl ether at 0 °C, followed by warming to room temperature, gave the corresponding indenyl complex **2** in 74% yield (Scheme 1). Although the indenyl ligand is chiral, owing to the menthyl substituent, it possesses homotopic π-faces and can form only one chiral indenyl metal complex after metalation. The crude product was obtained by removing the solvent, and purified by chromatography under an inert atmosphere on dried alumina with *n*-

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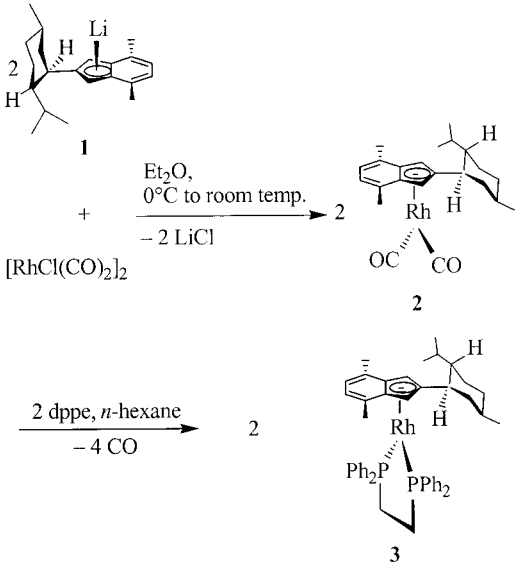
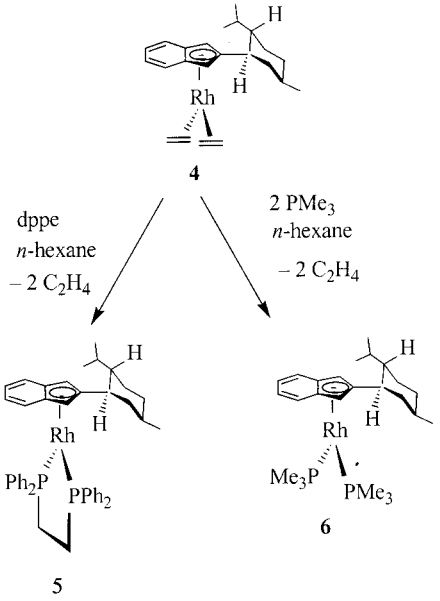
hexane as eluent, followed by crystallization from *n*-pentane. Contact with even traces of oxygen during chromatography led to the immediate decomposition of the complex and dimerization of the indenyl ligand to give 1,1′-bis(2-menthyl-4,7-dimethylindene) and 1,1′-bis(2-menthylindene), respectively.[10] Upon addition of bis(diphenylphosphanyl)ethane to **2**, followed by prolonged heating, **3** was obtained in 73% yield (Scheme 1).



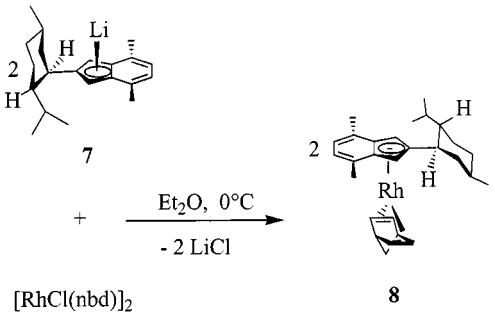
Scheme 1

The same substitution procedure could be used to obtain **5** and **6** by adding bis(diphenylphosphanyl)ethane or trimethylphosphane, respectively, to (−)-bis(η²-ethylene)(η⁵-2-menthylindenyl)rhodium(I) (**4**) (Scheme 2).



Scheme 2

The rhodium complex **8** was synthesized and isolated in 87% yield by the metathesis reaction of two equivalents of the lithium salt **7** with the binuclear rhodium complex [(nbd)Rh(μ-Cl)$_2$Rh(nbd)] (Scheme 3).



Scheme 3

In contrast to their solutions, pure crystalline **2**, **3**, **5**, and **8** are stable to air and moisture, while **6** readily decomposes. The complexes are soluble in polar solvents such as THF, pyridine, and diethyl ether as well as in aromatic solvents such as toluene, and in nonpolar solvents such as *n*-hexane.

Compounds **2**, **3**, and **6** gave suitable single crystals for X-ray diffraction analysis upon recrystallization from *n*-pentane. They crystallized in the same orthorhombic space group $P2_12_12_1$ with one or three crystallographically independent molecules in the asymmetric unit. The solid state structures of these molecules are shown in Figure 1, Figure 2, and Figure 3, respectively. The trimethylphosphane groups in **6** are disordered about two positions, with occupancy factors of 0.504(4) and 0.496(4), as shown in Figure 4.

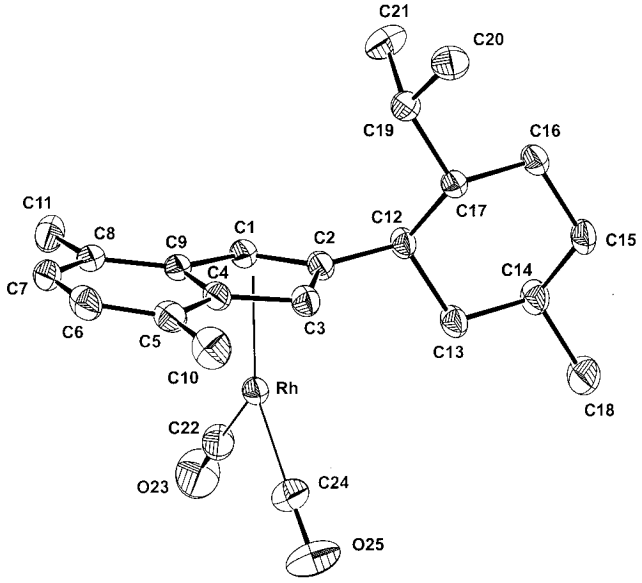


Figure 1. ORTEP drawing[11] of the molecular structure and numbering scheme of **2**, with 50% probability thermal ellipsoids; all hydrogens have been removed for clarity; selected bond lengths [Å] and bond angles [°] with estimated standard deviations:[12] Rh−Cg 1.9557(8), Rh−C(22) 1.861(2), Rh−C(24) 1.865(3), C(1)−C(2) 1.412(3), C(2)−C(3) 1.423(3), C(3)−C(4) 1.464(3), C(4)−C(9) 1.416(3), C(1)−C(9) 1.476(3), C(22)−O(23) 1.132(3), C(24)−O(25) 1.141(3); Cg−Rh−C(22) 135.24(8), Cg−Rh−C(24) 134.45(8), C(22)−Rh−C(24) 90.19(11), Rh−C(22)−O(23) 178.0(3), Rh−C(24)−O(25) 177.8(3)

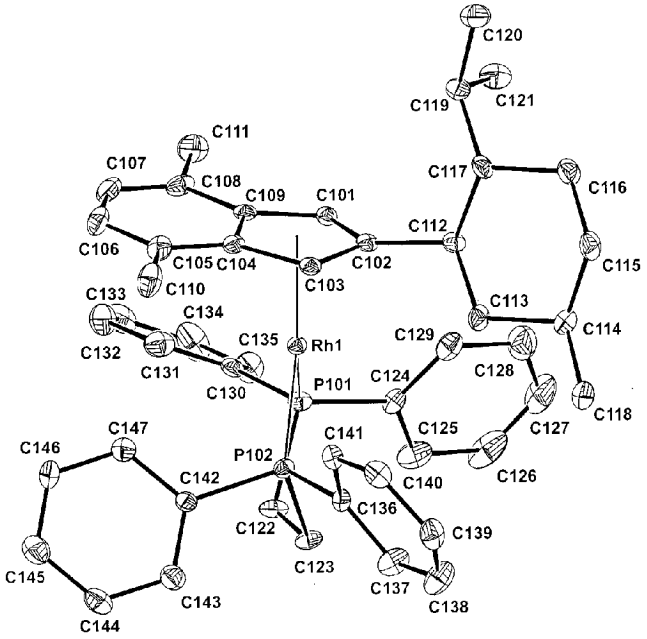


Figure 2. ORTEP drawing[11] of the molecular structure and numbering scheme of **3** (only one of the three crystallographically independent molecules is shown), with 30% probability thermal ellipsoids; all hydrogens have been removed for clarity; selected bond lengths [Å] and bond angles [°] with estimated standard deviations:[13] Rh(1)−Cg(1) 1.9782(19), Rh(2)−Cg(2) 1.9617(19), Rh(3)−Cg(3) 1.9880(19), Rh(1)−P(101) 2.2036(12), Rh(1)−P(102) 2.2063(13), Rh(2)−P(201) 2.1775(13), Rh(2)−P(202) 2.2094(14), Rh(3)−P(301) 2.1763(14), Rh(3)−P(302) 2.2322(13), C(101)−C(102) 1.435(6), C(102)−C(103) 1.418(6), C(103)−C(104) 1.461(6), C(104)−C(109) 1.436(7), C(101)−C(109) 1.440(6), C(201)−C(202) 1.443(6), C(202)−C(203) 1.421(6), C(203)−C(204) 1.442(7), C(204)−C(209) 1.432(7), C(201)−C(209) 1.437(7), C(301)−C(302) 1.437(6), C(302)−C(303) 1.407(6), C(303)−C(304) 1.456(6), C(304)−C(309) 1.428(7), C(301)−C(309) 1.450(6); Cg(1)−Rh(1)−P(101) 137.02(7), Cg(1)−Rh(1)−P(102) 138.57(7), Cg(2)−Rh(2)−P(201) 133.42(8), Cg(2)−Rh(2)−P(202) 141.36(8), Cg(3)−Rh(3)−P(301) 130.88(7), Cg(3)−Rh(3)−P(302) 143.98(7), P(101)−Rh(1)−P(102) 84.22(5), P(201)−Rh(2)−P(202) 85.20(5), P(301)−Rh(3)−P(302) 84.76(5), C(122)−P(101)−Rh(1) 111.28(16), C(123)−P(102)−Rh(1) 110.76(16), C(222)−P(201)−Rh(2) 110.59(16), C(223)−P(202)−Rh(2) 109.95(16), C(322)−P(301)−Rh(3) 109.36(18), C(323)−P(302)−Rh(3) 109.56(16)

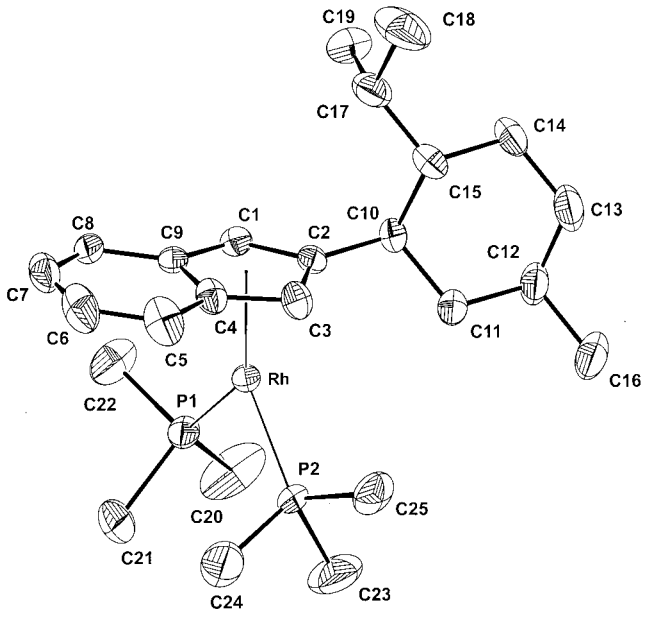


Figure 3. ORTEP drawing[11] of the molecular structure and numbering scheme of **6**, with 50% probability thermal ellipsoids; all hydrogens have been removed for clarity, and the disorder of the PMe_3 groups is omitted; selected bond lengths [Å] and bond angles [°] with estimated standard deviations:[14] Rh−Cg 1.9583(13), Rh−P(1a) 2.138(3), Rh−P(2a) 2.285(3), Rh−P(1b) 2.312(2), Rh−P(2b) 2.154(3), C(1)−C(2) 1.417(4), C(2)−C(3) 1.430(4), C(3)−C(4) 1.451(4), C(4)−C(9) 1.422(4), C(1)−C(9) 1.447(4), P(1a)−C(20a) 1.841(9), P(1a)−C(21a) 1.838(8), P(1a)−C(22a) 1.798(8), P(2a)−C(23a) 1.804(19), P(2a)−C(24a) 1.846(8), P(2a)−C(25a) 1.828(4), P(1b)−C(20b) 1.7758(13), P(1b)−C(21b) 1.836(8), P(1b)−C(22b) 1.823(7), P(2b)−C(23b) 1.828(16), P(2b)−C(24b) 1.817(8), P(2b)−C(25b) 1.810(8); Cg−Rh−P(1a) 136.14(9), Cg−Rh−P(2a) 125.68(10), Cg−Rh−P(1b) 123.64(8), Cg−Rh−P(2b) 141.07(9), P(1a)−Rh−P(2a) 96.19(10), P(1b)−Rh−P(2b) 94.64(9)

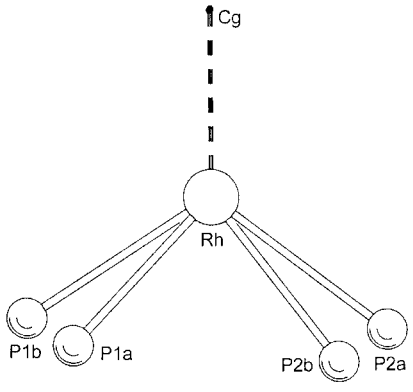


Figure 4. Disorder of **6** in the crystal[14]

All four complexes are monomeric, free of solvent, diastereomerically pure and clearly show the characteristic three stereocenters of the menthyl moiety. In all cases the transition metals of the formal oxidation state +1 are coordinated in a trigonal planar arrangement by the centroids of the cyclopentadienyl systems and the neutral ligands. It is particularly noteworthy that the terpene moiety adopts similar conformations, with the menthyl moiety being nearly perpendicular to the indenyl plane and the bulky isopropyl group pointing away from the metal. The corresponding dihedral angles[15] are: **2**: −8°; **3**: 24°, 29°, 17°; **6**: 14°. The average bonding distances of rhodium to the five-membered indenyl rings are 2.30 Å (**2**, **6**) and 2.32 Å (**3**); the average bond lengths for rhodium to the neutral ligands are 1.86 Å for complex **2**, 2.20 Å for complex **3**, and 2.22 Å for complex **6**. These distances are in close agreement with the bond lengths given for dicarbonyl(η^5-indenyl)rhodium (2.29 Å and 1.86 Å),[16] dicarbonyl(η^5-4,5,6,7-tetramethylindenyl)rhodium (2.29 Å and 1.86 Å),[17] (η^5-indenyl)bis(trimethylphosphane)rhodium(I) (2.32 Å and 2.21 Å),[18] and (η^5-indenyl)(methyl)[1,2-bis(diphenylphosphanyl)propane]-rhodium(III) (2.28 Å and 2.27 Å).[19] The CO−Rh−CO angle of 90.2° in **2** (91.7°[16] and 92.5°[17]) and the P(1)−Rh−P(2) angles of 84.2°, 85.2°, and 84.8° for **3** as well as 96.2° and 94.6° for **6** (96.7°[18] and 85.2°[19]) correlate with the corresponding angles in related complexes. The carbonyl ligands are almost linearly coordinated (177.9°). The average methyl−P−methyl angle of 99.9° is smaller

than the expected tetrahedral angle of 109.5°. It correlates with 101.5° in the compound $[Al_2Cl_2Me_4][(\eta^5$-cyclopentadienyl)bis(trimethylphosphane)rhodium(I)].[20]

The five-membered rings of the indenyl systems are not equally bound to Rh but resemble a distorted η^5-coordination. The bond lengths of the carbon atoms C(X01), C(X02), and C(X03) to the metal are 0.08−0.27 Å shorter than the bond lengths of the bridging atoms C(X04) and C(X09). In general, slip distortions Δ[21] and ring slippages RS[21] toward the C(X02) atoms are found. The values for Δ and RS are 0.186 Å and 0.189 Å in **2**, 0.157 Å, 0.152 Å, 0.177 Å and 0.175 Å, 0.180 Å, 0.243 Å in **3**, and 0.178 Å and 0.205 Å in **6**. The tendency towards a slight η^3-coordination accounts for the non-planar cyclopentadienyl ring and thus for the hinge angles HA[22] and fold angles FA.[22] The values for HA and FA are 10.6° and 10.5° in **2**, 7.7°, 6.8°, 8.0° and 8.3°, 5.4°, 8.1° in **3**, and 8.1° and 8.0° in **6**. The values are in the range expected for distorted η^5-coordination, as found in (COD)(η^5-indenyl)rhodium[23] (Δ = 0.152 Å, HA = 8.9°, FA = 7.4°), $(C_2H_4)_2$(η^5-indenyl)rhodium(I)[24] (Δ = 0.161 Å, HA = 8.1°, FA = 7.4°), bis(trimethylphosphane)(η^5-indenyl)rhodium(I)[25] (Δ = 0.201 Å, HA = 8.4°, FA = 7.9°) and fail to show the characteristics of η^3-coordination found in tris(dimethylphenylphosphane)(η^3-indenyl)rhodium(I)[26] (Δ = 0.79 Å, HA = 25°, FA = 28°). Such distortions are also detectable by the differences in the C−C bond lengths in the five-membered indenyl rings. The maximum variations of 0.06 Å (**2**), 0.05 Å (**3**), and 0.03 Å (**6**) are higher than can be accounted for by the influence of the condensed six-membered ring alone. In general the trend towards η^3-coordination is not strong; although the distortions are much higher than they are for the asymmetrical substituted (1-menthylindenyl)metal complexes, where the substitution patterns favor not only a distortion toward C(X02) but toward C(X03) as well.[8]

As the HOMO of the indenyl unit in rhodium complexes can best be stabilized at a rotation angle RA of 0°[16,18,24] the neutral ligands are aligned parallel to the longitudinal axis of indene. In these cases, values for RA of 0.1° (**2**), 1.8°, 11.4°, and 11.9° (**3**) as well as 6.3° and 3.5° (**6**) are observed.

NMR Spectra

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 on two-dimensional NOE experiments. All described transition metal complexes exhibit C_1 symmetry in their solution NMR spectra. The neutral ligands dppe in **5** and PMe_3 in **6** exhibit two ^{31}P NMR signals and thus do not seem to rotate around the indenyl−rhodium axis on the NMR time scale as has been found for similar complexes.[27] For the two CO ligands in **2**, for example, only one signal occurs and for the four coordinating carbon atoms of the nbd ligand only two signals occur. This gives rise to an empirical low induction of the chiral indenyl ligand on the remote neutral ligands or to rotating ligands on the ^{13}C NMR time scale.

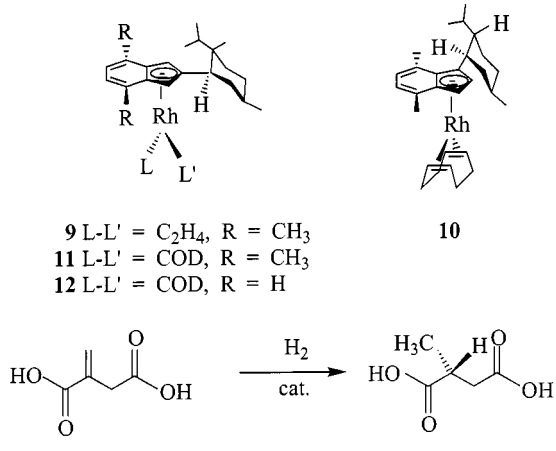
Characteristic $^1J_{CRh}$ coupling constants varying between 1.0 and 7.9 Hz for the five-membered indenyl rings and from 10.3 to 85.4 Hz for the neutral ligands could be determined. Higher coupling constants correlate to higher electron density, therefore the bridging atoms C^8 and C^9 are more weakly bonded in comparison to the atoms C^1 to C^3, which show higher values. This is consistent with the $\eta^2+\eta^3$-coordination found in the solid state structures. The higher $^1J_{XRh}$ 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 **3** and **8** in Et_2O/D_2O (3:1) were recorded and chemical shifts between δ = −143.4 and −834.1 relative to hexachlororhodate in D_2O were observed. The intensity of the high-field shift increases along with the stronger σ-donor bonded to the metal[28] and higher alkylation of the indenyl ligand.[8]

Catalysis

Catalytical Hydrogenation

The applicability of the rhodium complex **3** and of the related compounds (−)-bis(η^2-ethylene)(η^5-2-menthyl-4,7-dimethylindenyl)rhodium(I) (**9**),[29] (−)-(cycloocta-1,5-diene)(η^5-1-menthyl-4,7-dimethylindenyl)rhodium(I) (**10**),[8] (−)-(cycloocta-1,5-diene)(η^5-2-menthyl-4,7-dimethylindenyl)rhodium(I) (**11**),[29] and (−)-(cycloocta-1,5-diene)(η^5-2-menthylindenyl)rhodium(I) (**12**)[29] (Scheme 4), described by us earlier, as hydrogenation catalysts was studied. The prochiral itaconic acid was chosen as the substrate.



Scheme 4

All tested catalysts proved highly active. Usually a quantitative yield of the methylsuccinic acid was obtained within 4 h at 60−70 °C. However, only the two COD-containing rhodium-menthylindenyl complexes **10** and **11** were found to induce chirality, and lead to the formation of (*S*)-(−)-methylsuccinic acid in 18 and 16% *ee*, respectively. Complex **11** only has the chiral influence of the menthyl substituent, and the observed low stereoselectivity is similar to that seen with menthylcyclopentadienyl metal complexes.[30] Complex **10**, however, contains an additional facial chirality element, and gave an unexpectedly lower selectivity than other bis(1-menthylindenyl)metal catalyzed reactions.[31] It is rather

surprising that catalyst **12**, which has also a COD moiety but differs from **11** by having no indenyl-bound methyl groups, does not promote enantioselective hydrogenation of the itaconic acid.

Catalytic Hydroformylation

The observation that cyclohexene is hydroformylated in the presence of catalyst **2** at 120 °C and 40 bar CO/H_2, giving a quantitative yield of cyclohexanecarboxaldehyde within 3 h, led us to investigate the transformation of an olefin which can yield isomeric products. Using styrene as a prochiral substrate our rhodium complexes afforded 2- and 3-phenylpropanal (branched and linear products) in 23−100% yield. The results of some representative experiments are summarized in Table 1.

Table 1. Hydroformylation of styrene in the presence of some rhodium catalysts

Entry	Catalyst[a]	Total yield after 22 h	Linear/branched ratio
1	**2**	25	1:7.8[b]
2	**2**[c]	26	1:9.0
3	**3**	30	1:14.0
4	**4**	61	1:3.4
5	**10**	89[d]	1:6.2[e]
6	**11**	23	1:3.9
7	**12**	83	1:1.6

[a] Reaction conditions: 0.1 mol of styrene, 1 mmol of catalyst, 10 mL of toluene, 20 bar H_2, 20 bar CO, 60 °C, 22 h. [b] At 100−120 °C (2−4 h) the ratio became 1:0.8. [c] The complex was entrapped in a silica sol-gel matrix according to ref.[32]. [d] After 36.5 h. [e] At 100 °C the ratio became 1:1.1.

Due to the stereogenic centers in the catalyst precursors one would expect the chirality to be transferred to the branched aldehyde. However, styrene was found to undergo quantitative hydroformylation at 100 °C in the presence of **10** to give nearly identical amounts of the linear and the racemic branched aldehyde. As no chirality could be detected in the branched product, we lowered the temperature to 60 °C. At this temperature catalysts **2**, **3**, **4**, **11**, and **12** led to 23−83% aldehydes after 22 h, and even under these conditions no appreciable chirality transfer was observed: the highest *ee* value of 3% was obtained with catalyst **3** (entry 3).

Although we did not visually detect the separation of any metallic rhodium during the hydroformylation that could have been responsible for the achiral processes, we performed an experiment with sol-gel entrapped complex **2** to prevent any possible decomposition of the original chiral catalyst (entry 2). We found, however, that the homogeneous and the immobilized catalysts gave almost identical results and no significant enantioselectivity could be detected. Another reason for the atactic activity might have been the formation of achiral complexes of the type $RhH(CO)_2(L)(L')$ by substitution of the indenyl moiety. However, these complexes could still not explain the different linear/branched ratios, as they vary with changes of the indenyl (entry 6 vs. 7) and the neutral ligands. Values between 1:0.78 (catalyst **2** at 120 °C) and 1:14 (catalyst **3** at 60 °C) were found. The highest selectivity is obtained using the bulky dppe ligand, and the selectivity decreases with increasing temperature. Typically, linear/branched ratios of 1:1 and 1:3 are mentioned in the literature.[33]

In addition to styrene, *n*-dodecene was also reacted in the presence of catalyst **2** at different temperatures and pressures. Samples of the reaction mixture were withdrawn every hour and analyzed by GC and ^1H NMR spectroscopy. After 6 h (80 bar total pressure) conversions of 97% were obtained at 80 °C. If the temperature was lowered to 60 °C only 38% yield was obtained.

When using 1-dodecene as a substrate partial isomerization of the double bond occurred prior to the hydroformylation. In addition to 1-tridecanal and 2-methyldodecanal in the ratio 1:0.7, 3-ethylundecanal and 4-propyldecanal were formed in 8 and 7% yield (80 °C and 80 bar). This isomerization of 1-dodecene to 2- and 3-dodecene does not occur at 60 °C.[34]

Conclusions

Metathesis reactions of $[RhCl(L)(L')]_2$, with chiral, menthyl-functionalized indenyl salts and ligand substitution reactions provide a convenient entry into chiral rhodium complexes. X-ray diffraction analyses of the monomeric, stereomerically pure complexes **2**, **3**, and **6** confirm the enantiomeric purity of the stereogenic centers in the ligands and that the indenyl moiety is $\eta^2+\eta^3$-coordinated. Complex **3** and the analogeous rhodium complexes **9**, **10**, **11**, and **12** show a high activity in the catalytic hydrogenation of itaconic acid. Both catalysts **10** and **11** induced chirality in the product. Complexes **2**−**4** and **10**−**12** show considerable activity in the hydroformylation of olefins with highly varying linear/branched ratios between 1:0.78 and 1:14 but promote very little chirality transfer.

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 apparatus and are uncorrected. Optical rotations were determined on a Schmidt+Haensch Polartronic-D and a Perkin−Elmer model 141 polarimeter. The NMR spectra were recorded on a Bruker ARX 200 (^1H: 200 MHz; ^{13}C: 50.32 MHz; ^{31}P: 80.94 MHz) or ARX 400 (^1H: 400 MHz; ^{13}C: 100.64 MHz; ^{103}Rh: 12.60 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm relative to the ^1H or the ^{13}C signal of the deuterated solvents. Chemical shifts of ^{31}P and ^{103}Rh are given relative to 85% phosphoric acid in D_2O and hexachlororhodate in D_2O. 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 significant fragments containing the isotopes of the highest abundance are listed. Relative intensities in % are given in parentheses. Elemental analyses were performed on a Perkin−Elmer Series II CHNS/O Analyzer 2400. (−)-(2-Men-

thyl-4,7-dimethylindenyl)lithium (**1**),[7] (−)-(2-menthylindenyl)lithium (**7**),[7] tetracarbonyldi-μ-chlorodirhodium(I),[35] (−)-bis(η²-ethylene)(η⁵-2-menthyl-4,7-dimethylindenyl)rhodium(I) (**9**),[29] (−)-bis(η²-ethylene)(η⁵-2-menthylindenyl)rhodium(I) (**4**),[29] (−)-(cycloocta-1,5-diene)(η⁵-1-menthyl-4,7-dimethylindenyl)rhodium(I) (**10**),[8] (−)-(cycloocta-1,5-diene)(η⁵-2-menthyl-4,7-dimethylindenyl)rhodium(I) (**11**),[29] and (−)-(cycloocta-1,5-diene)(η⁵-2-menthylindenyl)rhodium(I) (**12**)[29] were prepared according to published procedures. 1,2-Bis(diphenylphosphanyl)ethane and di-μ-chlorobis(η⁴-norbornadiene)dirhodium(I) were used as purchased without further purification.

(−)-Dicarbonyl(η⁵-2-menthyl-4,7-dimethylindenyl)rhodium(I) (2): (−)-(η⁵-2-menthyl-4,7-dimethylindenyl)lithium (**1**) (0.62 g, 2.15 mmol) was added to a solution of tetracarbonyldi-μ-chlorodirhodium(I) (0.42 g, 1.08 mmol) in diethyl ether (15 mL) at 0 °C. The suspension was stirred for 3 h, heated to 25 °C and stirred for further 10 h. The solvent was removed under vacuum (10^{-2} mbar), leaving a solid which was subsequently suspended in *n*-hexane (2 mL) and fractionally chromatographed under nitrogen on alumina. Elution with *n*-hexane initially gave colorless and finally yellow solutions. The solvents of the yellow fractions were removed under vacuum (10^{-2} mbar) yielding an orange solid. Recrystallization from warm *n*-pentane (5 mL) gave 0.70 g (74%) of **2** as orange crystals, m.p. 125 °C dec. $[\alpha]_D^{25} = -31.8$ (*c* = 7.6, *n*-hexane). ^{1}H NMR ([D$_6$]benzene, 400 MHz): δ = 0.67 (d, ^3J = 7.0 Hz, 3 H, H$^{7'/9'/10'}$), 0.68 (d, ^3J = 6.9 Hz, 3 H, H$^{7'/9'/10'}$), 0.93 (d, ^3J = 6.5 Hz, 3 H, H$^{7'/9'/10'}$), 0.80−2.05 (m, 10 H, H$^{1',2',3',4',5',6',8'}$), 2.14 (s, 3 H, H$^{10/11}$), 2.15 (s, 3 H, H$^{10/11}$), 4.48 (d, ^4J = 2.0 Hz, 1 H, H$^{1/3}$), 5.50 (d, ^4J = 2.0 Hz, 1 H, H$^{1/3}$), 6.67 (m, 2 H, H^{5,6}). ^{13}C{^{1}H} NMR ([D]chloroform, 50.32 MHz): δ = 15.6, 18.07, 18.11, 21.6, 22.8 (C$^{7',9',10,10',11}$), 25.0, 35.4, 47.8 (C$^{2',5',6'}$), 28.2, 33.6, 40.2, 50.5 (C$^{1',3',4',8'}$), 72.1 (d, $^1J_{CRh}$ = 3.2 Hz, C$^{1/3}$), 75.9 (d, $^1J_{CRh}$ = 3.1 Hz, C$^{1/3}$), 114.3 (d, $^1J_{CRh}$ = 2.1 Hz, C$^{8/9}$), 115.8 (d, $^1J_{CRh}$ = 2.0 Hz, C$^{8/9}$), 128.1 (d, $^1J_{CRh}$ = 1.6 Hz, C^2), 125.07, 125.08 (C^{4,7}), 125.5, 125.6 (C^{5,6}), 191.3 (d, $^1J_{CRh}$ = 85.4 Hz, CO). IR (CsI): $\tilde{\nu}$ = 3043 cm^{-1} (w), 3025 (w), 2953 (s), 2929 (s), 2919 (s), 2877 (m), 2868 (m), 2859 (m), 2847 (m), 2031 (s), 2016 (m), 1971 (s), 1942 (m), 1835 (w), 1819 (m), 1699 (w), 1634 (w), 1589 (w), 1502 (m), 1445 (m), 1377 (m), 1367 (m), 1362 (m), 1348 (m), 1307 (m), 1288 (m), 1274 (m), 1261 (m), 1247 (w), 1182 (m), 1165 (w), 1139 (w), 1127 (m), 1084 (m), 1036 (m), 1004 (m), 922 (m), 860 (m), 818 (m), 684 (w), 574 (w), 569 (w), 563 (w), 552 (m), 543 (w), 510 (m), 502 (m), 491 (m), 279 (m). MS (68 °C): *m*/*z* (%) = 440 (5) [M]$^+$, 412 (11) [(CO)(C$_{21}$H$_{29}$)Rh]$^+$, 384 (4) [(C$_{21}$H$_{29}$)Rh]$^+$, 382 (100) [C$_{21}$H$_{27}$Rh]$^+$, 245 (1) [C$_{11}$H$_{10}$Rh]$^+$. C$_{23}$H$_{29}$O$_2$Rh (440.39): calcd. C 62.73, H 6.64; found C 62.30, H 6.23.

(−)-(η⁵-2-Menthyl-4,7-dimethylindenyl){η²-1,2-bis(diphenylphosphanyl)ethane}rhodium(I) (3): 1,2-Bis(diphenylphosphanyl)ethane (0.32 g, 0.80 mmol) was added to a solution of **2** (0.35 g, 0.79 mmol) in *n*-hexane (40 mL) at 0 °C. The orange solution (gas evolution!) was stirred for 2 h at room temperature and heated for 10 h to 60 °C. The solvent was removed under vacuum (10^{-2} mbar), leaving a solid which was suspended in *n*-hexane (10 mL), filtered with a d4 frit and washed three times with *n*-hexane (10 mL). The filtrate was cooled to −78 °C, decanted and the solvent was removed under vacuum (10^{-2} mbar). Fractional chromatography under nitrogen on alumina using *n*-hexane and *n*-hexane/ethyl acetate (10:1) as eluent gave yellow solutions. The solvent was removed under vacuum (10^{-2} mbar) yielding an orange solid. Recrystallization from warm *n*-pentane (5 mL) gave 0.45 g (73%) of **3** as orange crystals, m.p. > 240 °C. $[\alpha]_D^{25} = -76.0$ (*c* = 0.5, diethyl ether). ^{1}H NMR ([D$_6$]benzene, 200 MHz): δ = 0.67 (d, ^3J = 6.9 Hz, 3 H, H$^{9'/10'}$), 0.77 (d, ^3J = 6.9 Hz, 3 H, H$^{9'/10'}$), 0.81 (d, ^3J = 6.5 Hz, 3 H, H$^{7'}$), 0.81−1.95 (m, 14 H, H$^{1',2',3',4',5',6',8'}$, PCH_2), 2.03 (s, 3 H, H$^{10/11}$), 2.19 (s, 3 H, H$^{10/11}$), 5.23 (m, 1 H, H$^{1/3}$), 5.37 (m, 1 H, H$^{1/3}$), 6.93 (m, 2 H, H^{5,6}), 7.04−7.55 [m, 20 H, C*H*(Phenyl)]. ^{13}C{^{1}H} NMR ([D$_6$]benzene, 50.32 MHz): δ = 15.6, 18.8, 19.5, 21.7, 23.3 (C$^{7',9',10,10',11}$), 30.1 (d, $^1J_{CP}$ = 24.8 Hz, P*C*H$_2$), 30.6 (d, $^1J_{CP}$ = 24.7 Hz, P*C*H$_2$), 25.3, 35.8, 46.3 (C$^{2',5',6'}$), 28.0, 34.1, 41.2, 51.0 (C$^{1',3',4',8'}$), 71.6 (m, C$^{1/3}$), 74.4 (m, C$^{1/3}$), 114.3 (d, $^1J_{CRh}$ = 1.6 Hz, C$^{8/9}$), 115.7 (d, $^1J_{CRh}$ = 1.6 Hz, C$^{8/9}$), 120.6, 121.8 (C^{5,6}), 123.3 (C$^{4/7}$), 123.4 (d, $^1J_{CRh}$ = 7.9 Hz, C^2), 124.2 (C$^{4/7}$), 127.5−133.6 [m, *C*H(Phenyl)], 140.3 [d, $^1J_{CP}$ = 35.4 Hz, *C*^{q}(Phenyl)]. ^{31}P NMR ([D$_6$]benzene, 80.94 MHz): δ = 75.01 (m). ^{103}Rh NMR ([D]chloroform/diethyl ether (1:3), 12.60 MHz): δ = −834.10. IR (CsI): $\tilde{\nu}$ = 3070 cm^{-1} (m), 3052 (m), 3002 (w), 2954 (s), 2915 (s), 2870 (m), 2852 (m), 1586 (w), 1571 (w), 1482 (m), 1433 (s), 1385 (w), 1374 (m), 1367 (m), 1337 (w), 1095 (s), 921 (m), 824 (m), 815 (m), 792 (w), 743 (m), 699 (s), 694 (s), 683 (m), 527 (s), 489 (m), 446 (w), 203 (m). MS (209 °C): *m*/*z* (%) = 782 (33) [M]$^+$, 739 (3) [C$_{44}$H$_{46}$P$_2$Rh]$^+$, 501 (21) [(C$_{26}$H$_{24}$P$_2$)Rh]$^+$. C$_{47}$H$_{53}$P$_2$Rh (782.79): calcd. C 72.12, H 6.82; found C 71.76, H 6.48.

(+)-(η⁵-2-Menthylindenyl){η²-1,2-bis(diphenylphosphanyl)ethane}rhodium(I) (5): In analogy to the preparation of **3**, (−)-bis(η²-ethylene)(η⁵-2-menthylindenyl)rhodium(I) (**4**) (0.42 g, 1.02 mmol) was reacted at room temperature with 1,2-bis(diphenylphosphanyl)ethane (0.40 g, 1.00 mmol) in *n*-hexane (20 mL) at 0 °C. After 3 days, workup, chromatography and recrystallization from *n*-pentane at −28 °C, red crystals of **5** (0.52 g, 69%) were obtained, m.p. 119 °C dec. $[\alpha]_D^{25} = 63.7$ (*c* = 1.4, benzene). ^{1}H NMR ([D$_6$]benzene, 400 MHz): δ = 0.65 (m, 1 H, H$^{2'}$), 0.66 (d, ^3J = 6.8 Hz, 3 H, H$^{9'/10'}$), 0.73 (d, ^3J = 6.8 Hz, 3 H, H$^{9'/10'}$), 0.80 (d, ^3J = 6.8 Hz, 3 H, H$^{7'}$), 0.82 (m, 1 H, H$^{6'}$), 0.95 (m, 1 H, H$^{5'}$), 1.04 (m, 1 H, H$^{4'}$), 1.24 (m, 1 H, H$^{1'}$), 1.29 (m, 4 H, PCH_2), 1.60 (m, 1 H, H$^{5'}$), 1.70 (m, 1 H, H$^{6'}$), 1.82 (m, 1 H, H$^{2'}$), 1.86 (m, 1 H, H$^{8'}$), 1.89 (m, 1 H, H$^{3'}$), 5.16 (m, 1 H, H$^{1/3}$), 5.36 (m, 1 H, H$^{1/3}$), 7.01, 7.02, 7.04, 7.05 (m, 4 H, H^{4,5,6,7}), 7.08−7.54 [m, 20 H, C*H*(Phenyl)]. ^{13}C{^{1}H} NMR ([D$_6$]benzene, 100.64 MHz): δ = 15.6, 21.7 (C$^{9'/10'}$), 23.1 (C$^{7'}$), 25.2 (C$^{5'}$), 27.9 (C$^{8'}$), 29.5 (m, P*C*H$_2$), 33.9 (C$^{1'}$), 35.6 (C$^{6'}$), 40.9 (C$^{3'}$), 46.2 (C$^{2'}$), 50.8 (C$^{4'}$), 74.0 (m, C$^{1/3}$), 74.3 (m, C$^{1/3}$), 114.6 (d, $^1J_{CRh}$ = 1.0 Hz, C$^{8/9}$), 116.7 (d, $^1J_{CRh}$ = 1.2 Hz, C$^{8/9}$), 117.1, 117.4, 119.5, 120.9 (C^{4,5,6,7}), 124.7 (d, $^1J_{CRh}$ = 6.5 Hz, C^2), 126.7−134.5 [m, *C*H(Phenyl)], 139.5−141.0 [m, *C*^{q}(Phenyl)]. ^{31}P NMR ([D$_6$]benzene, 80.94 MHz): δ = 73.76 (m, $^1J_{PRh}$ = 213.4 Hz), 78.11 (m, $^1J_{PRh}$ = 225.1 Hz). IR (CsI): $\tilde{\nu}$ = 3096 cm^{-1} (m), 3049 (m), 2958 (s), 2927 (s), 2912 (s), 2868 (m), 2847 (m), 1585 (w), 1484 (m), 1459 (m), 1434 (s), 1431 (s), 1248 (s), 1095 (m), 922 (m), 747 (m), 735 (s), 696 (s), 681 (m), 527 (s), 491 (m), 449 (w). MS (83 °C): *m*/*z* (%) = 754 (100) [M]$^+$, 711 (2) [C$_{42}$H$_{42}$P$_2$Rh]$^+$, 501 (51) [C$_{26}$H$_{24}$P$_2$Rh]$^+$, 424 (9) [C$_{20}$H$_{19}$P$_2$Rh]$^+$, 356 (1) [(C$_{19}$H$_{25}$)Rh]$^+$. C$_{45}$H$_{49}$P$_2$Rh (754.74): calcd. C 71.61, H 6.54; found C 72.05, H 6.51. Mol wt. cryosc in benzene: 783.

(−)-(2-Menthylindenyl)bis(trimethylphosphane)rhodium(I) (6): In analogy to the preparation of **5**, a mixture of **4** (0.49 g, 1.19 mmol) and trimethylphosphane (0.30 g, 3.94 mmol) in *n*-hexane (20 mL) was reacted at 0 °C. After 10 h at room temperature, workup, chromatography and recrystallization from warm *n*-pentane, red crystals of **6** (0.47 g, 77%) were obtained, m.p. 157 °C. $[\alpha]_D^{25} = -47.7$ (*c* = 0.5, diethyl ether). ^{1}H NMR ([D$_6$]benzene, 400 MHz): δ = 0.81 (d, ^3J = 7.0 Hz, 3 H, H$^{9'/10'}$), 0.88 (d, ^3J = 6.8 Hz, 3 H, H$^{9'/10'}$), 0.94 (m, 1 H, H$^{6'}$), 0.99 (d, ^3J = 6.4 Hz, 3 H, H$^{7'}$), 1.04 [m, 9 H, P^2(CH_3)$_3$], 1.06 (m, 1 H, H$^{2'}$), 1.07 (m, 1 H, H$^{5'}$), 1.08 [m, 9 H, P^1(CH_3)$_3$], 1.27 (m, 1 H, H$^{4'}$), 1.39 (m, 1 H, H$^{1'}$), 1.70 (m, 1

H, H$^{5'}$), 1.76 (m, 1 H, H$^{6'}$), 2.17 (m, 1 H, H$^{8'}$), 2.22 (m, 1 H, H$^{3'}$), 2.41 (m, 1 H, H$^{2'}$), 4.80 (m, 1 H, H$^{1/3}$), 4.96 (m, 1 H, H$^{1/3}$), 6.91 (m, 1 H, H^{5,6}), 7.06 (m, 2 H, H^{4,7}). $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 100.64 MHz): δ = 15.9, 21.9 (C$^{9',10'}$), 23.1 (C$^{7'}$), 23.5 [dvt, $^1J_{CP}$ = 8.6, $^2J_{CRh}$ = 2.2 Hz, P(*C*H$_3$)$_3$], 23.8 [dvt, $^1J_{CP}$ = 8.6, $^2J_{CRh}$ = 2.2 Hz, P(*C*H$_3$)$_3$], 25.3 (C$^{5'}$), 27.9 (C$^{8'}$), 33.8 (C$^{1'}$), 35.7 (C$^{6'}$), 41.5 (C$^{3'}$), 48.9 (C$^{2'}$), 50.7 (C$^{4'}$), 69.1 (dd, $^2J_{CP}$ = 14.5, $^1J_{CRh}$ = 3.2 Hz, C$^{1/3}$), 73.0 (dd, $^2J_{CP}$ = 14.5, $^1J_{CRh}$ = 3.2 Hz, C$^{1/3}$), 113.67, 113.69 (C^{4,7}), 116.9, 118.4 (C^{8,9}), 119.5, 119.6 (C^{5,6}), 125.6 (d, $^1J_{CRh}$ = 7.5 Hz, C^2). $^{31}P\{^1H\}$ NMR spectroscopy ([D$_6$]benzene, 80.94 MHz): δ = −6.60 (d, $^1J_{P(2)Rh}$ = 120.4, $^2J_{P(1)P(2)}$ = 50.4 Hz, P^2), −3.95 (dd, $^1J_{P(1)Rh}$ = 119.2, $^2J_{P(1)P(2)}$ = 50.4 Hz, P^1). MS (114 °C): *m*/*z* (%) = 508 (100) [M]$^+$, 493 (1) [$C_{24}H_{40}P_2Rh$]$^+$, 465 (1) [$C_{22}H_{36}P_2Rh$]$^+$, 432 (3) [$C_{22}H_{34}PRh$]$^+$, 356 (1) [($C_{19}H_{25}$)Rh]$^+$, 255 (4) [$C_6H_{18}P_2Rh$]$^+$. $C_{25}H_{43}P_2Rh$ (wt 508.47): calcd. C 59.05, H 8.52; found C 59.54, H 8.52.

(−)-(η^5-2-Menthylindenyl)(η^4-norbornadiene)rhodium(I) (8): In a similar manner to the synthesis of **2**, di-μ-chlorobis(η^4-norbornadiene)dirhodium(I) (0.96 g, 2.08 mmol) was reacted with **7** (1.21 g, 4.65 mmol) in diethyl ether (20 mL) at 0 °C. A yellow powder of **7** (1.63 g, 87%) was obtained after workup, chromatography, and recrystallization from warm *n*-pentane, m.p. 104 °C. $[\alpha]_D^{25}$ = −64.0 (*c* = 2.3, diethyl ether). ^1H NMR ([D$_6$]benzene, 400 MHz): δ = 0.72 (d, ^3J = 7.0 Hz, 3 H, H$^{9'/10'}$), 0.75 (d, ^3J = 6.9 Hz, 3 H, H$^{9'/10'}$), 0.82 [m, 2 H, C*H*$_2$(nbd)], 0.98 (m, 1 H, H$^{6'}$), 1.05 (m, 1 H, H$^{5'}$), 1.11 (d, ^3J = 6.5 Hz, 3 H, H$^{7'}$), 1.13 (m, 1 H, H$^{4'}$), 1.33 (m, 1 H, H$^{2'}$), 1.52 (m, 1 H, H$^{1'}$), 1.67 (m, 1 H, H$^{5'}$), 1.75 (m, 1 H, H$^{8'}$), 1.80 (m, 1 H, H$^{6'}$), 2.30 (m, 1 H, H$^{3'}$), 2.71 (m, 1 H, H$^{2'}$), 3.05 [m, 2 H, C*H*CH$_2$(nbd)], 3.30 [m, 4 H, C*H*(nbd)], 4.88 (s. br., 1 H, H$^{1/3}$), 4.94 (s. br., 1 H, H$^{1/3}$), 7.05 (m, 2 H, H^{5,6}), 7.23 (m, 2 H, H^{4,7}). $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 50.32 MHz): δ = 15.7, 21.7 (C$^{9',10'}$), 23.2 (C$^{7'}$), 25.2 (C$^{5'}$), 27.9 (C$^{8'}$), 33.9 (C$^{1'}$), 35.6 (C$^{6'}$), 37.8 [d, $^1J_{CRh}$ = 15.4 Hz, *C*H(nbd)], 38.1 [d, $^1J_{CRh}$ = 10.3 Hz, *C*H(nbd)], 41.1 (C$^{3'}$), 47.9 [d, $^2J_{CRh}$ = 2.7 Hz, *C*HCH$_2$(nbd)], 48.2 (C$^{2'}$), 50.6 (C$^{4'}$), 58.3 [d, $^3J_{CRh}$ = 6.7 Hz, *C*H$_2$(nbd)], 72.0 (d, $^1J_{CRh}$ = 4.6 Hz, C$^{1/3}$), 75.5 (d, $^1J_{CRh}$ = 4.6 Hz, C$^{1/3}$), 108.8 (d, $^1J_{CRh}$ = 3.2 Hz, C$^{8/9}$), 110.4 (d, $^1J_{CRh}$ = 3.1 Hz, C$^{8/9}$), 119.3, 119.5 (C^{4,7}), 121.6 (d, $^1J_{CRh}$ = 6.1 Hz, C^2), 122.0 (C$^{5/6}$), 122.3 (C$^{5/6}$). ^{103}Rh NMR ([D]chloroform/diethyl ether (1:3), 12.60 MHz): δ = −143.40. IR (CsI): $\tilde{\nu}$ = 3053 cm^{-1} (m), 2981 (m), 2954 (s), 2919 (s), 2868 (m), 2850 (m), 1713 (m), 1605 (w), 1454 (m), 1383 (m), 1347 (m), 1299 (m), 1260 (w), 1171 (m), 1063 (m), 748 (s), 735 (s), 567 (m), 493 (m), 459 (w), 358 (m), 309 (w). MS (103 °C): *m*/*z* (%) = 448 (100) [M]$^+$, 405 (16) [$C_{23}H_{26}Rh$]$^+$, 356 (3) [($C_{19}H_{25}$)Rh]$^+$, 309 (22) [$C_{16}H_{14}Rh$]$^+$, 217 (1) [C_9H_6Rh]$^+$, 195 (3) [C_7H_8Rh]$^+$. $C_{26}H_{33}Rh$ (448.46): calcd. C 69.64, H 7.42; found C 69.73, H 7.62.

Hydrogenation of Itaconic Acid: Typically, a mini-autoclave was charged under nitrogen in a glove box with the chiral rhodium catalyst (1 mmol) and a solution of itaconic acid (2.6 g, 20 mmol) in methanol (7 mL). The autoclave was sealed, purged three times with H_2 and pressurized to 14 bar. The reaction vessel was placed in a preheated oil bath thermostated at the desired temperature (accuracy ±0.5 °C). After 4 h the autoclave was cooled, opened and its contents were treated with 10% aqueous NaOH (5 mL). The rhodium catalyst was extracted with diethyl ether (3 × 5 mL). Addition of excess 3 M HCl to the aqueous solution, threefold extraction with diethyl ether (20 mL), drying with Na_2SO_4 and removal of the solvent under vacuum (10^{-2} mbar) afforded methylsuccinic acid as a colorless powder in quantitative yield. When catalyst **10** was employed at 60 °C or catalyst **11** at 70 °C, the *ee* values of the resulting (−)-methylsuccinic acid were 18 and 16%, respec-

Table 2. Crystal data and structure refinement for **2**, **3**, and **6**

Compound	**2**	**3**	**6**
Empirical formula	$C_{23}H_{29}O_2Rh$	$C_{47}H_{53}P_2Rh$	$C_{25}H_{43}P_2Rh$
M_r [g·mol^{-1}]	440.39	728.79	508.47
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a [Å], α [°]	11.0197(2), 90	19.5844(1), 90	8.7390(16), 90
b [Å], β [°]	13.0781(2), 90	22.8322(1), 90	8.838(2), 90
c [Å], γ [°]	14.9456(3), 90	27.4046(4), 90	34.919(10), 90
V [Å^3]	2153.91(7)	12254.1(2)	2697.1(11)
Z	4	12	4
ρ $_{calcd.}$ [g/cm^3]	1.358	1.273	1.252
μ (Mo-K_α) [mm^{-1}]	0.806	0.527	0.760
F(000)	912	4920	1072
Cystal size [mm^3]	0.63 × 0.52 × 0.32	0.40 × 0.32 × 0.28	0.58 × 0.23 × 0.22
θ $_{min}$, θ $_{max}$ [°]	2.07, 27.49	1.28, 27.50	1.17, 27.50
Index ranges	$-11 \le h \le 14$	$-25 \le h \le 25$	$-7 \le h \le 11$
	$-13 \le k \le 16$	$-15 \le k \le 29$	$-11 \le k \le 10$
	$-18 \le l \le 19$	$-35 \le l \le 34$	$-45 \le l \le 42$
Reflections collected	16446	95295	20726
Independent reflections	4946 [R_{int} = 0.0361]	28116 [R_{int} = 0.1051]	6183 [R_{int} = 0.0482]
Max., min. transmission	0.7477, 0.5332	0.8955, 0.7370	0.8832, 0.7132
Data, restraints, parameters	4946/0/240	28116/0/1366	6183/0/334
GOF on F^2	1.038	1.030	1.000
R indices [$I > 2\sigma(I)$]	R_1 = 0.0214	R_1 = 0.0567	R_1 = 0.0335
	wR_2 = 0.0498	wR_2 = 0.0797	wR_2 = 0.0687
R indices (all data)	R_1 = 0.0231	R_1 = 0.0988	R_1 = 0.0437
	wR_2 = 0.0506	wR_2 = 0.0916	wR_2 = 0.0737
Abs. structure param.	−0.03(2)	−0.043(17)	0.01(3)
Residual el. density	max. 0.236	max. 0.468	max. 0.342
[e/Å^3]	min. −0.534	min. −0.535	min. −0.859

tively. Complexes **3**, **9** and **12** proved equally active as hydrogenating catalysts but did not induce asymmetry in the product.

Hydroformylation Reactions: In a typical experiment a mini-autoclave was charged under nitrogen in a glove box with a mixture of styrene (10.4 g, 0.1 mol), the appropriate rhodium complex (1 mmol) and toluene (10 mL). The reaction vessel was purged three times with nitrogen and loaded with 20 bar each of H_2 and CO. The autoclave was placed in a thermostated oil bath and heated at 60 °C for 22 h. After cooling, the autoclave was opened, the toluene was distilled off, and the catalyst was removed by filtration through a silica 60 column, using hexane as eluent. The hexane also eluted the linear aldehyde, $C_6H_5CH_2CH_2CHO$. The branched product $C_6H_5CH(CHO)CH_3$, was eluted with a 8:2 ratio of hexane/diethyl ether. The ratio of the two products was determined by NMR spectroscopy. Polarimetric measurements indicated that the enantiomeric excess of (−)-$C_6H_5CH(CHO)CH_3$ was low in all experiments and did not exceed 3%. The hydroformylation experiments with the various catalysts are summarized in Table 1.

Crystal Structure Determination: Data were collected on a Siemens SMART CCD diffractometer (graphite monochromated Mo-K_α radiation, $\lambda = 0.71073$ Å) with an area detector by use of ω scans at room temperature for **2** and at 173 K for **3** and **6**. The structures were solved by direct methods using SHELXS-97[36] and refined on F^2 using all reflections with SHELXL-97.[37] 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 X−C bond. Absolute structure parameters were determined according to Flack[38] with SHELX-97. SADABS[39] was used to perform area-detector scaling and absorption corrections. The maximum and minimum transmission factors and the resulting crystallographic data are given in Table 2. The geometrical aspects of the structures were analyzed by using the PLATON program.[40]

Crystallographic Data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-165792 (**2**), CCDC-165793 (**3**), and CCDC-165794 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[14] Cg defines the centroid of the ring atoms C(1), C(2), C(3), C(4), C(9); P(1), C(20), C(21), C(22) and P(2), C(23), C(24), C(25) are disordered about positions a and b, with occupancy factors of 0.504(4) and 0.496(4).
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[22] 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).[17]
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