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Synthesis, structure determination and immobilization of some dirhodium complexes with chiral binding thiolato ligands. Investigation of their catalytic activity for enantioselective hydrogenation

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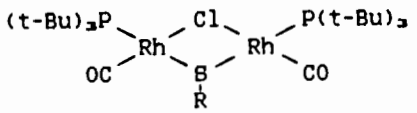
Abstract

(−)-*cis*-[Dicarbonyl-μ-chloro-[μ-6,6-dimethylbicyclo[3.1.1]heptane-2-methanethiolato-*S:S*)]]bis[tris(1,1-dimethylethyl)phosphine]dirhodium (**5a**) and (+)-*cis*-[dicarbonyl-μ-chloro-[μ-5β-methyl-2α-(1-methylethyl)cyclohexanethiolato-*S:S*]]bis[tris(1,1-dimethylethyl)phosphine]dirhodium (**5b**) were prepared from $[Rh(CO)_2]_2(\mu\text{-}Cl)_2$, P(t-Bu)$_3$ and the corresponding sulfides (−)-*cis*-(myrtanethio)trimethylsilane (**4a**) and (+)-(neomenthanethio)trimethylsilane (**4b**). The molecular structures of **5a** and **5b** were determined by single-crystal X-ray diffraction (**5a**: $C222_1$, $a = 13.749(4)$, $b = 23.509(9)$, $c = 27.271(9)$ Å, $Z = 8$, $R = 0.0443$, $R_w = 0.0491$. **5b**: $P\bar{1}$, $a = 16.209(6)$, $b = 14.150(5)$, $c = 9.899(3)$ Å, $Z = 2$, $R = 0.058$, $R_w = 0.094$). Complex **5b** was found to exist in the crystal as a pair of *1R,2R,5S*- and *1S,2R,5S*-epimers. Both chiral complexes have been immobilized by attachment to divinylbenzene-crosslinked polystyrene resins. Application of the chiral dirhodium complexes as catalysts for hydrogenation of methyl α-acetamidocinnamate revealed that while **5b** leads to optically active *N*-acetylphenylalanine methyl ester (up to 50% *ee*) **5a** gives only the racemic product. The immobilization of the complexes proved to improve the enantioselectivity of **5a** but decreases the ability of **5b** to induce asymmetric reduction.

Introduction

Previously we have shown that both homogeneous and supported dirhodium complexes of general formula **1** act as highly active catalysts for various hydrogen transfer processes [1]. We have also demonstrated that the replacement of the two tri-tert-butylphosphines in **1** by chiral (+)-neomenthyldiphenylphosphine ligands converts the complexes into enantioselective catalysts for the hydrogenation of dehydroamino acid derivatives [2].

In this paper we describe the syntheses and immobilization of compounds of type **1** in which chiral *cis*-myrtanyl and neomenthyl moieties have been introduced in the bridging SR group, and present an investigation on their utilization as hydrogenation catalysts for prochiral methyl acetamidocinnamate.



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Experimental

(−)-cis-Myrtanyl methanesulfonate (6b)

To a solution of 14.89 g (0.13 mol) of methanesulfonyl chloride in 50 ml of anhydrous ether was added dropwise at −20 °C a solution of 9.72 g (63 mmol) of (−)-*cis*-myrtanol and 26.7 ml (0.19 mmol) of triethylamine in 100 ml ether. The mixture was stirred at −20 °C for 20 min and then allowed to warm up to 20 °C. Neutralization with 1 N HCl followed by the usual workup gave 12.71 g (86%) of **6b** as a colorless oil. $[\alpha]_{578}^{20} = -19.9°$. 200 MHz ^{1}NMR ($C_6D_6$): δ 0.875 (s, 3H, CCH_3), 1.026–1.100 (m, 2H), 1.147 (s, 3H, CCH_3), 1.200–2.334 (m, 7H),

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2.376 (s, 3H, SO_2CH_3), 3.993 (dd, 2H, $J_1=1.2$ Hz, $J_2=7.8$ Hz, OCH_2). *Anal.* Calc. for $C_{11}H_{20}O_3S$: C, 56.86; H, 8.68. Found: C, 56.74; H, 8.40%.

(−)-cis-Myrtanyl thioacetate (6c)

A mixture of 12.71 g (55 mmol) of **6b**, 23.89 g (155 mmol) of cesium thioacetate and 100 ml of anhydrous DMF was stirred at 55 ± 0.5 °C for 23 h. Fractional distillation afforded 6.66 g (57%) of **6c** as a colorless oil; b.p. 103 °C (0.7 mm). $[\alpha]_D^{20}=-22.1°$ (neat). IR (neat): 1720 cm^{-1} (C=O). 200 MHz ^1H NMR (C_6D_6): δ 0.839 (m, 2H), 1.052 (s, 3H, CH_3), 1.219 (s, 3H, CH_3), 1.300–1.958 (m, 4H), 2.042 (s, 3H, $COCH_3$), 2.083–2.521 (m, 3H), 3.042 (dd, 2H, $J_1=1$ Hz, $J_2=8$ Hz, SCH_2). *Anal.* Calc. for $C_{12}H_{20}OS$: C, 68.87; H, 9.49. Found: C, 68.59; H, 9.67%.

(−)-cis-Myrtanethiol (6d)

To a stirred suspension of 1.18 g (31 mmol) of $LiAlH_4$ in 15 ml of anhydrous ether was added dropwise at 4 °C a solution of 6.58 (31 mol) of **6c** in 10 ml of the same solvent. Stirring was continued for 3 h at room temperature and the mixture decomposed with cold 2 N H_2SO_4. Workup in the usual manner furnished 5.08 g (96%) of **6d** as a colorless oil; b.p. 100 °C (0.7 mm). $[\alpha]_D^{20}=-20.5°$ (neat). 200 MHz ^1H NMR (C_6D_6): δ 0.795 (m, 1H), 0.888 (s, 3H, CH_3), 0.912 (m, 1H, SH), 1.186 (s, 3H, CH_3), 1.329 (m, 1H), 1.676–2.242 (m, 4H), 2.370 (m, 3H), 3.422 (dd, 2H, $J_1=1.5$ Hz, $J_2=8$ Hz, SCH_2). *Anal.* Calc. for $C_{10}H_{18}S$: C, 70.52; H, 10.65. Found: C, 70.59; H, 10.51%.

(−)-cis-Myrtanethiol lead salt (6e)

To a stirred solution of 5 g (30 mmol) of **6d** in 70 ml EtOH was added dropwise under Ar a solution of 6.6 g (15 mmol) of $Pb(OAc)_2\cdot 3H_2O$ in 170 ml of water. The yellow crystalline mass was stirred at room temperature for 24 h, filtered and washed successively with EtOH. Drying at 0.05 mm yielded 7.13 g (87%) of **6e**; m.p. 158 °C (dec.). $[\alpha]_D=-16.1°$ ($c=0.2$, $CHCl_3$). *Anal.* Calc. for $C_{20}H_{34}PbS$: C, 44.01; H, 6.27. Found: 44.48; H, 6.25%.

(−)-(cis)-(Myrtanylthio)trimethylsilane (4a)

A Schlenk tube was charged under Ar with 7.09 g (13 mmol) of **6e** and 20 ml of $ClSiMe_3$. The mixture was stirred for 20 h and the precipitate filtered off through a sintered glass filter (D 3) and washed (×2) with 10 ml of $ClSiMe_3$. The excessive reagent was removed under reduced pressure and the residue distilled at 0.1 mm. Yield 4.62 g (73%); b.p. 89 °C (0.1 mm). $[\alpha]_{578}^{20}=-26.66°$ ($c=1.5$, MeOH). 300 MHz ^1H NMR (C_6D_6): δ 0.222 [s, 9H, $Si(CH_3)_3$], 0.777 (m, 1H), 0.910 (s, 3H, CH_3), 1.130 (s, 3H, CH_3), 1.462 (m, 1H), 1.688–2.420 (m, 7H), 2.540 (d, 2H, $J=8$ Hz, SCH_2). 75 MHz $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.08, 22.54, 23.31, 26.54, 28.26, 33.48, 33.78, 38.86, 41.97, 44.80, 45.86. *Anal.* Calc. for $C_{13}H_{26}SSi$: C, 64.38; H, 10.80. Found: C, 64.18; H, 10.75%.

(−)-cis-Dicarbonyl-μ-chloro-[μ-6,6-dimethylbicyclo-[3.1.1]heptane-2-methanethiolato-S:S)[]bis[tris(1,1-dimethylethyl)phosphine]dirhodium (5a)

To a carefully dried Schlenk tube with 340 mg (0.87 mmol) of freshly sublimed tetracarbonyl-μ-dichlorodirhodium (**2**) was added slowly under Ar a solution of 333 mg (1.64 mmol) of tri-tert-butylphosphine in 20 ml of pentane (A.R. grade). The orange solution was heated with agitation for 30 min to 35 °C. After 2 h at this temperature there was syringed into the reaction vessel a solution of 211 mg (0.87 mmol) of **4a** in 20 ml of pentane. The yellow mixture was stirred for 4 h, the solvent was decanted off under Ar and the precipitate washed (×3) with 3 ml pentane. Drying at 0.05 mm yielded 360 mg (47%) of **5a**; m.p. 192–194 °C (dec.). $[\alpha]_{578}^{20}=-1.36°$ ($c=0.735$, PhH). IR (KBr): 1936, 1949 cm^{-1} (RhC≡O). 300 MHz ^1H NMR (C_6D_6): δ 1.072 (s, 3H, CH_3), 1.106 (s, 3H, CH_3), 1.427 [d, 54H, $^3J_{P,H}=10$ Hz, $C(CH_3)_3$], 1.519 (m, 1H), 1.812–1.889 (m, 4H), 2.275–2.372 (m, 2H), 2.554 (m, 1H), 2.889 (m, 1H), 3.275 (d, 2H, $J=6$ Hz, SCH_2). 75 MHz $^{13}C\{^1H\}$ NMR (C_6D_6): δ 28.82, 23.42, 26.72, 28.15, 33.21 (d, $^3J_{P,C}=3.2$ Hz), 33.90, 38.93, 39.88 (d, $^1J_{P,C}=7.4$ Hz), 40.82, 41.92, 54.30, 46.05. 81 MHz ^{31}P NMR (C_6D_6, 85% H_3PO_4): δ 93.263 (d, $J_{Rh,P}=146$ Hz). *Anal.* Calc. for $C_{36}H_{71}ClO_2P_2Rh_2S$: C, 49.63; H, 8.21; P, 7.11. Found: C, 49.24; H, 7.55; P, 7.03%.

A suitable crystal for X-ray diffraction analysis was obtained by slow recrystallization from a 1:1 mixture of MeOH–CH_2Cl_2 at −30 °C. The crystal data, the experimental conditions, and a summary of the solution and refinement details are presented in Table 1. The positional coordinates and isotropic equivalent thermal parameters for all non-hydrogen atoms are listed in Table 2, and selected bond distances and bond angles are given in Table 3. An ORTEP drawing is shown in Fig. 1. See also 'Supplementary material'.

(+)-(Neomenthanethio)trimethylsilane (4b)

In the manner described for the preparation of **6e**, 10.52 g (61 mmol) of (+)-neomentanethiol of >99.5% *ee* [5] were reacted with 11.64 g (30 mmol) of $Pb(OAc)_2\cdot 3H_2O$ to give 14.52 g (87%) of the lead thiolate; m.p. 182 °C (dec.). $[\alpha]_D^{20}=+22.5°$ ($c=0.2$, $CHCl_3$). *Anal.* Calc. for $C_{20}H_{38}PbS_2$: C, 43.68; H, 6.98. Found: C, 43.75; H, 6.92%).

A quantity of 14.11 g (26 mmol) of the foregoing salt was then heated in a Schlenk tube under Ar

TABLE 1. Crystal data and details of structure determination for **5a** and **5b**

Compound	**5a**	**5b**
Crystal data		
Formula	$C_{36}H_{71}ClO_2P_2Rh_2S \cdot CH_2Cl_2$	$C_{36}H_{73}ClO_2P_2Rh_2S$
Molecular weight	1041.1	873.3
Space group	$C222_1$	$P\bar{1}$
Crystal system	orthorhombic	triclinic
a^a (Å)	13.749(4)	16.209(6)
b (Å)	23.509(9)	14.150(5)
c (Å)	27.271(9)	9.899(3)
α (°)		109.69(3)
β (°)		93.12(5)
γ (°C)		79.65(2)
V (Å^3)	8814.6(6)	2102.8(8)
ρ_{calc} (g cm^{-3})	1.355	1.38
$F(000)$	4271.97	915.99
μ(Mo Kα) (cm^{-1})	10.93	9.03
Data collection and reduction		
Diffractometer	Enraf-Nonius CAD 4	PW1100/20
Radiation (Å)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71069)
Temperature (K)	110–115	295–298
Crystal dimensions (mm)	0.18 × 0.18 × 0.22	0.33 × 0.36 × 0.55
Scanation technique	ω–2θ	ω–2θ
2θ, min., max. (°)	1–50	4–50
Scanning speed (°/min)		3.0
Check reflections	3	3
Frequency, h	2	1
No reflections measured	8134	7317
No. unique reflections	6587	7317
No. observed reflections	4253	5794
σ criterion	$F > 6\sigma(F)$	$F > 6\sigma(F)$
Structure determination and refinement		
Method of phase determination	direct methods	direct methods
Programs	SHELX-76[b]	SHELXS-86[c]
$R = \Sigma\|\|F_o\| - \|F_o\|\|/\Sigma\|F_o\|$	0.044	0.058
$R_w = [\Sigma w(\|F_o\| - \|F_o\|)^2/\Sigma wF_o]^{1/2}$	0.046	0.094
Weight	$1.5807[\sigma^2(F_o) + 0.000352F_o^2]^{-1}$	$1.7324[\sigma^2(F_o) + 0.001309F_o^2]^{-1}$

[a]Cell dimensions were determined by least-squares fit of the setting angles of 24 reflections with 2θ in the range 16.8–23° for **5a** and 11–15° for **5b**. [b]Ref. 3. [c]Ref. 4.

with 20 ml of $ClSiMe_3$ for 10 days. Workup as described for **4a** afforded 10.75 g (85%) of **4b** as a colorless oil; b.p. 91 °C (0.1 mm). $[\alpha]_D^{20} = +80.4°$ (c = 2, MeOH). 300 MHz ^{1}H NMR (C_6D_6): δ 0.238 [s, 9, Si(C*H*$_3$)$_3$]; 0.768–0.831 (m, 3H), 0.859–1.018 [m, 9H, CH(C*H*$_3$)$_2$, C*H*$_3$], 1.204 (m, 1H), 1.478–1.865 (m, 4H), 2.217 (m, 1H), 3.334 (dt, 1H, J_1 = 2.4 Hz, J_2 = 2.5 Hz, SC*H*). 75 MHz ^{13}C{^{1}H} NMR (C_6D_6): δ 1.77, 20.95, 21.08, 22.40, 25.28, 26.08, 30.17, 35.90, 43.16, 45.24, 50.06. *Anal.* Calc. for $C_{13}H_{28}SSi$: C, 63,86; H, 11.54. Found: C, 64.23; H, 11.73%.

(+)-cis[Dicarbonyl-μ-chloro[μ-[5β-methyl-2α-(1-methylethyl)cyclohexanethiolato-S:S]]bis[tris(1,1-dimethylethyl)phosphine]dirhodium (5b)

In the manner described for the preparation of **5a**, 300 mg (0.77 mmol) of **2** was reacted with 300 mg (1.48 mmol) of tri-tert-butylphosphine and 188 mg (0.77 mmol) of **4b**. Yield 390 mg (58%) of **5b**. Orange crystals, m.p. 180–190 °C (dec.). $[\alpha]_D^{20} = +7.7°$ (c = 0.012, PhH). IR (KBr): 1948, 1955 cm^{-1} (RhC≡O). 300 MHz ^{1}H NMR (C_6D_6): δ 1.009 (m, 1H), 1.126 (d, 3H, J = 6.5 Hz, CH_3CHCH_3), 1.453 (d, 3H, J = 6.5 Hz, CH_3CHCH_3), 1.275 (m, 1H), 1.445 [d, 54H, $J_{P,H}$ = 12 Hz, C(C*H*$_3$)$_3$], 1.603 (m, 1H), 1.682 (d, 3H, J = 6.5 Hz, CHC*H*$_3$), 1.693–1.936 (m, 2H), 2.180 (m, 1H), 2.720–2.969 (m, 2H), 3.642 (m, 1H), 4.430 (m, 1H, SC*H*). 50 MHz ^{13}C{^{1}H} NMR (C_6D_6): δ 22.06, 23.28, 23.94, 25.17, 26.68, 30.02, 30.56, 32.78 (d, $^3J_{P,C}$ = 1.8 Hz), 35.58, 40.67, 49.99, 50.56 (d, $^1J_{P,C}$ = 26 Hz). 81 MHz ^{31}P NMR (C_6D_6, 85% H_3PO_4): δ 92.437 (d, $J_{Rh,P}$ = 144 Hz). *Anal.* Calc. for $C_{36}H_{73}ClO_2P_2RH_2S$: C, 49.52; H, 8.43. Found: C, 49.87; H, 8.29%.

A suitable crystal for X-ray diffraction was obtained by slow recrystallization from benzene. Details of

TABLE 2. Refined positional and isotropic thermal parameters for **5a** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Rh1	0.8468(1)	0.8244(0)	0.3671(0)	1.80
Rh2	0.8414(1)	0.6834(0)	0.3694(0)	1.87
Cl	0.7602(1)	0.7539(1)	0.3182(1)	2.04
S	0.9610(1)	0.7519(2)	0.3521(1)	2.25
P1	0.7286(2)	0.8982(1)	0.3736(1)	1.73
P2	0.7222(2)	0.6111(1)	0.3757(1)	1.89
O1	0.9862(6)	0.8685(4)	0.4385(3)	4.37
O2	0.9693(6)	0.6383(4)	0.4457(3)	5.15
C1	1.2303(7)	0.7922(4)	0.4115(4)	2.54
C2	1.1509(7)	0.7829(4)	0.3732(4)	2.76
C3	1.1937(6)	0.7607(5)	0.3246(3)	3.55
C4	1.3050(6)	0.7532(7)	0.3222(3)	3.63
C5	1.3541(6)	0.7689(3)	0.3697(4)	3.85
C6	1.3138(7)	0.8256(4)	0.3873(5)	4.26
C7	1.3051(6)	0.7423(7)	0.4148(3)	3.41
C8	1.3661(6)	0.7437(7)	0.4611(3)	4.53
C9	1.2721(8)	0.6794(5)	0.4082(4)	4.65
C10	1.0670(5)	0.7497(6)	0.3922(3)	2.76
C11	0.9290(8)	0.8557(4)	0.4085(4)	3.07
C12	0.9140(7)	0.6522(5)	0.4167(4)	2.52
C13	0.6633(8)	0.8904(4)	0.4350(4)	3.06
C14	0.6485(8)	0.8258(4)	0.4427(4)	4.28
C15	0.5640(7)	0.9207(4)	0.4396(4)	3.82
C16	0.7246(8)	0.9099(4)	0.4758(3)	3.51
C17	0.7766(8)	0.9744(4)	0.3697(4)	2.66
C18	0.8735(7)	0.9779(4)	0.3989(4)	2.77
C19	0.8072(8)	0.9881(4)	0.3184(5)	4.60
C20	0.7076(8)	1.0206(4)	0.3889(4)	2.61
C21	0.6344(7)	0.8940(4)	0.3232(4)	1.89
C22	0.6881(7)	0.8825(4)	0.2729(3)	1.68
C23	0.5638(7)	0.8438(4)	0.3296(5)	3.16
C24	0.5665(8)	0.9475(4)	0.3144(5)	4.36
C25	0.6247(7)	0.6183(4)	0.3243(4)	2.18
C26	0.6746(8)	0.6282(4)	0.2753(4)	3.53
C27	0.5632(7)	0.6694(4)	0.3346(3)	2.61
C28	0.5605(7)	0.5655(4)	0.3188(4)	1.84
C29	0.6546(7)	0.6174(4)	0.4373(3)	2.23
C30	0.6397(6)	0.6799(4)	0.4491(4)	2.94
C31	0.5564(7)	0.5877(4)	0.4417(4)	3.57
C32	0.7224(8)	0.5960(5)	0.4803(4)	3.50
C33	0.7769(7)	0.5354(4)	0.3731(4)	3.83
C34	0.8694(8)	0.5281(5)	0.4009(5)	7.77
C35	0.8027(8)	0.5216(5)	0.3174(3)	4.52
C36	0.7076(9)	0.4893(4)	0.3896(4)	5.23

TABLE 3. Selected bond lengths (Å) and angles (°) for **5a** with e.s.d.s in parentheses

Bond lengths					
Rh1–Cl	2.439(3)	Rh2–C12	1.79(1)	C3–C4	1.54(1)
Rh1–S	2.355(3)	S–C10	1.82(1)	C4–C5	1.51(1)
Rh1–P1	2.383(2)	C1–C2	1.53(1)	C5–C6	1.52(1)
Rh1–C11	1.76(1)	C1–C6	1.54(2)	C5–C7	1.54(2)
Rh2–Cl	2.438(3)	C1–C7	1.56(2)	C7–C8	1.52(1)
Rh2–S	2.350(3)	C2–C3	1.54(1)	C7–C9	1.56(2)
Rh2–P2	2.367(2)	C2–C10	1.49(1)		
Bond angles					
Cl–Rh1–C11	161.5(4)		C1–C2–C3	110.9(9)	
Cl–Rh1–P1	101.8(1)		C1–C2–C10	111.6(9)	
Cl–Rh1–S	74.1(1)		C3–C2–C10	114.6(9)	
C11–Rh1–P1	95.2(4)		C2–C3–C4	117.9(9)	
C11–Rh1–S	88.9(4)		C3–C4–C5	112.0(9)	
P1–Rh1–S	174.3(2)		C4–C5–C6	109(1)	
Cl–Rh2–C12	161.6(4)		C4–C5–C7	113.2(8)	
Cl–Rh2–S	75.0(1)		C6–C5–C7	86(1)	
C12–Rh2–P2	92.1(4)		C1–C6–C5	88.5(8)	
C12–Rh2–S	92.2(4)		C1–C7–C5	87(1)	
P2–Rh2–S	172.3(2)		C1–C7–C8	113(1)	
Rh1–Cl–Rh2	85.7(1)		C1–C7–C9	120(1)	
Rh1–S–C10	116.5(5)		C5–C7–C8	115(1)	
Rh2–S–C10	115.3(5)		C5–C7–C9	115(1)	
C2–C1–C6	107(1)		C8–C7–C9	106(1)	
C2–C1–C7	114.5(9)		S–C10–C2	112.9(8)	
C6–C1–C7	84.6(8)				

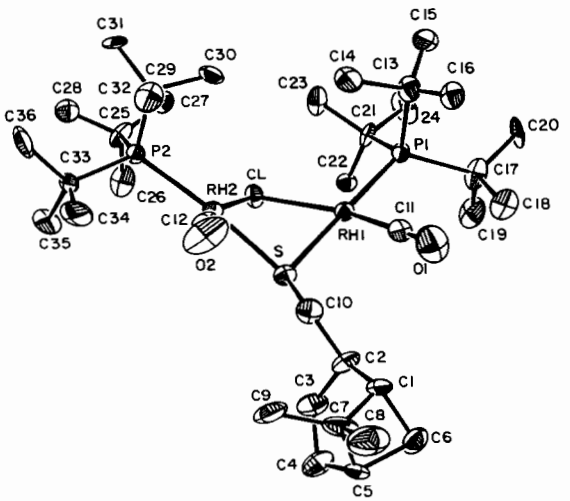


Fig. 1. Molecular structure (ORTEP) of **5a**.

the crystal data, the experimental conditions and a summary of the solution and refinement details are given in Table 1. The positional coordinates equivalent isotropic thermal parameters are listed in Table 4. Selected bond distances and angles are presented in Table 5. A stereoscopic view of one half of the unit cell is shown in Fig. 2. ORTEP drawings of the two epimers of **5b** are shown in Fig. 3. See also 'Supplementary material'.

Anchoring of complexes 5a and 5b to diphenylphosphinated polystyrene resins

In a typical experiment a mixture of 156 mg of diphenylphosphine bound to polystyrene crosslinked with 2% divinylbenzene (phosphorus content 0.74 mequiv. g^{-1}), 56.2 mg (6.45×10^{-2} mmol) of **5a** and 20 ml of dry benzene was refluxed and stirred under Ar for 8 days. The solvent was decanted and the solid residue washed with hot benzene until the

TABLE 4. Refined positional and isotropic thermal parameters for **5b** with e.s.d.s in parentheses[a]

Atom	x	y	z	B_{eq} (Å)
Rh1	0.26686(4)	0.26098(5)	0.31784(6)	2.66
Rh2	0.21146(4)	0.51104(5)	0.43825(6)	2.56
P1	0.2449(1)	0.1296(2)	0.0996(2)	2.79
P2	0.1490(1)	0.6377(2)	0.3448(2)	2.73
S	0.2904(1)	0.3872(2)	0.5392(2)	2.81
C1	0.2986(1)	0.3908(2)	0.2271(2)	3.37
O1	0.2092(5)	0.1671(6)	0.5104(7)	6.31
O2	0.1437(5)	0.5991(6)	0.7258(7)	5.47
C1,1'	0.4040(5)	0.3948(6)	0.5331(8)	2.97
C2	0.438(1)	0.453(2)	0.687(2)	4.44
C3,3'	0.4381(7)	0.3835(9)	0.779(1)	5.73
C4	0.493(1)	0.281(2)	0.723(2)	5.52
C5,7'	0.4608(6)	0.2199(7)	0.562(1)	5.15
C6	0.454(1)	0.289(1)	0.478(2)	3.68
C7,5'	0.3936(6)	0.5606(7)	0.7595(9)	3.70
C8	0.385(1)	0.620(1)	0.646(2)	5.00
C9	0.437(2)	0.610(2)	0.889(3)	6.31
C10	0.517(2)	0.130(2)	0.538(6)	11.04
C2'	0.460(1)	0.355(1)	0.610(2)	3.47
C4'	0.449(1)	0.491(2)	0.841(2)	4.73
C6'	0.415(1)	0.512(1)	0.595(2)	4.18
C8'	0.486(2)	0.177(1)	0.391(3)	5.78
C9'	0.526(2)	0.176(3)	0.648(5)	12.36
C10'	0.419(2)	0.663(2)	0.818(3)	6.31
C11	0.2323(5)	0.1972(7)	0.430(1)	3.86
C12	0.1720(5)	0.5694(7)	0.612(1)	4.08
C13	0.2886(6)	0.1492(7)	−0.0654(9)	4.00
C14	0.2954(7)	0.0527(9)	−0.212(1)	5.92
C15	0.3762(7)	0.1755(8)	−0.031(1)	5.28
C16	0.2322(7)	0.2387(8)	−0.097(1)	5.05
C17	0.1262(5)	0.1324(7)	0.075(1)	3.73
C18	0.0961(7)	0.0809(8)	−0.081(1)	5.36
C19	0.0941(7)	0.0833(8)	0.177(1)	5.21
C20	0.0838(6)	0.2464(8)	0.124(1)	4.81
C21	0.2951(6)	−0.0060(7)	0.094(1)	4.15
C22	0.2604(7)	−0.0924(8)	−0.018(1)	5.28
C23	0.3926(8)	−0.0210(9)	0.068(1)	6.23
C24	0.2864(7)	−0.0191(9)	0.240(1)	5.52
C25	0.1515(7)	0.7763(6)	0.465(1)	4.21
C26	0.1426(7)	0.7884(9)	0.628(1)	5.92
C27	0.2372(9)	0.807(1)	0.456(1)	7.18
C28	0.0870(9)	0.855(1)	0.435(1)	7.34
C29	0.0341(5)	0.6195(8)	0.321(1)	4.63
C30	−0.0101(8)	0.6574(9)	0.472(1)	6.31
C31	−0.0181(8)	0.672(1)	0.225(1)	6.63
C32	0.0349(7)	0.5048(9)	0.259(1)	5.60
C33	0.1908(6)	0.6266(7)	0.1598(9)	4.31
C34	0.1566(8)	0.717(1)	0.106(1)	4.70
C35	0.1684(7)	0.5315(8)	0.045(1)	5.28
C36	0.2890(7)	0.6174(9)	0.173(1)	5.99

[a]Numbers marked with a prime refer to the carbon atoms of the myrtanyl moiety in the second epimer of **5b**.

TABLE 5. Selected bond lengths (Å) and angles (°) for **5b** with e.s.d.s in parentheses[a]

Bond lengths					
Rh1–P1	2.387(2)	C1,1'–C6	1.59(2)	C5,7'–C10	1.38(3)
Rh1–S	2.378(2)	C1,1'–C2'	1.49(2)	C5,7'–C2'	1.53(2)
Rh1–Cl	2.438(3)	C1,1'–C6'	1.60(2)	C5,7'–C8'	1.64(3)
Rh1–C11	1.81(1)	C2–C3,3'	1.54(3)	C5,7'–C9'	1.50(5)
Rh2–P2	2.385(2)	C2–C7,5'	1.51(2)	C7,5'–C8	1.61(3)
Rh2–S	2.381(2)	C3,3'–C4	1.50(2)	C7,5'–C9	1.45(3)
Rh2–Cl	2.439(2)	C3,3'–C2'	1.61(2)	C7,5'–C4'	1.60(2)
Rh2–C12	1.803(9)	C3,3'–C4'	1.48(3)	C7,5'–C6'	1.57(2)
S–C1,1'	1.868(8)	C4–C5,7'	1.65(2)	C7,5'–C10'	1.49(3)
C1,1'–C2	1.59(2)	C5,7'–C6	1.46(3)		
Bond angles					
P1–Rh1–S	177.92(7)	C1,1'–C2–C7,5'	116(1)		
P1–Rh1–Cl	101.19(7)	C3,3'–C2–C7,5'	113(1)		
P1–Rh1–C11	93.7(4)	C2–C3,3'–C4	115(1)		
S–Rh1–Cl	80.63(7)	C2'–C3,3'–C4'	113(1)		
S–Rh1–C11	84.6(4)	C3,3'–C4–C5,7'	108(1)		
Cl–Rh1–C11	163.2(4)	C4–C5,7'–C6	107(1)		
P2–Rh2–S	177.87(9)	C4–C5,7'–C10	98(3)		
P2–Rh2–Cl	101.52(8)	C6–C5,7'–C10	127(2)		
P2–Rh2–C12	94.3(3)	C2'–C5,7'–C8'	106(1)		
S–Rh2–Cl	80.54(8)	C2'–C5,7'–C9'	108(1)		
S–Rh2–Cl2	83.6(3)	C8–C5,7'–C9'	111(2)		
Cl–Rh2–C12	163.6(3)	C1,1'–C6–C5,7'	121(1)		
Rh1–S–Rh2	87.35(7)	C2–C7,5'–C8	109(1)		
Rh1–S–C1,1'	104.3(3)	C2–C7,5'–C9	111(2)		
Rh2–S'–C1,1'	104.1(2)	C8–C7,5'–C9	113(1)		
Rh1–Cl–Rh2	84.72(7)	C4'–C7,5'–C6'	109(1)		
S–C1,1'–C2	111.6(8)	C4'–C7,5'–C10'	106(1)		
S–C1,1'–C6	109.2(8)	C6'–C7,5'–C10'	110(1)		
S–C1,1'–C2'	114.2(7)	C1,1'–C2'–C3,3'	109(1)		
S–C1,1'–C6'	108.7(9)	C1,1'–C2'–C5,7'	118(1)		
C2–C1,1'–C6	109(1)	C3,3'–C2'–C5,7'	109(1)		
C2'–C1,1'–C6'	111(1)	C3,3'–C4'–C7,5'	111(1)		
C1,1'–C2–C3,3'	107(1)	C1,1'–C6'–C7,5'	112(1)		

[a]Numbers marked with a prime refer to the carbon atoms of the myrtanyl moiety in the second epimer of 5b.

washings were colorless. The beads were dried at room temperature at 5×10^{-2} mm and stored under Ar. The combined benzene solutions were evaporated and the Rh content in the residue was determined by atomic absorption [6]. From the difference between the Rh in **5a** and in the washings the metal content in **8a** was calculated.

The same procedure was applied for the preparation of **8b** from **5b**. For the preparation of the rigid immobilized catalysts diphenylphosphine bound to polystyrene crosslinked with 20% of divinylbenzene (phosphorus content 0.43 mequiv. g^{-1}) was used.

Preparation of 9a

To 300 mg (0.77 mequiv. Rh) of **2** in 10 ml of hexane was added dropwise under Ar a solution of 480 mg (1.48 mmol) of (+)-neomenthyldiphenylphosphine (**10**) in 10 ml of the same solvent, and

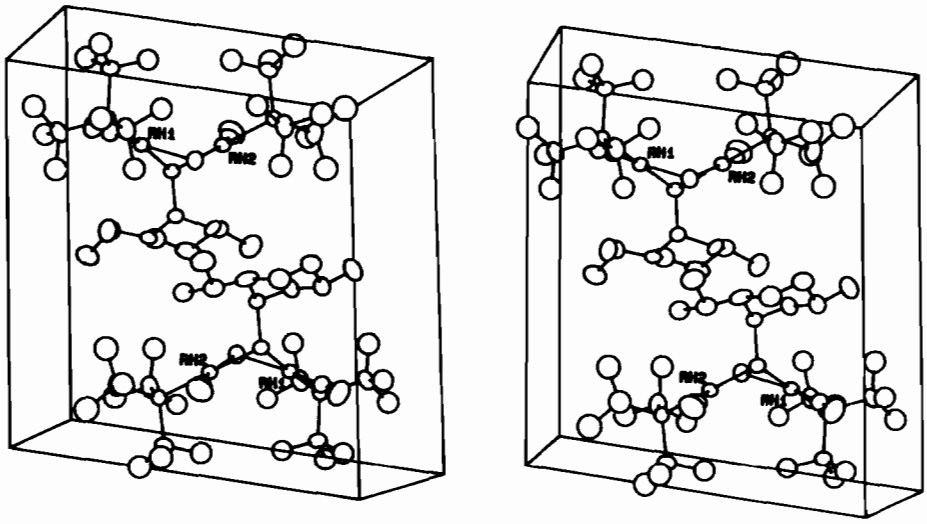


Fig. 2. Stereoscopic view of one half unit cell of **5b**.

the mixture was stirred at room temperature. After 4 h 35.5 mg of trimethyl-silylated 2% divinylbenzene-crosslinked polymer **12** (containing 0.77 mequiv. of Si) was added (prepared as previously described [1c]). The mixture was stirred for a further 12 h and then filtered under Ar. The remaining beads were washed with warm pentane until the washings were colorless Drying of the beads at 10^{-3} mm afforded 358 mg of **9a**. From the difference between the Rh content of **2** and the metal content in the filtrate and washings, the beads were found to contain 1.486 mequiv. Rh per g catalyst.

General procedure for hydrogenation of 13

Typically, a mixture of 0.156 mmol of **13**, 7.81×10^{-3} mmol of the catalyst, 1 ml of absolute MeOH and 2 ml of dry benzene was placed in a mini autoclave. The autoclave was sealed, purched with Ar (×3) and charged with 100 psi H_2. The reaction mixture was stirred at 120 ± 0.5 °C for 20 h, cooled to room temperature and the autoclave opened under Ar. When a homogeneous catalyst had been applied the solvents were removed under reduced pressure and the residue separated on neutral alumina-90 with mixtures of CH_2Cl_2–MeOH as eluent. The product was analyzed by GC with the aid of a glass column packed with 5% OV-101 on Chromosorb Q, by ^1H NMR spectroscopy, and by optical rotation measurements. When an immobilized catalyst had been used the liquid reaction mixture was decanted, and the amount of rhodium leaching was determined by atomic absorption [6]. The remaining beads were washed with five 0.5 ml portions of MeOH, dried in a stream of Ar and either recycled immediately or stored under Ar.

Results and discussion

Syntheses and crystal structures of the homogeneous catalysts

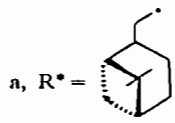
The soluble dirhodium compounds **5a** and **5b** were obtained by modification of the general synthesis of μ-alkylthiolato-μ-chlorodicarbonylbis(tri-tert-butylphosphine)dirhodium complexes outlined in eqns. (1) and (2) [1a, 7].

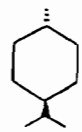
$$[Rh(CO)_2(\mu\text{-}Cl)]_2 + 2P(t\text{-}Bu)_3 \longrightarrow \underset{\mathbf{2}}{}$$

$$\underset{\mathbf{3}}{[(t\text{-}Bu)_3P(CO)Rh]_2(\mu\text{-}Cl)_2} + 2CO \quad (1)$$

$$\mathbf{3} + R^*SSiMe_3 \longrightarrow \underset{\mathbf{4}}{}$$

$$\underset{\mathbf{5}}{[(t\text{-}Bu)_3P(CO)Rh]_2(\mu\text{-}Cl)(\mu\text{-}SR^*)} + ClSiMe_3 \quad (2)$$

a, R* = 

b, R* = 

The thio ether **4a** was formed in a sequence of reactions in which (−)-*cis*-myrtanol (**6a**) was initially converted into the thioacetate **6c** (via the methanesulfonate **6b**), followed by lithium aluminium hydride reduction to (−)-*cis*-myrtanethiol (**6d**).

a, X = OH **d**, X = SH
b, X = OSO_2CH_3 **e**, X = $SPb_{1/2}$
c, X = $SCOCH_3$

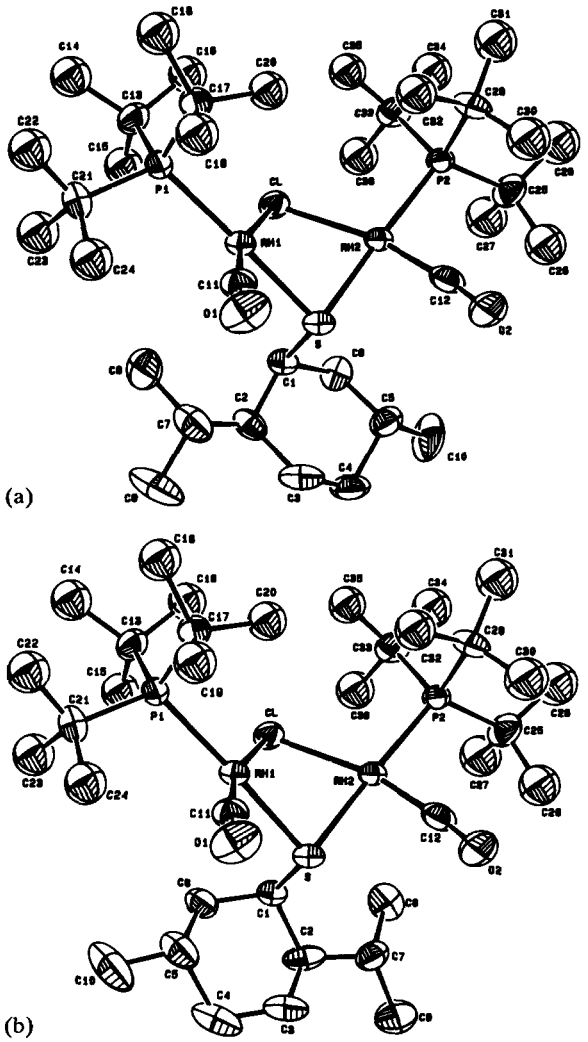
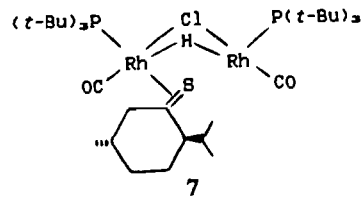


Fig. 3. ORTEP drawings of (a) the 1*S*,2*R*,5*S*-isomer of **5b**; (b) the 1*R*,2*R*,5*S*-isomer of **5b**.

The latter was then treated with lead diacetate, and the least salt **6e** reacted with trimethylchlorosilane. The reaction of chlorodicarbonylrhodium dimer (**2**) with tri-tert-butylphosphine and **4a** gave smoothly (−)-*cis*-[dicarbonyl-μ-chloro-[μ-(6,6-dimethylbicyclo[3.1.1]heptane-2-methanethiolato)]bis[tris(1,1-dimethyl)phosphine]dirhodium (**5a**) as the only isolable product. The structure of **5a** was determined by X-ray diffraction analysis (see Table 1–3). The ORTEP drawing (Fig. 1) shows that the two metals and the bridging Cl and S atoms form a distorted rhombus in which both the Rh1–Cl and Rh2–Cl distances equal to 2.43 Å and the bond lengths Rh1–S and Rh2–S are 2.36 and 2.35 Å, respectively. The corresponding bond angles Rh1–Cl–Rh2, Rh1–S–Rh2, Cl–Rh1–S and Cl–Rh2–S were found to be 86, 90, 75 and 75°. Each of the two metal atoms is formally univalent and is surrounded by a distorted square planar coordination sphere. Such an arrangement is usually observed when a Rh–Rh bond exists (32 electrons). The X-ray data reveal, however, that the Rh1–Rh2 distance is too large (3.31 Å) for such a metal–metal interaction [8]. In contrast to some other *cis*-dicarbonyl-bis(tri-tert-butylphosphine)dirhodium complexes [7] the sulfur-bound cyclohexane moiety occupies a pseudo-equatorial position in the dimetallo-cyclobutane ring.

The starting sulfide for (+)-*cis*-[dicarbonyl-μ-chloro-[μ-[5β-methyl-2α-(1-methylethyl)cyclohexanethiolato]]bis[tris(1,1-dimethylethyl)phosphine]dirhodium (**5b**) was (+)-(neomenthanethio)-trimethylsilane (**4b**) [9]. Although this compound was of >99.5% optical purity (as evidenced (*i*) by Horeau's method [10], (ii) by the chiral lanthanide shift reagent technique, and (iii) by hydrolysis to >99.5% optically pure (+)-neomenthanethiol [5]), X-ray diffraction analysis (see Tables 1, 4 and 5) revealed that during the process of eqn. (2), epimerization at carbon 1 of the cyclohexane moiety took place. Each unit cell of the crystals was found to consist of two *cis*-oriented pairs of epimers: one pair in which the chiral moiety has the (1*S*,2*R*,5*S*)-configuration, and one in which it has the (1*R*,2*R*,5*S*)-configuration (see Fig. 2 for a stereoscopic view of one half of the unit cell). ORTEP drawings of the two isomers of **5b** are presented in Fig. 3(a) and (b). By placing the Figure in such a way that all the atoms of both molecules, with the exception of those of the chiral portion, are superimposed, atoms C1 and C3 of the methylisopropyl-cyclohexane moieties also become superimposable, but C5 of one molecule occupies the position of C7 in the other and vice versa. A similar epimerization process has recently been observed when **4b** was reacted with $[(t\text{-}Bu_3)As(CO)Rh]_2(\mu\text{-}Cl)_2$ [9]. We explain this phenomenon by a reversible formation of a hydride bridged dirhodium intermediate **7**.



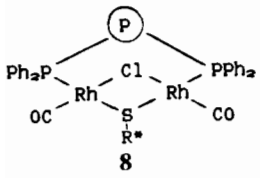
7

As in **5a**, atoms Rh1, Rh2, Cl and S of **5b** also form a distorted rhombus with sides Rh1–Cl = Rh2–Cl = 2.44 Å, and Rh1–S = Rh2–S = 2.38 Å, and angles Cl–Rh1–S, Cl–Rh2–S, Rh1–Cl–Rh2 and Rh1–S–Rh2 of 80.5, 80.5, 85 and 87°, respectively. Here too, the Rh1–Rh2 distance of 3.28 Å does not permit metal–metal interaction. In contrast to the situation in **5a**, the sulfur-bound cyclohexane group

of **5b** occupies a pseudo-axial position in the four membered ring.

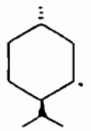
Immobilized complexes

Since we have already noticed [1, 2] that attachment of dirhodium complexes of type **1** to insoluble supports both decreases their sensitivity towards oxygen, and usually improves their catalytic properties, we attached compounds **5a** and **5b** (by the phosphine exchange technique [1, 2]) to various crosslinked diphenylphosphinated polystyrene resins. Thus, indeed, we obtained highly stable and recyclable catalysts with considerably better performances than the soluble complexes (*vide infra*). Although no structure studies of the hybrid catalysts have been performed (except (i) destructive MS measurements by which we proved that the dinuclearic arrangement was retained, and (ii) FT-IR measurements that indicated close similarity between the Rh–C≡O band patterns in the free and in the supported complexes), we assume that part of the soluble compounds are attached to the polystyrene as in **8** (cf., ref. 1).

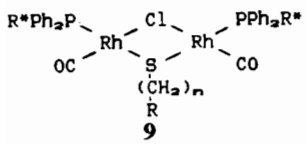


8

a, R* = 

b, R* = 

Ⓟ = divinylbenzene-crosslinked polystyrene resin



9

R* = 1α*R*-(5β-methyl-2α-(1-methylethyl)cyclohexyl]
a, $n = 1$, R = 2% divinylbenzene-crosslinked polystyrene resin
b, $n = 0$, R = CMe_3
c, $n = 2$, R = $Si(OEt)_3$
d, $n = 2$, R = $Si(O)_3$-silica

For comparison we prepared polystyrene-bound (+)-dicarbonyl-μ-chloro-(μ-methanethiolato-*S*:*S*)-bis[[5-methyl-2-(1-methylethyl)cyclohexyl]diphenylphosphinite-*P*]dirhodium (**9a**) which is an immobilized version of the previously studied bis-neomenthyldiphenylphosphine complexes **9b** and **9c** [2]. The synthesis of **9a** was accomplished by a modification of Rollmann's method [11] for the attachment of polystyrene to thiolato bridges as shown in eqns. (3) and (4).

$$\underset{\mathbf{10}}{2} + 2R^*Ph_2P \longrightarrow \underset{\mathbf{11}}{[R^*Ph_2P(CO)Rh]_2(\mu\text{-}Cl)_2} + 2CO \quad (3)$$

$$\underset{\mathbf{12}}{\mathbf{11}} + Ⓟ\text{-}CH_2SSiMe_3 \longrightarrow \mathbf{9a} + ClSiMe_3 \quad (4)$$

R* = 1α*R*-[5β-methyl-2α-(1-methylethyl)cyclohexyl]
Ⓟ = 2% divinylbenzene-crosslinked polystyrene resin

Catalytic activity of 5a, 5b, 8a, 8b and 9a

Both the homogeneous and the hybrid catalysts were found to act as highly active catalysts for the hydrogenation of simple alkenes. Cyclohexene, for example, could be transformed under atmospheric pressure at room temperature by each of these dirhodium compounds to cyclohexane in a comparable, or even higher rate, than by the Wilkinson catalyst [12]. Hydrogenation of derivatives of prochiral dehydroamino acids, however, proceeded rather slowly even at 120 °C and 100–750 psi of H_2 with only low or medium enantioselectivity. For example, when methyl α-acetamidocinnamate (**13**) was used as substrate the optical purity of the resulting (*S*)-(+)-*N*-acetylphenylalanine methyl ester (**14**) (eqn. (5)) did not exceed 50% *ee*

$$\underset{\mathbf{13}}{Z\text{-}PhCH{=}C(NHCOMe)COOMe} + H_2 \longrightarrow \underset{\mathbf{14}}{(S)\text{-}(+)\text{-}PhCH_2CH(NHCOMe)COOMe} \quad (5)$$

Although we have already shown [2] that the application of dirhodium catalysts **9b** and **9c**, in which the chiral elements are incorporated in the phosphine ligands, leads to **14** of higher optical purity (up to 97% *ee*), the present study gives us an overview on the various experimental factors that affect the yield and the enantioselectivity.

Representative results of hydrogenation of **13** by **5a, 5b, 8a, 8b** and **9a** are summarized in Table 6.

Table 6 reveals that structural factors of the catalyst, the nature of the medium, the reaction time and temperature, and the hydrogen pressure substantially affect both the efficiency and the enantioselectivity.

Experiments 1 and 2 show that the myrtanyl complex **5a** fails to induce asymmetric induction in **14**. On the other hand, **5b** leads under certain conditions to products with considerable optical activity (see expts. 3–6). The difference between the enantioselectivity of **5a** and **5b** is particularly remarkable because **5a** is a single optical isomer while **5b** exists in the crystal as a pair of epimers (*vide supra*). We

TABLE 6. Hydrogenation of methyl α-acetamidocinnamate (**13**) to (*S*)-(+)-*N*-acetylphenylalanine methyl ester (**14**) in the presence of several homogeneous and immobilized dirhodium catalysts[a]

Expt.	Catalyst	Reaction time (h)	Solvent (ml)		Yield (%)	*ee* (%)
			MeOH	PhH		
1	**5a**	20[b]	1	2	18	0
2	**5a**	0.5	0	3	98	0
3	**5b**	20[b]	1	2	50	20
4	**5b**	0.5	0	3	29	50
5	**5b**	1	0	3	33	45
6	**5b**	2	0	3	38	38
7	**5b**	20[b]	0	3	98	0
8	**8a**[c]	20	1	2	15[d-f]	7[d-f]
9	**8a**[c, g]	20	1	2	58[d, h]	8[d, h]
10	**8a**[c, i]	20	1	2	4	10
11	**8a**[j]	20	1	2	40–98[k]	0
12	**8a**[c]	20[l]	1	1	68	0
13	**8a**[c]	0.5	0	3	8	0
14	**8a**[c]	3	0	3	23	0
15	**8a**[c]	20	0	3	42	0
16	**8a**[c]	20[b]	3	0	28	1
17	**8a**[c]	20	2	1	27	1
18	**8b**[c]	20	1	2	29[m]	5[m]
19	**8b**[c]	20	0	3	51[n]	1[n]
20	**9a**[g]	20	1	2	2–25[o]	0–4[o]
21	**9a**	20	1	2	11[p]	42[p]

[a]Except when otherwise stated, 0.156 mmol of **13** was hydrogenated at 120±0.1 °C under H_2 pressure of 100 psi in the presence of 7.8×10^{-3} mequiv. of the Rh catalyst. All results are the average of at least three experiments in which the yields and *ee* values did not differ by more than ±2%. [b]Partial decomposition of the catalyst to metallic rhodium was noticed. [c]Support: 2% divinylbenzene crosslinked polystyrene. [d]In 5 consecutive runs the same yields and *ee* values were recorded. [e]At 50 psi H_2 both the yield and *ee* were 8%. [f]Upon raising the H_2 pressure up to 750 psi the yield did not change but the optical activity raised gradually to 13% *ee*. [g]Amount of catalyst 1.56×10^{-2} mequiv. (molar ratio Rh:substrate 1:10). [h]At 50 psi H_2 the yield and *ee* values were 35 and 9%, respectively. [i]Amount of catalyst 3.9×10^{-3} mequiv. (Rh:substrate 1:40). [j]Support: 20% divinylbenzene-crosslinked polystyrene [k]1st run 40%; 2nd run 62%; 3rd run 94%. All following runs 98%. [l]At 160 °C. [m]Gradual decrease in yield and optical purity was noted in consecutive runs. [n]Neither the yield nor the optical purity changed in consecutive runs. [o]The respective yields and *ee* values were 2 and 0 in the 1st run, 5 and 1 in the 2nd run, 25 and 4 in the 3rd and 4th runs. [p]Results of the 5th run. Significant deterioration of the catalyst took place in the following runs.

assume that this difference is associated in part with the fact that the chiral centers in **5a** are more remote from the metal atoms than in **5b**. In **5a**, for example, the distances Rh1–C2 and Rh2–C2 are 4.28 and 4.85 Å, respectively, while in **5b** the distances between Rh1 and Rh2 and the nearest chiral carbon atoms are only 3.36 and 3.37 Å. Thus, owing to the large distance in the former complex the metal cannot differentiate between the two enantiotopic faces of the approaching prochiral substrate.

As in the catalytic hydrogenation of **13** by **9c** [2], the nature of the solvent affects both the yield and the optical purity. Reactions in aromatic solvents, such as benzene, were found to proceed much faster than in alcohol containing media. Thus, for example, **13** has been hydrogenated by **5a** in pure PhH in almost quantitative yield within 30 min, while the yield in a 1:2 mixture of MeOH–PhH was only 18% after 20 h. In the **5b** catalyzed reaction the use of alcohol-free PhH caused significant retardation in the enantioselectivity as compared with PhH–MeOH mixtures (compare, for example, expt. 3 with expt. 7). Reactions that were conducted in pure MeOH gave products of highest optical purity, but rapid decomposition of the catalyst into metallic rhodium rendered this solvent impractical. The improvement in enantioselectivity by MeOH may be associated with the following reasons: (i) the polar solvent stabilizes the diastereometric transition states, and thus allows preferential attack on one over the other [13], (ii) the MeOH decreases not only the rate of hydrogenation, but also that of the undesired racemization of the optically active product. We have already shown by mass spectral studies [14] that optically active **14** which is formed initially during **9d**-catalyzed hydrogenation of **13** undergoes a slow

catalytic transformation to the racemate. Furthermore, we found now that (*S*)-(+)-**14** undergoes racemization in PhH, when heated under reflux with catalytic amounts of either **5a** or **5b** in the presence of 10% of **13** (in the absence of the unsaturated starting ester no racemization was observed). The relatively fast racemization in PhH is also reflected by expts. 4–7 in Table 6. In these experiments the loss in optical activity could be slowed down by addition of MeOH to the reaction mixture.

The attachment of the chiral dirhodium complexes to 'inert' supports strongly affects their catalytic activity. We have already shown that while the hydrogenation of **13** by **9c** gives (*S*)-(+)-**14**, its attachment to silica gel as in **9d** results in the formation of (*R*)-(−)-**14** [2]. The attachment of **5a** and **5b** to 2% divinylbenzene-crosslinked diphenylphosphinated polystyrene resin does not reverse the sign of the product, but it has an opposite effect on the catalytic activity of the two complexes. The myrtanyl compound **5a** which is absolutely non-enantioselective in its homogeneous version is capable of inducing some asymmetry after immobilization (compare expt. 1 with expts. 8 and 9). On the other hand, conversion of **5b** into **8b** results in significant loss in enantioselectivity (compare expt. 3 with expt. 18). Upon replacement of the flexible 2% divinylbenzene-crosslinked polymer of **8a** and **8b** by a rigid 20% divinylbenzene-crosslinked support, the efficiency, in terms of yield increases, but the enantioselectivity is completely lost (expt. 11). The flexible and rigid supported complexes differ also in their mode of activation. While the flexible catalysts reach maximum activity already during the first run, the rigid ones require three to four 20 h cycles before full activation is achieved (see footnote k of Table 6).

The hybrid catalyst **9a** in which the polystyrene resin is part of the thiolato bridge has quite different properties than **8a** and **8b**. It is air sensitive and decomposes after several runs (cf., ref. 1c). Although the resin in **9a** is of the flexible type, four to five runs are required to achieve maximum enantioselectivity. In expt. 21 the product reached 42% in the fifth run but the optical activity dropped sharply in consecutive cycles owing to decomposition of the catalyst.

Supplementary material

Tables of thermal parameters, hydrogen coordinates, complete listings of bond lengths and angles, and observed and calculated structure factors for **5a** and **5b** as well as stereoscopic views of **5a** and of the two isomers of **5b** are available from the authors upon request.

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