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Optically active transition metal complexes. Part 119:[1] New rhodium(I) complexes containing two different types of optically active ligands

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Abstract

The synthesis of novel rhodium(I) complexes containing two different chiral ligands is described. These ligands are on the one hand (−)-diop and on the other hand various optically active pyrroleimines, which derive from 1-phenylethylamine or 1-cyclohexylethylamine with an (R)- or (S)-configuration. The resulting (−)-diop–pyrrolylimine–rhodium(I) complexes are diastereomers and are expected to give different stereoselectivities in enantioselective catalysis (double stereoselection). In addition, the synthesis of novel rhodium(I) complexes containing 1,5-cyclooctadiene and various chiral pyrroleoxazoline ligands is described. All the complexes are used in the enantioselective hydrogenation of ketopantolactone (see following paper).

1. Introduction

Rhodium(I) complexes containing 1,5-cyclooctadiene and bidentate chiral nitrogen ligands, such as (R)- or (S)-configured pyrrolylimines, are well known.[2,3] If a further chiral ligand instead of 1,5-cyclooctadiene, i.e. the C_2-symmetric bidentate chiral phosphine (−)-(R,R)-diop [(4R,5R)-trans-4,5-bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane] is used, a stereochemically interesting situation arises. The combination of (R,R)-diop with the (R)-pyrrolylimine leads to the (RR-R) configured diop–pyrrolylimine–rhodium(I) complex, the S-pyrrolylimine gives the diastereomeric (RR-S) complex. They are formed in synthesis with the correct stereoisomers of the ligands without separation. Used in enantioselective catalysis, one of the diastereomers could turn out to be the matched catalyst, which gives higher enantioselectivity, the other the mismatched catalyst, which gives lower enantioselectivity (double stereoselection).[4] In the present paper, new rhodium(I) complexes containing (−)-diop and (R)-

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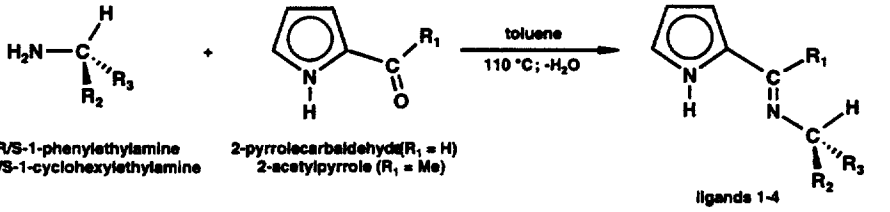
or (S)-pyrrolylaldimines, (R)- or (S)-pyrrolylketimines and (R)- or (S)-pyrrolyloxazolines, respectively, are described. These compounds have been used as catalysts in the enantioselective hydrogenation of ketopantolactone (see following paper).

2. Synthesis and characterization of the ligands and complexes

The optically active pyrroleimines **1–4** for the synthesis of the (−)-diop–pyrroleimine–rhodium(I) complexes **5–8** were prepared by Schiff base condensation of the corresponding aldehyde or ketone with primary chiral amines (Scheme 1).[2] The air-sensitive products **1–4** were distilled under high vacuum. They form pale yellow oils.



	1a	1b	2a	2b	3	4a	4b
R_1	H	H	H	H	H	Me	Me
R_2	Ph	Me	Cyhex	Me	H	Ph	Me
R_3	Me	Ph	Me	Cyhex	Ph	Me	Ph

Scheme 1.

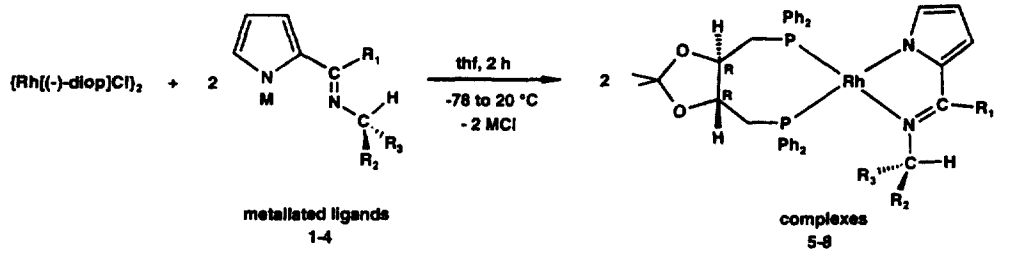
For the synthesis of the rhodium complexes **5–8** containing (−)-diop, and the pyrroleimines, the precursor {Rh[(−)-diop]Cl}$_2$ was used.[5] It was obtained from [Rh(cod)Cl]$_2$ and (−)-diop as described or, alternatively, from [Rh(C_2H_4)$_2$Cl]$_2$ and (−)-diop. The ethylene ligands were easily replaced by the phosphine without recoordination. {Rh[(−)-diop]Cl}$_2$, obtained in this way, could be used without isolation for the subsequent reaction with the sodium or potassium salts of the pyrroleimines.

The pyrroleimines **1–4** were deprotonated with NaH or KO^{t}Bu, respectively, in diethyl ether. The solutions of the salts were added at −78°C to the tetrahydrofuran solution of the [Rh(C_2H_4)$_2$Cl]$_2$/(−)-diop reaction (Scheme 2). The diastereomerically pure complexes **5–8** were chromatographed on silica and recrystallized from methanol or methanol/tetrahydrofuran (**6b**).

An alternative synthesis of the complexes **5–8** started from [Rh(cod)(−)-diop]PF_6.[6–8] The exchange of 1,5-cyclooctadiene for the deprotonated pyrroleimine was only possible in the solvent acetonitrile. The complexes **5–8** were used as catalysts in the asymmetric hydrogenation of ketopantolactone and Z-(α)-N-acetamidocinnamic acid (see following paper).

The new (−)-diop–pyrrolylimine–rhodium(I) complexes were characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. The two phosphorus atoms of each complex form the AB part of an ABX system (8 signals). The P–P coupling constants are between 57.0 and 58.6 Hz and the P–Rh coupling constants are between 173.2 and 176.2 Hz. The chemical shifts are centered between 31.67 and 37.81 ppm.

2D and DEPT NMR experiments allowed a complete assignment of all hydrogen and carbon signals. The protons of the diop methylene groups were diastereotopic and occurred as 4 signals. The same holds for the protons of the diop methyl groups (2 signals). The ortho protons of the diphenylphosphanyl groups



complex	R_1	R_2	R_3	configuration
5a	H	Ph	Me	RR-R
5b	H	Me	Ph	RR-S
6a	H	Cyhex	Me	RR-R
6b	H	Me	Cyhex	RR-S
7	H	H	Ph	RR
8a	Me	Ph	Me	RR-R
8b	Me	Me	Ph	RR-S

Scheme 2.

were detected with a marked low field shift. The signals of the methine groups appeared at δ=3.95 and 4.42 ppm.

An X-ray structure analysis of **6b** proved the planar geometry of the complex (Fig. 1). Trans-effects were visible in the Rh–P and Rh–N bond lengths:[9] short Rh–N bonds are opposite to long Rh–P bonds and vice versa. The phenyl groups form angles of 20 to 30° with the P1–Rh1–P2 plane. Only phenyl C1–C6 is found in an axial position (angle 80.1°).

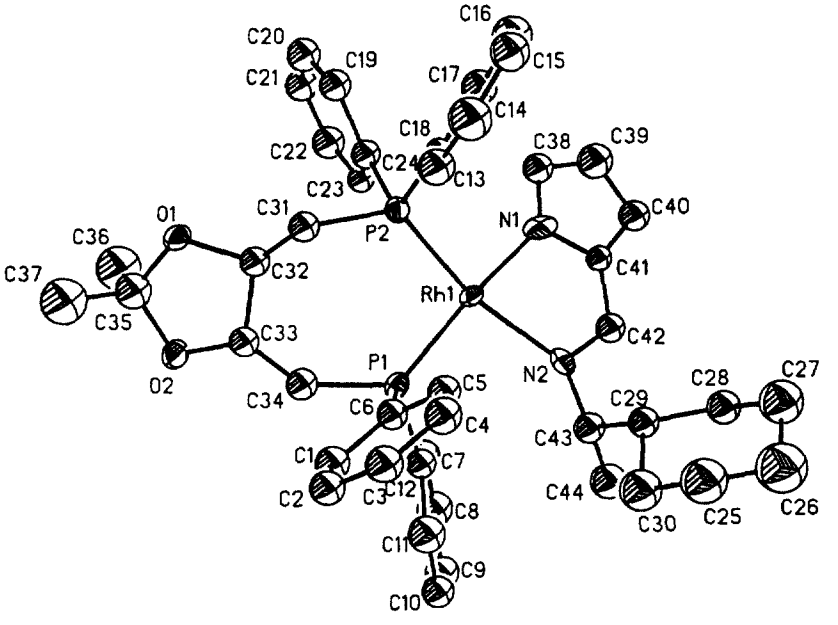
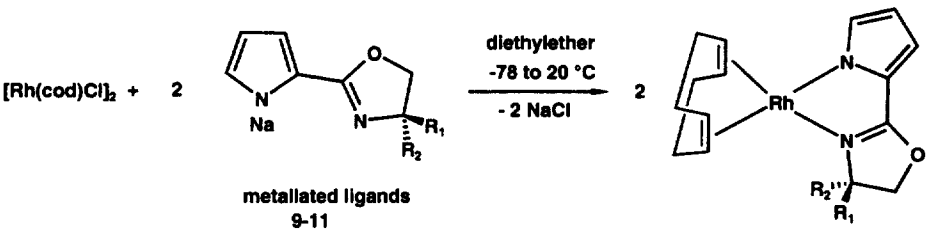


Figure 1. Molecular structure of **6b** (ORTEP plot). Selected bond lengths [Å] and angles [°]: Rh1–P1 2.214, Rh1–P2 2.209, Rh1–N1 2.101, Rh1–N2 2.131, N1–Rh1–N2 78.6, N2–Rh1–P1 95.3, P1–Rh1–P2 95.3, P2–Rh1–N1 93.3

New 1,5-cod–pyrroleoxazoline–rhodium(I) complexes were synthesized with methyl, ethyl or benzyl substituents in the 4-position of the oxazoline ring (Scheme 3).[10]



ligand	9a	9b	10a	10b	11
complex	12a	12b	13a	13b	14
R_1	Me	H	Et	H	H
R_2	H	Me	H	Et	CH_2Ph

Scheme 3.

The chiral pyrroleoxazolines **9–11** were deprotonated with NaH in diethyl ether. The reaction with $[Rh(cod)Cl]_2$ in tetrahydrofuran gave the complexes **12–14**, which were chromatographed on silica. The air-stable products crystallized from toluene/pentane as pale yellow needles. A complete assignment of all hydrogen and carbon signals was possible on the basis of 2D and DEPT NMR experiments. The protons of the methylene and methine groups of the oxazoline system formed an ABM system complicated by additional coupling with the oxazoline substituents.

3. Experimental

All the ligands and complexes were prepared under an atmosphere of dried argon. Solvents were dried and distilled prior to use, according to standard procedures. ^1H-, ^{13}C- and ^{31}P-NMR spectra: Bruker AC 250 and ARX 400 spectrometer [250 or 400 MHz (^1H), 63 or 100 MHz (^{13}C) and 162 MHz (^{31}P)], chemical shifts in ppm downfield from TMS or 85% H_3PO_4 or solvent, respectively. FD mass spectra: Finnigan MAT 95 instrument. Optical rotations: Perkin–Elmer 241 polarimeter. Microanalyses: Microanalytical Laboratory of the University of Regensburg. $[Rh(C_2H_4)_2Cl]_2$ was prepared by the method of Cramer.[11]

3.1. General procedure for the synthesis of the ligands 2a,b; 3[2]

2-Formylpyrrole (4.76 g, 50 mmol) and (R)- and (S)-1-cyclohexylethylamine (7.0 g, 55 mmol) or benzylamine (5.89 g, 55 mmol) were dissolved in benzene. After addition of Na_2SO_4 (10 g) the mixture was refluxed for 3 h. Then the solution was filtered and concentrated. The product was distilled in high vacuum.

3.1.1. (−)-2-N-[(R)-1-Cyclohexylethyl]pyrrolecarbaldimine 2a

A pale yellow oil. Yield 8.36 g (82%), bp 75°C/10^{-4} torr. ^1H NMR ($CDCl_3$): δ 8.01 (s, 1H, CH=N), 6.81 (m, 1H, py-5H), 6.43 (m, 1H, py-3H), 6.21 (m, 1H, py-4H), 2.94 (m, 1H, C*H*CH_3), 0.78–1.79 (br, 11H, CH_{cyhex}), 1.17 (d, ^3J=6.4 Hz, 3H, CHC*H*$_3$). MS (EI): *m/z* 204 (M^+). $[\alpha]_{589}=-131$ (c 1, toluene). $C_{13}H_{20}N_2$ (204.32): calcd C 76.42, H 9.87, N 13.71, found C 76.41, H 10.01, N 13.68%.

*3.1.2. (+)-2-N-[(S)-1-Cyclohexylethyl]pyrrolecarbaldimine **2b***

Yield 7.81 g (77%), b.p. 75°C/10^{-4} torr. $[\alpha]_{589}$=+127 (c 1, toluene). $C_{13}H_{20}N_2$ (204.32): calcd C 76.42, H 9.87, N 13.71, found C 76.37, H 10.04, N 13.65%.

*3.1.3. 2-N-(Benzyl)pyrrolecarbaldimine **3***

After distillation in high vacuum, the product solidified to a colourless powder. Yield 6.30 g (68%), mp 102°C. ^{1}H NMR ($CDCl_3$): δ 10.10–9.30 (br, 1H, NH), 8.16 (m, 1H, CH=N), 7.42–7.20 (m, 5H, $H_{arom.}$), 6.66 (m, 1H, py-5H), 6.50 (m, 1H, py-3H), 6.19 (m, 1H, py-4H), 4.7 (s, 2H, CH_2). MS (EI): *m/z* 184 (M^+). $C_{12}H_{12}N_2$ (184.24): calcd C 78.23, H 6.56, N 15.20, found C 78.32, H 6.74, N 14.97%.

*3.2. General procedure for the synthesis of the (−)-diop–pyrrolylaldimine–rhodium(I) complexes **5**, **6**, **7***

To a solution of $[Rh(C_2H_4)_2Cl]_2$ (58.3 mg, 0.15 mmol) in 20 ml of tetrahydrofuran, (−)-diop [(4R,5R)-trans-4,5-bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane] (149.6 mg, 0.30 mmol), dissolved in 20 ml of tetrahydrofuran, was added in 30 min at 20°C. The solution changed its colour from red to orange.

The solution of the pyrrolealdimine (0.45 mmol) in 60 ml of diethyl ether was stirred with an excess of NaH (24.0 mg, 1.0 mmol) for 1 h at 20°C and then filtered through glass wool into a dropping funnel. The sodium salt of the pyrrolealdimine was added in 30–60 min to the orange solution of the $[Rh(C_2H_4)_2Cl]_2$/(−)-diop reaction, which had been cooled to −78°C. After 2 h the solvents were removed. The orange product was dissolved in 3 ml of toluene:acetone (15:1) and chromatographed on silica. After removal of the solvents the residue crystallized from methanol as a microcrystalline orange powder. The (S)-configured cyclohexyl derivative formed orange crystals in methanol:tetrahydrofuran (10:1), which were suitable for an X-ray structure analysis.

*3.2.1. (+)-(4R,5R)-trans-4,5-Bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane{2-N-[(R)-1-phenylethyl]pyrrolylcarbaldimine}rhodium(I) **5a***

The ligand (−)-2-N-[(R)-1-phenylethyl]pyrrolecarbaldimine **1a** (89.2 mg, 0.45 mmol) was used. Yield 131.8 mg (55%), mp 123–133°C. ^{1}H NMR (C_6D_6): δ 8.11 (m, 4H, H_{ortho} in PPh_2), 7.93, 7.85 (2m, 4H, H_{ortho} in PPh_2), 7.75 (dd, J=6.5, 2.2 Hz, 1H, CH=N), 7.23–6.72 (m, 18H, $H_{arom.}$, py-5H), 6.54 (s, 1H, py-3H), 6.29 (m, 1H, py-4H), 4.42, 3.95 (2m, 2H, CH), 4.10 (m, 1H, C*H*CH_3), 3.10, 2.87 (2m, 2H, CH_2), 1.90 (ddd, ^{2}J=13.4 Hz, ^{3}J=9.4 Hz, ^{2}J(CH–P)=2.4 Hz, 1H, CH_2), 1.75 (ddd, ^{2}J=13.4 Hz, ^{3}J=10.1 Hz, ^{2}J(CH–P)=2.7 Hz, 1H, CH_2), 1.25, 1.22 (2s, 6H, $C(CH_3)_2$), 1.00 (d, ^{3}J=6.6 Hz, 3H, CHCH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 159.17 (s, CH=N), 146.10 (s, C_{ipso} in $CHCH_3Ph$), 142.90 (d, J=2.1 Hz, py-2C), 139.74 (m, py-3C), 139.01, 138.56, 137.05, 136.70 (dddd, J=36.4, J=39.0, 37.7, 39.0 Hz, C_{ipso} in PPh_2), 134,20, 134.03, 133.48, 132.01 (dddd, J=11.9, 11.9, 12.7, 11.4 Hz, C_{ortho} in PPh_2), 129.68, 129.56, 129.51, 129.13 (dddd, J=2.1, 2.0, 2.1, 1.9 Hz, $C_{arom.}$ in PPh_2), 128.34–127.68 (m, $C_{arom.}$), 116.43 (d, J=1.3 Hz, py-5C), 111.37 (d, J=3.8 Hz, py-4C), 108.01 (s, *C*$(CH_3)_2$), 78.85, 78.76 (dd, J=2.5, 2.2 Hz, CH), 61.66 (s, *C*HCH_3), 34.13, 33.83, 31.09, 30.85 (4m, CH_2), 27.33, 27.19 (2s, C(*C*$H_3)_2$), 22.12 (s, CH*C*H_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 35.03, 30.88 (ddd, ^{1}J(P1–Rh)=178.5 Hz, ^{1}J(P2–Rh)=174.7 Hz, ^{2}J(P1–P2)=57.2 Hz, 2P). MS (FD, toluene): m/e=798 (M^+). $[\alpha]_{589}$=+64 (c 3.9, toluene).

*3.2.2. (−)-(4R,5R)-trans-4,5-Bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane{2-N-[(S)-1-phenylethyl]pyrrolylcarbaldimine}rhodium(I) **5b***

The ligand (+)-2-N-[(S)-1-phenylethyl]pyrrolecarbaldimine **1b** (89.2 mg, 0.45 mmol) was used. Yield 151.0 mg (63%), m.p. 129–139°C. ^{1}H NMR (C_6D_6): δ 8.36, 7.98 (2m, 4H, H_{ortho} in PPh_2), 8.08 (m, 4H,

H_{ortho} in PPh_2), 7.65 (m, 1H, CH=N), 7.18–6.82 (m, 17H, $H_{arom.}$), 6.72 (m, 1H, py-5H), 6.50 (s, 1H, py-3H), 6.23 (m, 1H, py-4H), 4.26 (q, ^{3}J=6.7 Hz, 1H, C*H*CH_3), 3.97, 3.68 (2m, 2H, CH), 3.03, 2.87, 2.30, 2.01 (4m, 4H, CH_2), 1.16, 1.14 (2s, 6H, $C(CH_3)_2$), 0.79 (d, ^{3}J=6.7 Hz, 3H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 159.73 (s, CH=N), 145.71 (s, C_{ipso} in $CHCH_3Ph$), 142.90 (d, J=2.1 Hz, py-2C), 141.16, 139.14, 135.74 (ddd, J=37.5, 42.8, 33.1 Hz, C_{ipso} in PPh_2), 139.42 (d, J=2.4 Hz, py-3C), 135.74, 135.31, 133.13, 131.94 (dddd, J=12.8, 13.9, 11.2, 10.8 Hz, C_{ortho} in PPh_2), 130.40, 130.26, 129.13, 129.08 (dddd, J=1.8 Hz, $C_{arom.}$ in PPh_2), 128.71–126.90 (m, $C_{arom.}$ in PPh_2, $CHCH_3Ph$, solvent), 116.61 (s, py-5C), 111.26 (d, J=4.0 Hz, py-4C), 108.42 (s, *C*$(CH_3)_2$), 78.74, 77.54 (2d, J=8.8, 10.0 Hz, CH), 62.21 (m, *C*HCH_3), 35.94–35.10 (br, CH_2), 27.14, 27.11 (2s, C(*C*$H_3)_2$), 21.59 (s, CH*C*H_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 36.78, 35.72 (ddd, ^{1}J(P1–Rh)=176.2 Hz, ^{1}J(P2–Rh)=174.7 Hz, ^{2}J(P1–P2)=57.2 Hz, 2P). MS (FD, toluene): m/e=798 (M^+). $[\alpha]_{589}$=−13 (c 1.98, toluene).

*3.2.3. (−)-(4R,5R)-trans-4,5-Bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane{2-N-[(R)-1-cyclohexylethyl]pyrrolylcarbaldimine}rhodium(I) **6a***

The ligand (−)-2-N-[(R)-1-cyclohexylethyl]pyrrolecarbaldimine **2a** (91.9 mg, 0.45 mmol) was used. Yield 123.1 mg (51%), mp 128–138°C. ^{1}H NMR (C_6D_6): δ 8.11, 8.03, 7.90, 7.79 (4m, 8H, H_{ortho}), 7.67 (dd, ^{4}J(P–CH)=6.8 Hz, J=2.2 Hz, 1H, CH=N), 7.16–6.62 (m, 13H, $H_{arom.}$, py-5H), 6.57 (s, 1H, py-3H), 6.29 (m, 1H, py-4H), 5.12, 4.12 (2m, 2H, CH), 3.50, 2.84, 2.51 (3m, 3H, CH_2), 2.90 (m, 1H, C*H*CH_3), 2.06 (m, 3H, CH_2, CH_2 (cyhex)), 1.90–1.62 (m, 5H, CH_2 (cyhex), CH_2), 1.37, 1.35 (2s, 6H, $C(CH_3)_2$), 1.43–0.74 (m, 4H, CH_2 (cyhex)), 0.48 (d, ^{3}J=6.6 Hz, 3H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 157.38 (s, CH=N), 143.18 (d, J=2.2 Hz, py-2C), 139.89, 139.51, 137.52, 135.63 (dddd, J=29.6, 33.2, 40.3, 36.8 Hz, C_{ipso}), 139.30 (m, py-3C), 134.44, 133.74, 132.95, 131.73 (dddd, J=12.1, 12.1, 12.6, 11.2 Hz, C_{ortho}), 129.51 (m, $C_{arom.}$), 129.23, 129.06, 128.26, 128.16, 127.90, 127.66 (dddddd, J=1.8, 1.8, 9.0, 9.4, 9.9, 9.4 Hz, $C_{arom.}$), 115.35 (s, py-5C), 111.01 (d, J=4.0 Hz, py-4C), 108.03 (s, *C*$(CH_3)_2$), 79.42 (dd, J=8.8, 2.7 Hz, CH), 76.77 (dd, J=14.4, 4.0 Hz, CH), 63.96 (d, J=3.1 Hz, *C*HCH_3), 45.69 (s, C_1-cyhex), 33.65 (dd, J=31.1, 4.8 Hz, CH_2), 31.42, 28.12, 27.16, 27.04, 27.02 (5s, CH_2 (cyhex)), 29.67 (d, J=19.8 Hz, CH_2), 27.42, 27.19 (2s, C(*C*$H_3)_2$), 15.50 (s, CH*C*H_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 34.90, 28.44 (ddd, ^{1}J(P1–Rh)=178.5 Hz, ^{1}J(P2–Rh)=176.2 Hz, ^{2}J(P1–P2)=57.0 Hz, 2P). MS (FD, toluene): m/e=804 (M^+). $[\alpha]_{589}$=−59 (c 2.28, toluene).

*3.2.4. (+)-(4R,5R)-trans-4,5-Bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane{2-N-[(S)-1-cyclohexylethyl]pyrrolylcarbaldimine}rhodium(I) **6b***

The ligand (+)-2-N-[(S)-1-cyclohexylethyl]pyrrolecarbaldimine **2b** (91.9 mg, 0.45 mmol) was used. Yield 115.9 mg (48%), mp 133–143°C. ^{1}H NMR (C_6D_6): δ 8.31 (m, 4H, H_{ortho}), 8.18, 8.03 (2m, 4H, H_{ortho}), 7.57 (dd, ^{4}J(P–CH)=6.6 Hz, J=2.0 Hz, 1H, CH=N), 7.19–6.92 (m, 12H, $H_{arom.}$), 6.77 (m, 1H, py-5H), 6.42 (s, 1H, py-3H), 6.25 (d, J=1.7 Hz, py-4H), 3.87, 3.67 (2m, 2H, C*H*CH_2), 3.00 (m, 2H, CH_2, C*H*CH_3), 2.89 (m, 1H, CH_2), 2.32 (dd, ^{3}J=14.2 Hz, ^{1}J=11.2 Hz, 1H, CH_2), 2.11 (m, 1H, CH_2), 1.64–0.70 (m, 11H, CH (cyhex), CH_2 (cyhex)), 1.15, 1.13 (2s, 6H, $C(CH_3)_2$), 0.22 (d, ^{3}J=6.8 Hz, 3H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (toluene-d_8): δ 157.66 (s, CH=N), 143.11 (d, J=2.2 Hz, py-2C), 141.30, 139.54, 135.51, 133.50 (4d, J=39.2, 43.2, 26.4, 30.0 Hz, C_{ipso}), 138.63 (d, J=2.4 Hz, py-4C), 135.87, 133.26, 131.95 (3d, J=13.2, 11.3, 10.7 Hz, C_{ortho}), 130.65, 130.37, 129.12 (3d, J=1.8, 1.8, 7.3 Hz, $C_{arom.}$), 128.84–124.86 (m, $C_{arom.}$), 115.57 (s, py-5C), 110.66 (d, J=3.9 Hz, py-3C), 108.35 (s, *C*$(CH_3)_2$), 78.74, 77.65 (2d, J=10.0, 9.5 Hz, CH), 64.03 (s, *C*HCH_3), 44.69 (s, C_1-cyhex), 37.01, 35.24 (2m, CH_2), 31.14, 27.56, 27.20, 27.07, 26.77 (5s, CH_2 (cyhex)), 27.09 (s, C(*C*$H_3)_2$), 15.28 (s, CH*C*H_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 37.26, 36.12 (ddd, ^{1}J(P1–Rh)=177.0 Hz, ^{1}J(P2–Rh)=175.5 Hz, ^{2}J(P1–P2)=58.0 Hz, 2P). MS (FD, toluene): m/e=804 (M^+). $[\alpha]_{589}$=+88 (c 1.09, toluene).

*3.2.5. X-Ray structure analysis of **6b***

$C_{44}H_{51}N_2O_2P_2Rh$ (804.76); crystal dimensions 0.05×0.15×0.75 mm^3; crystal system rhombic; space group D_2^4, $P2_12_12_1$, (19); Z=4; unit cell dimensions: a=11.75(1), b=12.56(1), c=28.90(2) Å, α=β=γ=90°, V=4265 $Å^3$, d_{calc}=1.25 g/cm^3, μ(Mo-K_α)=0.5 mm^{-1}, scan: θ–2θ; total no. of reflections 4859, reflections with I>2.5×σ(I): 2724; F(000)=1680; R=8.6%, Rw=7.1%. The structure was solved by direct methods using the SHELXTL PLUS release 4.11/V program system. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository CSD number 408885.

3.2.6. (+)-(4R,5R)-trans-4,5-Bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane[2-N-(benzyl)pyrrolylcarbaldimine]rhodium(I) 7

The ligand 2-N-(benzyl)pyrrolecarbaldimine **4** (82.9 mg, 0.45 mmol) was used. Yield 98.9 mg (42%), mp 123–133°C. ^{1}H NMR (C_6D_6): δ 8.19, 8.09 (2m, 4H, H_{ortho} in PPh_2), 7.85 (m, 4H, H_{ortho} in PPh_2), 7.35 (d, ^{4}J(P–CH)=5.5 Hz, 1H, CH=N), 7.30–6.71 (m, 18H, $H_{arom.}$, py-5H), 6.52 (s, 1H, py-3H), 6.24 (m, 1H, py-4H), 4.35, 3.90 (2m, 2H, CH), 3.79 (d, ^{2}J=15.5 Hz, 1H, CH_2Ph), 3.55 (d, ^{2}J=15.5 Hz, 1H, CH_2Ph), 3.03, 2.74 (2m, 2H, CH_2), 1.82 (m, 2H, CH_2), 1.24, 1.23 (2s, 6H, $C(CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 163.39 (s, CH=N), 141.96 (d, J=2.1 Hz, py-2C), 141.19 (s, C_{ipso} in CH_2Ph), 140.16, 138.15, 136.75, 136.12 (dddd, J=37.3, 37.7, 40.3, 36.4 Hz, C_{ipso} in PPh_2), 139.88 (m, py-3C), 134.33, 134.19, 133.70, 131.67 (dddd, J=12.6, 12.1, 13.0, 11.2 Hz, C_{ortho} in PPh_2), 129.84, 129.63, 129.47, 129.20 (dddd, J=2.2, 1.8, 1.8, 1.8 Hz, $C_{arom.}$ in PPh_2), 128.43–126.85 (m, $C_{arom.}$ in PPh_2, $C_{arom.}$ in CH_2Ph), 116.39 (s, py-5C), 111.34 (d, J=3.6 Hz, py-4C), 108.01 (s, $C(CH_3)_2$), 79.03, 78.94 (dd, J=2.2 Hz, CH), 61.68 (s, CH_2Ph), 33.98 (dd, J=30.6, 4.5 Hz, CH_2), 30.90 (d, J=22.7 Hz, CH_2), 27.30, 27.24 (2s, $C(CH_3)_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 36.62, 30.51 (ddd, ^{1}J(P1–Rh)=178.5 Hz, ^{1}J(P2–Rh)=173.2 Hz, ^{2}J(P1–P2)=57.2 Hz, 2P). MS (FD, toluene): m/e=784 (M^+). $[\alpha]_{589}$=+8 (c 3.21, toluene).

3.3. General procedure for the synthesis of the (–)-diop–pyrrolylketimine–rhodium(I) complexes 8

To the solution of pyrroleketimine (95.5 mg, 0.45 mmol) in 60 ml of diethyl ether, KO^{t}Bu (50.5 mg, 0.45 mmol) was added. The mixture was stirred for 1 h at 20°C. The precursor {Rh[(–)-diop]Cl}$_2$, produced as described from $[Rh(C_2H_4)_2Cl]_2$ and (–)-diop, was added in 60 min at –78°C. After 2 h of stirring with slow warming up to 20°C, the solvents were removed. The residue was dissolved in 3 ml of toluene:acetone (15:1) and treated as described for the pyrrolylaldimine complexes. The products could be recrystallized from methanol at –30°C.

3.3.1. (+)-(4R,5R)-trans-4,5-Bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane{2-N-[(R)-1-phenylethyl]pyrrolylmethylketimine}rhodium(I) 8a

The ligand (–)-2-N-[(R)-1-phenylethyl]pyrrolemethylketimine **4a** was used. Yield 109.7 mg (45%), mp 133–143°C. ^{1}H NMR (C_6D_6): δ 8.35, 7.77 (2m, 4H, H_{ortho} in PPh_2), 8.18 (m, 4H, H_{ortho} in PPh_2), 7.15–6.76 (m, 17H, $H_{arom.}$), 6.55 (d, ^{3}J=3.6 Hz, 1H, py-5H), 6.51 (s, 1H, py-3H), 6.15 (m, 1H, py-4H), 4.97 (m, 1H, $CHCH_3$), 4.23, 3.80 (2m, 2H, CH), 3.06, 2.92 (2m, 2H, CH_2), 2.21–2.07 (m, 2 H, CH_2), 1.65 (s, 3H, H_3CC=N), 1.19, 1.18 (2s, 6H, $C(CH_3)_2$), 1.12 (d, ^{3}J=7.0 Hz, 3H, $CHCH_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 170.95 (s, H_3CC=N), 145.84 (d, J=1.7 Hz, py-2C), 145.47 (s, C_{ipso} in $CHCH_3Ph$), 139.13 (dd, J=38.5, 1.7 Hz, C_{ipso}), 138.00 (d, J=34.3 Hz, C_{ipso}), 137.90 (m, py-3C), 136.65 (dd, J=34.5, 1.2 Hz, C_{ipso}), 135.61 (dd, J=31.4, 1.4 Hz, C_{ipso}), 135.18, 134.75, 133.16, 132.28 (dddd, J=11.9, 13.1, 11.0, 10.6 Hz, C_{ortho} in PPh_2), 130.15, 130.09, 129.23, 128.88 (dddd, J=1.7 Hz, $C_{arom.}$ in PPh_2), 128.33–127.67

(m, $C_{arom.}$ in PPh_2, $C_{arom.}$ in $CHCH_3Ph$), 114.61 (s, py-5C), 109.68 (d, J=3.8 Hz, py-4C), 108.36 (s, $C(CH_3)_2$), 78.42 (dd, J=9.7, 1.7 Hz, CH), 77.78 (dd, J=10.7, 2.5 Hz, CH), 62.93 (d, J=6.4 Hz, $CHCH_3$), 35.05 (m, CH_2), 27.19, 27.12 (2s, $C(CH_3)_2$), 19.97 (s, $CHCH_3$), 19.19 (m, H_3CC=N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 36.10, 35.37 (ddd, ^1J(P1–Rh)=177.8 Hz, ^1J(P2–Rh)=173.2 Hz, ^2J(P1–P2)=58.0 Hz, 2P). MS (FD, toluene): m/e=812 (M^+). $[\alpha]_{589}$=+174 (c 2.4, toluene).

3.3.2. (−)-(4R,5R)-trans-4,5-bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane{2-N-[(S)-1-phenylethyl]pyrrolylmethylketimine}rhodium(I) 8b

The ligand (+)-2-N-[(S)-1-phenylethyl]pyrrolemethylketimine **4b** was used. Yield 97.5 mg (40%), mp 140–150°C. ^1H NMR (C_6D_6): δ 8.46 (m, 2H, H_{ortho} in PPh_2), 8.13 (m, 6H, H_{ortho} in PPh_2), 7.37 (m, 2H, $H_{arom.}$), 7.20–6.83 (m, 15H, $H_{arom.}$), 6.65 (m, 2H, py-5H, py-3H), 6.16 (m, 1H, py-4H), 4.86 (m, 1H, $CHCH_3$), 3.79, 3.56 (2m, 2H, CH), 2.97 (m, 2H, CH_2), 2.25, 2.06 (2m, 2H, CH_2), 1.67 (s, 3H, H_3CC=N), 1.12, 1.10 (2s, 6H, $C(CH_3)_2$), 0.64 (d, ^3J=7.0 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 170.86 (s, H_3CC=N), 145.93 (s, C_{ipso} in $CHCH_3Ph$), 145.48 (d, J=1.8, py-2C), 141.40, 140.04, 135.39, 131.65 (4d, J=35.9, 43.6, 30.5, 28.3 Hz, C_{ipso}), 140.26, 139.82, 129.09, 128.90 (4d, J=1.4, 1.8, 1.8, 1.8 Hz, $C_{arom.}$), 137.66 (m, py-3C), 136.08, 135.77, 132.55, 132.16 (dddd, J=13.0, 14.8, 10.3, 10.8 Hz, C_{ortho}), 130.61 (s, $C_{arom.}$), 128.46–125.86 (m, $C_{arom.}$, solvent), 115.00 (s, py-5C), 109.63 (d, J=3.6 Hz, py-4C), 108.45 (s, $C(CH_3)_2$), 78.68, 77.52 (dd, J=7.6, 9.9 Hz, CH), 63.34 (d, J=6.7 Hz, $CHCH_3$), 37.37, 35.85 (2m, CH_2), 27.19, 27.17 (2s, $C(CH_3)_2$), 20.00 (s, $CHCH_3$), 19.21 (m, H_3CC=N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 38.25, 37.38 (ddd, ^1J(P1–Rh)=176.3 Hz, ^1J(P2–Rh)=174.4 Hz, ^2J(P1–P2)=58.6 Hz, 2P). MS (FD, toluene): m/e=812 (M^+). $[\alpha]_{589}$=−19 (c 1.5, toluene).

3.4. General procedure for the synthesis of the 1,5-cyclooctadiene–pyrrolyloxazoline–rhodium(I) complexes 12–14

The solution of the pyrroleoxazoline[10] (0.80 mmol) in 100 ml of diethyl ether was stirred with an excess of sodium hydride (60.0 mg, 2.5 mmol) for 30 min at 20°C, filtered through glass wool and cooled to −78°C. $[Rh(cod)Cl]_2$ (155.6 mg, 0.40 mmol) was dissolved in 20 ml of tetrahydrofuran. After cooling to −78°C, both solutions were combined. The colour changed from orange to pale yellow. After slowly warming up to 20°C the solvents were removed, the residue was dissolved in 3 ml of toluene and chromatographed on silica. The product crystallized in pale yellow needles from toluene:pentane (1:1).

3.4.1. (−)-(η⁴-1,5-Cyclooctadiene){2-[(4R)-4,5-dihydro-4-methyl]pyrrolyloxazol}rhodium(I) 12a

The ligand (4R)-(+)-4,5-dihydro-2-(2-pyrrolyl)-4-methyloxazol **9a** (119.7 mg, 0.80 mmol) was used. Yield 216.2 mg (75%), mp 179.5°C. ^1H NMR (C_6D_6): δ 6.98 (dd, J=3.6, 1.1 Hz, 1H, py-3H), 6.79 (bs, 1H, py-5H), 6.49 (m, 1H, py-4H), 4.54 (m, 2H, CH (cod)), 4.21, 3.97 (2m, 2H, CH (cod)), 3.64 (dd, ^2J=8.2 Hz, ^3J=8.7 Hz, 1H, ox-CH_2), 3.23 (dd, ^2J=8.2 Hz, ^3J=6.4 Hz, 1H, ox-CH_2), 3.14 (4q, ^3J=^3J=6.4 Hz, ^3J=8.7 Hz, 1H, ox-CH), 2.44–2.32, 2.23–2.01, 1.86–1.75, 1.61–1.42 (4m, 8H, CH_2 (cod)), 0.57 (d, ^3J=6.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 171.74 (d, ^2J(Rh–C)=1.3 Hz, C=N), 132.52 (d, ^2J(Rh–C)=2.5 Hz, py-5C), 127.10 (bs, py-2C), 113.43 (d, ^3J(Rh–C)=1.3 Hz, py-3C), 110.74 (d, ^3J(Rh–C)=1.3 Hz, py-4C), 78.31, 76.51, 76.50, 75.97 (dddd, ^1J(Rh–C)=12.3, 11.9, 13.0, 13.6 Hz, CH (cod)), 76.71 (d, ^3J(Rh–C)=0.8 Hz, ox-CH_2), 56.91 (d, ^3J(Rh–C)=2.5 Hz, ox-CH), 32.31, 31.41, 30.78, 29.53 (4s, CH_2 (cod)), 21.10 (s, CH_3). MS (FD, THF): 360.1 (M^+). $[\alpha]_\lambda$=−107 (589 nm), −112 (578 nm), −124 (546 nm) (c 1.50, toluene). $C_{16}H_{21}N_2ORh$ (360.29): calcd C 53.34, H 5.87, N 7.78, found C 52.90, H 6.03, N 7.71%.

3.4.2. (+)-(η⁴-1,5-Cyclooctadiene){2-[(4S)-4,5-dihydro-4-methyl]pyrrolyloxazol}rhodium(I) ***12b***

The ligand (4S)-(−)-4,5-dihydro-2-(2-pyrrolyl)-4-methyloxazol **9b** (119.7 mg, 0.80 mmol) was used. Yield 181.6 mg (63%), mp 179.5°C. $[\alpha]_\lambda$=+108 (589 nm), +113 (578 nm), +125 (546 nm) (c 1.55, toluene). $C_{16}H_{21}N_2ORh$ (360.29): calcd C 53.34, H 5.87, N 7.78, found C 53.20, H 6.00, N 7.75%.

3.4.3. (−)-(η⁴-1,5-Cyclooctadiene){2-[(4R)-4,5-dihydro-4-ethyl]pyrrolyloxazol}rhodium(I) ***13a***

The ligand (4R)-(+)-4,5-dihydro-2-(2-pyrrolyl)-4-ethyloxazol **10a** (131.0 mg, 0.8 mmol) was used. Yield 206.6 mg (69%), mp 167.5°C. ^{1}H NMR (C_6D_6): δ 6.99 (dd, J=3.6, 1.1 Hz, 1H, py-3H), 6.79 (bs, 1H, py-5H), 6.45 (m, 1H, py-4H), 4.54 (m, 2H, CH (cod)), 4.19, 3.99 (2m, 2H, CH (cod)), 3.66 (dd, ^{2}J=8.6 Hz, ^{3}J=9.0 Hz, 1H, ox-CH_2), 3.50 (dd, ^{2}J=8.6 Hz, ^{3}J=6.0 Hz, 1H, ox-CH_2), 3.14 (m, 1H, ox-CH), 2.46, 2.34, 2.21–2.01, 1.86, 1.76, 1.60–1.41 (m, 8H, CH_2 (cod)), 1.45–0.93 (m, 2H, CH_2), 0.43 (t, ^{3}J=7.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 172.02 (d, ^{2}J(Rh–C)=1.3 Hz, C=N), 132.49 (d, ^{2}J(Rh–C)=2.1 Hz, py-5C), 127.10 (s, py-2C), 113.43 (d, ^{3}J(Rh–C)=1.3 Hz, py-3C), 110.76 (d, ^{3}J(Rh–C)=1.3 Hz, py-4C), 78.51, 76.55, 76.54, 75.95 (d, ^{1}J(Rh–C)=11.9, 13.0, 12.1, 13.6 Hz, CH (cod)), 74.20 (s, ox-CH_2), 62.19 (d, ^{3}J(Rh–C)=2.1 Hz, ox-CH), 32.38, 31.49, 30.74, 29.46 (4s, CH_2 (cod)), 27.48 (s, CH_2CH_3), 8.25 (s, CH_2CH_3). MS (FD, THF) 374.1 (M^+). $[\alpha]_\lambda$=−146 (589 nm), −151 (578 nm), −172 (546 nm) (c 1.50, toluene). $C_{17}H_{23}N_2ORh$ (374.29): calcd C 54.55, H 6.19, N 7.48, found C 54.62, H 6.26, N 7.49%.

3.4.4. (+)-(η⁴-1,5-Cyclooctadiene){2-[(4S)-4,5-dihydro-4-ethyl]pyrrolyloxazol}rhodium(I) ***13b***

The ligand (4S)-(−)-4,5-dihydro-2-(2-pyrrolyl)-4-ethyloxazol **10b** (131.0 mg, 0.80 mmol) was used. Yield 215.6 mg (72%), mp 167.5°C. $[\alpha]_\lambda$=+146 (589 nm), +152 (578 nm), +175 (546 nm) (c 1.51, toluene). $C_{17}H_{23}N_2ORh$ (374.29): calcd C 54.55, H 6.19, N 7.48, found C 54.44, H 6.15, N 7.46%.

3.4.5. (+)-(η⁴-1,5-Cyclooctadiene){2-[(4S)-4,5-dihydro-4-benzyl]pyrrolyloxazol}rhodium(I) ***14***

The ligand (4S)-(+)-4,5-dihydro-2-(2-pyrrolyl)-4-benzyloxazol **11** (119.7 mg, 0.80 mmol) was used. Yield 276.4 mg (79%), mp 145°C. ^{1}H NMR (C_6D_6): δ 7.08–6.76 (m, 7H, py-3H, py-5H, $H_{arom.}$), 6.45 (m, 1H, py-4H), 4.57, 4.28–4.06 (2m, 4H, CH (cod)), 3.79–3.42 (m, 3H, ox-CH_2, ox-CH), 2.70–1.39 (5m, 10H, CH_2 (cod), CH_2Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ 172.40 (s, C=N), 137.25 (s, py-2C), 132.90 (d, ^{2}J(Rh–C)=2.5 Hz, py-5C), 129.69–126.84 (m, $C_{arom.}$), 113.80 (d, ^{3}J(Rh–C)=1.3 Hz, py-3C), 110.98 (s, py-4C), 79.10, 76.95, 76.95, 76.23 (dddd, ^{1}J(Rh–C)=12.1, 11.4, 11.4, 13.3 Hz, CH (cod)), 74.56 (s, ox-CH_2), 62.59 (d, ^{2}J(Rh–C)=2.0 Hz, ox-CH), 41.49 (s, CH_2Ph), 32.54, 31.71, 30.83, 29.52 (4s, CH_2 (cod)). MS (FD, THF): 437.4 (M^+). $[\alpha]_\lambda$=+207 (589 nm), +219 (578 nm), +259 (546 nm) (c 1.40, toluene). $C_{22}H_{26}N_2ORh$ (437.37): calcd C 60.40, H 5.99, N 6.40, found C 60.21, H 6.11, N 6.39%.

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