Enantiomerically Pure Rhodium Complexes Bearing 1,5-Diphenyl-1,5-cyclooctadiene as a Chiral Diene Ligand. Their Use as Catalysts for Asymmetric 1,4-Addition of Phenylzinc Chloride

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Experimental

General.

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded at 500 MHz for $^1$H, and 125 MHz for $^{13}$C). Chemical shifts are reported in δ ppm referenced to an internal SiMe$_4$ standard for $^1$H NMR and chloroform-$d$ (δ 77.05) for $^{13}$C NMR.

Materials.

THF, benzene, and dioxane were distilled from sodium benzophenone-ketyl under nitrogen. (R)-1,1'-Binaphthyl-2,2'-diamine was purchased from Wako Pure Chemicals and used as received. PdCl$_2$(dppf),$^1$ 1,5-dibromo-1,5-cyclooctadiene,$^2$ and [RhCl(C$_2$H$_4$)$_2$]$^3$ were prepared according to the reported procedures.

1,5-Diphenyl-1,5-cyclooctadiene (Ph-cod, 1)

To a mixture of 1,5-dibromo-1,5-cyclooctadiene (400 mg, 1.50 mmol) and PdCl$_2$(dppf) (22.0 mg, 30.0 µmol) in 10 mL of Et$_2$O was added phenylmagnesium bromide (3.0 mL, 2.0 M, 6.0 mmol) in Et$_2$O at room temperature, and the mixture was heated to reflux for 12 h. After cooled to room temperature, the mixture was quenched with aqueous ammonium chloride, and extracted with Et$_2$O three times. The combined organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (benzene/hexane = 1/10) to give 353 mg of 1 (90% yield). $^1$H NMR (CDCl$_3$) δ 2.60 (dt, $J = 7.1, 6.7$ Hz, 4H), 2.88 (t, $J = 7.1$ Hz, 4H), 5.89 (t, $J = 6.7$ Hz, 2H), 7.20 (t, $J = 7.2$ Hz, 2H),
7.27 (t, $J = 7.2$ Hz, 4H), 7.32 (d, $J = 7.2$ Hz, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 27.7, 31.1, 126.1, 126.5, 126.8, 128.2, 140.6, 144.8; Anal. Calcd for C$_{20}$H$_{20}$: C, 92.26; H, 7.74. Found: C, 92.37; H, 7.73.

$[\text{RhCl(Ph-cod)}]_2$ $dl$-$2$

A suspension of $[\text{RhCl(ethylene)}]_2$ (280 mg, 1.44 mmol Rh) and Ph-cod 1 (347 mg, 1.30 mmol) in 15 mL of benzene was stirred at 50 °C for 12 h. After cooled to room temperature, the reaction mixture was filtered through celite and the filtrate was concentrated under reduced pressure to give a quantitative yield of $[\text{RhCl(Ph-cod)}]_2$ $dl$-$2$. $^1$H NMR (CDCl$_3$) $\delta$ 1.71 (ddd, $J = 13.7$, 11.6, 8.2 Hz, 4H), 2.19 (dd, $J = 14.8$, 8.2 Hz, 4H), 2.28 (dd, $J = 13.8$, 10.5 Hz, 4H), 3.15 (dddd, $J = 14.8$, 11.6, 10.5, 6.9 Hz, 4H), 4.34 (d, $J = 6.1$ Hz, 4H), 7.26 (m, 12H), 7.40 (m, 8H); $^{13}$C NMR (CDCl$_3$) $\delta$ 34.4, 36.4, 72.2 (d, $J_{C-Rh} = 12.9$ Hz), 91.6 (d, $J_{C-Rh} = 14.5$ Hz), 126.4, 126.8, 127.6, 148.0; Anal. Calcd for C$_{40}$H$_{40}$Cl$_2$Rh$_2$: C, 60.24; H, 5.06. Found: C, 60.36; H, 5.33.

$[\text{Rh((R)-Ph-cod)((R)-1,1''-binaphthyl-2,2''-diamine)}]BF_4$ ($R,R$)-3

To a solution of racemic $[\text{RhCl(Ph-cod)}]_2$ $dl$-$2$ (325 mg, 0.817 mmol Rh) and ($R$)-1,1''-binaphthyl-2,2''-diamine ($R$)-4 (232 mg, 0.817 mmol) in dichloromethane (2.8 mL) was added silver tetrafluoroborate (167 mg, 0.858 mmol). The reaction mixture was stirred at room temperature for 1 h. The precipitate was removed by filtration through celite, and the filtrate was concentrated under reduced pressure to give a quantitative yield of a mixture of diastereomers 3, which was recrystallized from tetrahydrofuran and benzene to give ($R,R$)-3 (177 mg, 29% yield) as a single diastereomer (>99% de determined by $^1$H NMR analysis).

($R,R$)-3: $^1$H NMR (CDCl$_3$) $\delta$ 1.19 (d, $J = 9.7$ Hz, 2H), 1.81 (dddd, $J = 14.0$, 8.4, 8.0, 5.0 Hz, 2H), 2.16 (ddd, $J = 15.3$, 8.0, 3.1 Hz, 2H), 2.83 (dddd, $J = 14.0$, 11.0, 8.4, 3.1 Hz, 2H), 3.08 (ddd, $J = 15.3$, 11.0, 8.4 Hz, 2H), 4.35 (d, $J = 9.7$ Hz, 2H), 4.82 (dd, $J = 8.4$, 5.0 Hz, 2H), 6.63 (m, 8H), 7.27 (t, $J = 7.2$ Hz, 2H), 7.41 (t, $J = 7.1$ Hz, 2H), 7.48 (br, 4H), 7.88 (d, $J = 8.2$ Hz, 2H), 8.07 (d, $J = 8.9$ Hz, 2H), 8.11 (d, $J = 8.9$ Hz, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 29.9, 39.5, 71.6 (d, $J_{C-Rh} = 12.8$ Hz), 99.9 (d, $J_{C-Rh} = 13.9$ Hz), 119.1, 120.3, 124.6, 125.7, 126.7, 127.5,
128.0, 128.3, 128.5, 131.2, 132.1, 137.6, 143.6; Anal. Calcd for C_{40}H_{36}BF_4N_2Rh: C, 65.41; H, 4.93; [α]_{20}^D –634 (c 0.450, CHCl_3).

(S,R)-3: 1H NMR (CDCl_3) δ 1.72 (br, 2H), 1.87 (ddd, J = 16.2, 13.7, 8.7 Hz, 2H), 2.37 (dd, J = 14.3, 10.3 Hz, 2H), 2.41 (dd, J = 15.5, 8.2 Hz, 2H), 3.38 (dddd, J = 16.2, 10.7, 10.3, 6.1 Hz, 2H), 4.46 (d, J = 8.9 Hz, 2H), 5.00 (d, J = 6.1 Hz, 2H), 6.63 (m, 6H), 7.00 (t, J = 7.7 Hz, 2H), 7.11 (t, J = 7.6 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.48 (br, 6H), 7.54 (t, J = 6.8 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H); 13C NMR (CDCl_3) δ 34.0, 37.2, 75.4 (d, J_{C-Rh} = 10.4 Hz), 96.6 (d, J_{C-Rh} = 13.9 Hz), 118.9, 119.3, 125.1, 125.3, 126.2, 127.0, 127.8, 130.1, 131.4, 131.7, 136.2, 146.4.

[RhCl((R)-Ph-cod)]_2 (R)-2

A mixture of (R,R)-3 (180 mg, 0.245 mmol) in acetonitrile (5 mL) and concentrated hydrochloric acid (1 mL) was stirred at room temperature for 10 h, and it was extracted with benzene three times. The combined organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC (chloroform and then ethyl acetate/hexane = 1/10) to give [RhCl((R)-Ph-cod)]_2 (R)-2 (94.0 mg, 96% yield); [α]_{20}^D –322 (c 1.00, CHCl_3).

[Rh((R)-Ph-cod)(MeCN)_2]BF_4 (R)-5

A mixture of (R)-[RhCl((R)-Ph-cod)]_2 (R)-2 (80.0 mg, 0.200 mmol Rh) and silver tetrafluoroborate (48.0 mg, 0.240 mmol) in acetonitrile (0.50 mL) and dichloromethane (2 mL) was stirred at room temperature for 30 min. The precipitate was removed by filtration through celite. The filtrate was evaporated under reduced pressure to give a quantitative yield (106 mg) of [Rh((R)-Ph-cod)(MeCN)_2]BF_4. 1H NMR (CDCl_3) δ 1.89 (S, 6H), 2.09 (dt, J = 17.7, 8.9 Hz, 2H), 2.44 (m, 2H), 2.68 (dd, J = 13.7, 10.5, 2.2 Hz, 2H), 3.27 (dtd, J = 15.3, 10.0, 7.2 Hz, 2H), 5.05 (d, J = 7.0 Hz, 2H), 7.28 (m, 6H), 7.65 (d, J = 7.1 Hz, 4H); 13C NMR (CDCl_3) δ 2.01, 33.2, 36.3, 76.6, 101.4, (J_{C-Rh} = 12.9 Hz), 126.5, 128.2, 128.4, 145.7; [α]_{20}^D –227 (c 0.32, CHCl_3).
**General Procedure for Catalytic Asymmetric 1,4-Addition for Phenylzinc Reagent to α,β-Unsaturated Ketones and Esters.**

To a solution of catalyst (9.0 µmol Rh) in 1.0 mL of tetrahydrofuran was added a substrate 6 (0.30 mmol). The solution was cooled to 0 °C. Chlorotrimethylsilane (58 µL, 0.45 mmol) and phenylzinc chloride (0.78 mL, 0.42 mmol, 0.54 M in tetrahydrofuran and diethyl ether) were added in one portion. After stirring at 0 °C for 20 min, the reaction was quenched with 3 N HCl aq (0.10 mL). The resulting mixture was stirred at 0 °C for 30 min, and it was passed through a short silica gel column (eluent: diethyl ether). Evaporation of the solvent followed by preparative TLC (silica gel, hexane/ethyl acetate = 3/1) gave the corresponding 1,4-addition product (R)-7a-d.

**X-ray Crystal Structure of [RhCl((R)-Ph-cod)]_2·CH_2Cl_2**

**Data Collection**

A deep red dichloromethane solution of [RhCl((R)-Ph-cod)]_2 was prepared. Crystals suitable for X-ray analysis were obtained by layering hexane at room temperature.

A prism red crystal of Rh_2Cl_4C_41H_40 having approximate dimensions of 0.20 x 0.40 x 0.40 mm was mounted in a glass capillary. All measurements were made on a Bruker Smart APEX X-Ray diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

\[
\begin{align*}
a &= 10.8101(5) \text{ Å} \\
b &= 15.2076(7) \text{ Å} \\
c &= 21.8748(9) \text{ Å} \\
V &= 3596.1(3) \text{ Å}^3
\end{align*}
\]

For Z = 4 and F.W. = 880.39, the calculated density is 1.63 g/cm^3. The systematic absences

- h00: h ± 2n
- 0k0: k ± 2n
- 00l: l ± 2n
uniquely determine the space group to be:

\[ P2_12_12_1 \ (\#19) \]

The data were collected at a temperature of 23 ± 1°C to a maximum 2q value of 56.5°.

**Data Reduction**

Of the 22224 reflections that were collected, 4664 were unique \( (R_{int} = 0.018) \).

The linear absorption coefficient, \( m \), for Mo-Kα radiation is 12.4 cm⁻¹. The data were corrected for Lorentz and polarization effects.

**Structure Solution and Refinement**

The structure was solved by direct methods⁴ and expanded using Fourier techniques.⁵ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement⁶ on F was based on 4664 observed reflections \( (I > 2σ(I)) \) and 467 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

\[
R = \frac{S \|Fo\| \cdot |Fc|}{S |Fo|} = 0.028
\]

\[
R_w = \sqrt{\frac{\sum S w (|Fo| - |Fc|)^2 / S w Fo^2}{\sum S w Fo^2}} = 0.032
\]

The standard deviation of an observation of unit weight⁷ was 1.12. A Robust-resistant weighting scheme was used.⁸ Plots of \( S w (|Fo| - |Fc|)^2 \) versus \|Fo\|, reflection order in data collection, sin q/l and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.19 and -0.84 e/Å³, respectively. The flack parameter⁹ is -0.06(3).
Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in Fcalc; the values for Df' and Df" were those of Creagh and McAuley. The values for the mass attenuation coefficients are those of Creagh and Hubbell. All calculations were performed using the CrystalStructure crystallographic software package.

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 283694). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula \( \text{Rh}_2\text{Cl}_4\text{C}_4\text{H}_40 \)

Formula Weight 880.39

Crystal Color, Habit red prism

Crystal Dimensions 0.20 X 0.40 X 0.40 mm

Crystal System orthorhombic

Lattice Type Primitive

Lattice Parameters
\[
a = 10.8101(5) \text{ Å} \\
b = 15.2076(7) \text{ Å} \\
c = 21.8748(9) \text{ Å} \\
V = 3596.1(3) \text{ Å}^3
\]

Space Group \( \text{P2}_1\text{2}_1\text{2}_1 \) (#19)

Z value 4

Dcalc 1.626 g/cm\(^3\)

F000 1776.00

\( \mu(\text{MoKa}) \) 12.42 cm\(^{-1}\)

B. Intensity Measurements

Detector Bruker CCD

Goniometer Bruker SMART APEX

Radiation MoKa (\( l = 0.71069 \text{ Å} \))
**Detector Aperture**
70 mm x 70 mm

**2q max**
56.5°

**No. of Reflections Measured**
Total: 22224
Unique: 4664 (R_{int} = 0.018)

**Corrections**
Lorentz-polarization

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**C. Structure Solution and Refinement**

**Structure Solution**
Direct Methods (SIR88)

**Refinement**
Full-matrix least-squares on F

**Function Minimized**
S w (|Fo| - |Fc|)^2

**Least Squares Weights**
Chebychev polynomial with 3 coefficients: 0.2200, 0.1583, 0.0848,

**2q max cutoff**
56.5°

**Anomalous Dispersion**
All non-hydrogen

**No. Observations (All reflections)**
4664

**No. Variables**
467

**Reflection/Parameter Ratio**
9.99

**Residuals: R (All reflections)**
0.029

**Residuals: R (I>2.00s(I))**
0.028

**Residuals: Rw (All reflections)**
0.032

**Goodness of Fit Indicator**
1.122

**Flack Parameter**
-0.06(3)

**Max Shift/Error in Final Cycle**
0.008

**Maximum peak in Final Diff. Map**
2.19 e/Å³

**Minimum peak in Final Diff. Map**
-0.84 e/Å³


(6) Least Squares function minimized:
\[ S_w(|F_o|-|F_c|)^2 \] where \( w \) = Least Squares weights.

(7) Standard deviation of an observation of unit weight.
\[ \left[ S_w(|F_o|-|F_c|)^2 / (N_o-N_v) \right]^{1/2} \]
where: \( N_o \) = number of observations
\( N_v \) = number of variables


[Rh(Ph-cod)(IR-4)]BF₄

a mixture of diastereoisomers (3)