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Chiral Organometallic Triangles with Rh–Rh Bonds. 2. Compounds Prepared from Enantiopure *cis*-$Rh_2(C_6H_4PPh_2)_2(OAc)_2(HOAc)_2$ and Their Catalytic Potentials

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Enantiomers of the orthometalated dirhodium compound *cis*-$Rh_2(C_6H_4PPh_2)_2(OAc)_2(HOAc)_2$ (*R*-**1** and *S*-**1**) were prepared from carboxylate exchange reactions of the resolved diasteroisomers of *cis*-$Rh_2(C_6H_4PPh_2)_2(protos)_2(H_2O)_2$ (protos = *N*-4-methylphenylsulfonyl-L-proline anion) and acetic acid. These compounds react with excess Me_3OBF_4 in CH_3CN, producing the enantiomers of [*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6](BF_4)_2$ (*R*-**2** and *S*-**2**) which have six labile and replaceable CH_3CN ligands in equatorial and axial positions. Reactions of *R*-**2** and *S*-**2** with tetraethylammonium salts of the linear dicarboxylic acids, terephthalic acid ($HO_2CC_6H_4CO_2H$), oxalic acid (HO_2CCO_2H), and 4,4′-diphenyl-dicarboxylic acid ($HO_2CC_6H_4C_6H_4CO_2H$) afford the enantiopure triangular supramolecules [*cis*-$Rh_2(C_6H_4PPh_2)_2(O_2CC_6H_4CO_2)(py)_2]_3$, *RRR*-**3** and *SSS*-**3**, Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_5(CH_2Cl_2)$, *RRR*-**4** and *SSS*-**4**, and Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4C_6H_4CO_2)_3(py)_4(CH_2Cl_2)_2$, *RRR*-**5** and *SSS*-**5**, respectively. The absolute structures of each of the enantiomers of **1**, **3**, **4**, and **5** were determined by X-ray diffraction analyses. The enantiomers of **3**, **4**, and **5** were found to be enantiomorphically isostructural, whereas *R*-**1** and *S*-**1** crystallized in different space groups. In **4** and **5**, CH_2Cl_2 molecules coordinate to rhodium atoms in the axial positions. The ^1H and $^{31}P\{^1H\}$ NMR spectra of all compounds are reported. The triangular compounds are redox-active, and their electrochemistry is also discussed. An assay of the catalytic activity/selectivity performance of the triangles for typical metal carbene transformation, using the model intermolecular cyclopropanation of styrene with ethyl diazoacetate in both homogeneous and heterogeneous phases, show that these chiral triangles are very active and have remarkable selectivity when compared with simple Rh_2 paddlewheel catalysts with chiral amidate ligands.

Introduction

The use of metal atoms (or ions) as key elements in the self-assembly of metal−organic supramolecular arrays has been of great interest over the past decade.[1] A great variety of supramolecular architectures have been realized, including triangles, squares, and other polygons, as well as helices and 2-D and 3-D structures, by using the proper choice of metal-containing units and ligand−metal interactions.

Recently, significant work has been done in efforts to incorporate functional features into the supramolecular assemblies because design and synthesis of chiral metal−organic frameworks may provide new approaches to enantioselective recognition, sensing, and catalysis.[2] Unfortu-

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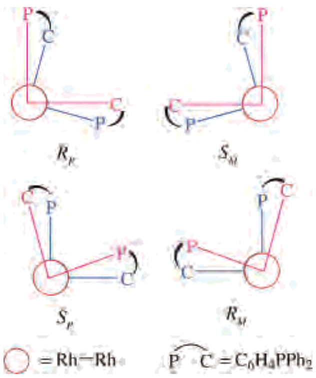
nately, most metal centers in metal−organic assemblies are coordinatively saturated, which generally prevents their use in metal-based catalysis. Thus, only a few examples of applications of enantiopure supramolecular assemblies have been reported so far. The first application of an enantiopure supramolecular material in enantioselective separation and catalysis was reported in 2000 by Kim and co-workers.[3] Later, the first successful asymmetric catalyzed reaction which employed a chiral organometallic triangle was described.[4] The successful application of this method was then demonstrated in asymmetric Michael additions[5] and carbonyl-ene reactions.[6]

Electroactivity is another appealing and potentially useful functionality to be introduced into supramolecular systems as a combination of electroactivity and complexation of supramolecules may lead to fascinating molecular sensing materials. A remarkable example of how this can be used is provided by a modification of an electrode surface by using a molecular square which serves as a receptor for π-donor substrates.[7] More recently, a new example was reported of ferrocene-based electrochemical sensing of neutral species via a metalloporphyrin-centered binding process mediated by two kinetically labile ligands in axial positions.[8] To date, only a few redox-active polygons are known with single metal corner pieces because the majority of the reported entities have metal ions such as Pd^{2+}, Pt^{2+}, and Zn^{2+}, which do not allow for alteration of charge by electrochemical or other means without collapse of the structures.

Beginning in early 1998 in this laboratory, the use of dimetal units (e.g., Mo_2^{4+}, Rh_2^{4+}, and Ru_2^{n+}) to build higher-order structures (so-called supramolecules) has been pioneered.[9] These higher-order structures include pairs, loops, triangles, squares, tubes, sheets, and 2-D and 3-D structures. Importantly, all of these compounds are electroactive, and those containing Ru_2^{5+} units are also paramagnetic.[9c] Recently, we reported that the *cis*-$Rh_2(C_6H_4PPh_2)_2^{2+}$ units, in which there are two cisoid orthometalated anions derived from a triphenylphosphine molecules bridging a metal−metal bonded dirhodium unit, can be a useful metal-based building block capable of making both chiral and redox-active supramolecules.[10]

Because of the head-to-tail arrangement of the two orthometalated bridging ligands, the *cis*-$Rh_2(C_6H_4PPh_2)_2^{2+}$ unit is chiral, and compounds containing these entities are accordingly chiral. Details of the chirality and associated nomenclature have been described previously.[10] There are two sources of chirality found in these Rh_2 units. In addition to the one arising from the head-to-tail relationship of the orthometalated phosphine ligands (designated as *R* and *S*), there is another one due to the twist pattern of each phosphine ligand (designated as *P* and *M*),[10] as shown in Scheme 1. The chirality induced by the latter factor is only secondary when compared to the chirality that arises from the head-to-tail arrangement of the phosphine ligands.[10] The interconversion of *R* and *S* is a process that requires bond-breaking, and it is not expected to occur at ordinary temperatures because of the large energy barrier for such process. In contrast, the interconversion of the secondary chirality (*P* and *M*) may be easier. In this report, we will generally refer to the *R* and *S* configurations, and *P* and *M* will only be used for the description of the overall chirality.

Scheme 1



The compounds containing the *cis*-$Rh_2(C_6H_4PPh_2)_2^{2+}$ unit are usually electroactive and catalytically active,[11] and like most compounds containing singly bonded Rh_2 units, they have kinetically labile axial ligands. The electrode potentials of these compounds is sensitive to the presence of different neutral electron donors in solution as indicated by the electrochemistry of racemic *cis*-$Rh_2(C_6H_4PPh_2)_2(OAc)_2(HOAc)_2$ in CH_2Cl_2 in the presence of various potential axial ligands.[12] It is expected that supramolecules containing the Rh_2 unit may have potential applications in molecular sensor materials and homogeneous or heterogeneous asymmetric catalysis. In this second of a series of reports, we are concerned with the preparation and X-ray structures of three enantiopure molecular triangles based on *cis*-$Rh_2(C_6H_4PPh_2)_2^{2+}$ units and two enantiopure dirhodium compounds which are used as precursors for the triangles. In addition, an evaluation of the catalytic ability of the triangles in both homogeneous and heterogeneous phases by the model intermolecular cyclopropanation of styrene with ethyl diazoacetate is also reported.

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Experimental Section

Materials and Methods. Unless otherwise stated, all manipulations and procedures were conducted in air. The solvents for the catalytic tests were purified before use as follows. CH_2Cl_2 was distilled over calcium hydride and then passed through a pad of anhydrous K_2CO_3, and n-C_5H_{12} was passed through a column of silica gel, followed by distillation. Solvents used for syntheses were used as received. Tetraethylammonium salts of dicarboxylic acids were prepared and isolated as white solids by neutralization of the corresponding diacids with 2 equiv of 35% Et_4NOH in water followed by thorough drying under vacuum. All other reagents were purchased from commercial sources and used as received. Resolved diastereoisomers of *cis*-$Rh_2(C_6H_4PPh_2)_2(protos)_2(H_2O)_2$ (protos = *N*-4-methylphenylsulfonyl-L-proline anion) were prepared using the method described in the literature.[11b] Both of the *R* and *S* enantiomers of each compound reported herein were synthesized, but because they were made following the same procedure and in essentially the same yields, only the synthesis for the *R* enantiomer of each compound is described below.

Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a CH Instruments model-CH1620A electrochemical analyzer in 0.1 M Bu_4NPF_6 solution (CH_2Cl_2) with a Pt working and auxiliary electrodes, an Ag/AgCl reference electrode, and a scan rate of 100 mV/s for the CV. All potential values are referenced to the Ag/AgCl electrode, and under the present experimental conditions, the $E_{1/2}$ (Fc^+/Fc) occurred at 440 mV. ^1H NMR (using the residual proton of the deuterated solvent CD_2Cl_2 or $CDCl_3$ as reference) and $^{31}P\{^1H\}$NMR (with H_3PO_4 in $CDCl_3$ as reference) spectra were recorded on a Mercury-300 NMR spectrometer.

Preparation of *R-cis*-$Rh_2(C_6H_4PPh_2)_2(OAc)_2(HOAc)_2$ (*R*-1). A solution of *R*-*cis*-$Rh_2(C_6H_4PPh_2)_2(protos)_2(H_2O)_2$ (183 mg, 0.140 mmol) in a mixture of 3 mL of CH_3CN and 3 mL of CH_3COOH was stirred overnight. The mixture was dried in a vacuum. The solid was washed with 3 × 20 mL of water, dried in a vacuum again, and then dissolved in 5 mL of CH_2Cl_2. To this solution was added 2 mL of acetic acid and 20 mL of isomeric hexanes. The resulting clear solution was concentrated in air. After 1 day, diffraction-quality crystals were obtained. Yield: 62 mg, 46%. ^1H NMR (CD_2Cl_2, δ, ppm): 7.636 (m, 4H, aromatic), 7.392 (m, 6H, aromatic), 7.234 (t, 2H, aromatic), 7.030 (t, 4H, aromatic), 6.727−6.894 (m, 8H, aromatic), 6.527−6.608 (m, 4H, aromatic), 2.152 (s, 6H, CH_3COOH), 1.192 (s, 6H, CH_3COO). ^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 19.403 (d, $^1J_{PRh} = 162.55$ Hz). Anal. Calcd for $C_{44}H_{42}O_8P_2Rh_2$: C, 54.68; H, 4.38%. Found: C, 54.50; H, 4.32%. $[\alpha]^{23}_D = +244.33$ ($c = 1.06 \times 10^{-3}$, in a mixture of CH_2Cl_2 and CH_3COOH)

Preparation of *R*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6](BF_4)_2$ (*R*-2). The procedure for the preparation of compounds *R*-**2** and *S*-**2** was similar to that for racemic *RS*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6](BF_4)_2$.[10] A mixture of *R*-**1** (146 mg, 0.150 mmol) and Me_3OBF_4 (150 mg, 0.96 mmol) in 3 mL of acetonitrile was stirred at ambient temperature for about 10 min. When the mixture became a clear red solution, ether was added while stirring until a precipitate was observed. The mixture was allowed to stand overnight to let the product deposit from the solution. After filtration, the crystals were washed with ether. Yield (140 mg, 81.3%). ^1H NMR ($CDCl_3$, δ, ppm): 7.788 (t, 4H, aromatic), 7.503 (m, 6H, aromatic), 7.317 (t, 2H, aromatic), 7.117 (t, 4H, aromatic), 6.745−6.894 (m, 8H, aromatic), 6.663 (t, 2H, aromatic), 6.362 (q, 2H, aromatic), 2.034 (s, 18H, CH_3CN). Anal. Calcd for $C_{48}H_{46}N_6B_2F_8P_2Rh_2$: C, 50.17; H, 4.04, N, 7.32%. Found: C, 50.50; H, 4.25; N, 7.01%. $[\alpha]^{23}_D = 126.0$ ($c = 7.5 \times 10^{-3}$ in CH_3CN)

Preparation of *RRR*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(O_2CC_6H_4CO_2)(py)_2]_3$ (*RRR*-3). A mixture of *R*-**2** (75 mg, 0.065 mmol) and $(Et_4N)_2O_2CC_6H_4C_6H_4CO_2$ (40 mg, 0.094 mmol) in 4 mL of CH_2Cl_2 and 5 mL of methanol was stirred at ambient temperature for 10 min. The mixture of solvents was removed under vacuum. The residue was washed with 3 × 30 mL of water, dried in air, and then dissolved in a mixture of 5 mL of CH_2Cl_2 and two drops of pyridine. Deep red crystals of the product were obtained by layering the solution with methanol over a period of one week. (Yield: 65 mg, 78%). ^1H NMR (CD_2Cl_2, δ, ppm): 8.770 (d, 12H, pyridine C−H), 7.805 (t, 6H, pyridine C−H), 6.387−7.253 (m, 108 H, aromatic C−H). ^{31}P $\{^1H\}$ NMR (CD_2Cl_2, δ, ppm): 21.433 (d, $^1J_{PRh} = 167.08$ Hz). Anal. Calcd for $C_{162}H_{126}N_6O_{12}P_6Rh_6$: C, 61.71; H, 4.03; N, 2.66%. Found: C, 61.22; H, 4.36; N, 2.49%. $[\alpha]^{23}_D = 191.2$ ($c = 3.6 \times 10^{-4}$, in a mixture of CH_2Cl_2 and pyridine).

Preparation of *RRR*-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_5(CH_2Cl_2)$ (*RRR*-4). A mixture of *R*-**2** (75 mg, 0.065 mmol) and $(Et_4N)_2O_2CCO_2$ (30 mg, 0.086 mmol) in 5 mL of CH_2Cl_2 and 5 mL of methanol was stirred for 10 min. The mixture of solvents was removed in a vacuum. The purple residue[13] was washed with 3 × 30 mL of water, dried in air, and then dissolved in 5 mL of CH_2Cl_2. Orange crystals of the product were obtained from a CH_2Cl_2 solution, to which 3 drops of pyridine had been added, and then layering with isomeric hexanes over a period of 5 days. Yield: 56 mg, 82%. ^1H NMR (CD_2Cl_2, δ, ppm): 8.730 (d, 10H, pyridine), 7.35 (t, 5H, pyridine), 6.364−7.228 (m, 94 H, aromatic), 5.332 (s, 2H, CH_2Cl_2). ^{31}P $\{^1H\}$ NMR (CD_2Cl_2 and C_5D_5N, δ, ppm): 22.675 (d, $^1J_{PRh} = 173.08$ Hz). Anal. Calcd for $C_{140}H_{111}N_5O_{12}Cl_2P_6Rh_6$: C, 57.40; H, 3.82; N, 2.39%. Found: C, 57.66; H, 3.84; N, 2.40%. $[\alpha]^{23}_D = 51.9$ ($c = 5.2 \times 10^{-4}$, in a mixture of CH_2Cl_2 and pyridine).

Preparation of *RRR*-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4C_6H_4CO_2)_3(py)_4(CH_2Cl_2)_2$ (5). A solution of compound *R*-**2** (30 mg, 0.026 mmol) and $(Et_4N)_2O_2CC_6H_4C_6H_4CO_2$ (13 mg, 0.026 mmol) in a mixture of 3 mL of CH_2Cl_2 and 1 mL of methanol was stirred for 10 min. After filtration, 3 drops of pyridine were added to the filtrate. The resulting solution was layered with 10 mL of methanol to afford red crystals that were separated by decantation. Yield: 29 mg, 81%. ^1H NMR (CD_2Cl_2, δ, ppm): 8.690 (d, 8H, pyridine), 7.859 (t, 4H, pyridine), 6.547−7.501 (m, 116 H, aromatic), 5.333 (s, 4H, CH_2Cl_2). ^{31}P $\{^1H\}$ NMR (CD_2Cl_2 and C_5D_5N, δ, ppm): 22.796 (d, $^1J_{PRh} = 167.08$ Hz). Anal. Calcd for $C_{172}H_{132}N_4O_{12}Cl_4P_6Rh_6$: C, 60.92; H, 3.93; N, 1.65%. Found: C, 60.43; H, 3.76; N, 1.80%. $[\alpha]^{23}_D = 48.2$ ($c = 3.8 \times 10^{-4}$, in a mixture of CH_2Cl_2 and pyridine).

Cyclopropanation of Styrene with Ethyl Diazoacetate. A solution of ethyl diazoacetate (18 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) was added, under argon atmosphere with the aid of a syringe pump over 5 h (1 mL/h) to a refluxing, stirred solution of the catalyst (1 mol%) and a 10-fold excess of styrene (0.18 mL, 1.5 mmol) in CH_2Cl_2 (20 mL). After complete addition, the reaction mixture was stirred at reflux for an additional 4 h and then cooled

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(13) A CH_2Cl_2 solution of the purple residue layered with methanol over a period of one month produced crystals of *SSS*-$\{Rh_6$(*cis*-$C_6H_4PPh_2)_6(C_2O_4)(CH_3OH)_5(H_2O)\}$. The ^1H NMR spectra of this compound exposed to air overnight and that of the purple residue were the same, (CD_2Cl_2, δ, ppm): 6.439−7.244 (m, 84H, aromatic), 1.956 (s, H_2O). The spectra indicated that, when the solutions are exposed to air, all of the methanol ligands in axial positions were readily replaced by water. Crystal data: $a = 11.180(8)$ Å, $b = 27.89(2)$ Å, $c = 19.28(1)$ Å, $\beta = 101.94(1)°$, $V = 5881(7)$ Å^3, $Z = 2$, space group $P2_1$, R1 and wR2 = 0.0556 and 0.0962, Flack parameter = −0.01(2)

Table 1. Crystallographic Data and Structure Refinement Parameters

compound	*R*-**1**	*S*-**1**	*SSS*-**3**·1.5CH$_3$OH·7.25CH$_2$Cl$_2$·1.5H$_2$O	*SSS*-**4**·2CH$_2$Cl$_2$	*RRR*-**5**·7CH$_3$OH·5CH$_2$Cl$_2$
chemical formula	$C_{44}H_{42}O_8P_2Rh_2$	$C_{44}H_{42}O_8P_2Rh_2$	$C_{170.75}H_{149.5}Cl_{14.5}N_6O_{15}P_6Rh_6$	$C_{142}H_{115}Cl_6N_5O_{12}P_6Rh_6$	$C_{184}H_{170}Cl_{14}N_4O_{19}P_6Rh_6$
fw	966.54	966.54	3842.77	3099.37	4040.82
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1$	$P2_1$	$P2_1$	$C222_1$
a(Å)	10.667(3)	12.6777(9)	22.366(3)	15.210(1)	24.069(2)
b(Å)	15.152(4)	18.368(1)	21.519(3)	27.015(2)	36.637(3)
c(Å)	25.053(6)	18.145(1)	36.118(4)	16.9670(2)	22.257(2)
α(deg)	90	90	90	90	90
β(deg)	90	94.648(1)	91.152(2)	113.032(1)	90
γ(deg)	90	90	90	90	90
V(Å^3)	4049(2)	4211.4(5)	17380(4)	6417(1)	19626(3)
Z	4	4	4	2	4
d_{calcd} (g cm^{-3})	1.585	1.524	1.469	1.604	1.368
μ(Mo K$_\alpha$) (mm^{-1})	0.948	0.911	0.895	1.018	0.791
T, °C	−60	−60	−100	−100	−100
GOF	1.073	1.022	1.149	1.055	1.101
R1,[a] wR2[b] ($I > 2\sigma$)	0.0184, 0.0456	0.0278, 0.0601	0.1168, 0.2869	0.0353, 0.0826	0.0611, 0.1567
Flack parameter	−0.02(1)	0.00(2)	0.14(5)	−0.01(2)	0.03(5)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2(F_c^2)]/3$.

to room temperature. The solution was filtered through a short silica gel chromatography column to eliminate the catalyst. The column was further washed with CH$_2$Cl$_2$ (10 mL), and the solvent from the combined solutions was evaporated. The yield was determined using ^{1}H NMR spectroscopy.

X-Ray Structure Determinations. Mounting of crystals on the diffractometer was done as quickly as possible to minimize the loss of solvent molecules, and data collection was done at −100 °C because crystals of all triangular compounds rapidly lost interstitial solvent molecules. Some of crystals decayed quickly even at −60 °C. Diffraction data were collected using a Bruker SMART 1000 CCD area detector system. Cell parameters were determined using the program SMART.[14] Data reduction and integration were performed with the software SAINT,[15] and absorption corrections were applied by using the program SADABS.[16] The positions of the Rh atoms were found via direct methods using the program SHELXTL.[17] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were added in idealized positions for the calculation of the structure factors. The absolute structure for each compound was assigned on the basis of the value of the Flack parameter, *x*.[18] Disordered phenyl groups on the phosphine ligand and solvent molecules were refined with distance constraints. Some additional details of data collection and refinement are given in Table 1. Crystallographic data are available as Supporting Information.

The modest quality of the crystal of *SSS*-**3** resulted in a large Flack parameter of 0.14(5), which is greater than those for the other compounds reported here. Refinement including an "inversion twin" model did not improve the structure analysis, indicating that the crystal was not twinned. Furthermore, a CH$_2$Cl$_2$ solution of *SSS*-**3** which had been layered with methanol afforded crystals of *SSS*-Rh$_6$(*cis*-C$_6$H$_4$PPh$_2$)$_6$(O$_2$CC$_6$H$_4$CO$_2$)$_3$(py)$_3$(CH$_3$OH)$_3$ with a small Flack parameter.[19] Crystallization of *SSS*-Rh$_6$(*cis*-C$_6$H$_4$PPh$_2$)$_6$(O$_2$CC$_6$H$_4$CO$_2$)$_3$(py)$_3$(CH$_3$OH)$_3$ in CH$_2$Cl$_2$ from a solution containing an excess of pyridine gave back crystals of *SSS*-**3**. Therefore, it is reasonable to believe that *SSS*-**3** is as enantiopure as *SSS*-**4** which was synthesized from the same starting material, namely compound *S*-**2**.

In the crystal structure of *RRR*-**5**, the axial ligands in the crystallographically independent Rh$_2$ units are disordered over two orientations with occupancies of 0.695 and 0.305 for CH$_2$Cl$_2$ in one axial position and 0.648 and 0.352 for pyridine in another position.

Results and Discussion

Syntheses. The dirhodium compound *cis*-Rh$_2$(C$_6$H$_4$PPh$_2$)$_2$(OAc)$_2$(HOAc)$_2$ is composed of a singly bonded inherently chiral *cis*-Rh$_2$(C$_6$H$_4$PPh$_2$)$_2$$^{2+}$ unit and two labile acetate groups in cis positions. The racemic compound, *RS-cis*-Rh$_2$(C$_6$H$_4$PPh$_2$)$_2$(OAc)$_2$(HOAc)$_2$, was prepared readily from the reaction of Rh$_2$(OAc)$_4$ with PPh$_3$ in acetic acid under reflux conditions.[12] The enantiomers of this racemate can be resolved using a general diastereoisomer separation method. The reactions involved are shown in eqs 1 and 2. The dirhodium products of eq 1 are a mixture of diastereoisomers. This mixture can be separated using chromatography on silica gel. The pure diastereoisomers can then be converted to pure enantiomers of the corresponding acetate compound used as starting material (eq 2).

$$\begin{aligned} &RS\text{-}cis\text{-}Rh_2(C_6H_4PPh_2)_2(OAc)_2(HOAc)_2 + \\ &\qquad \text{excess Hprotos} + 2H_2O \rightarrow \\ &R \text{ and } S\text{-}cis\text{-}Rh_2(C_6H_4PPh_2)_2(\text{protos})_2(H_2O)_2 + 4CH_3COOH \end{aligned} \quad (1)$$

$$\begin{aligned} &R \text{ or } S\text{-}cis\text{-}Rh_2(C_6H_4PPh_2)_2(\text{photos})_2(H_2O)_2 + \\ &\qquad \text{excess } CH_3COOH \rightarrow \\ &R \text{ or } S\text{-}cis\text{-}Rh_2(C_6H_4PPh_2)_2(OAc)_2(HOAc)_2 + 2\text{Hprotos} + 2H_2O \end{aligned} \quad (2)$$

Although compounds *R*-**1** and *S*-**1** could be used directly as reactants to synthesize the target macrocyclic supramolecules, in practice, we have found it is best to convert

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(14) *SMART for Windows NT,* version 5.618; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2001.

(15) *SAINT Data Reduction Software. Verson 6.36A*; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2001.

(16) *SADABS. Area Detector Absorption and other Corrections Software, Version 2.05*; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2001.

(17) Sheldrick, G. M. *SHELXTL, version 6.12*; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2002.

(18) (a) Flack, H. D. *Acta Crystallogr. A* **1983**, *39*, 876. (b) Flack, H. D.; Bernardinelli, G. *J. Appl. Crystallogr.* **2000**, *33*, 1143.

them to pure enantiomers of [*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6$]$(BF_4)_2$ (*R*-**2** and *S*-**2**), which contain six easily replaceable equatorial and axial CH_3CN ligands. Compounds *R*-**2** and *S*-**2** react smoothly and readily with the dicarboxylate linkers to afford the desired products. The enantiopure compounds *R*-**2** and *S*-**2** were prepared from the reactions of **1** with Me_3OBF_4 in CH_3CN in a synthesis similar to that of the racemic compounds.[10] The formation and purity of **2** have been attested by the NMR spectra.

The preparations of enantiopure triangular compounds were accomplished from the reaction of **2** with the desired dicarboxylate anion in the presence of a strong donor solvent which can provide axial ligands. We have reported that the reaction of the racemic compound [*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6$]$(BF_4)_2$ and linear dicarboxylate dianions affords only triangular molecules.[10] Likewise, the reactions of either of the enantiopure compounds *R*-**2** and *S*-**2** with oxalate, terephthalate, and 4,4′-diphenyl-dicarboxylate dianions provide only triangular compounds. Crystals of compounds *RRR*-**3** and *SSS*-**3** were obtained from a solution in a mixture of CH_2Cl_2 and pyridine by layering with methanol. The crystal structure analysis revealed that all the axial positions of **3** are occupied by pyridine molecules. It is interesting that, when oxalate dianion was used under the same conditions, methanol competes with CH_2Cl_2 for the axial positions. A mixture of red crystals of Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_{4.75}(CH_3OH)_{1.25}$,[20] which is composed of 50% of Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_5(CH_3OH)$ and 50% of Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_{4.5}(CH_3OH)_{1.5}$, and a small amount of orange crystals of **4** were isolated. A product containing only **4** was obtained from a CH_2Cl_2 solution in the presence of additional pyridine by layering with isomeric hexanes. The reaction of **2** with $(Et_4N)_2(O_2CC_6H_4C_6H_4CO_2)$ provided the triangle Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4C_6H_4CO_2)_3(py)_4(CH_2Cl_2)_2$ (**5**), in high yield, under similar conditions in which a CH_2Cl_2 solution was layered with hexanes in the presence of excess pyridine.

It should be noted that, with the paddlewheel geometry of the Rh_2 group, a square with Rh_2 units at the corners and four rigid dicarboxylate linkers at the sides would also be expected to form with the same stoichiometry. While compounds **3**−**5** have been shown to be triangles in the crystalline state, this is no guarantee that a transformation, full or partial, to squares in solution might not occur. Thus, it is important and meaningful to study the solution properties of these compounds.

The ^{31}P NMR spectrum of **3** in CD_2Cl_2 has one sharp signal at 21.433 ppm, which is a doublet due to coupling of the P atom to the $I = {}^1/_2$ ^{103}Rh nucleus. This indicates that there is only one highly symmetric species present, which is consistent with the triangular structure of **3** in the crystals.

The $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2 shows a broad signal around 20 ppm. The appearance of a broad signal instead of six doublets, as expected from the X-ray structure, is consistent with the labile character of the axial ligands of the dirhodium units. The ^1H NMR spectra of **4** and **5** in which there is only one set of signals for pyridine reflect this property too. The broad signal in the $^{31}P\{^1H\}$ NMR spectrum became a sharp doublet (19.86 ppm with $^1J_{PRh} = 169.42$ Hz) when an excess of pyridine was added to ensure that all the axial positions are occupied by the same ligand, so that only one highly symmetrical species, presumably Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_6$, is present in this solution.

The crystals of **5** dissolve sparingly in CD_2Cl_2 but much more in the mixed solvent of CD_2Cl_2 and C_5D_5N. The solutions of **5** in CD_2Cl_2 are not concentrated enough to provide a discernible $^{31}P\{^1H\}$ NMR signal even with thousands of transients. Like the spectra of **4**, the $^{31}P\{^1H\}$ NMR spectrum of **5** in a mixed solvent of CD_2Cl_2 and C_5D_5N again is a doublet, attributable to Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4C_6H_4CO_2)_3(py)_6$.

There is no change observed for the $^{31}P\{^1H\}$ NMR spectra of these triangular compounds for days. In addition, as we shall see, the electrochemical study of compound **4** in CH_2Cl_2 and py demonstrates that there are three well-separated consecutive one-electron redox processes, which supports the presumption that the only species in solution are triangular molecules. The triangular identity of the species in solution is also consistent with the fact that the racemic product *RRR*(*SSS*)-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4CO_2)_3$ can be isolated from a mixture of equivalent amounts of *RRR*-**3** and *SSS*-**3**.[21]

As reported previously,[10] the racemic triangle of *RRS-(SSR)*-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4CO_2)_3$, which has two Rh_2 corners of one chirality and one corner of the other chirality in each triangular molecule, can be prepared from the reaction of the racemic compound *RS*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6$]$(BF_4)_2$ and the terephthalate salt. No evidence of the formation of *RRR(SSS)*-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4CO_2)_3$ in which all the Rh_2 corners are of the same chirality was observed in that reaction. Using enantiopure starting materials, the racemic triangular compound *RRR-(SSS)*-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4CO_2)_3$ was isolated from a solution containing equal amounts of *RRR*-**3** and *SSS*-**3** in

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(19) Crystallographic data for *SSS*-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4CO_2)_3(py)_3(CH_3OH)_3\cdot(CH_3OH)_6\cdot(CH_2Cl_2)_{3.25}\cdot(H_2O)_{4.25}$: $a = 21.651(4)$ Å, $b = 21.922(4)$ Å, $c = 22.055(4)$ Å, $\alpha = 82.113(3)°$, $\beta = 61.153(3)°$, $\gamma = 64.889(3)°$, $V = 8272(2)$ Å^3, $Z = 2$, space group *P1*, R1 and wR2 = 0.0871 and 0.2187, Flack parameter = −0.06(5).

(20) *SSS*-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_{4.75}(CH_3OH)_{1.25}$ crystallizes in space group $P2_1$ with two independent triangular molecules, Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_5(CH_3OH)$ and Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_{4.5}(CH_3OH)_{1.5}$, and with four CH_2Cl_2 and three CH_3OH solvent molecules in each asymmetric unit. In the molecule of Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_{4.5}(CH_3OH)_{1.5}$, four of six axial positions are occupied by pyridine molecules, one is occupied by a methanol molecule, and the other one is partially occupied by 0.5 pyridine and 0.5 methanol. The crystal data and refinement of the crystal are: $a = 13.4000(5)$ Å, $b = 53.882(2)$ Å, $c = 18.2036(6)$ Å; $\beta = 90.048(1)°$; $V = 13143.3(8)$ Å^3; $Z = 2$; space group $P\bar{1}$, R1 = 0.0425, wR2 = 0.0972 ($I > 2\sigma$); $T = 173$ K.; GOF = 1.088. Flack parameter = 0.02(2).

(21) Equivalent amounts of *RRR*-**3** and *SSS*-**3** was dissolved in CH_2Cl_2. The solution was allowed to stand for about one week and then layered with methanol. The orange crystals of racemic *RRR*(*SSS*)-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4CO_2)_3(py)_{1.5}(CH_3OH)_{4.5}\cdot 4.5CH_2Cl_2\cdot 7.5CH_3OH$ were isolated quantitatively after a period of one month. $^{31}P\{^1H\}$ NMR ($CDCl_3$ and C_5D_5N, δ, ppm): 22.001 (d, $^1J_{PRh} = 165.38$ Hz). The crystal data and refinement of the crystal are: $a = 16.139(3)$ Å, $b = 22.787(4)$ Å, $c = 24.622(4)$ Å; $\alpha = 81.053(3)°$, $\beta = 75.193(3)°$, $\gamma = 81.430(3)°$; $V = 8591(3)$ Å^3; $Z = 2$; R1 = 0.0757, wR2 = 0.2130 ($I > 2\sigma$); $T = 213$ K; GOF = 1.034.

CH_2Cl_2. The chirality and purity of this racemic compound were established by both the single-crystal structure and the $^{31}P\{^1H\}$ NMR spectrum. The syntheses of the two types of racemic triangular compounds, *RRS(SSR)* and *RRR(SSS)*, by different methods, and the lack of interconversion of the two types indicates that these molecular triangles retain their integrity in solution.

The axial coordination of CH_2Cl_2 as in the enantiopure compounds **4** and **5** is uncommon.[22] There are over 1500 dirhodium complexes with axial coordination reported so far,[23] but these are the only two compounds that have been found with CH_2Cl_2 in axial positions. The occurrence of this rare coordination is not easily explained, but it is possible that the relative solubilities of these compounds controls the crystallization process since compounds *RRR*-**5** and *SSS*-**5** are only slightly soluble in CH_2Cl_2 but are quite soluble in the presence of additional pyridine. In the presence of excess pyridine, compounds *RRR*-**5** and *SSS*-**5** are likely to become the highly symmetric compound $Rh_6(cis\text{-}C_6H_4PPh_2)_6(O_2CC_6H_4C_6H_4CO_2)_3(py)_6$ as revealed by their $^{31}P\{^1H\}$ NMR spectra. However, under the crystallization conditions, perhaps $Rh_6(C_6H_4PPh_2)_6(O_2CC_6H_4C_6H_4CO_2)_3(py)_6$ can exist only in solution and is converted to compounds *RRR*-**5** and *SSS*-**5** in the crystalline solid because the latter is less soluble and easier to crystallize.

Crystal Structures. Both enantiomers of compounds **1**, **3**, **4**, and **5** were crystallized, and their absolute structures were determined by X-ray diffraction analysis. The enantiomers of **3**, **4**, and **5** form enantiomorphic crystals. Only one enantiomer of each compound is reported herein. However, crystals of *R*-**1** and *S*-**1** crystallize in different space groups. The structures and crystal data of both enantiomers are described in this paper. It is likely that both enantiomers form both polymorphs, and the selection of a different polymorph in each case was fortuitous.

Compound *R*-*cis*-$Rh_2(C_6H_4PPh_2)_2(OAc)_2(HOAc)_2$ (*R*-**1**) was obtained in the orthorhombic system, space group $P2_12_12_1$, with one molecule in the asymmetric unit and no interstitial solvent molecules. A thermal ellipsoid depiction of the structure of this compound is shown in Figure 1, and selected bond distances and angles are listed in Table 2. The bond distances and angles are very close to the values in the previously studied racemic compound *RS*-*cis*-$Rh_2(C_6H_4PPh_2)_2(OAc)_2(HOAc)_2$.[12] The Rh−Rh distance is 2.5086(5) Å. The Rh−P and Rh−C bond distances are in the normal range. The Rh−O distances trans to Rh−P bonds are slightly shorter than those trans to Rh−C bonds, as expected from the difference in the trans influence of Rh−P and Rh−C bonds.

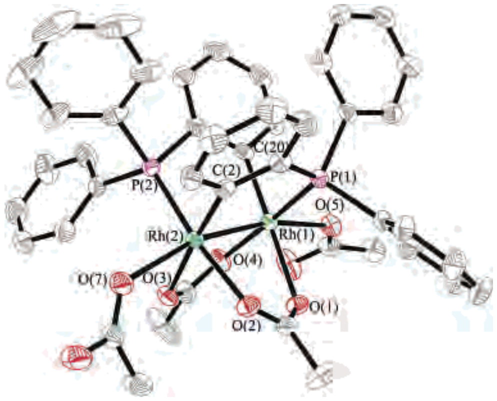

Figure 1. The structure of *R*-**1**. Displacement ellipsoids are drawn at the 40% probability level. All hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for *R*-**1**

Rh(1)−Rh(2)	2.5086(5)	Rh(1)−O(1)	2.1363(15)
Rh(1)−P(1)	2.2123(6)	Rh(1)−O(3)	2.2197(15)
Rh(2)−P(2)	2.2202(7)	Rh(1)−O(5)	2.2735(14)
Rh(1)−C(20)	1.986(2)	Rh(2)−O(2)	2.1891(15)
Rh(2)−C(2)	1.989(2)	Rh(2)−O(4)	2.1249(15)
		Rh(2)−O(7)	2.4146(15)
C(20)−Rh(1)−O(1)	92.32(7)	C(2)−Rh(2)−O(4)	87.72(7)
O(1)−Rh(1)−O(3)	85.04(6)	O(4)−Rh(2)−O(2)	87.58(6)
P(1)−Rh(1)−O(3)	95.14(5)	O(2)−Rh(2)−P(2)	95.47(4)
C(20)−Rh(1)−P(1)	87.59(6)	C(2)−Rh(2)−P(2)	89.28(6)
O(5)−Rh(1)−Rh(2)	167.91(4)	O(7)−Rh(2)−Rh(1)	165.51(4)

Table 3. Selected Bond Distances (Å) and Angles (deg) for *S*-**1**

Rh(1)−Rh(2)	2.5019(8)	Rh(1)−O(1)	2.197(4)
Rh(1)−P(1)	2.204(2)	Rh(1)−O(3)	2.150(4)
Rh(2)−P(2)	2.199(2)	Rh(1)−O(5)	2.288(5)
Rh(1)−C(20)	2.002(6)	Rh(2)−O(2)	2.141(4)
Rh(2)−C(2)	2.001(6)	Rh(2)−O(4)	2.185(4)
		Rh(2)−O(7)	2.309(5)
C(20)−Rh(1)−P(1)	87.8(2)	C(2)−Rh(2)−P(2)	90.6(2)
C(20)−Rh(1)−O(3)	94.7(2)	O(4)−Rh(2)−P(2)	95.0(1)
O(3)−Rh(1)−O(1)	83.2(2)	O(2)−Rh(2)−O(4)	85.5(2)
O(1)−Rh(1)−P(1)	94.3(1)	C(2)−Rh(2)−O(2)	89.0(2)
O(5)−Rh(1)−Rh(2)	168.3(1)	O(7)−Rh(2)−Rh(1)	165.8(1)

As expected, all the bridging ligands are twisted. The torsion angles are 9.99(6)° for P(1)−Rh(1)−Rh(2)−C(2), 11.67(6)° for P(2)−Rh(2)−Rh(1)−C(20), 15.32(2)° for O(1)−Rh(1)−Rh(2)−O(2), and 18.15(6)° for O(3)−Rh(1)−Rh(2)−O(4). In this complex, the torsion angle of P(1)−Rh(1)−Rh(2)−P(2) is 99.06(3)°. Therefore, the overall chirality of this dirhodium compound is R_P. The torsion angle of P−Rh−Rh−P is usually larger than that of C(20)−Rh(1)−Rh(2)−C(2) (−77.40(8)°), which is due to the steric repulsions of the bulky phenyl groups in the phosphines.

The enantiomer *S*-**1** was obtained in the monoclinic system, space group $P2_1$. There are two independent dirhodium molecules in each asymmetric unit. Again, there is no solvent molecule in the crystal. The molecular structure is shown in Figure S1. Selected bond distances and angles are listed in Table 3. The bonding parameters of *R*-**1** and *S*-**1** are almost the same, and the small differences may be attributed to the different packing forces in the two kinds of

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(22) For examples of compounds with CH_2Cl_2 coordination: (a) Newbound, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762. (b) Fernandez, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. (c) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349 and references therein. (d) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (e) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831. (f) Forniés, J.; Martínez, F.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **1996**, *15*, 1813. (g) Huang, D.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 7398. (h) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1998**, *120*, 6808.

(23) Cotton, F. A.; Murillo, C. A.; Walton, R. A. Eds. *Multiple Bonds between Metal Atoms*, 3rd ed.; Springer Science and Business Media, Inc.: New York, 2005.

crystals. The average of P−Rh−Rh−P torsion angles is −103.5°. The torsion angles of P−Rh−Rh−C are in the range of −12.6(2) to 15.8(2)°. The chirality of this enantiomer is found to be S_M.

There are only a few reports in which structure analyses of both enantiomers have been carried out. Possibly, this has not been worthwhile because usually the crystal structure of the second enantiomer is that of the opposite enantiomorph. Recently, the polymorphism of enantiomers has been of interest due to the needs of the pharmaceutical industry.[24] A detailed analysis of the various types of polymorphism that are theoretically possible with enantiomers has been discussed,[25] but relatively few examples have been found.[26] The structures of *R*-**1** and *S*-**1** are another example of enantiomeric polymorphism.

Compound *SSS*-$Rh_6(cis\text{-}C_6H_4PPh_2)_6(O_2CC_6H_4CO_2)_3(py)_6$ (*SSS*-**3**) crystallizes in the chiral monoclinic space group $P2_1$ with two triangular species together with interstitial solvent molecules in each asymmetric unit. The two independent triangles are essentially identical in structure. One of them is shown in Figure 2, and selected bond distances and angles are listed in Table 4. This triangular molecule has idealized D_3 symmetry with a C_3 axis through the center of the triangle and three C_2 axes each through the midpoint of a dirhodium unit. All six P atoms are equivalent, which is consistent with the $^{31}P\{^1H\}$ NMR spectrum. The triangular molecule has one short (2.529(2) Å) and two long (2.562(2) and 2.556(2) Å) Rh−Rh bonds. The Rh−P distances are in the narrow range between 2.196(5) and 2.223(5) Å and Rh−N distances vary from 2.24(1) to 2.28(1) Å. The Rh−O distances are in the normal range. The terephthalate linkers are both bent and twisted: the carboxylate groups make angles between 6(3)° and 25(2)° with the C_6H_4-ring plane and in the range 12(3)°−37(3)° with each other.

Unlike the racemic triangular compounds reported previously,[10] in which the chirality of each Rh_2 unit is either R_P or S_M, the overall chirality of the enantiopure compound *SSS*-**3** was found to be $S_PS_MS_M$. In other words, in one of the Rh_2 units (the Rh(1)−Rh(2) unit in Figure 2), the P−Rh−Rh−P angle (−75.3(2)°) is smaller than the C−Rh−Rh−C angle (118.7(6)°). Thus, the signs of P(1)−Rh(1)−Rh(2)−C(2)(18.9(4)°) and C(20)−Rh(1)−Rh(2)−P(2) (24.5(4)°) angles are positive. This is very uncommon for simple dirhodium complexes, and the only example reported so far is that of $Rh_2(C_6H_4PPh_2)_2(O_2CCPh_3)_2$, which has two bulky carboxylate ligands in cis positions.[11c] The difference between the P−Rh−Rh−P angle (−94.6(2)°) and the C−Rh−Rh−C angle (87.3(8)°) in the Rh_3−Rh_4 unit is small as compared to those in other units. The Rh(5)−Rh(6) unit is similar to that in compound *S*-**1**, where the P(5)−Rh(5)−Rh(6)−P(6) torsion angle (−103.2(2)°) is greater than the C(92)−Rh(5)−Rh(6)−C(74) (76.0(5)°) angle. The torsion angles of P−Rh−Rh−C and O−Rh−Rh−O are close to those in *R*-**1** except for the P−Rh−Rh−C angles in the Rh_3−Rh_4 units, which are 1.9(5)° for P(4)−Rh(4)−Rh(3)−C(56) and −5.4(7)° for P(3)−Rh(3)−Rh(4)−C(38).

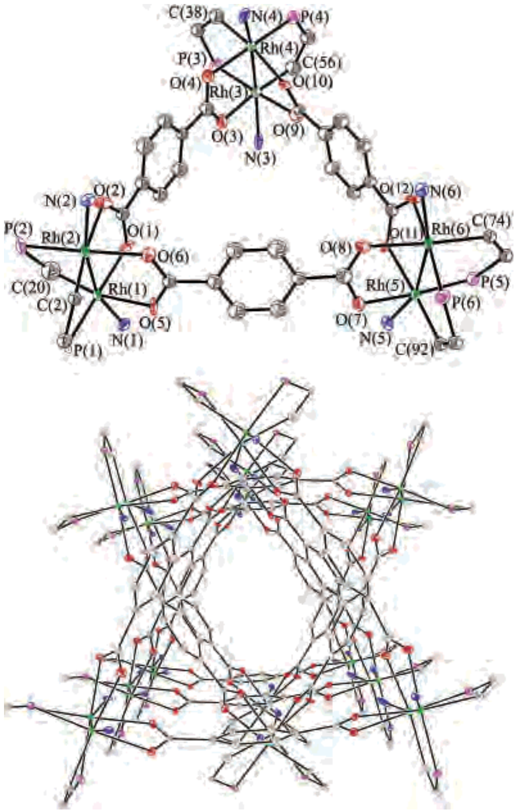

Figure 2. The core structure (top) and packing pattern (bottom) of *SSS*-**3**. Displacement ellipsoids for the core structure are drawn at the 40% probability level. Some carbon atoms in phosphine groups and pyridine ligands, solvent molecules, and hydrogen atoms are omitted for clarity. Note that molecules stack on top of each other, but out of register, leaving a chiral channel.

Table 4. Selected Bond Distances (Å) and Angles (deg) for *SSS*-**3**

Rh(1)−Rh(2)	2.529(2)	Rh(1)−N(1)	2.26(1)
Rh(3)−Rh(4)	2.562(2)	Rh(2)−N(2)	2.24(1)
Rh(5)−Rh(6)	2.556(2)	Rh(1)−O(1)	2.11(1)
Rh(1)−P(1)	2.196(5)	Rh(1)−O(5)	2.14(1)
Rh(2)−P(2)	2.198(5)	Rh(2)−O(2)	2.20(1)
Rh(1)−C(20)	2.065(9)	Rh(2)−O(6)	2.09(1)
Rh(2)−C(2)	2.047(9)		
C(20)−Rh(1)−O(1)	83.1(5)	C(2)−Rh(2)−O(6)	89.6(5)
O(1)−Rh(1)−O(5)	82.9(5)	O(6)−Rh(2)−O(2)	84.3(5)
O(5)−Rh(1)−P(1)	94.0(4)	O(2)−Rh(2)−P(2)	91.9(4)
C(20)−Rh(1)−P(1)	98.9(5)	C(2)−Rh(2)−P(2)	94.2(4)
N(1)−Rh(1)−Rh(2)	163.8(3)	N(2)−Rh(2)−Rh(1)	165.1(3)

The compound *SSS*-$Rh_6(C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_5(CH_2Cl_2)$ (*SSS*-**4**) has five axial pyridine ligands, and the sixth axial position is occupied by a CH_2Cl_2 molecule. Complex *SSS*-**4** crystallizes in the space group $P2_1$ with only one independent triangle together with 2.5 CH_2Cl_2 molecules in each asymmetric unit. Figure 3 shows the ellipsoid plot of this triangle, and selected bond distances and angles are listed in Table 5. The Rh−Rh distances are 2.5252(5), 2.5567(5), and 2.5626(5) Å. The Rh−Rh bond connecting with a CH_2Cl_2 has the shortest distance, which is consistent with that CH_2Cl_2 molecule being a weaker electron donor than

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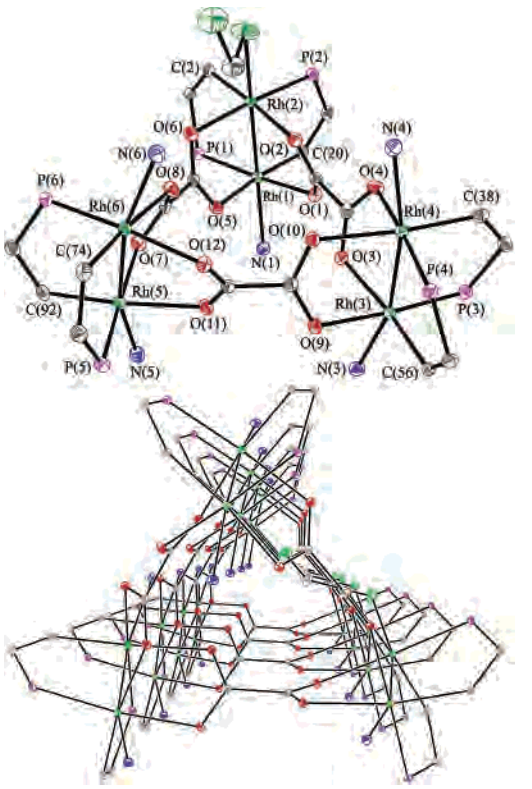

Figure 3. The core structure (top) and packing pattern (bottom) of *SSS*-**4**. Displacement ellipsoids for the core structure are drawn at the 40% probability level. Some carbon atoms in phosphine groups and pyridine ligands, solvent molecules, and hydrogen atoms are omitted for clarity. Note that all molecules stack, leaving a chiral channel.

Table 5. Selected Bond Distances (Å) and Angles (deg) for *SSS*-**4**

Rh(1)−Rh(2)	2.5252(5)	Rh(1)−O(1)	2.117(4)
Rh(3)−Rh(4)	2.5567(5)	Rh(1)−O(5)	2.183(3)
Rh(5)−Rh(6)	2.5626(5)	Rh(2)−O(2)	2.182(4)
Rh(1)−P(1)	2.218(2)	Rh(2)−O(6)	2.122(3)
Rh(2)−P(2)	2.209(1)	Rh(1)−N(1)	2.229(4)
Rh(1)−C(20)	2.029(5)	Rh(2)−Cl(2)	2.636(2)
Rh(2)−C(2)	1.996(5)		
C(20)−Rh(1)−O(1)	88.7(2)	C(2)−Rh(2)−O(6)	93.5(2)
O(1)−Rh(1)−O(5)	80.9 (1)	O(6)−Rh(2)−O(2)	82.1(1)
O(5)−Rh(1)−P(1)	96.0(1)	C(2)−Rh(2)−P(2)	90.2(1)
C(20)−Rh(1)−P(1)	94.2(2)	O(2)−Rh(2)−P(2)	94.3(1)
N(1)−Rh(1)−Rh(2)	165.3(1)	Rh(1)−Rh(2)−Cl(2)	164.78(4)

pyridine. The axial Rh−Cl (CH_2Cl_2) bond distance is 2.636(2) Å, which is significantly shorter than the sum of van der Waals radii for Rh and Cl atoms (about 3.10 Å). This distances is in the range of M−Cl distances 2.4−3.0 Å reported for metal dichloromethane complexes.[22] It is much shorter than the Cr···Cl (3.335(4) Å) and Mo···Cl (3.390(3)Å) separations in the dichloromethane adducts of tetraamidodichromium(II) and tetraamidodimolybdenum(II), in which CH_2Cl_2 is not engaged in significant bonding.[27]

The oxalate linkers in *SSS*-**4** are twisted about the central C−C bonds, with dihedral angles of 41.3−47.7° between the carboxylate groups of the oxalate bridge. All three Rh_2 corners in this triangle have the same twist pattern. The overall chirality of this triangle can be described as $R_PR_PR_P$.

Table 6. Selected Bond Distances (Å) and Angles (deg) for *RRR*-**5**

Rh(1)−Rh(2)	2.523(1)	Rh(2)−O(2)	2.158(7)
Rh(3)−Rh(3A)	2.529(2)	Rh(2)−O(6)	2.114(7)
Rh(1)−P(1)	2.198(3)	Rh(3)−O(3)	2.155(7)
Rh(2)−P(2)	2.193(3)	Rh(3)−O(4)	2.201(7)
Rh(3)−P(3)	2.208(3)	Rh(1)−N(1A)	2.17(3)
Rh(1)−C(20)	2.021(9)	Rh(1)−N(1B)	2.27(6)
Rh(2)−C(2)	1.99(1)	Rh(2)−Cl(1B)	2.61(6)
Rh(3)−C(38A)	2.02(1)	Rh(2)−Cl(1A)	2.79(2)
Rh(1)−O(1)	2.140(7)	Rh(3)−N(2)	2.25(1)
Rh(1)−O(5)	2.193(6)		
C(20)−Rh(1)−O(1)	91.1(3)	O(2)−Rh(2)−P(2)	95.7(2)
O(1)−Rh(1)−O(5)	84.5(3)	Rh(1)−Rh(2)−Cl(1B)	167(1)
O(5)−Rh(1)−P(1)	95.(2)	Rh(1)−Rh(2)−Cl(1A)	164.5(5)
C(20)−Rh(1)−P(1)	88.8(2)	C(38A)1−Rh(3)−O(3)	87.2(3)
N(1A)−Rh(1)−Rh(2)	161.7(8)	O(3)−Rh(3)−O(4)	84.2(3)
N(1B)−Rh(1)−Rh(2)	164(2)	C(38A)−Rh(3)−P(3)	96.4(3)
C(2)−Rh(2)−O(6)	91.7(3)	O(4)−Rh(3)−P(3)	92.1(2)
O(6)−Rh(2)−O(2)	84.8(3)	N(2)−Rh(3)−Rh(3A)	163.5(3)
C(2)−Rh(2)−P(2)	87.8(3)		

In each Rh_2 unit, the torsion angle of P−Rh−Rh−P is bigger than that of C−Rh−Rh−C. The torsion angles of P−Rh−Rh−P and C−Rh−Rh−C are −105.49(5)°, −100.89(5)°, and −108.73(5)° and 78.7(2)°, 78.0(2)°, and 77.7(2)°, respectively. The torsion angles of P−Rh−Rh−C fall in the range of −10.5(2)° to −17.3(2)°. The O−Rh−Rh−O angles are between 17.6(1)° and 20.1(2)°.

The compound *RRR*-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CC_6H_4C_6H_4$-$CO_2)_3(py)_4(CH_2Cl_2)_2$ (*RRR*-**5**) crystallizes in the orthorhombic chiral space group $C222_1$. The triangle resides on a position of C_2 symmetry. Only half of a triangular molecule is independent, and a C_2 axis generates the entire triangle. The six axial positions of this molecular triangle are occupied by four pyridine ligands and two CH_2Cl_2 ligands. The core structure of this compound is shown in Figure S2, and selected bond distances and angles are listed in Table 6.

In *RRR*-**5**, one of the Rh_2 units has two pyridine axial ligands and the others have one pyridine and one CH_2Cl_2. In the Rh_2 unit with two axial pyridine ligands, the Rh−Rh distance of 2.529(2) Å is close to the shortest one in compound *SSS*-**3**. The Rh−Rh distances in the Rh_2 units with one pyridine ligand and one CH_2Cl_2 ligand in the axial positions, 2.523(1) Å, are comparable to the bond distance in the analogous Rh_2 unit in *SSS*-**4**. In the crystal structure, the axial CH_2Cl_2 is disordered in two positions and the average of the Rh−Cl distances is 2.70 Å, which is again much shorter than the sum of van der Waals radii for Rh and Cl. Like the bridging linkers in *SSS*-**3** and *SSS*-**4**, the 4,4′-diphenyl-dicarboxylate dianions in *SSS*-**4** are bent and twisted. The carboxylate groups have dihedral angles between 7.3(5)° and 22(1)° with the C_6H_4-ring plane and angles (13.9(5)° and 40(1)°) with each other. The dihedral angles of the C_6H_4-ring with each other are 33.3(6)° and 36.1(6)°.

As in *SSS*-**3**, there is one Rh_2 unit (Rh(3)−Rh(3A) unit in Figure S2) in which the P−Rh−Rh−P angle (75.8(1)°) is smaller than the C−Rh−Rh−C angle (−116.9(6)°). In the other two Rh_2 units, the P−Rh−Rh−P angle (101.1(1)°) is larger than the C−Rh−Rh−C angle (−74.9(4)°). The torsion angles are 13.5(3)° for P(1)−Rh(1)−Rh(2)−C(2), 12.7(2)° for P(2)−Rh(2)−Rh(1)−C(20), and −20.5(3)° for P(3)−

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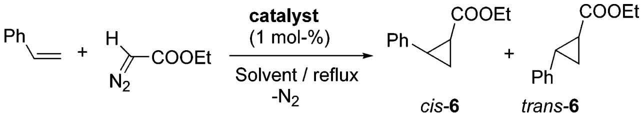
Scheme 2



Rh(3)−Rh(3A)-C(38). The O−Rh−Rh−O angles are in the range of 15.2(3)−18.0(3)°.

The molecular structures of **3**−**5** can each be described as an equilateral triangle composed of three Rh_2 units linked by dicarboxylate dianions. The edges of the triangles are about 11.1, 6.8, and 15.4 Å for **3**, **4**, and **5**, respectively. The space inside each triangle is large enough to accommodate small molecules, and there are some disordered solvent molecules inside the triangles in *SSS*-**3** and *RRR*-**5**. The packing patterns of these compounds are also interesting. The chiral molecules stack together to form asymmetric environments. In *SSS*-**3**, the triangular molecules stack on top of each other but out of register, i.e., with alternating orientations differing by about 60° (Figure 2). Thus, a projection in the stacking direction has a hexagonal cross section, and the channel is filled with disordered solvent molecules. In *SSS*-**4**, the triangular molecules stack in register resulting in the formation of a triangular channel (Figure 3). In *RRR*-**5**, the triangular molecules stack with alternating orientations differing by about 60°, such as in *SSS*-**3**, and the centers of the molecules have alternating displacement from the mean stacking axis. Thus, a distorted hexagonal channel is created by the stacking of *RRR*-**5** (Figure S2).

Asymmetric Cyclopropanation of Styrene with Ethyl Diazoacetate Catalyzed by Rh_2-Chiral Organometallic Triangles. The search for new asymmetric dirhodium(II) catalysts capable of inducing high enantiocontrol in transformations of diazo compounds is growing because of (i) the impressive accomplishment achieved with such catalysts in many asymmetric metal carbene transformations involved in the synthesis of complex molecules such as natural products and (ii*)* the limited enantiocontrol achieved so far in the transformation of α-diazo ketones and α-diazo ester.[28] In this context, it has been reported some time ago that chiral dirhodium(II) complexes with a variety of orthometalated bridging phosphines are superior catalysts for the enantioselective intermolecular cyclopropanation of styrenes with ethyl diazoacetate (Scheme 2).[11a,c] Such enantiopure catalysts are based on discrete Rh−Rh units with two orthometalated phosphines in cis positions and two bridging carboxylate ligands. Since the $(Rh-Rh)_3$-enantiomerically pure triangular supramolecules were constructed from an asymmetric catalyst, namely, the Rh−Rh units with orthometalated triphenyl phosphine ligands, it was pertinent to evaluate the catalytic activity/selectivity performance of the chiral organometallic triangles for a typical metal carbene transformation, such as the model intermolecular cyclopropanation reaction of styrene with ethyl diazoacetate.[29]

Table 7. Asymmetric Catalytic Cyclopropanation of Styrene with Ethyl Diazoacetate in Refluxing CH_2Cl_2 or *n*-C_5H_{12}

				% ee[d]	
catalyst	solvent	yield **6**, %[b]	cis/trans[c]	*cis*-**6**[e]	*trans*-**6**[e]
3	CH_2Cl_2	50	40:60	70	80
3	*n*-C_5H_{12}	74	40:60	32	60
4	CH_2Cl_2	55	55:45	14	25
4	*n*-C_5H_{12}	64	58:42	32	28
5	CH_2Cl_2	45	35:65	62	58
7[a]	CH_2Cl_2	55	48:52	91	87

[a] Reference 11c. [b] Cyclopropanes yields based on ethyl diazoacetate. [c] Ratio determined by GC analysis and ^1H NMR spectroscopy. [d] Values determined by GC on a 2,3-di-*O*-acetyl-6-*O*-(*ter*-butyldimethylsilyl)-*β*-CDX column. [e] The configuration of *cis*-**6** *(1S,2R)* and *trans*-**6** *(1S, 2S)* cyclopropanes obtained with catalysts **3**−**5** were determined by correlation of the sign of the rotation of polarized light with those cyclopropane enantiomers previously published (ref 30b).

The catalytic activity of three triangular organometallic compounds, namely *SSS*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(C_8H_4O_4)(py)_2]_3$ (**3**), *SSS*-{*cis*-$Rh_6(C_6H_4PPh_2)_6(C_2O_4)(py)_5(CH_2Cl_2)$} (**4**), and *SSS*-{*cis*-$Rh_6(C_6H_4PPh_2)_6(C_{14}H_8O_4)(py)_4(CH_2Cl_2)_2$} (**5**), was evaluated in the intermolecular cyclopropanation reaction of styrene with ethyl diazoacetate in both dichloromethane and pentane as solvents. The diastereoselectivity and enantioselectivity results are shown in Table 7. The catalytic results of the previously reported discrete enantiopure *S*-{*cis*-$Rh_2(C_6H_4PPh_2)_2(O_2CCF_3)(H_2O)_2$} (**7**) in dichloromethane are also reported for comparison. While *S*-{*cis*-$Rh_2(C_6H_4PPh_2)_2(O_2CCF_3)(H_2O)_2$} induced low diastereoslectivity (cis/trans, 48:52) and higher enantioselectivity, the triangular organometallic compounds, particularly **3** and **5** gave higher trans selectivity (up to 35:65 cis/trans with compound **3**) and good enantioselectivity (ca. 70 and 80% for *cis*-**6** and *trans*-**6** cyclopropanes, respectively) with enantiopure compound **3**. Use of the triangular organometallic compound **4** resulted in an increase in cis selectivity but lower enantioselectivity in dichloromethane.

The enantiocontrol achieved, particularly with catalysts **3** and **5**, is superior to that of the known dirhodium(II) catalysts with chiral carboxamide ligands such as Rh_2(*5S*-MEPY)$_4$ (ca. 33 and 58% for *cis*-**6** and *trans*-**6**, respectively),[30] as well as with those dirhodium(II) compounds with chiral carboxylates ligands,[31] where enantioselectivities did not exceed 12% ee for the same intermolecular cyclopropanation reaction between styrene and ethyl diazoacetate. However, the enantiocontrol performances of catalysts **3**−**5** were found to be less than those achieved using discrete dirodium(II) with orthometalated aryl phosphine ligands, such as triphenyl phosphine ligands. The higher enantiocontrol achieved with the discrete catalysts having orthometalated aryl ligands was rationalized using a model transition state, which shows that the cyclopropanation between styrene and ethyl diazoacetate preferentially occurs in the area of the carboxylate ligands,

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thus entailing smaller steric effects for the orientation and stabilization of the Rh−CHCOOEt species.[11c]

Solvent effects on activity and selectivity of dirhodium(II) catalysts in reactions of diazo compounds has been demonstrated.[32] The polarity of the solvent used in the reaction of diazo compound transformation can increase or decrease the enantiocontrol of the process depending on the dirhodium(II) catalysts and the type of the carbene transfer reaction. It seems that the solvent can affect to some extent the alignment of the ligands on chiral dirhodium(II) compounds, thereby affecting the enantiocontrol over the diazo compound transformation.[33]

To evaluate such solvent effects, we exposed compounds **3** and **5** to ethyl diazoacetate and styrene in pentane (n-C_5H_{12}) and followed the outcome of the cyclopropanation reaction in terms of activity and selectivity. The results are shown in Table 7 and are compared with those obtained in CH_2Cl_2. The first observation is that the yield was remarkably increased to 64 and 74% when using catalysts **3** and **4**, respectively. A slight increase in the cis selectivity was observed for compound **4**, as well as an increase in the enantioselectivity (ca. 32 and 28% for *cis*-**6** and *trans*-**6**, respectively). However, a decrease in enantioselectivity was observed with compound **3**. It is important to mention that the triangular organometallic supramolecules were practically insoluble in pentane, which indicates that they were acting as heterogeneous catalysts in the intermolecular cyclopropanation. Their separation from the reaction products was easily conducted by filtration. Despite the insolubility of these supramolecular catalysts in a nonpolar solvent such as pentane, they have shown remarkable catalytic activity with a notable enantiocontrol when compared with known heterogeneous catalysts used for metal carbene transformation.

The present results on the catalytic activity/selectivity of chiral organometallic triangles containing chiral building units with Rh−Rh bonds are promising. They are very active and remarkably selective catalysts when compared to the rest of dirhodium(II) catalysts. Their size permits the performance of the catalytic reactions either *homogeneously or heterogeneously* depending on the reaction solvent. Further studies aiming to extend the utilization of these catalysts to intramolecular diazo compound transformations such as cyclopropanation of α-diazo ketones and α-diazo ester and C−H insertions are of unusual interest because of the lack of higher enantiocontrol in transformations of these types.

Electrochemistry. Compounds **3**, **4**, and **5** have been studied by both CV and DPV. The CV of **3** in a solution of 10 mL of CH_2Cl_2 containing 0.02 mL of pyridine shows a redox process with a maximum wave at $E_{red} = 0.441$ V and $E_{ox} = 0.716$ V. Its DPV has a broad signal with a maximum at 0.596 V. The CV and DPV of **5** in 10 mL of CH_2Cl_2 containing 0.15 mL of pyridine are similar to those of **4**, with CV at $E_{red} = 0.457$ V and $E_{ox} = 0.695$ V, and DPV at 0.528 V. As expected, compound **4** has a higher degree of electronic communication between the Rh_2 units. Electrochemical measurements of **4** in CH_2Cl_2 show three reversible oxidation processes with $E_{1/2}$'s at 0.615, 0.737 and 0.952 V (from DPV). The $E_{1/2}$ values were shifted negatively to 0.459, 0.599 and 0.653 V as 0.02 mL of pyridine was added. The triangular configuration of these compounds remains stable in different axial coordinations, as shown by the single-crystal structures of the compounds *SSS*-Rh_6(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_{4.75}(CH_3OH)_{1.25}$[20] and *SSS*-$Rh_6$(*cis*-$C_6H_4PPh_2)_6(O_2CCO_2)_3(CH_3OH)_5(H_2O)$.[13] The oxidation of the Rh_2 units in **4** remains reversible in the presence of various coordinating ligands. The combination of electroactivity and the complexation features of these triangular molecules in the axial positions suggest that they have potential as sensory materials. The axial positions of these molecules may serve as receptors for the complexation of electron-donor substrates. The binding of the substrates in the triangular molecules will change their $E_{1/2}$ values and enable electrochemical sensing.

Conclusion

The preparation and structural characterization of compounds **3**−**5** show that enantiopure organometallic molecular triangles can be prepared readily from the self-assembly reaction of rigid dicarboxylate linkers and an enantiopure orthometalated dirhodium compound *cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6(BF_4)_2$. Compounds **4** and **5** are the only isolated dirhodium compounds with axial dichloromethane ligands ever found. The interesting electrochemical properties of **4** suggest potential application in neutral molecular sensing. The structural characterization of both enantiomers of compound **1** fortuitously provides an example of polymorphism.

This work is another step in our effort to synthesize enantiomerically selective catalysts and molecular sensors based on supramolecular compounds. The catalytic evaluation of the enantiopure triangles showed that they are catalytically active and provided good results for the intermolecular cyclopropanation between styrene and ethyl diazoacetate. The use of these triangles as catalysts in the intramolecular cyclopropanation of diazo compounds and in other uses is of interest and will be investigated further.

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Supporting Information Available: X-ray crystallographic files in CIF format for *R*-**1**, *S*-**1**, *SSS*-**3**, *SSS*-**4**, *RRR*-**4**, *RRR*-**5**, *SSS*-Rh_6-

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$(cis\text{-}C_6H_4PPh_2)_6(C_2O_4)(CH_3OH)_5(H_2O)$, *SSS*-$Rh_6(cis\text{-}C_6H_4PPh_2)_6(O_2CC_6H_4CO_2)_3(py)_3(CH_3OH)_3$, *SSS*-$Rh_6(cis\text{-}C_6H_4PPh_2)_6(O_2CCO_2)_3(py)_{4.75}(CH_3OH)_{1.25}$, and *RRR*(*SSS*)-$Rh_6(cis\text{-}C_6H_4PPh_2)_6(O_2CC_6H_4CO_2)_3(py)_{1.5}(CH_3OH)_{4.5}$; displacement ellipsoid plots of *S*-**1** and *RRR*-**5** (Figures S1 and S2, respectively) in pdf format. This material is available free of charge via the Internet at http://pubs.acs.org.

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