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Chiral Supramolecules: Organometallic Molecular Loops Made from Enantiopure *R*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6](BF_4)_2$

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Two enantiopure molecular loops, *RR*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(py)_2O_2C(CF_2)_nCO_2]_2$ (**1**, $n = 2$ and **2**, $n = 3$) have been made from the reaction in CH_2Cl_2 and CH_3OH of the inherently chiral dirhodium compound, *R*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6](BF_4)_2$, and $HO_2C(CF_2)_nCO_2H$ in the presence of an excess of pyridine. Single-crystal structure analyses reveal that each of these compounds is composed of two *R*-*cis*-$Rh_2(C_6H_4PPh_2)_2(\text{ax-py})_2^{2+}$ units, and two equatorial perfluorodicarboxylate linkers, which form a loop oligomer. The ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ and C_5D_5N indicate that only one type of highly symmetric species exists in each solution, which is consistent with the solid-state structures.

Introduction

The study of metal-based units as key elements in self-assembly of supramolecular arrays is a topic of great interest in supramolecular chemistry.[1−3] This field of research began with the use of *cis*-ML_2^{2+} units (where M is a single metal atom, usually Pt^{2+}, Pd^{2+}, Zn^{2+}, or Cd^{2+} and L represents a monodentate or half of a bidentate ligand) as the metallic component.[2] Such supramolecules are usually ionic with high charges. Beginning in early 1998, metal−metal bonded dinuclear species bridged with two or three formamidinate ligands have been used in this laboratory for the preparation of redox-active neutral supramolecules.[3] Appropriate selection of metal−ligand interactions, proper choice of the metal-containing units, and the use of suitable linkers have led to the self-assembly of numerous interesting supramolecular architectures, such as triangles, squares and other polygons, helices, and polyhedra, as well as 2D and 3D infinite structures.[2,3] These compounds not only show interesting structural features but also have various potential applications, for example in catalysis, chemical sensing, and chemical separation.

The use of chiral transition metal complexes to catalyze the synthesis of single enantiomers of chiral organic compounds is now an important contemporary technique in both laboratory-scale and industrial chemistry.[4] Introduction of chirality into supramolecular architectures might provide new approaches to asymmetric catalysis. However, there have been few reports on the catalysis of chiral metallo-supramolecules[5] because most such compounds are coordinately saturated, and this hinders their application in metal-based catalysis.

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The preparation and structure of *cis*-$Rh_2(C_6H_4PPh_2)_2(OAc)_2(HOAc)_2$ was reported in 1985;[6] it was synthesized from the reaction of $Rh_2(OAc)_4$ and PPh_3 in acetic acid under reflux. Its structure is composed of a singly bonded Rh−Rh subunit with two cisoid, head-to-tail, orthometalated $C_6H_4PPh_2$ groups and two cisoid acetate anions in the equatorial sites, as well as two acetic acid molecules in the axial positions. The *cis*-$Rh_2(C_6H_4PPh_2)_2^{2+}$ unit is inherently chiral because the head-to-tail arrangement excludes the existence of an improper axis. The absolute chirality of this dirhodium unit can be defined by the relationship of the phosphine ligands and the torsion angle of each phosphine ligand as described before.[7]

We have reported that racemic neutral molecular triangles which have six kinetically labile ligands in axial positions can be prepared from the self-assembly of racemic mixtures containing the dirhodium units and linear rigid-dicarboxylate anions.[7] Interestingly, only triangular compounds have been isolated and there is no evidence of molecular squares, even though the formation of squares is enthalpically favored by the near 90° angle subtended at the dimetal unit when linear rigid dicarboxylate linkers are used. The enantiomers of these triangles have also been prepared, and homogeneous and heterogeneous asymmetric catalysis by these chiral triangles in the intermolecular carbenoid transfer reaction of ethyl diazo ester has shown that these chiral triangles are very active and have remarkable selectivity when compared with simple Rh_2 paddlewheel catalysts with chiral amidate ligands.[8]

We report here the preparation, structures, and multinuclear NMR spectra of two enantiopure molecular loops, *RR*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(py)_2O_2C(CF_2)_nCO_2]_2$ (**1**, $n = 2$ and **2**, $n = 3$), which were prepared from the reaction of perfluorinated dicarboxylates and enantiopure *R*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6](BF_4)_2$, which was made using a procedure similar to that for the preparation of the racemic analogue[7] in which the resolved diastereoisomer *R*-*cis*-$Rh_2(C_6H_4PPh_2)_2(protos)_2(H_2O)_2$ (protos = *N*-4-methylphenylsulfonyl-L-proline anion)[4e] was employed as starting material. Compounds **1** and **2** are the first examples of chiral molecular loops formed with chiral metal components, achiral ligands, and labile axial ligands. They may have potential applications in homogeneous or heterogeneous asymmetric catalysis,[9] e.g., in the decomposition reaction of diazo compounds. A few molecular loops containing dimetal components have been produced previously from the self-assembly of [*cis*-$M_2(DAniF)_2(CH_3CN)_4](BF_4)_2$ (M = Mo[10] and Rh[10,11]) and bent or flexible dicarboxylate dianions. However, to our knowledge, only two chiral molecular loops with two dimetal building blocks linked with chiral bridges have been made, *cis*-$Mo_2(DAniF)_2(O_2CCH{=}C{=}CHCO_2)_2$[12] and *cis*-$Mo_2(DAniF)_2$(*p*-$O_2CCH(CH_3)C_6H_4CH(CH_3)CO_2)_2$.[13]

Experimental Section

Materials and Methods. Unless otherwise stated, all manipulations and procedures were conducted in air. Solvents were used as received. All other reagents were purchased from commercial sources and used as received. Enantiopure *R*-*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6(BF_4)_2$ was prepared following a procedure similar to that for the preparation of the racemic compound[7] but using *R*-$Rh_2(C_6H_4PPh_2)_2(protos)_2(H_2O)_2$ as starting material.[4e]

Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia. ^{1}H NMR (using the residual proton of $CDCl_3$ as reference), $^{31}P\{^1H\}$NMR (with H_3PO_4 in $CDCl_3$ as reference), and ^{19}F NMR (CF_3COOH in $CDCl_3$ as reference) spectra were recorded on an Inova-300 NMR spectrometer.

Preparation of *RR*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(py)_2O_2C(CF_2)_2CO_2]_2$, 1. A solution of *R*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6](BF_4)_2$ (30 mg, 0.028 mmol) and $HO_2C(CF_2)_2CO_2H$ (10 mg, 0.052 mmol) in 4 mL of CH_2Cl_2, 1 mL of methanol, and 5 drops of pyridine was layered with 5 mL of methanol. Orange crystals were isolated after two weeks when the diffusion was complete. Yield: 22 mg, 72%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.609 (d, 8H, pyridine), 7.603 (t, 4H, aromatic), 7.331 (t, 4H, aromatic), 6.697−7.042 (m, 56 H, aromatic), 6.418 (t, 4H, aromatic). $^{31}P\{^1H\}$ NMR ($CDCl_3$ and C_5D_5N, δ, ppm): 24.25 (d, $^1J_{PRh} = 170.79$ Hz). ^{19}F NMR ($CDCl_3$ and C_5D_5N, δ, ppm): −42.10 (dd, $^4J_{FRh} = 646.04$ and 256.37 Hz). Anal. Calcd for $C_{100}H_{76}N_4F_8O_8P_4Rh_4$: C 55.86, H 3.57, N 2.61%. Found: C 55.72, H 3.41, N 2.49%.

Preparation of *RR*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(py)_2O_2C(CF_2)_3CO_2]_2$, 2. A solution of *R*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6](BF_4)_2$ (30 mg, 0.028 mmol) and $HO_2C(CF_2)_3CO_2H$ (10 mg, 0.040 mmol) in 3 mL of CH_2Cl_2, 1 mL of methanol, and 5 drops of py was layered with 5 mL of methanol. Orange crystals were isolated after three weeks when diffusion was complete. Yield: 25 mg, 79%. ^{1}H NMR (CD_2Cl_2, δ, ppm): 8.580 (d, 8H, pyridine), 7.589 (t, 4H, aromatic), 7.310 (dd, 4H, aromatic), 6.677−7.161 (m, 56 H, aromatic), 6.385 (t, 4H, aromatic). $^{31}P\ \{^1H\}$ NMR ($CDCl_3$ and C_5D_5N, δ, ppm): 22.14-(d, $^1J_{PRh} = 170.34$ Hz). ^{19}F NMR ($CDCl_3$ and C_5D_5N, δ, ppm): −40.75(dd, $^4J_{FRh} = 663.76$ and 282.04 Hz), −44.74 (s, central CF_2) Anal. Calcd for $C_{102}H_{76}N_4F_{12}O_8P_4Rh_4$: C 54.45, H 3.41, N 2.49%. Found: 54.33, H 3.35, N 2.39%.

X-Ray Structure Determination. Data were collected on 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] while absorption corrections were applied by using the program SADABS.[16] The positions of the Rh atoms were found via direct methods

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Table 1. Crystallographic Data for the Molecular Loops **1** and **2**

compound	**1**·3CH_2Cl_2·CH_3OH·0.5H_2O	**2**·3.5CH_2Cl_2·2CH_3OH
chemical formula	$C_{104}H_{87}Cl_6F_8N_4O_{9.5}P_4Rh_4$	$C_{107.5}H_{91}Cl_7F_{12}N_4O_{10}P_4Rh_4$
fw	2445.00	2610.51
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1$
a (Å)	15.65(1)	12.971(3)
b (Å)	17.64(2)	18.364(4)
c (Å)	19.21(2)	23.397(5)
β (deg)	99.30(2)	105.347(4)
V (Å^3)	5231(8)	5374(2)
Z	2	2
d_{calcd} (g cm^{-3})	1.552	1.613
μ(Mo K$_\alpha$) (mm^{-1})	0.907	0.918
T, °C	−60	−60
GOF	1.007	1.057
R1,[a] wR2[b]($I > 2\sigma$)	0.0603, 0.1615	0.0549, 0.1381
abs structure param (Flack)	−0.04(3)	−0.01(3)

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

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. All hydrogen atoms were included in the calculation of the structure factors. Non-hydrogen atoms in the molecular loops, except those that were disordered, were refined with anisotropic displacement coefficients.

The $-(CF_2)_3-$ groups in compound **2** are disordered over two orientations in a ratio of ca. 1:1. Other details of data collection and refinement are given in Table 1. Crystallographic data are available as Supporting Information.

Results and Discussion

Syntheses. The net reactions used to prepare **1** and **2** are summarized by the following equation:

$$2R\text{-}[cis\text{-}Rh_2(C_6H_4PPh_2)_2(CH_3CN)_6](BF_4)_2 + 2HO_2C(CF_2)_nCO_2H + 8py \rightarrow RR\text{-}[Rh_2(C_6H_4PPh_2)_2(py)_2O_2C(CF_2)_nCO_2]_2 + 4pyHBF_4$$

When the reaction was carried out in a mixture of CH_2Cl_2, pyridine, and methanol, a clear solution was obtained. This solution was then layered with methanol to give an analytically pure product in high yield. The use of the polar solvent methanol is helpful in keeping reactants and intermediates, as well as the byproduct $pyHBF_4$, in solution.

For the reactions to proceed smoothly, it is also very important to use an excess of pyridine for two main reasons. First, the dirhodium unit, *cis*-$Rh_2(C_6H_4PPh_2)_2^{2+}$, has a strong tendency to axially coordinate electron donors, such as acetic acid, methanol, water, and pyridine.[6,7] Only when an excess of pyridine is used is the pure pyridine adduct, i.e., one with a py ligand in every axial position obtained. Second, pyridine neutralizes the strong acid HBF_4 that would otherwise be liberated and prevent the reactions from going to completion.

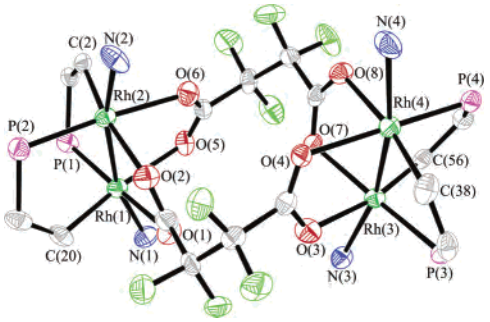

Figure 1. Core structure of the chiral molecular loop *RR*-*cis*-$[Rh_2(C_6H_4PPh_2)_2(py)_2(O_2CCF_2CF_2CO_2)]_2$. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and some of the carbon atoms in the orthometalated $C_6H_4PPh_2$ group and pyridine molecules are omitted for clarity.

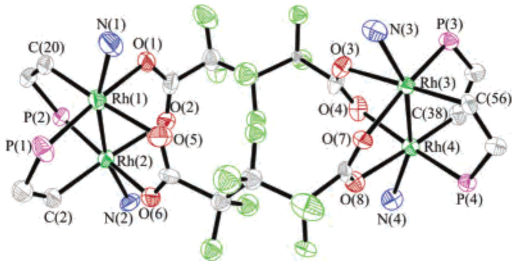

Figure 2. Core structure of *RR*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(py)_2(O_2CCF_2CF_2CF_2CO_2)]_2$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and some of the carbon atoms in the $C_6H_4PPh_2$ group and pyridine molecules are omitted for clarity.

Compounds **1** and **2** are very soluble in CH_2Cl_2 and $CDCl_3$. In each case, the ^{1}H NMR, ^{19}F NMR, and ^{31}P{^{1}H} NMR spectra are consistent with the presence of only one highly symmetric species in solution. Again, the addition of an excess of C_5D_5N to the NMR samples was necessary to guarantee that the labile axial sites are all occupied by the same molecules. Each ^{31}P{^{1}H} NMR spectrum shows only one doublet. The doublet structure is due to coupling of the P atom to the ^{103}Rh atom to which it is bound. There is a doublet of doublets in the ^{19}F NMR spectra of each of these compounds that have been assigned to the F atoms of the CF_2 groups adjacent to the carboxylate groups. For **2**, the signal for the central CF_2 group is a singlet. The appearance of the doublet of doublets is due to the coupling of the F nuclei with two ^{103}Rh nuclei ($I = {}^1/_2$) which, while chemically equivalent, have different atoms (C or P) trans to each of the $-CF_2CO_2$ oxygen atoms.

Structures. Compounds **1** and **2** both crystallize along with interstitial molecules in the monoclinic chiral space group $P2_1$ with $Z = 2$. The core structures are depicted in Figures 1 and 2. Selected bond distances, bond angles, and torsion angles are listed in Tables 2 and 3. Each compound is composed of two inherently chiral dirhodium units. Each dirhodium unit contains two cisoid, head-to-tail orthometalated $C_6H_4PPh_2^-$ ligands and two carboxylate groups. The dirhodium units are linked by two perfluorodicarboxylate bridges ($-(CF_2)_2-$ in **1** or $-(CF_2)_3-$ in **2**) to form molecular loops. The axial positions of the dirhodium units are all occupied by pyridine molecules. The idealized overall symmetry is D_2, which is consistent with the NMR spectra,

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

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Table 2. Selected Bond Distances (Å), Bond Angles, and Torsion Angles (deg) for **1**

Rh(1)−Rh(2)	2.538(2)	Rh(2)−N(2)	2.280(8)
Rh(3)−Rh(4)	2.537(2)	Rh(3)−N(3)	2.280(8)
Rh(1)−P(1)	2.222(3)	Rh(4)−N(4)	2.276(7)
Rh(2)−P(2)	2.196(3)	Rh(1)−O(1)	2.170(7)
Rh(3)−P(3)	2.218(3)	Rh(1)−O(5)	2.150(6)
Rh(4)−P(4)	2.198(3)	Rh(2)−O(2)	2.189(7)
Rh(1)−C(20)	1.978(8)	Rh(2)−O(6)	2.171(6)
Rh(2)−C(2)	1.978(9)	Rh(3)−O(3)	2.174(6)
Rh(3)−C(56)	2.010(9)	Rh(3)−O(7)	2.214(7)
Rh(4)−C(38)	1.979(9)	Rh(4)−O(4)	2.167(6)
Rh(1)−N(1)	2.208(8)	Rh(4)−O(8)	2.148(7)
N(1)−Rh(1)−Rh(2)	164.4(2)	N(3)−Rh(3)−Rh(4)	168.2(2)
C(20)−Rh(1)−O(1)	86.5(3)	C(56)−Rh(3)−O(7)	85.1(4)
O(5)−Rh(1)−O(1)	84.2(3)	O(3)−Rh(3)−O(7)	86.3(2)
O(5)−Rh(1)−P(1)	93.3(2)	O(3)−Rh(3)−P(3)	90.8(2)
C(20)−Rh(1)−P(1)	95.9(3)	C(56)−Rh(3)−P(3)	97.7(3)
N(2)−Rh(2)−Rh(1)	166.0(2)	N(4)−Rh(4)−Rh(3)	164.8(2)
C(2)−Rh(2)−O(6)	83.1(3)	C(38)−Rh(4)−O(4)	85.6(3)
O(6)−Rh(2)−O(2)	87.4(2)	O(8)−Rh(4)−O(4)	84.1(2)
O(2)−Rh(2)−P(2)	92.7(2)	O(8)−Rh(4)−P(4)	94.0(2)
C(2)−Rh(2)−P(2)	96.8(3)	C(38)−Rh(4)−P(4)	96.1(2)
P(1)−Rh(1)−Rh(2)−P(2)	75.7(1)	P(3)−Rh(3)−Rh(4)−P(4)	74.56(9)
C(20)−Rh(1)−Rh(2)−C(2)	−116.9(4)	C(56)−Rh(3)−Rh(4)−C(38)	−119.2(4)
P(1)−Rh(1)−Rh(2)−C(2)	−21.0(3)	P(3)−Rh(3)−Rh(4)−C(38)	−21.5(2)
C(20)−Rh(1)−Rh(2)−P(2)	−20.3(3)	C(56)−Rh(3)−Rh(4)−P(4)	−23.1(3)
O(1)−Rh(1)−Rh(2)−O(2)	−13.6(2)	O(3)−Rh(3)−Rh(4)−O(4)	−16.0(3)
O(5)−Rh(1)−Rh(2)−O(6)	−10.5(2)	O(7)−Rh(3)−Rh(4)−O(8)	−14.0(2)

Table 3. Selected Bond Distances (Å), Bond Angles, and Torsion Angles (deg) for **2**

Rh(1)−Rh(2)	2.580(1)	Rh(2)−N(2)	2.297(5)
Rh(3)−Rh(4)	2.5816(9)	Rh(3)−N(3)	2.289(7)
Rh(1)−P(1)	2.221(2)	Rh(4)−N(4)	2.272(7)
Rh(2)−P(2)	2.220(2)	Rh(1)−O(1)	2.207(5)
Rh(3)−P(3)	2.211(2)	Rh(1)−O(5)	2.175(5)
Rh(4)−P(4)	2.209(2)	Rh(2)−O(2)	2.157(5)
Rh(1)−C(20)	2.017(7)	Rh(2)−O(6)	2.199(6)
Rh(2)−C(2)	2.004(7)	Rh(3)−O(3)	2.186(5)
Rh(3)−C(56)	2.014(7)	Rh(3)−O(7)	2.185(5)
Rh(4)−C(38)	2.013(6)	Rh(4)−O(4)	2.174(5)
Rh(1)−N(1)	2.257(7)	Rh(4)−O(8)	2.187(4)
N(1)−Rh(1)−Rh(2)	166.0(2)	N(3)−Rh(3)−Rh(4)	162.0(2)
C(20)−Rh(1)−O(5)	91.1(2)	C(56)−Rh(3)−O(3)	91.9(3)
O(5)−Rh(1)−O(1)	83.9(2)	O(7)−Rh(3)−O(3)	85.3(2)
O(1)−Rh(1)−P(1)	96.5(2)	O(7)−Rh(3)−P(3)	93.1(1)
C(20)−Rh(1)−P(1)	88.4(2)	C(56)−Rh(3)−P(3)	89.8(2)
N(2)−Rh(2)−Rh(1)	165.0(2)	N(4)−Rh(4)−Rh(3)	161.4(2)
C(2)−Rh(2)−O(2)	91.0(2)	C(38)−Rh(4)−O(8)	91.6(2)
O(2)−Rh(2)−O(6)	85.4(2)	O(4)−Rh(4)−O(8)	86.6(2)
O(6)−Rh(2)−P(2)	94.5(2)	O(4)−Rh(4)−P(4)	93.2(1)
C(2)−Rh(2)−P(2)	89.2(2)	C(38)−Rh(4)−P(4)	88.8(2)
P(1)−Rh(1)−Rh(2)−P(2)	99.00(8)	P(3)−Rh(3)−Rh(4)−P(4)	100.66(7)
C(20)−Rh(1)−Rh(2)−C(2)	−77.8(3)	C(56)−Rh(3)−Rh(4)−C(38)	−77.3(3)
P(1)−Rh(1)−Rh(2)−C(2)	10.2(2)	P(3)−Rh(3)−Rh(4)−C(38)	12.1(2)
C(20)−Rh(1)−Rh(2)−P(2)	11.0(2)	C(56)−Rh(3)−Rh(4)−P(4)	11.2(2)
O(1)−Rh(1)−Rh(2)−O(2)	16.6(2)	O(3)−Rh(3)−Rh(4)−O(4)	13.2(2)
O(5)−Rh(1)−Rh(2)−O(6)	15.1(2)	O(7)−Rh(3)−Rh(4)−O(8)	14.5(2)

but the molecular loop is located on a general position in the X-ray structure.

In compound **1**, the Rh−Rh bond distances of 2.538(2) and 2.537(2) Å are similar to those found in other orthometalated dirhodium complexes[7,18] as are the Rh−P and Rh−C distances. One of the four Rh−N distances (2.208(8) Å) is much shorter than the others (about 2.280(8) Å). Because there is no obvious chemical reason for such a difference, it is possible that crystal packing forces might be the cause. The P−Rh−Rh−C torsion angles are in the range of −20.3(3)° to −23.1(3)°, and those for O−Rh−Rh−O are between −10.5(2)° and −16.0(3)°. In this complex, the P−Rh−Rh−P torsion angles (75.7(1)° and 74.56(9)°) are smaller than those of C−Rh−Rh−C (−116.9(4)° and −119.2(4)°). Therefore, the overall chirality of this dirhodium compound is R_MR_M.[19] This is uncommon for simple dirhodium compounds, in which the torsion angle of P−Rh−Rh−P is usually larger than that of C−Rh−Rh−C[18] because of steric repulsions between the bulky phenyl groups in the phosphines.

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(18) (a) Barceló, F.; Cotton, F. A.; Lahuerta, P.; Sanaú, M.; Schwotzer, W.; Ubeda, M. A. *Organometallics* **1987**, *6*, 1105. (b) Lahuerta, P.; Martínez-Mañez, R.; Paya, J.; Peris, E. *Inorg. Chim. Acta* **1990**, *173*, 99. (c) Morrison, E. C.; Tocher, D. A. *J. Organomet. Chem.* **1991**, *408*, 105. (d) Lahuerta, P.; Payá, J.; Peris, E.; Aguirre, A.; García-Granda, S.; Gómez-Beltrán, F. *Inorg. Chim. Acta* **1992**, *192*, 43. (e) Borrachero, M. V.; Estevan, F.; García-Granda, S.; Lahuerta, P.; LaTorre, J.; Peris, E.; Sanaú. M. *Chem. Commun.* **1993**, 1864. (f) Estevan, F.; Lahuerta, P.; Peris, E.; Ubeda, M. A.; García-Granda, S.; Gómez-Beltrán, F.; Pérez-Carreño, E.; González, G.; Martínez, M. *Inorg. Chim. Acta* **1994**, *218*, 189. (g) Estevan, F.; García-Granda, S.; Lahuerta, P.; LaTorre, J.; Peris E.; Sanaú, M. *Inorg. Chim. Acta*. **1995**, *229*, 365. (h) Lahuerta, P.; Pereira, I.; Pérez-Prieto, J.; Sanaú, M.; Stiriba, S.-E.; Taber, D. F. *J. Organomet. Chem.* **2000**, *612*, 36. (i) Estevan, F.; Krueger, P.; Lahuerta, P.; Moreno, E.; Pérez-Prieto, J.; Sanaú, M.; Werner, H. *Eur. J. Inorg. Chem.* **2001**, 105.

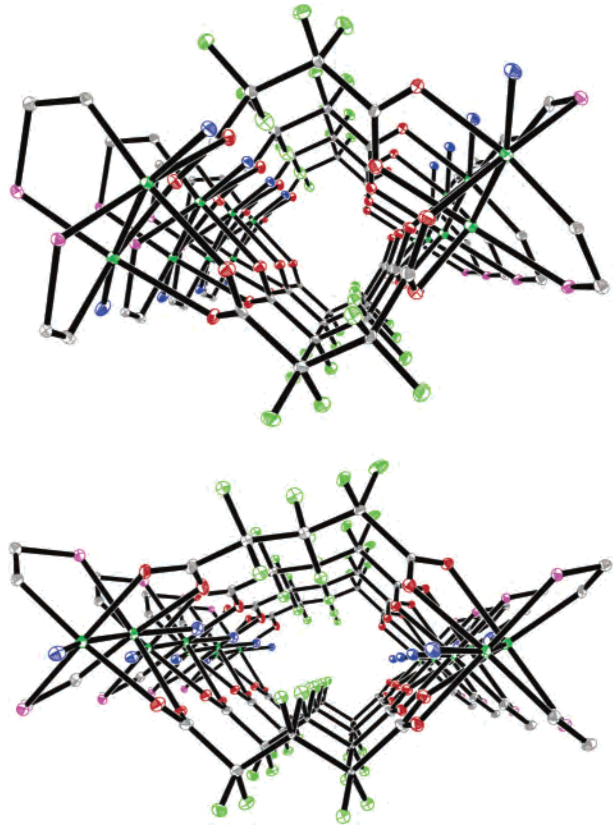

Figure 3. Crystal packing of the molecular loops in **1**·$3CH_2Cl_2$·CH_3OH·$0.5H_2O$ (upper) and **2**·$3.5CH_2Cl_2$·$2CH_3OH$ (lower) showing the chiral channels formed by the molecules. The hydrogen atoms, carbon atoms in pyridine molecules, some of the carbon atoms in the $C_6H_4PPh_2$ ligand, and the interstitial molecules have been omitted for clarity.

For compound **2**, the Rh−Rh distances, 2.580(1) and 2.5816(9) Å, are about 0.04 Å longer than those in **1**. The difference is believed to arise from crystal packing forces. The Rh−N distances are distributed through the range 2.26−2.30 Å. Other bond distances are in the normal range. In contrast to compound **1**, here the P−Rh−Rh−P torsion angles (99.00(8)° and 100.66(7)°) are larger than those for C−Rh−Rh−C (−77.8(3)° and −77.3(3)°). Therefore, the overall chirality of this dirhodium compound is R_PR_P.[19,20] The torsion angles for P−Rh−Rh−C and O−Rh−Rh−O are in a relatively small range as shown in Table 3.

In contrast with the formation of triangles when rigid dicarboxylate linkers have been used,[7] the formation of loops requires linkers to form curves, which the $O_2(CF_2)_xCO_2$ groups can do. However, unlike “permanently bent” linkers, such as malonate dianion, they might also be able to participate in the formation of squares or triangles. However, the multinuclear NMR spectra for **1** and **2** are consistent with there being only one species in solution. The exclusive formation of molecular loops in these reactions demonstrates again the key influence of entropy in supramolecular chemistry.[21]

Finally, the crystal packing patterns of these compounds are also interesting. As shown in Figure 3, the molecular loops stack directly on top of each other, creating chiral channels. This packing pattern, which is common for the supramolecular compounds with dinuclear building blocks,[3] may be a key element for future development of the chemistry of these entities.

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Supporting Information Available: X-ray crystallographic files in CIF format for *RR*-[*cis*-$Rh_2(C_6H_4PPh_2)_2(py)_2O_2C(CF_2)_nCO_2]_2$ (**1**·$3CH_2Cl_2$·CH_3OH·$0.5H_2O$, $n = 2$ and **2**·$3.5CH_2Cl_2$·$2CH_3OH$, $n = 3$). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) For a definition of R_MR_M and R_PR_P, see ref 7 or Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

(20) The reasons for why the conformation in compound **1** is R_MR_M while that of compound **2** is R_PR_P have not systematically investigated. However, it is possible that the chirality of these molecular loops is affected by the length of the alkyl chain.

(21) For examples where the effect of entropy is notorious, see for example: (a) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 575. (b) Schweiger, M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3467.