Synthesis and Structures of (2,2-*cis*)-Dirhodium(II) Tetrakis[methyl 1-acyl-2-oxoimidazolidine-4(*S*)-carboxylates]. Chiral Catalysts for Highly Stereoselective Metal Carbene Transformations

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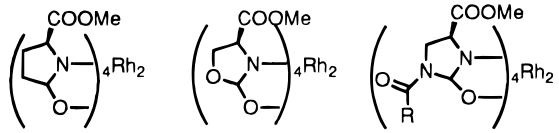
Dirhodium(II) tetracarboxamidates derived from chiral methyl 1-acyl-2-oxoimidazolidine-4(*S*)-carboxylates are highly enantioselective and diastereoselective catalysts for metal carbene transformations of diazoacetates. Four of these catalysts have been prepared by ligand substitution with dirhodium(II) acetate and characterized spectroscopically and by X-ray structural analysis. The simplest member of the series, (2,2-*cis*)-dirhodium(II) tetrakis[methyl 1-acetyl-2-oxoimidazolidine-4(*S*)-carboxylate], (2,2-*cis*)-Rh_2(4*S*-MACIM)$_4$, forms monoclinic crystals in space group $P2_1$ with cell constants of $a = 9.959(1)$ Å, $b = 20.100(1)$ Å, $c = 11.678(1)$ Å, $\beta = 107.61(1)°$, $V = 2228.1(3)$ Å^3, and $Z = 2$. (2,2-*cis*)-Rh_2(4*S*-MBOIM)$_4$, whose 1-acyl group is phenyl, forms tetragonal crystals in space group $P4_12_12$ with cell constants of $a = 18.352(1)$ Å, $c = 17.067(1)$ Å, $V = 5748.1(6)$ Å^3, and $Z = 4$. The most enantioselective catalyst in many metal carbene transformations is the one with 3-phenylpropanoyl at the 1-position, (2,2-*cis*)-Rh_2(4*S*-MPPIM)$_4$; crystals are monoclinic in space group $P2_1$ with cell constants of $a = 11.589(1)$ Å, $b = 12.225(1)$ Å, $c = 21.802(2)$ Å, $\beta = 94.429(8)°$, $V = 3079.6(5)$ Å^3, and $Z = 2$. The highest level of diastereocontrol has been achieved with the dirhodium(II) 1-acyl-2-oxoimidazolidine having the 1-acyl group equal to cyclohexylacetyl, (2,2-*cis*)-Rh_2(4*S*-MCHIM)$_4$, whose crystals are triclinic in space group $P1$ with cell constants of $a = 11.720(1)$ Å, $b = 12.067(1)$ Å, $c = 12.773(1)$ Å, $\alpha = 71.794(3)°$, $\beta = 75.765(4)°$, $\gamma = 72.789(3)°$, $V = 1615.5(2)$ Å^3, and $Z = 1$. The (3,1) isomer in which ligand orientation places three nitrogens and one oxygen on one rhodium and three oxygens and one nitrogen bound to the second rhodium is formed as a byproduct of the (2,2-*cis*) isomer in three of the four catalyst preparations; for (3,1)-Rh_2(4*S*-MACIM)$_4$, crystals are orthorhombic in space group $P2_12_12_1$ with cell constants of $a = 11.568(1)$ Å, $b = 19.344(1)$ Å, $c = 19.551(2)$ Å, $V = 4375.0(6)$ Å^3, and $Z = 4$. A third tetrasubstituted isomer, proposed to be (4,0)-Rh_2(4*S*-MACIM)$_4$ based on spectral information and the absence of enantiocontrol in selected metal carbene transformations, is also formed, but in amounts that do not exceed 5% of the total, and this compound isomerizes during the time course of the substitution reaction. Under the reaction conditions employed for their synthesis, the (2,2-*cis*) and (3,1) isomers reach equilibrium at 85:15. The effectiveness of these chiral dirhodium(II) oxazolidinones as catalysts for enantioselective and diastereoselective intramolecular reactions of diazoacetates has been evaluated.

Introduction

The advantages of chiral dirhodium(II) carboxamidates for highly enantioselective catalytic metal carbene transformations are now well documented.[2] With few exceptions, dirhodium(II) tetrakis[methyl 2-oxopyrrolidin-5(*R* or *S*)-carboxylate], Rh_2(5*R*-MEPY)$_4$ or Rh_2(5*S*-MEPY)$_4$ (**1**),[3] which is representative of the class of oxopyrrolidine-ligated catalysts, is preferred for intramolecular cyclopropanation reactions of allylic and homoallylic diazoacetates,[4−6] for intermolecular cyclopropenation of 1-alkynes,[7] and, among others,[8,9] for C−H insertion reactions of *N*-diazoacetylazacycloalkanes that produce β-lactams.[10] Dirhodium(II) tetrakis[methyl 2-oxooxazolidine-4(*R* or *S*)-carboxylate], Rh_2(4*R*-MEOX) or Rh_2(4*S*-MEOX)$_4$ (**2**),[11] which



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is representative of the class of oxooxazolidine-ligated catalysts, is most effective for C−H insertion on rigid frameworks of

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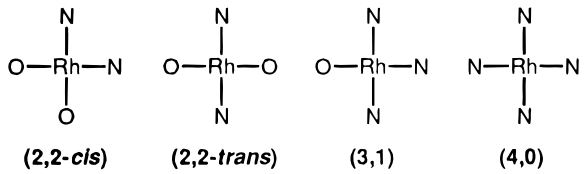
Chart 1



substituted cyclohexyl and adamantyl diazoacetates[11] and for enantiomer differentiation in intramolecular cyclopropanation reactions of racemic secondary allylic diazoacetates.[12] Ester derivatives of Rh_2(5*S*-MEPY)$_4$, where methyl is replaced by ethyl, isopropyl, neopentyl, and octadecyl,[13,14] do not significantly influence enantiocontrol, although increasing the hydrocarbon content provides increased solubility in hydrocarbon solvents. In their structures the dirhodium(II) core is surrounded by four bridging amide ligands so that the two nitrogen and two oxygen donor atoms bonded to each rhodium are oriented cis (2,2-*cis*);[3,11] none of the three other isomers (Chart 1) has been observed from the syntheses of **1**, **2**, or their analogs.

We have recently reported enhanced enantioselectivity and/or diastereodifferentiation for a variety of intramolecular metal carbene transformations catalyzed by chiral dirhodium(II) *N*-acyl-2-oxoimidazolidine-4-carboxylate esters (**3**). Dirhodium(II) tetrakis[methyl 1-acetyl-2-oxoimidazolidine-4(*S*)-carboxylate], Rh_2(4*S*-MACIM)$_4$ (**3**, R = Me), is the catalyst of choice for highly enantioselective and diastereoselective intramolecular C−H insertion reactions of cyclohexyl diazoacetates[15,16] and for high diastereocontrol in intramolecular C−H insertion reactions of chiral pyrrolidinediazoacetamides directed to the synthesis of pyrrolizidine bases.[17] The extended *N*-acyl derivative, dirhodium(II) tetrakis[methyl 1-(3-phenylpropanoyl)-2-oxoimidazolidine-4(*S*)-carboxylate], Rh_2(4*S*-MPPIM)$_4$ (**3**, R = $PhCH_2CH_2$), is the preferred catalyst for intramolecular C−H insertion reactions of 3-aryl-1-propyl diazoacetates leading to lignan lactones[18] and, among others, for enhancement of enantiocontrol in intramolecular cyclopropanation reactions of certain substituted allylic diazoacetates.[19]

The design of the imidazolidinone-ligated catalysts has provided the opportunity to construct a dirhodium(II) framework in which both the carboxylate ester at the 4-position and the *N*-acyl group at the 1-position are placed in close proximity to the reaction center. The *N*-acyl groups are formally in position to enhance reaction selectivity, especially diastereoselectivity. Applications have proven the validity of this rationale, but information concerning the structures of the imidazolidinone-ligated dirhodium(II) catalysts that could suggest the cause(s) of enhanced stereocontrol has been absent. We now report the synthesis, characterization, and X-ray structures of representatives in this class of catalysts, suggest the cause of chiral dirhodium(II) carboxamidate synthetic selectivity that permits often exclusive formation of the (2,2-*cis*) isomer, and provide comparative structural analysis of imidazolidinone-ligated dirhodium(II) complexes with those having 2-oxopyrrolidine and 2-oxooxazolidine ligands.

Experimental Section

General Considerations. Dirhodium(II) tetraacetate was obtained from Degussa and was recrystallized from methanol[20] prior to use. *N*-((Benzyloxy)carbonyl)-L-asparagine (**4**) from Aldrich was used without further purification; *N*-((benzyloxy)carbonyl)-D-asparagine was prepared from D-asparagine by the standard method.[21] The syntheses of 3-((benzyloxy)carbonyl)-2-oxoimidazolidin-4(*S*)-carboxylic acid (**5**) and methyl 3-((benzyloxy)carbonyl)-2-oxoimidazolidin-4(*S*)-carboxylate (**6**) have been previously reported;[4] the syntheses of the *R*-enantiomer of these compounds followed the same procedures. The preparations of Rh_2(5*R*-MEPY)$_4$,[3] Rh_2(5*S*-MEPY)$_4$,[3] Rh_2(4*R*-MEOX)$_4$,[11] Rh_2(4*S*-MEOX)$_4$,[11] and Rh_2(4*S*-MACIM)$_4$[4] by acetate displacement from $Rh_2(OAc)_4$ have been described. The specific rotation, $[\alpha]^{23}_D$, of 4*S*-MACIMH (**8a**) is +55.7 (*c* 3.34, CH_2Cl_2) and its mp is 65−67 °C and not the values previously reported.[4] Chlorobenzene, acetonitrile, and dichloromethane were distilled from calcium hydride prior to use. Procedures for the preparation and catalytic diazo decomposition of diazo esters have been previously reported.[4,14,16,19] Enantiomeric excesses were determined by GC with baseline separation on Chiraldex columns.[4,14,19] ^{1}H NMR spectra were obtained on a Varian VXR-300 instrument, and ^{13}C NMR spectra were recorded by the same spectrometer at 75 MHz; spectra were obtained as solutions in $CDCl_3$, unless indicated otherwise, and chemical shifts are reported in parts per million (ppm, δ) downfield from internal Me_4Si (TMS). Infrared spectra were obtained from a Nicolet Model 550 FTIR spectrometer. Elemental analyses were performed at Texas Analytical Laboratories, Inc.

Dirhodium(II) Tetrakis[methyl 1-acetyl-2-oxoimidazolidine-4(*S*)-carboxylate], Rh_2(4*S*-MACIM)$_4$ (3a). The preparation and spectral characterization of Rh_2(4*S*-MACIM)$_4$, whose structure was that of the (2,2-*cis*) isomer, has been described.[4] Crystals suitable for X-ray analysis were grown from acetonitrile as red-orange prisms by slow evaporation. In the chromatographic separation of the crude product on reverse phase silica (BAKERBOND Cyano 40 μm prep LC packing, 25 cm), eluting with methanol, three purple bands were evident. After isolation of the first band, which was (2,2-*cis*)-Rh_2(4*S*-MACIM)$_4$, two purple bands remained on the column. They were collected together using MeCN as the eluent, the solvent was removed under reduced pressure, and the resulting red powder was rechromatographed on a 5-cm column of reverse phase silica (BAKERBOND Cyano) eluting with methanol. The first purple band was collected, and anhydrous MeCN was added to the purple solution with resulting color change to red-orange. Evaporation of the solvent under reduced pressure gave 0.194 g (16% yield) of a purple-red powder (>99.9% pure by HPLC on a μ-Bondapak-CN reverse phase column) identified as **(3,1)-Rh_2(4*S*-MACIM)$_4$(CH_3CN)**: $[\alpha]^{20}_D$ = −279 (*c* 0.105, CH_3CN); ^{1}H NMR (acetone-d_6) δ 4.38 (dd, *J* = 10.1, 4.3 Hz, 1 H), 4.26 (dd, *J* = 10.1, 6.0 Hz, 1 H), 4.12 (dd, *J* = 10.4, 3.3 Hz, 1 H), 3.97−3.85 (comp, 4 H), 3.81−3.58 (comp, 5 H), 3.75 (s, 3 H), 3.74 (s, 3 H), 3.62 (s, 3 H), 3.55 (s, 3 H), 2.27 (s, 3 H), 2.24 (s, 3 H), 2.21 (s, 3 H), 2.18 (s, 3 H); ^{13}C NMR (acetone-d_6) δ 174.9, 174.8, 174.6 (2 C), 168.6, 168.4, 168.3 (2C), 166.2, 166.0, 165.6, 165.4, 117.6, 59.7, 59.1, 59.0, 58.3, 52.7, 52.5, 51.9 (2C), 48.5, 48.2, 47.9, 47.5, 23.7, 23.5, 23.4 (2C), 1.4. Crystals grew as small orange-red prisms by slow evaporation from an acetonitrile solution. Anal. Calcd for $C_{30}H_{39}N_9O_{16}Rh_2$: C, 36.49; H, 3.98; N, 12.77. Found: C, 36.52; H, 4.06; N, 12.70.

The second purple band remained at the baseline during elution with methanol. With 95:5 methanol−acetonitrile, however, this remaining

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band passed down the column and was collected. Evaporation of the solvent under reduced pressure gave 0.049 g (4% yield) of a purple-red powder (> 99.9% pure by HPLC) whose structure is proposed, based primarily on the absence of asymmetric induction in its catalytic uses for inter- and intramolecular reactions of diazoacetates, to be **(4,0)-Rh_2(4*S*-MACIM)$_4$(CH_3CN)$_2$**: $[\alpha]^{21}_D = -385°$ (*c* 0.14, CH_3CN); ^{1}H NMR (acetone-d_6) δ 4.00−3.90 (comp, 8 H), 3.76 (s, 12 H), 3.74−3.68 (comp, 4 H), 2.22 (s, 12 H), 2.08 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 174.9, 168.2, 166.5, 60.1, 52.7, 48.7, 23.3. Anal. Calcd for $C_{32}H_{42}N_{10}O_{16}Rh_2$: C, 37.37; H, 4.12; N, 13.62. Found: C, 37.28; H, 4.20; N, 13.53.

Methyl 1-Benzoyl-3-((benzyloxy)carbonyl)-2-oxoimidazolidine-4(*S*)-carboxylate (7b). To a solution of methyl 3-((benzyloxy)-carbonyl)-2-oxoimidazolidine-4(*S*)-carboxylate (**6**, 4.30 g, 15.5 mmol) and 4-(dimethylamino)pyridine (DMAP, 183 mg, 1.50 mmol) in 25 mL of pyridine was added benzoyl chloride (3.2 g, 23 mmol) dropwise at 0 °C. After the mixture was stirred at 0 °C for 2 h and then at room temperature for 6 h, 150 mL of CH_2Cl_2 was added to the reaction mixture, and the resulting solution was washed three times with 80-mL portions of 2 M aqueous HCl, then once with saturated $NaHCO_3$, and, finally, with saturated NaCl. The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and then chromatographed on silica gel (hexanes:ethyl acetate = 1:1; R_f 0.47) to give 5.54 g of **7b** (94% yield) as a white solid: mp 103−104 °C; $[\alpha]^{23}_D = +32.7$ (*c* 0.44, CH_2Cl_2); ^{1}H NMR δ 7.65−7.33 (m, 10 H), 5.38 (d, J = 12.2 Hz, 1 H), 5.21 (d, J = 12.2 Hz, 1 H), 4.80 (dd, J = 9.7, 3.7 Hz, 1 H), 4.22 (dd, J = 11.7, 9.7 Hz, 1 H), 3.98 (dd, J = 11.7, 3.7 Hz, 1 H), 3.79 (s, 3 H); ^{13}C NMR δ 169.9, 169.5, 150.9, 148.7, 134.6, 133.0, 132.3, 130.1, 129.0, 128.6, 128.4, 127.9, 68.9, 53.2, 52.6, 43.5; IR ($CHCl_3$) $\tilde{\nu}$ 1821, 1798, 1760, 1738, 1685 cm^{-1}. Anal. Calcd for $C_{20}H_{18}N_2O_6$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.90; H, 4.75; N, 7.28.

Methyl 1-Benzoyl-2-oxoimidazolidine-4(*S*)-carboxylate (8b). A solution of **7b** (3.07 g, 8.00 mmol) containing 5% Pd/C (120 mg) in 60 mL of methanol was shaken in a Parr hydrogenator under H_2 (35 psi) for 8 h. The Pd/C catalyst was removed by filtration through a Celite plug, and the filtrate was concentrated to give a crude product that, after recrystallization from 1:2 hexanes:ethyl acetate, provided 1.9 g of **8b** (95% yield) as a white solid: mp 132−133 °C; $[\alpha]^{24}_D = +40.0$ (*c* 0.74, CH_2Cl_2); ^{1}H NMR δ 7.61 (dd, J = 7.2, 1.5 Hz, 2 H), 7.49 (dt, J = 7.4, 1.5 Hz, 1 H), 7.40 (dt, J = 7.2, 1.5 Hz, 2 H), 6.04 (s, 1 H), 4.35−4.15 (m, 3 H), 3.83 (s, 3 H); ^{13}C NMR δ 170.8, 169.8, 154.9, 133.7, 131.6, 128.9, 127.5, 53.0, 49.8, 46.1; IR ($CHCl_3$) $\tilde{\nu}$ 1760, 1677 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.28. Found: C, 58.12; H, 4.85; N, 11.23.

Dirhodium(II) Tetrakis[methyl 1-benzoyl-2-oxoimidazolidine-4(*S*)-carboxylate], Rh_2(4*S*-MBOIM)$_4$ (3b). Dirhodium(II) acetate (128 mg, 0.290 mmol), **8b** (1.31 g, 5.28 mmol) and 20 mL of anhydrous chlorobenzene were mixed in a round bottom flask fitted with a Soxhlet extraction apparatus into which was placed a cellulose thimble containing 5 g of an oven-dried mixture of two parts Na_2CO_3 and one part sand. The resulting mixture in chlorobenzene was refluxed under nitrogen for 3 h, at which time HPLC analysis (μ-Bondapak-CN reverse-phase column, MeOH) showed the reaction to be complete and that only one tetrasubstituted product was formed. After this was cooled to room temperature, the solvent was removed under reduced pressure, and the purple residue, dissolved in methanol containing a minimal volume of MeCN, was purified by column chromatography on reverse phase silica (BAKERBOND Cyano 40 μm prep LC packing) eluting with methanol. The fraction eluting prior to the rose colored band was collected, and unreacted **8b** (1.01 g, 99% recovery) was reclaimed. The rose-colored band was collected and, following removal of the solvent under reduced pressure, pure (2,2-*cis*)-Rh_2(4*S*-MBOIM)$_4$(CH_3CN)$_2$ was collected as a red solid (330 mg, 89% yield): $[\alpha]^{25}_D = -447$ (*c* 0.13, MeCN); ^{1}H NMR δ 7.54−7.38 (comp, 12 H), 7.32−7.21 (comp, 8 H), 4.17−4.04 (comp, 4 H), 4.03−3.85 (comp, 8 H), 3.76 (s, 6 H), 3.42 (s, 6 H), 1.97 (s, 6 H); ^{13}C NMR δ 173.0, 172.7, 167.9, 167.5, 164.3, 163.7, 135.1, 134.8, 130.7, 130.6, 129.4, 129.1, 129.0, 128.8, 127.2, 127.1, 127.0, 126.9, 114.1, 59.8, 59.0, 58.4, 52.5, 52.3, 48.2, 47.6, 17.6, 2.5. Crystals grew as red-orange prisms by slow crystallization from acetonitrile. Anal. Calcd for $C_{52}H_{50}N_{10}O_{16}Rh_2$: C, 48.91; H, 3.95; N, 10.97. Found: C, 48.82; H, 4.06; N, 10.91.

Methyl 1-(3-Phenylpropanoyl)-3-((benzyloxy)carbonyl)-2-oxoimidazolidine-4(*S*)-carboxylate (7c). Hydrocinnamoyl chloride (6.74 g, 40.0 mmol) was added dropwise into an ice-bath cooled solution of **6** (5.56 g, 20.0 mmol) in anhydrous CH_2Cl_2 (25 mL) containing pyridine (3.2 mL, 40 mmol) and 4-(dimethylamino)pyridine (244 mg, 2.00 mmol). The resulting mixture was stirred at 0 °C for 0.5 h then heated at reflux for 12 h. After the mixture was cooled to room temperature, 100 mL of CH_2Cl_2 was added, and the resulting solution was washed with cold 1 M aqueous HCl (3 × 40 mL), saturated $NaHCO_3$, and brine. After the solution was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (hexanes:EtOAc, 2:1) to give 7.95 g of a white solid, mp 81−82 °C, identified as the title compound (19.4 mmol, 97% yield): $[\alpha]^{23}_D = -21.6$ (*c* 1.41, $CHCl_3$); ^{1}H NMR δ 7.41−7.14 (m, 10 H), 5.37 (d, J = 12.2 Hz, 1 H), 5.25 (d, J = 12.2 Hz, 1 H), 4.69 (dd, J = 9.9, 3.7 Hz, 1 H), 3.96 (dd, J = 12.0, 9.9 Hz, 1 H), 3.87 (dd, J = 12,0, 3.8 Hz, 1 H), 3.71 (s, 1 H), 3.37−3.18 (comp, 2 H), 3.05−2.90 (comp, 2 H); ^{13}C NMR δ 172.6, 169.4, 150.7, 149.0, 140.3, 134.6, 128.6 (2 C), 128.4, 128.3, 128.2, 126.1, 68.8, 53.0, 52.2, 42.1, 37.5, 30.0; IR (CHCl3) $\tilde{\nu}$ 1813, 1760, 1738, 1707 cm^{-1}. Anal. Calcd for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.42; H, 5.47; N, 6.78.

Methyl 1-(3-Phenylpropanoyl)-2-oxoimidazolidine-4(*S*)-carboxylate (8c) was prepared by an 8 h hydrogenolysis of the CBz-derivative of the title compound (6.70 g, 16.3 mmol) in 130 mL of methanol with H_2 (35 psi) catalyzed by 5% Pd/C (268 mg) in a Parr hydrogenator. After filtration of the reaction mixture through a Celite pad and evaporation of the solvent under reduced pressure, 4.50 g of **8c** (100% yield) was isolated as a colorless oil: $[\alpha]^{23D} = +26.0$ (*c* 1.82, $CHCl_3$); ^{1}H NMR δ 7.31−7.14 (m, 5 H), 6.47 (br s, 1 H), 4.24 (dd, J = 8.6, 6.3 Hz, 1 H), 4.14−4.07 (comp, 2 H), 3.77 (s, 3 H), 3.30−3.14 (comp, 2 H), 3.00−2.94 (comp, 2 H); ^{13}C NMR δ 172.5, 170.8, 155.5, 140.8, 128.4, 128.3, 126.0, 52.9, 49.6, 44.9, 36.9, 30.3; IR ($CHCl_3$) $\tilde{\nu}$ 1753, 1692 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.78; H, 5.83; N, 10.12.

Dirhodium(II) Tetrakis[methyl 1-(3-phenylpropanoyl)-2-oxoimidazolidine-4(*S*)-carboxylate], Rh_2(4*S*-MPPIM)$_4$ (3c). Rhodium(II) acetate (228 mg, 0.516 mmol), **8c** (1.70 g, 6.15 mmol), and 20 mL of anhydrous chlorobenzene were mixed in a round bottom flask fitted with a Soxhlet extraction apparatus into which was placed a thimble containing 5 g of an oven-dried mixture of two parts Na_2CO_3 and one part sand, and the resulting blue-green solution was refluxed under nitrogen for 18 h. The progress of ligand displacement was followed by HPLC (μ-Bondapak-CN column, MeOH); the initial $Rh_2(OAc)_4$ band disappeared and was replaced by several bands with longer retention volumes until one principal band (the (2,2-*cis*) isomer) and two later bands, in addition to that for the ligand, were observed. The latter two bands were assigned as (3,1)-**3c** and (4,0)-**3c**, and by 18 h of reflux the band for (4,0)-**3c** had disappeared. The resulting blue solution was cooled to room temperature, and the solvent was evaporated under reduced pressure. The residue in a minimal volume of MeOH containing 5% MeCN was chromatographed on reverse phase silica (BAKERBOND Cyano 40 mm prep LC packing) eluting with MeOH to isolate unreacted ligand (1.05 g, 93% recovery) and, in a second fraction, the red-orange band consisting of Rh_2(4*S*-MPPIM)$_4$ (purity >98%). The (3,1)-**3c** isomer remained on the column. Recrystallization of the chromatographed dirhodium(II) compound from methanol containing a minimal amount of MeCN afforded 0.415 g of analytically pure **(2,2-*cis*)-Rh_2(4*S*-MPPIM)$_4$(CH_3CN)$_2$** (57% yield): $[\alpha]^{23}_D = -311$ (*c* 0.10, MeCN); ^{1}H NMR δ 7.28−7.11 (comp, 20 H), 4.08 (dd, J = 10.1, 5.0 Hz, 2 H), 4.00−3.70 (comp, 10 H), 3.72 (s, 6 H), 3.46 (s, 6 H), 3.32−3.10 (comp, 4 H), 2.98−2.78 (comp, 12 H), 1.84 (s, 6 H, CH_3CN); ^{13}C NMR δ 173.2, 172.9, 170.6, 170.5, 164.9, 164.8, 141.7, 141.4, 128.6, 128.4, 128.3, 128.2, 126.0, 125.9, 116.0, 59.6, 59.1, 52.3, 51.7, 47.0, 37.6, 37.2, 31.4, 31.3, 1.9. Crystals suitable for X-ray analysis grew as red-orange prisms by slow crystallization from acetonitrile. Anal. Calcd for $C_{60}H_{66}N_{10}O_{16}Rh_2$: C, 51.88; H, 4.79; N, 10.08. Found: C, 51.82; H, 4.85; N, 9.97.

The (3,1)-**3c** isomer as a purple-red band that had remained on the column was removed by elution with 1% MeCN in MeOH. Concentration of the resulting solution and drying gave 50 mg (8% yield) of a red powder that was assigned (3,1)-**Rh_2(4*S*-MPPIM)$_4$(CH_3CN)$_2$**: ^{1}H

NMR δ 7.34−7.10 (comp, 20 H), 4.21−4.16 (comp, 2 H), 3.98−3.71 (comp, 10 H), 3.73 (s, 3 H), 3.65 (s, 3H), 3.46 (s, 3 H), 3.45 (s, 3 H), 3.26−3.18 (comp, 4 H), 3.10−2.70 (comp, 12 H), 1.93 (s, 6 H).

Isomerization of (2,2-*cis*)-Rh_2(4*S*-MPPIM)$_4$. The combination of (2,2-*cis*)-Rh_2(4*S*-MPPIM)$_4$ (21 mg, 0.015 mmol) and **8c** (100 mg, 0.24 mmol) in chlorobenzene (5 mL) was heated at reflux, and the progress of reaction was monitored by HPLC analysis (μ-Bondapak-CN reverse phase column, MeOH). Product analysis at 3 h and 6 h showed a mixture of (2,2-*cis*)-Rh_2(4*S*-MPPIM)$_4$ and (3,1)-Rh_2(4*S*-MPPIM)$_4$ in a 85:15 ratio.

Dirhodium(II) Tetrakis[methyl 1-(3-phenylpropanoyl)-2-oxoimidazolidine-4(*R*)-carboxylate], Rh_2(4*R*-MPPIM)$_4$, was prepared by an identical procedure to that described for Rh_2(4*S*-MPPIM)$_4$. Acylation of methyl 3-((benzyloxy)carbonyl)-2-oxoimidazolidine-4(*R*)-carboxylate was accomplished in 92% yield, and hydrogenolysis provided methyl 1-(3-phenylpropanoyl)-2-oxoimidazolidin-4(*R*)-carboxylate, $[\alpha]_D^{23} = -27.2$ (*c* 1.58, $CHCl_3$), quantitatively. The dirhodium(II) catalyst as the (2,2-*cis*) isomer was prepared in 48% yield after purification: $[\alpha]_D^{23} = +307$ (*c* 0.14, MeCN).

Methyl 1-(Cyclohexylacetyl)-3-((benzyloxy)carbonyl)-2-oxoimidazolidine-4(*S*)-carboxylate (7d). To a solution of **6** (2.78 g, 10.0 mmol), pyridine (1.58 g, 20.0 mmol) and 4-(dimethylamino)pyridine (122 mg, 1.00 mmol) in 30 mL of anhydrous CH_2Cl_2 was added cyclohexaneacetyl chloride, prepared from oxalyl chloride (3.4 mL, 40 mmol) and cyclohexaneacetic acid (2.84 g, 20.0 mmol), at room temperature. The resulting mixture was refluxed under nitrogen for 20 h. After being cooled to room temperature, the reaction mixture was diluted with 50 mL of CH_2Cl_2 and then washed three times with 30-mL portions of 1 M aqueous HCl, once with saturated $NaHCO_3$, and once with saturated NaCl. The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and then chromatographed on silica gel (hexanes:ethyl acetate = 2:1, R_f 0.40) to give 3.75 g of **7d** (93% yield) as a white solid: mp 113−114 °C; $[\alpha]_D^{23} = -22.2$ (*c* 0.98, $CHCl_3$); ^{1}H NMR δ 7.42−7.34 (comp, 5 H), 5.37 (d, J = 12.2 Hz, 1 H), 5.25 (d, J = 12.2 Hz, 1 H), 4.68 (dd, J = 10.0, 3.7 Hz, 1 H), 3.96 (dd, J = 12.0, 10.0 Hz, 1 H), 3.86 (dd, 12.0, 3.7 Hz, 1 H), 3.71 (s, 3 H), 2.86 (dd, J = 15.8, 6.9 Hz, 1 H), 2.80 (dd, J = 15.8, 6.9 Hz, 1 H), 1.94−1.76 (m, 1 H), 1.76−1.57 (comp, 5 H), 1.36−0.92 (comp, 5 H); ^{13}C NMR δ 172.8, 169.5, 150.7, 149.0, 134.6, 128.6, 128.2, 68.8, 53.0, 52.1, 43.0, 42.1, 34.0, 33.0, 32.9, 26.1, 25.9; IR ($CHCl_3$) $\tilde{\nu}$ 1813, 1785, 1768, 1735, 1700 cm^{-1}. Anal. Calcd for $C_{21}H_{26}N_2O_6$: C, 62.67; H, 6.51; N, 6.96. Found: C, 62.60; H, 6.48; N, 6.88.

Methyl 1-(Cyclohexylacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate (8d). A solution of **7d** (34.5 g, 8.57 mmol) containing 5% Pd/C (138 mg) in 70 mL of methanol was shaken in a Parr hydrogenator under H_2 (35 psi) for 4 h. After filtration of the reaction solution through a Celite pad, the filtrate was concentrated to give 2.30 g of the title compound (100% yield) as a colorless oil: $[\alpha]_D^{23} = +41.1$ (*c* 0.95, $CHCl_3$); ^{1}H NMR δ 5.82 (s, 1 H), 4.28 (dd, J = 8.9, 5.8 Hz, 1 H), 4.18−4.05 (comp, 2 H), 3.82 (s, 3 H), 2.83 (dd, J = 15.3, 6.8 Hz, 1 H), 2.76 (dd, J = 15.6, 6.8 Hz, 1 H), 1.92−1.78 (comp, 1 H), 1.78−1.59 (comp, 5 H), 1.36−0.91 (comp, 5 H); ^{13}C NMR δ 172.8, 170.9, 155.5, 52.8, 49.4, 44.9, 42.2, 34.3, 32.9, 26.0, 25.9; IR ($CHCl_3$) $\tilde{\nu}$ 1753, 1692 cm^{-1}. Anal. Calcd for $C_{13}H_{20}N_2O_4$: C, 58.19; H, 7.51; N, 10.44. Found: C, 58.13; H, 7.56; N, 10.40.

Dirhodium(II) Tetrakis[methyl 1-(cyclohexylacetyl)-2-oxoimidazolidine-4(*S*)-carboxylate], Rh_2(4*S*-MCHIM)$_4$ (3d). Dirhodium(II) acetate (240 mg, 0.544 mmol), **8d** (2.19 g, 8.16 mmol), and 20 mL of anhydrous chlorobenzene were mixed in a round bottom flask fitted with a Soxhlet extraction apparatus into which was placed a cellulose thimble containing 2:1 Na_2CO_3−sand. The resulting mixture in chlorobenzene was refluxed under nitrogen for 22 h, at which time HPLC analysis (μ-Bondapak-CN reverse phase column, MeOH) showed the reaction to be complete. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure, and the purple residue was purified by column chromatography on reverse phase silica (BAKERBOND Cyano 40 μm prep LC packing) eluting with methanol to isolate unreacted **8d** (1.55 g, 96% recovery) and the first of two bands of **3d** (purity >90%). This first band, which was the major product, was further purified by recrystallization (twice) from methanol containing a minimal amount of acetonitrile to provide pure red **(2,2-*cis*)-Rh_2(4*S*-MCHIM)$_4$(CH_3CN)$_2$** (295 mg, 40% yield): $[\alpha]_D^{23} = -375$ (*c* 0.12, MeCN); ^{1}H NMR δ 4.10 (dd, J = 10.1, 5.0 Hz, 2 H), 4.04−3.74 (comp, 10 H), 3.74 (s, 6 H), 3.57 (s, 6 H), 3.10 (dd, J = 14.3, 6.6 Hz, 2 H), 3.00 (dd, J = 13.2, 6.2 Hz, 2 H), 2.40−2.26 (comp, 4 H), 2.33 (s, 6 H), 1.80−1.55 (comp, 24 H), 1.31−0.89 (comp, 20 H); ^{13}C NMR δ 173.2, 172.9, 171.0, 170.8, 164.8, 164.7, 115.5, 59.6, 59.1, 52.3, 51.8, 46.9, 46.8, 42.4, 42.2, 35.6, 35.2, 33.3, 33.1, 33.0, 32.9, 26.3, 26.2, 2.3. Crystals grew as very large red-orange prisms by slow evaporation from acetonitrile−methanol solution. Anal. Calcd for $C_{56}H_{82}N_{10}O_{16}Rh_2$: C, 49.56; H, 6.09; N, 10.32. Found: C, 49.62; H, 6.15; N, 10.27.

After collection of the first band of **3d**, the second purple band was obtained by elution with 98:2 MeOH:MeCN. Concentration of this fraction provided 70 mg (10% yield) of a red powder identified by ^{1}H NMR spectroscopy to be **(3,1)-Rh_2(4*S*-MCHIM)$_4$(CH_3CN)** (98% pure by HPLC): ^{1}H NMR δ 4.40−4.19 (comp, 4 H), 4.25−3.59 (comp, 8 H), 3.76 (s, 3 H), 3.67 (s, 3 H), 3.64 (s, 3 H), 3.54 (s, 3 H), 3.25−2.00 (comp, 8 H), 2.44 (s, 3 H), 1.95−1.50 (comp, 24 H), 1.32−0.80 (comp, 20 H).

X-ray Structures of Dirhodium(II) Tetrakis[methyl 1-acyl-2-oxoimidazolidine-4(*S*)-carboxylates]. Details of the crystal data, data collection, and the structure refinement are listed in Table 1. The space group for **15** was uniquely determined from the systematically absent reflections. Choice of the space groups for the remaining complexes was narrowed down using the systematically absent reflections and/or the diffraction symmetry. Check reflections were remeasured periodically during data collection to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The data were corrected for *Lp* effects and absorption. For structures **9**, **10, 11**, and **15**, an absorption correction was applied using the semi-empirical method of SHELXA.[22] For structure **12**, an analytical absorption correction based on measured crystal faces was used.[23] Data reduction, decay correction, structure solution, and refinement were performed using the SHELXTL/PC software package.[23] The structures were solved by direct methods and refined on F^2 by full-matrix lease-squares with anisotropic thermal parameters for the non-H atoms. Hydrogen atoms were calculated in idealized positions (C−H 0.96 Å) with U_{iso} set to 1.2U_{eq} of the attached atom (1.5U_{eq} for methyl hydrogen atoms). The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (aP)^2 + (bP)]$, $P = (|F_o|^2 + 2|F_c|^2)/3$ and where the values for a and b are suggested during refinement. Initially, space group assignments were made given the known chirality of the complexes and were confirmed by the successful refinement of the structures. The absolute configurations were initially assigned by internal comparison to the known configuration of the 2-oxoimidazolidine ligand and were all subsequently confirmed by the X-ray diffraction results using the method of Flack.[24] The data were checked for secondary extinction effects and applied if the correction was significant. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from ref 25. All figures were generated using SHELXTL/PC.[23] Tables of crystal data and positional and thermal parameters, and figures are located in the Supporting Information.

Results

Synthesis. The preparation of enantiomerically pure 1-acyl-2-oxaimidazolidine-4(*S*)-carboxylates (**8**) was accomplished from a common precursor, *N*-((benzyloxy)carbonyl)-L-asparagine (**4**), by Hoffmann rearrangement, esterification, *N*-acylation, and hydrogenolysis (Scheme 1). Accordingly, methyl 1-acetyl-2-oxoimidazolidine-4(*S*)-carboxylate (MACIMH, **8a**), methyl 1-benzoyl-2-oxoimidazolidine-4(*S*)-carboxylate

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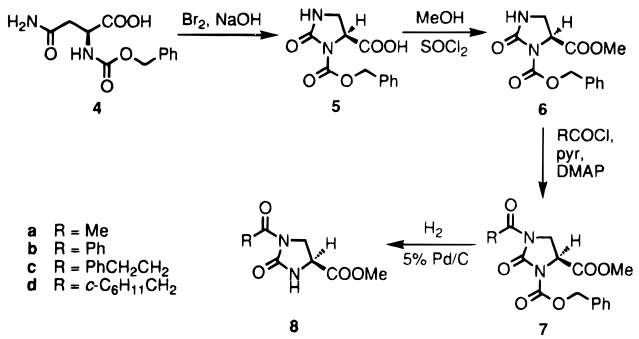
Table 1. Crystallographic Data for Dirhodium(II) Tetrakis[methyl 1-acyl-2-oxaimidazolidine-4(*S*)-carboxylates]

	(2,2-*cis*)-Rh_2(4*S*-MACIM)$_4$(CH_3CN)$_2$C (**9**)[a]	(3,1)-Rh_2(4*S*-MACIM)$_4$(CH_3CN)$_2$ (**15**)[a]	(2,2-*cis*)-Rh_2(4*S*-MBOIM)$_4$(CH_3CN)$_2$ (**10**)[a]	(2,2-*cis*)-Rh_2(4*S*-MPPIM)$_4$(CH_3CN)$_2$ (**11**)[b]	(2,2-*cis*)-Rh_2(4*S*-MCHIM)$_4$(CH_3CN)$_2$ (**12**)[b]
chem formula	$C_{32}H_{42}N_{10}O_{16}Rh_2\cdot 2CH_3CN$	$C_{32}H_{42}N_{10}O_{16}Rh_2\cdot 2CH_3CN$	$C_{52}H_{50}N_{10}O_{16}Rh_2\cdot CH_3CN$	$C_{60}H_{66}N_{10}O_{16}Rh_2$	$C_{56}H_{82}N_{10}O_{16}Rh_2\cdot CH_3OH$
fw	1110.68	1110.68	1317.89	1389.05	1389.18
a, Å	9.959(1)	11.568(1)	18.352(1)	11.589(1)	11.720(1)
b, Å	20.100(1)	19.344(1)	18.352(1)	12.225(1)	12.067(1)
c, Å	11.678(1)	19.551(2)	17.067(1)	21.802(2)	12.773(1)
α, deg	90.0	90.0	90.0	90.0	71.794(3)
β, deg	107.61(1)	90.0	90.0	94.429(8)	75.765(4)
γ, deg	90.0	90.0	90.0	90.0	72.789(3)
V, Å^3	2228.1(3)		5748.1(6)	3079.6(5)	1615.5(2)
Z	2	4	4	2	1
F(000)	1132	2176	2688	1428	724
$^{\rho}$calc, g cm^{-3}	1.66	1.62	1.57	1.50	1.43
μ, cm^{-1}	8.24	8.35	6.41	6.12	5.84
cryst syst	monoclinic	orthorhombic	tetragonal	monoclinic	triclinic
space group	$P2_1$	$P2_12_12_1$	$P4_12_12$	$P2_1$	$P1$
2θ range, deg	4−65	4−55	4−65	4−60	4−62.5
scan speed, °/min	5−10	4−8	4−8	6−12	4−8
scan range in ω, deg	1.0	1.0	1.2	1.2	1.2
range of *h*,*k*,*l*	$\bar{1}4\rightarrow15,\bar{1}\rightarrow30,\bar{1}7\rightarrow16$	$\bar{1}\rightarrow15,\bar{2}5\rightarrow25,\bar{2}5\rightarrow25$	$\bar{2}7\rightarrow27,\bar{1}9\rightarrow19,0\rightarrow25$	$\bar{1}6\rightarrow16,\bar{1}\rightarrow17,\bar{3}0\rightarrow30$	$\bar{1}6\rightarrow17,\bar{1}6\rightarrow16,\bar{1}8\rightarrow18$
no. of reflcns measd	15445	11785	11602	19688	20456
no. of unique reflcns	8584	6510	5811	10153	20456
R_{int} (F^2)	0.020	0.0670	0.0369	0.064	0.00
decay cor	0.988−1.01	0.987−1.02	1.00−1.02	0.986−1.01	0.974−1.00
cryst size, mm	0.34 × 0.40 × 0.40	0.16 × 0.22 × 0.22	0.38 × 0.46 × 0.49	0.4 × 0.5 × 0.7	0.36 × 0.44 × 0.56
transm factor range[b]	0.3711−0.9411	0.6669−0.9393	0.5728−0.9525	0.5180−0.9554	0.7281−0.8191
$R_w(F^2)$[c]	0.0768	0.0790	0.0902	0.0772	0.0665
a, *b*	0.041, 0.7189	0.0218, 0.0	0.0394, 2.559	0.0218, 0.9	0.0374, 0.4553
$R(F)$[d]	0.0306	0.0459	0.0373	0.0455	0.0261
$S(F^2)$, goodness of fit	1.066	1.005	1.022	1.055	1.046
extinction cor factor[d]	0.0038(3)	none	0.0017(1)	0.0013(1)	0.0124(4)
Flack *x* parameter	0.00(2)	−0.01(3)	−0.06(4)	0.00(3)	−0.02(1)
parameters	582	568	377	794	775
min, max peaks in final ΔF map, e$^-$/Å^3	−1.1, 1.0	−0.46, 0.45	−0.44, 0.74	−0.66, 0.60	−0.67, 0.96

[a] Data for all crystals were collected by the ω-scan technique at −100 °C on a Siemens P4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The temperature was controlled using a Nicolet LT-2 low-temperature device. Lattice parameters were obtained by least squares refinement of several high angles reflections in the 2θ range as follows: 45 reflections between 24.7 and 25.0° for **9**, 30 reflections between 17.2 and 23.9° for **15**; 42 reflections between 11.4 and 25.0° for **10**; 34 reflections between 22.5 and 24.9° for **11**; 46 reflections between 20.1 and 25.1° for **12**. [b] The absorption correction for **9**, **10**, **11**, and **15** was applied using SHLXA Version 1 (Sheldrick, G. Personal communication, 1990) the semi-empirical method using refined atomic coordinates and X-ray diffraction data. The absorption correction for **12** was based on measured crystal dimensions using SHELXTL/PC Version 5 (Sheldrick, G. Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995). [c] $R_w = \{\sum w(|F_o|^2 - |F_c|^2)2/\sum w(|F_o|^4)\}^{1/2}$ where the weight, $w = 1/\{\sigma^2(|F_o|^2) + (aP)^2 + bP\}$; $P = [^1/_3(\text{max. of } (0 \text{ or } |F_o|^2) + {}^2/_3|F_c|^2]$; $R(F) = \sum(|F_o| - |F_c|)/\sum(|F_o|)$ and observed reflections have $F_o > 4[\sigma(F_o))$; $S = [\sum w(|F_o|^2 - |F_c|^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters. [d] The correction is of the form: $F_{cor} = k[1 + 0.001X(F_{calc})^{2(\lambda 3)}/\sin(2\theta)]^{-1/4}$ where *X* is the extinction correction factor and *k* is the overall scale factor.

Scheme 1



(MBOIMH, **8b**), methyl 1-(3-phenylpropanoyl)-2-oxoimidazolidine-4(*S*)-carboxylate (MPPIMH, **8c**), and methyl 1-(cyclohexylacetyl)-2-oxoimidazolidine-4(*S*)-carboxylates (MCHIMH, **8d**), each having the *S* absolute configuration at the stereogenic 4-position, were synthesized in high yield. The combination of a 3−4 molar excess of **8** with $Rh_2(OAc)_4$ in refluxing chlorobenzene, performed in a Soxhlet extraction apparatus containing a thimble charged with Na_2CO_3, caused complete replacement of acetate for imidazolidinone ligands. In this semiautomated procedure, HOAc distills with chlorobenzene and is converted to NaOAc by Na_2CO_3; the equilibrium that normally exists between HOAc and the imidazolidinone-ligated dirhodium(II) intermediates is thereby driven to the tetrasubstituted imidazolidinone-ligated product **3**. After evaporation of the solvent and chromatographic recovery of unreacted **8** (93−99%), dirhodium(II) imidazolidinones **3** were isolated in moderate to high yield.

The conversions of $Rh_2(OAc)_4$ to **3** were followed by HPLC. In previously reported syntheses of Rh_2(MEPY)$_4$,[3] Rh_2(MEOX)[4,11] and related oxopyrrolidine− and oxooxazolidine-ligated dirhodium(II) compounds,[26,27] only one tetrasubstituted product, identified by X-ray structural analysis to be exclusively the (2,2-*cis*) isomer, was observed. In reactions of $Rh_2(OAc)_4$ with **8a**, **8c**, and **8d**, followed as a function of time, the

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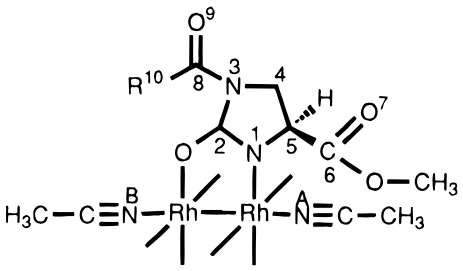
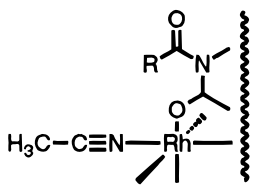
production of **3a**, **3c**, and **3d**, was seen to yield three tetrasubstituted products. The major isomer, as determined by spectral and X-ray structural analyses, was the (2,2-*cis*) isomer. A minor product, amounting to less than 20% of the total, was demonstrated to be the isomer in which three nitrogens and one oxygen are bound to one rhodium on the dirhodium(II) framework—the (3,1) isomer. However, although benzonitrile as a cosolvent with chlorobenzene enhances the solubility of the intermediate and final products and also decreases the time for complete substitution, use of this nitrile leads to an increase in (3,1)-**3a** production from 17% to 21−22%. The ratio of this isomer to the (2,2-*cis*) isomer remained constant over time, even with the disappearance of a third isomer, whose amount never exceeded 5 percent of the total, that was assigned the C_4-symmetric (4,0)-structure (*vide infra*). Heating analytically pure (2,2-cis)-**3c** with MPPIMH (**8c**) in chlorobenzene at reflux converted (2,2-cis)-**3c** to an equilibrium mixture of 85% (2,2-cis)-**3c** and 15% (3,1)-**3c**, and this was the same product composition as that obtained for the preparation of Rh_2(4*S*-MPPIM)$_4$ from $Rh_2(OAc)_4$. Thus, in the synthesis of **3a,c,d**, but not **3b**, (2,2-*cis*)-, (3,1)-, and (4,0)-2-oxoimidazolidine tetrasubstituted dirhodium(II) compounds are detectable products. The (4,0) isomer rearranges over time to the (3,1) isomer, and the (2,2-*cis*) and (3,1) isomers exist in equilibrium.

Structures of (2,2-*cis*)-3a−d. ORTEP diagrams for the (2,2-*cis*) isomers of Rh_2(4*S*-MACIM)$_4(CH_3CN)_2$ (**9**, Figure 1), Rh_2(4*S*-MBOIM)$_4(CH_3CN)_2$ (**10**, Figure 2), Rh_2(4*S*-MPPIM)$_4(CH_3CN)_2$ (**11**, Figure 3), and Rh_2(4*S*-MCHIM)$_4(CH_3CN)_2$ (**12**, Figure 4) describe the relevant structural features of these chiral dirhodium(II) 2-oxoimidazolidines. Selected bond lengths (Table 2) as well as bond and torsional angles (Table 3) are provided for structural comparisons (see **13** for numbering



13

scheme). In all four (2,2-*cis*)-**3** structures, viewed along the Rh−Rh axis, the nearest carboxylate groups at the 4-position of the imidazolidinone ligands (position 5 in **13**) are situated with a counterclockwise orientation, whereas those at the far end have a clockwise orientation, consistent with the (*S*)-configuration. The carbonyl groups of the 1-acyl substituents are directed anti from the ligated oxygens of the same ligands (**14**), presumably to avoid electronic repulsions, and this



14

conformation points the R-group of **9**−**12** toward the axially bound acetonitrile. The reversal from near 180° anti-orientation to near 0° syn-orientation (torsional angles) between two of the four 1-acyl carbonyl oxygens and their rhodium-ligated oxygens

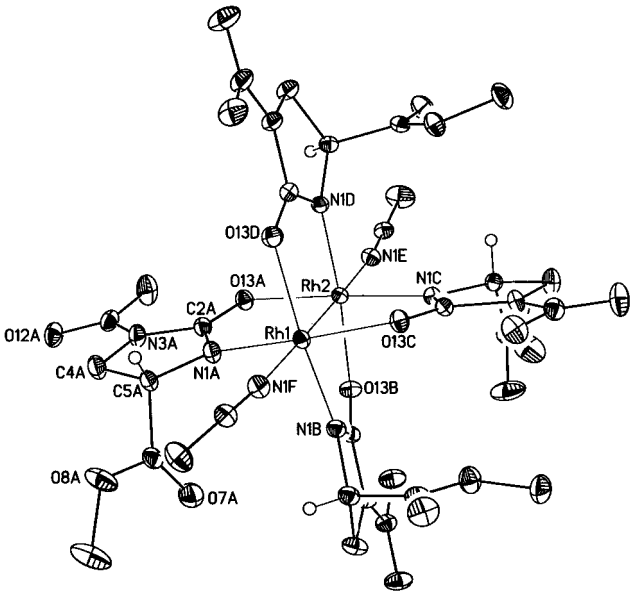


Figure 1. View of (2,2-*cis*)-Rh_2(4*S*-MACIM)$_4(CH_3CN)_2$·2CH_3CN (**9**) showing a partial atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary scale; most have been omitted for clarity.

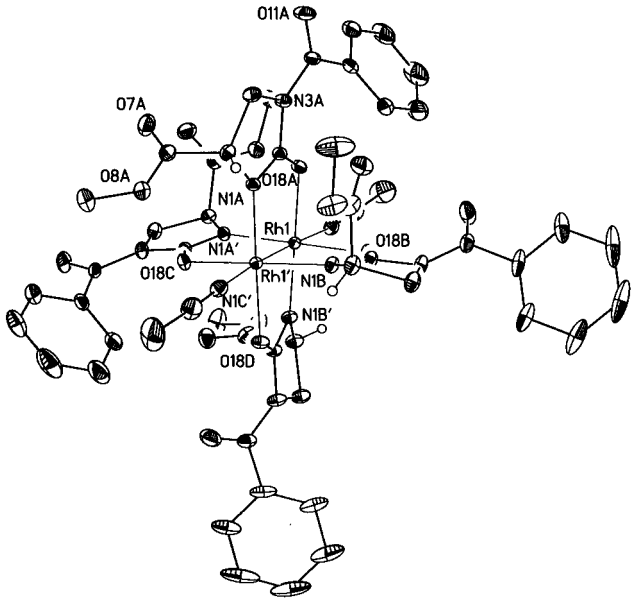


Figure 2. View of (2,2-*cis*)-Rh_2(4*S*-MBOIM)$_4(CH_3CN)_2$·2CH_3CN (**10**) showing a partial atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary scale; most have been omitted. The molecule lies on a crystallographic 2-fold axis passing perpendicular to the Rh−Rh axis. Atoms labeled by ′ are related by *y*, *x*, 1 − *z*.

seen with (2,2-*cis*)-Rh_2(MBOIM)$_4(CH_3CN)_2$ (**10**) suggests steric interactions arising from contacts with the benzoyl phenyl substituent. Torsional angles for the ester carbonyl relative to the 2-oxoimidazolidine ring are highly variable, but they generally portray the carbonyl group as being capable of alignment along the bond axis of the axial ligand.

Structure of (3,1)-Rh_2(4*S*-MACIM)$_4(CH_3CN)_2$ (15). The thermal ellipsoid representation of **15** is presented in Figure 5. Selected bond lengths (Table 2) and bond angles/torsional angles (Table 3) for **15** are provided for comparison. In this structure three nitrogens and one oxygen are attached to one rhodium atom, while the other rhodium is bonded to one nitrogen and three oxygens. The orientations of the 1-acetyl groups are, as expected, similar to those found with the (2,2-*cis*) isomer. The

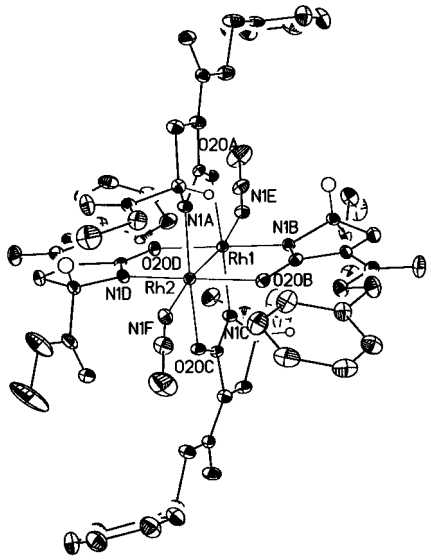


Figure 3. View of (2,2-*cis*)-Rh_2(4*S*-MPPIM)$_4$·2CH_3CN (**11**) showing a partial atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Most hydrogen atoms have been omitted for clarity and are drawn to an arbitrary scale.

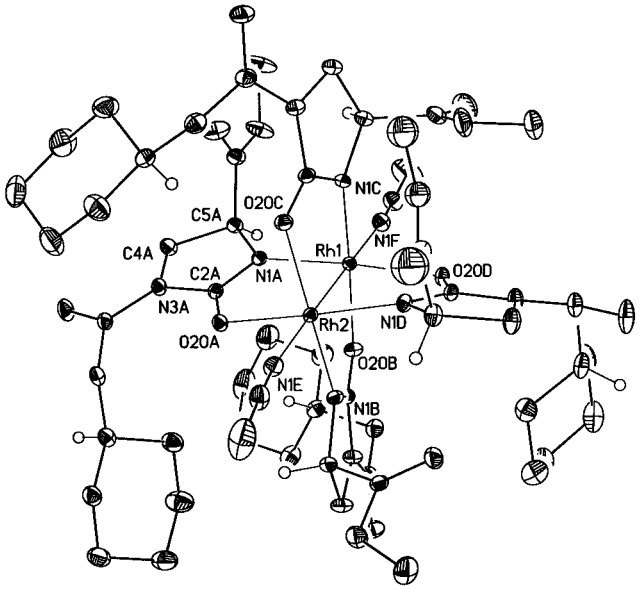


Figure 4. View of (2,2-*cis*)-Rh_2(4*S*-MCHIM)$_4$·2CH_3CN (**12**) showing a partial atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary scale; most have been omitted for clarity. The ester group on ligand D was disordered. The disorder was about two orientations, about 140° apart, rotated around the C5D−C6D bond to the imidazolidinone ring. The geometry of the two groups was idealized, and the affected atoms were refined with isotropic temperature factors. On ligand D, only the higher occupancy atoms on the disordered methyl ester group are shown.

Rh1−Rh2 bond length in **15** is the same as those for the (2,2-*cis*) isomers, and Rh−O and Rh−N bond lengths are not greatly affected. The Rh−N bond lengths to axially bound acetonitriles suggest one that is strongly bound and one that is weakly bound, which is consistent with experimental observations.

NMR spectra of the isomeric tetrasubstituted dirhodium(II) 2-oxoimidazolidines are consistent with their structural assignments. The number of absorptions for the ester methyl group(s) and for the amide acetyl group(s) provides a definitive pattern that defines their structure. The (2,2-cis)-**3a** isomer has two ^{1}H and two ^{13}C NMR absorptions for MeO and MeCO, and there are two carbonyl ^{13}C NMR absorptions for each carbonyl carbon.[4] The product assigned to be (3,1)-**3a** has four ^{1}H NMR absorptions each for MeO and MeCO, consistent with the asymmetry for this isomer. With the C_4-symmetric (4,0) isomer, one ^{1}H NMR absorption is expected for MeO and one for MeCO, and this is what is observed. (The same pattern is also expected for the C_2-symmetric (2,2-*trans*) isomer, and the chemical shift differences that might allow differentiation, although existing in COOMe resonances, cannot be uniquely assigned). Since acetone displaces the weakly coordinated acetonitrile, spectra in acetone-d_6 do not report acetonitrile absorptions.

Table 2. Selected Bond Lengths (Å) for Dirhodium(II) Tetrakis[methyl 1-acyl-2-oxoimidazolidine-4(*S*)-carboxylates][a]

bond	**9**	**15**	**10**	**11**	**12**
Rh−Rh	2.4586(3)	2.4597(8)	2.4611(3)	2.4637(5)	2.4508(2)
Rh−$N_{imid.}$	2.009(2)	2.023(3)[b]	2.008(2)	2.012(2)	2.007(1)
Rh−O	2.081(1)	2.054(2)[b]	2.072(2)	2.063(2)	2.073(1)
Rh−$N_{acetonitrile}$	2.220(3)	2.223(4)	2.210(3)	2.219(4)	2.216(3)
N1−C2	1.311(3)	1.306(4)	1.312(4)	1.311(4)	1.314(2)
N1−C5	1.458(3)	1.474(4)	1.466(4)	1.463(3)	1.457(2)
C2−O	1.263(3)	1.262(4)	1.257(4)	1.267(3)	1.260(2)
C2−N3	1.410(2)	1.410(4)	1.414(3)	1.408(3)	1.414(2)
N3−C4	1.457(3)	1.469(4)	1.476(4)	1.454(4)	1.462(2)
C4−C5	1.542(3)	1.543(5)	1.548(4)	1.543(4)	1.550(2)

[a] Except for the Rh−Rh bonds, the values listed are averaged values. The value for each bond length is the unweighted average value. The values in parenthesis are the estimated standard deviations and were calculated by $\sigma_{av} = [1/(\sum_i(1/\sigma_i)]^{1/2}$, where σ_i is the estimated standard deviation for each bond length contributing to the average. [b] The Rh−N bonds where a nitrogen atom is *trans* to another nitrogen atom are 2.037(6) and 2.043(5) Å for N1A and N1C to Rh2, respectively. For Rh−N bonds where a nitrogen atoms is *trans* to an oxygen atom, the bond lengths are 1.996(6) and 2.015(6) Å for N1B and N1D to Rh1, respectively. The Rh−O bonds where an oxygen atom is *trans* to another oxygen atom are 2.035(4) and 2.029(4) Å for O13A and O13C to Rh1, respectively. The Rh−O bonds where an oxygen atom is *trans* to a nitrogen atom are 2.100(5) and 2.054(5) Å for O13B and O13D to Rh2, respectively.

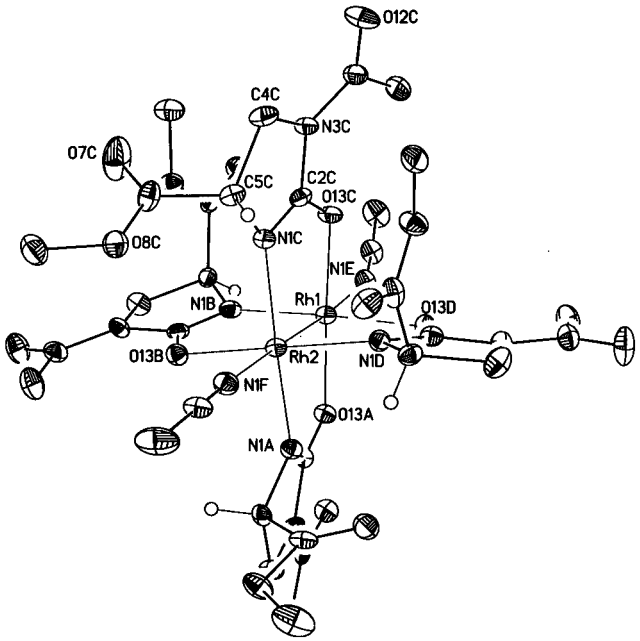


Figure 5. View of (3,1)-Rh_2(4*S*-MACIM)$_4$(CH_3CN)$_2$·2CH_3CN (**15**) showing a partial atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary scale; most have been omitted for clarity.

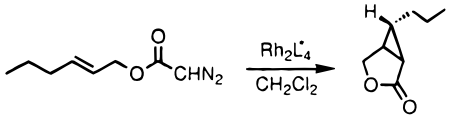
Selectivity of Catalysts. Comparisons of enantiocontrol and diastereocontrol in intramolecular reactions of diazoacetates, for which Rh_2(MEPY)$_4$ and Rh_2(MEOX)$_4$ catalysts gave low to moderate selectivities, were made with the (2,2-*cis*)-**3** catalysts. Intramolecular cyclopropanation of 2(*E*)-hexen-1-yl diazoacetate

Table 3. Selected Bond and Torsional Angles (deg) for Dirhodium(II) Tetrakis[methyl 1-acyl-2-oxoimidazolidine-4(*S*)-carboxylates][a]

bond angle (torsional angle)	**9**	**15**	**10**	**11**	**12**
Rh−Rh−N1	85.05(5)	85.0(1)	85.22(6)	85.98(5)	85.22(4)
Rh−Rh−O	89.90(4)	89.78(5)	89.77(5)	89.45(5)	89.27(3)
Rh−Rh−$N_{acetonitrile}$	177.71(5)	177.35(9)	176.24(9)	172.55(7)	179.21(8)
N1−Rh−O	89.94(5)	89.7(1)	90.30(7)	88.6(1)	89.94(4)
N1−Rh−N1	91.75(7)	90.6(1)	90.5(1)	92.3(1)	90.68(6)
N1−Rh−O	174.32(5)	174.5(1)	174.90(7)	175.2(1)	174.30(5)
O−Rh−O	87.95(7)	88.8(1)	88.5(1)	90.20(7)	88.92(5)
N1−Rh−$N_{acetonitrile}$	93.50(5)	94.9(1)	96.55(7)	99.0(1)	94.60(6)
O−Rh−$N_{acetronitrile}$	91.58(5)	90.3(1)	88.35(7)	86.4(1)	91.99(5)
Rh−N1−C2	122.1(1)	120.5(2)	121.7(1)	121.3(2)	120.8(1)
Rh−N1−C5	127.0(1)	127.4(2)	127.5(1)	127.9(2)	127.4(1)
Rh−O−C2	114.4(1)	115.3(2)	115.2(1)	115.9(2)	115.0(1)
N1−C2−N3	111.3(2)	112.0(3)	111.6(2)	111.8(2)	111.4(2)
C2−N3−C4	109.4(2)	109.2(3)	108.6(2)	108.7(2)	109.4(1)
N3−C4−C5	102.6(2)	102.4(3)	102.2(2)	102.5(2)	103.0(1)
C4−C5−N1	104.8(2)	104.7(3)	103.9(2)	104.1(2)	104.8(1)
C5−N1−C2	110.6(2)	110.2(3)	110.4(2)	109.8(2)	111.2(1)
N1−C2−O	127.1(2)	127.3(3)	126.9(2)	126.9(2)	126.8(1)
N3−C2−O	121.6(2)	120.6(3)	121.5(2)	121.2(2)	121.8(1)
$(C2-N3-C8-C10)_A$[b]	−2.0(6)	0.1(7)	173.4(4)	−19.9(9)	−0.4(4)
$(C2-N3-C8-C10)_B$[b]	−4.5(6)	7.4(11)	7.4(7)	−15.9(8)	−6.2(3)
$(N1-C5-C6-O7)_A$	−24.6(6)	−27.0(11)	−79.7(5)	−47.0(7)	−49.5(3)
$(N1-C5-C6-O7)_B$	124.3(4)	125.3(7)	−40.1(6)	−54.6(7)	−27.5(3)
$(N1-C5-C6-O7)_C$	64.2(5)	−80.2(9)	79.7(5)	−31.6(8)	119.2(3)
$(N1-C5-C6-O7)_D$	135.6(4)	130.6(7)	−40.1(6)	−40.8(8)	−69.7(5)

[a] The value for each bond length is the unweighted average value. The values in parenthesis are the estimated standard deviations and were calculated by $\sigma_{av} = [1/(\sum_i(1/\sigma_i))]^{1/2}$, where σ_i is the estimated standard deviation for each bond length contributing to the average. The bond angles around the Rh atoms having *cis* and *trans* stereochemistry were grouped seperately. For **15**, the N1A−Rh2−N1C bond angle is 170.2(2)° while the O13A−Rh1−O13C angle is 177.7(2)°. [b] For **15** $(C2-N3-C8-C10)_C = -80.2(9)°$ and $(C2-N3-C8-C10)_D = 130.6(7)°$.

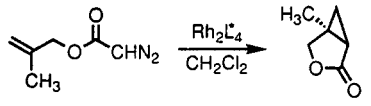
(**16**, eq 1)[4] and 2-methyl-2-propen-1-yl diazoacetate (**18**, eq 2)[4]



(1)

16 **17**

	yield, %	*ee, %*
Rh_2(5S-MEPY)$_4$	93	85
Rh_2(4S-MEOX)$_4$	65	52
Rh_2(4S-MACIM)$_4$	70	87
Rh_2(4S-MBOIM)$_4$	77	86
Rh_2(4S-MPPIM)$_4$	83	95
Rh_2(4S-MCHIM)$_4$	64	94



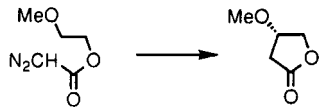
(2)

18 **19**

	yield, %	ee, %
Rh_2(5S-MEPY)$_4$	72	7
Rh_2(4S-MEOX)$_4$	84	1
Rh_2(4S-MACIM)$_4$	90	78
Rh_2(4S-MBOIM)$_4$	43	50
Rh_2(4S-MPPIM)$_4$	72	89
Rh_2(4S-MCHIM)$_4$	75	83

demonstrate the significant advantage of dirhodium(II) tetrakis-[methyl 1-acyl-2-oxaimidazolidine-4(*S*)-carboxylates] over Rh_2-(5*S*-MEPY)$_4$ and Rh_2(4*S*-MEOX)$_4$ for high enantiocontrol.[19] However, Rh_2(4*S*-MPPIM)$_4$ and Rh_2(4*S*-MCHIM)$_4$ are clearly superior to Rh_2(4*S*-MACIM)$_4$ for these transformations, and, among the four chiral imidazolidinone-ligated catalysts examined, Rh_2(4*S*-MBOIM)$_4$ gave the lowest level of enantiocontrol.

Similar advantages were seen in carbon−hydrogen insertion reactions. With 2-methoxy-1-ethyl diazoacetate (**20**, eq 3), for which high enantiocontrol had already been achieved with Rh_2-(5*S*-MEPY)$_4$[14] and Rh_2(4*S*-MEOX)$_4$,[11] slightly higher enantiomeric excesses could be found from reactions catalyzed by

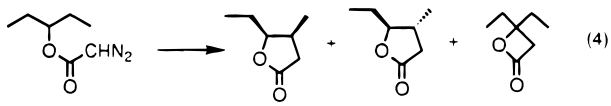


(3)

20 **21**

	yield, %	*ee, %*
Rh_2(5S-MEPY)$_4$	62	91
Rh_2(4S-MEOX)$_4$	65	92
Rh_2(4S-MACIM)$_4$	58	78
Rh_2(4S-MBOIM)$_4$	56	73
Rh_2(4S-MPPIM)$_4$	50	92
Rh_2(4S-MCHIM)$_4$	63	94

Rh_2(4*S*-MPPIM)$_4$ and Rh_2(4*S*-MCHIM)$_4$. However, when diastereocontrol was a determining factor for synthetic advantage (e.g., eq 4),[19] Rh_2(4*S*-MPPIM)$_4$ and Rh_2(4*S*-MCHIM)$_4$ were



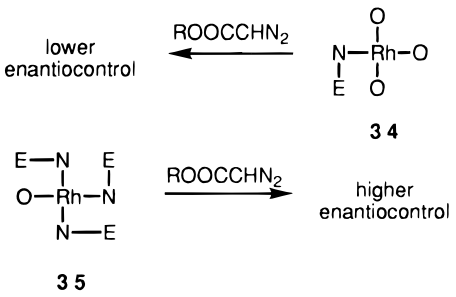
(4)

22 **23** **24** **25**

	yield, %	*23:24:25*	*ee, % 23*
Rh_2(5S-MEPY)$_4$	75	73:20:7	98
Rh_2(4S-MEOX)$_4$	86	60:27:13	98
Rh_2(4S-MACIM)$_4$	83	92:5:3	86
Rh_2(4S-MBOIM)$_4$	88	83:9:8	81
Rh_2(4S-MPPIM)$_4$	85	92:3:5	99
Rh_2(4S-MCHIM)$_4$	90	95:2:3	99

clearly superior to Rh_2(5*S*-MEPY)$_4$ and Rh_2(4*S*-MEOX)$_4$.

The (3,1)-Rh_2(4*S*-MACIM)$_4$ isomer was also evaluated in catalytic reactions of diazoacetate esters and, as can be seen from the results in Table 4, comparable yields but lower ee's, relative to (2,2-*cis*)-Rh_2(4*S*-MACIM)$_4$, were obtained in all cases. With the (3,1) isomer diazo decomposition can occur at the rhodium face on which three oxygens (**34**) or three nitrogens (**35**) are present. Enantiocontrol is expected to be significantly lower with **34**, where only one chiral attachment directs product formation, whereas higher ee's are expected for reactions that



occur on the rhodium face bearing three nitrogens (**35**) where three carboxylate groups are positioned to direct enantioselective product formation. The results in Table 4 are in accord with diazo decomposition taking place at both rhodium faces in proportions that are dependent on the diazo compounds that are employed.

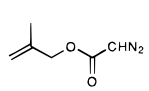
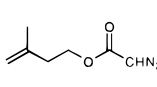
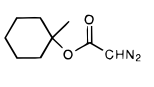
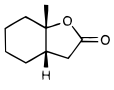
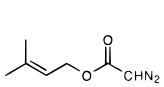
Proposed (4,0)-Rh$_2$(4*S*-MACIM)$_4$. Without definitive spectral data that could distinguish between the (2,2-*trans*)- and (4,0) isomers, and in lieu of an X-ray structure for the proposed (4,0) isomer, this dirhodium(II) compound was employed as a catalyst to evaluate enantioselectivity in metal carbene reactions. If the structure is, indeed, the (4,0) isomer, carbene reaction at the rhodium face bearing four oxygens should result in racemic product while that at the rhodium face bearing four nitrogens should give product with measurably high enantiomeric excess. On the other hand, if the structure of this isomer is that of the (2,2-*trans*) isomer then, like every other C_2-symmetric cyclopropanation catalyst,[2,13,28−30] moderate to high enantioselectivities are expected. Thus, only if the reaction takes place with the (4,0) isomer at the rhodium face having four oxygens would product enantiomeric excess be at 0%, and this is exactly what was observed in the intermolecular cyclopropanation of styrene with ethyl diazoacetate (64% yield, *cis:trans* = 58:42, ≤ 1% ee for both *cis*- and *trans*-2-phenylcyclopropanecarboxylates). The same result (≤3% ee) characterized intramolecular cyclopropanation of 3-methyl-2-buten-1-yl diazoacetate (**32** → **33**, 55% isolated yield).

Discussion

The extraordinary effectiveness of (2,2-*cis*)-dirhodium(II) tetrakis[methyl 1-acyl-2-oxoimidazolidine-4(*S*)-carboxylates] as catalysts for exceptional diastereocontrol and/or enantiocontrol in intramolecular metal carbene transformations is evident in the data from eqs 1−4. Compared to Rh$_2$(5*S*-MEPY)$_4$ and Rh$_2$(4*S*-MEOX)$_4$, however, their preparation by substitution of acetate on Rh$_2$(OAc)$_4$ is more complex and, with **3a,c,d**, results in the production of the (3,1) as well as the predominant (2,2-*cis*) isomers of the tetrasubstituted dirhodium(II) 2-oxoimidazolidines. The ratio of the (2,2-*cis*) isomer to the (3,1) isomer from reactions in refluxing chlorobenzene is approximately (±2%) 83:17 for **3a,c,d** and is invariant with imidazolidinone structure. The proposed (4,0) isomer, whose isomerization to the (3,1) isomer precluded isolation in quantities or crystalline form for structural analysis by X-ray diffraction, was a minor component, and no evidence for the formation of an alternative (2,2-*trans*) isomer was obtained.

The observation of (3,1)-dirhodium(II) tetrakis(carboxamidates) is not unprecedented. Kadish, Bear, and co-workers have reported the formation of (3,1)-dirhodium(II) tetrakis(*N*-phenylacetamidate) along with the (2,2-*cis*) isomer in the reaction of Rh$_2$(OAc)$_4$ with *N*-phenylacetamide.[31] Two isomers for each ligand substitution were observed, and a similar pattern was evident in HPLC analyses of products during reactions between Rh$_2$(OAc)$_4$ and **8a**, **8c**, and **8d**. The cause for formation of (3,1)-dirhodium(II) tetrakis(*N*-phenylacetamidate) has been attributed to steric effects in axial bond formation for the entering ligand and, if the substitution sequence suggested in Scheme 2 (Ac = acetyl) is operative, the pathway to eventual (2,2-*cis*) and (4,0) isomer formation begins with the substitution of the acetate trans to the first carboxamidate ligand. Substitution of the third acetate from **37** and **38** can form three products (**39**−**41**), although only two (**39** and **40**) are required for entry to the final tetrasubstituted products. According to this interpretation, axial coordination of carboxamide (**42**) occurs at either the nitrogen-

Table 4. Representative Results from Intramolecular Metal Carbene Reactions Catalyzed by (2,2-*cis*)- and (3,1)-Rh$_2$(4*S*-MACIM)$_4$[a]

reactant	product	catalyst	yield, %	ee, %
 26	 27	(2,2-*cis*)-Rh$_2$(4*S*-MACIM)$_4$	90	78
		(3,1)-Rh$_2$(4*S*-MACIM)$_4$	81	72
 28	 29	(2,2-*cis*)-Rh$_2$(4*S*-MACIM)$_4$	67	76
		(3,1)-Rh$_2$(4*S*-MACIM)$_4$	78	54
 30	 31	(2,2-*cis*)-Rh$_2$(4*S*-MACIM)$_4$	68[b]	90
		(3,1)-Rh$_2$(4*S*-MACIM)$_4$	49[c]	53
 32	 33	(2,2-*cis*)-Rh$_2$(4*S*-MACIM)$_4$	44	52
		(3,1)-Rh$_2$(4*S*-MACIM)$_4$	48	25
		(4,0)-Rh$_2$(4*S*-MACIM)$_4$	55	<3

[a] Reactions performed in CH_2Cl_2 using 1.0 mol % catalyst as previously described.[4,16] [b] Includes product from insertion into the methyl group (90:10). [c] Includes product from insertion into the methyl group (91:9).

Scheme 2

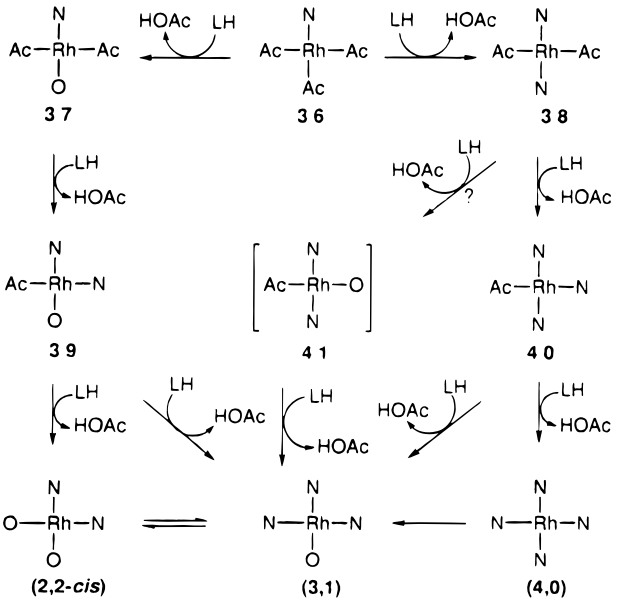


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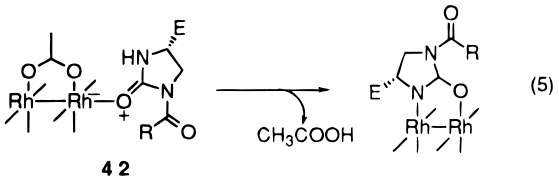
Table 5. Through Space Distances from Nitrile Nitrogen to *N*-Acyl and Ester Ligand Attachments

	distances, Å			
bond (**13**)	**9**	**10**[a]	**11**	**12**
N_A−O7A	3.648	4.345	3.598	3.795
N_A−O7B	3.768	4.583	3.027	3.920
N_A−C10C	4.793	4.930	4.575	5.036
N_A−C10D	5.033	6.795	4.545	4.944
N_B-O7C	4.166		3.514	4.366
N_B−O7D	3.366		3.543	3.346
N_B−C10A	4.903		4.588	4.796
N_B−C10B	4.815		4.521	4.986

[a] Contacts to N_B are identical with those to N_A by symmetry.

ligated or oxygen-ligated face (eq 5, E = COOMe) of dirhodium(II) in **36** but only at the oxygen ligated face to achieve formation of **40**. Isomerization of the presumed (4,0) isomer under the reaction conditions is consistent with this structure rather than the (2,2-*trans*) isomer which, like the (*cis*-2,2) isomer, should be stable under the reaction conditions. However, although Scheme 2 is consistent with the results of Bear/Kadish[31] and this study, other substitution sequences are possible and cannot be completely dismissed.



4 2 (5)

Although there is rotational flexibility for the *N*-acyl and ester ligand attachments in dirhodium(II) oxazolidinones **9**−**12**, the proximity of these functional groups to the carbene center in catalytic reactions with diazo compounds is an essential consideration in assessing stereoselectivity. In this regard, the acetonitrile complexes of these dirhodium(II) compounds are useful models, and the distances from the attached nitrile nitrogen to C10 and O7 (in **13**) provide reasonable estimates of similar distances within the carbene structures. Table 5 provides these distances for **9**−**12**. Consistently, the shortest N−O7 and N−C10 distances are seen with Rh_2(4*S*-MPPIM)$_4$($CH_3CN)_2$ (**11**), which is also, along with Rh_2(4*S*-MCHIM)$_4$($CH_3CN)_2$ (**12**), the catalyst that provides the highest levels of stereocontrol in metal carbene transformations. These same distances are longest with Rh_2(4*S*-MBOIM)$_4$($CH_3CN)_2$ (**10**), whose induced selectivities in catalytic reactions are the lowest among the four imidazolidinone-ligated dirhodium(II) catalysts. For comparison, ester carbonyl oxygen−nitrile nitrogen distances in Rh_2(5*R*-MEPY)$_4$($CH_3CN)_2$ are 3.28 and 4.67 Å,[3] the latter distorted, like Rh_2(4*S*-MCHIM)$_2$($CH_3CN)_2$, by an alcohol molecule in the crystalline lattice. With Rh_2(4*S*-MEOX)$_4$-($PhCN)_2$ these distances are 3.343 and 3.265 Å.

Among chiral (2,2-*cis*)-dirhodium(II) carboxamidates **1**−**3**, Rh−Rh bond lengths are independent of the ligand, 2.46 ± 0.01 Å, as are Rh−O and Rh−N bond lengths.[11] However, the C2−N3−C4 bond angles of **9**−**12** are 109° compared to 106° for C2−O3−C4 in dirhodium(II) oxazolidinones and 103° for C2−C3−C4 in the corresponding pyrrolidinone-ligated catalysts. The N3−C4−C5 bond angles of **9**, **11**, and **12** are 103° compared to 105° with Rh_2(4*S*-MEOX)$_4$ and 103° with Rh_2(5*S*-MEPY)$_4$.

Chiral dirhodium(II) oxazolidinones **3** have been synthesized and characterized, and their X-ray structures have revealed that their relative effectiveness as chiral catalysts is related to the orientation of the *N*-acyl group at the 1-position. The alkyl (aryl) group of the *N*-acyl linkage protrudes toward the axial-bound carbene. The outcome of this structural arrangement, that with (2,2-*cis*)-Rh(4*S*-MPPIM) and (2,2-*cis*)-Rh(4*S*-MCHIM) constructs a cavity in which the metal carbene is formed, is highly enantioselective and diastereoselective catalysis. Further elaboration of these catalytic systems is underway.

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Supporting Information Available: Text giving an X-ray experimental writeup for each structure, tables of positional and thermal parameters, and thermal ellipsoid diagrams (49 pages). Ordering information is given on any current masthead page.

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