New Dinuclear Catalysts $Rh_2(N-O)_2[(C_6H_4)P(C_6H_5)_2]_2$ with Imidate Ligands: Synthesis and Isomerization from Head-to-Tail to Head-to-Head Configuration of the Imidate Ligands

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Two new dirhodium(II) catalysts of general formula $Rh_2(N-O)_2[(C_6H_4)P(C_6H_5)_2]_2$ ($N-O = C_4H_4NO_2$) are prepared, starting from $Rh_2(O_2CCH_3)_2(PC)_2L_2$ [$PC = (C_6H_4)P(C_6H_5)_2$ (head-to-tail arrangement); $L = HO_2CCH_3$]. The thermal reaction of $Rh_2(O_2CCH_3)_2(PC)_2{\cdot}L_2$ with the neutral succinimide stereoselectively gives one compound that according to the X-ray structure determination has the formula $Rh_2(C_4H_4NO_2)_2[(C_6H_4)P(C_6H_5)_2]_2$ (**1**). It corresponds to the polar isomer with two bridging imidate ligands in a head-to-head configuration. However, stepwise reaction of $Rh_2(O_2CCH_3)_2(PC)_2{\cdot}L_2$ with $(CH_3)_3SiCl$ and potassium succinimidate yields a mixture of **1** and one of the two possible isomers (structure B) with a head-to-tail configuration of the imidate ligands, $Rh_2(C_4H_4NO_2)_2[(C_6H_4)P(C_6H_5)_2]_2$ (**2**), also characterized by X-ray methods. In solution, compound **2** undergoes slow isomerization to **1**; the rate of this process is enhanced by the presence of acetonitrile. Compounds **1** and **2** are obtained as pure enantiomers starting from (*M*)- and (*P*)-$Rh_2(O_2CCH_3)_2(PC)_2{\cdot}L_2$ rather than from the racemic mixture. Their enantioselectivities in cyclopropanation of 1-diazo-5-penten-2-one are similar to those reported for the dirhodium amidate catalysts.

Introduction

We have recently reported that chiral cyclometalated compounds of formula $Rh_2(O_2CCF_3)_2(PC)_2$ [$PC = (C_6H_4)P(C_6H_5)_2$, head-to-tail configuration] can induce enantioselectivity in the cyclization of α-diazocompounds.[1,2] As these compounds have backbone chirality, the observation of catalytic enantioselectivity is direct evidence of the involvement of the entire dinuclear species in the carbene transfer process.

Later on, we focused our interest on the synthesis and study of $Rh_2(L-L)_2(PC)_2$ compounds with an L−L ligand placing a donor group in the proximity of the axial Rh−C bond in the carbenoid, with the aim of increasing the selectivity of the carbene transfer process. A good candidate for this purpose could be the succinimidate ligand that, acting as a bridging N- and O-donor ligand, leaves an uncoordinated keto group in the vicinity of the axial catalytic site. The syntheses of compounds of the general formula $Rh_2(N-O)_4$ (N,O = carboxamidate) have been reported;[3−5] these compounds are formed by successive acetate ligand replacement from $Rh_2(O_2CCH_3)_4$. From the four possible isomers, the compound that contains four bridging amidate ligands with a *cis*-RhN_2O_2 coordination around each rhodium atom (2,2-cis arrangement) is usually obtained as the major or only reaction product. In some cases, (3,1) and (4,0) compounds have been characterized as minor reaction products.[4−6]

We report in this work the stereoselective synthesis of two rhodium compounds of formula $Rh_2(N-O)_2[(C_6H_4)P(C_6H_5)_2]_2$ by exchanging acetate with succinimidate in $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2$. The presence of two metalated phosphines in the head-to-tail (H−T) arrangement could have a direct influence in the substitution processes, as has been suggested in other related processes.[6] By careful procedures, the thermodynamically stable compound **1**, with head-to-head (H−H) configuration, and the compound **2**, with H−T configuration, have been synthesized. Surprisingly, the complete isomerization of **2** to **1** is observed, even under mild conditions. Catalytic studies performed on both compounds show that the succinimidate ligands do not have the expected influence on the selectivity.

Experimental Section

General Comments. $C_4H_5NO_2$ (Aldrich) was used as purchased. $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$ was prepared by literature procedure.[7] All solvents were of analytical grade and were degassed before use. NMR spectra were recorded on Varian Unity-300 and Varian Unity-400 spectrometers. Chemical shifts (δ) are given in ppm, relative to TMS (^{1}H,^{13}C) and 85% H_3PO_4 aqueous solution (^{31}P). Coupling constants (*J*) are given in hertz.

Synthesis of $Rh_2(C_4H_4NO_2)_2[(C_6H_4)P(C_6H_5)_2]_2$ (H−H) (1). To a solution of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2{\cdot}(HO_2CCH_3)_2$ (0.20 g, 0.21

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mmol) in toluene (50 mL) was added succinimide (0.16 g, 1.65 mmol), and the mixture was refluxed for 48 h. The solvent was evaporated, and the crude product was purified by column chromatography using dichloromethane as eluent solvent.

Yield: 85%.^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.4−2.4 (m, 8H), 6.49 (m, 1H), 6.60−7.25 (m, 17H), 7.36 (m, 6H), 7.56 (m, 4H). $^{13}C[^1H]$ NMR ($CDCl_3$, 400 MHz): δ 29.26, 29.78, 30.43, 32.65, 120−145 (m, aromatics), 166.00 (m), 193.46, 196.26, 198.53, 198.69. $^{31}P[^1H]$ NMR ($CDCl_3$, 300 MHz): δ 14.7 ($^1J_{Rh-P} = 146$ Hz, $^2J_{Rh-P} = 8$ Hz), 25.0 ($^1J_{Rh-P} = 178$ Hz, $^2J_{Rh-P} = 7$ Hz; values of J obtained from a simulated spectrum).

Synthesis of (*P*)-$Rh_2(C_4H_4NO_2)_2[(C_6H_4)P(C_6H_5)_2]_2$ (H−H) [(*P*)-1]. This compound was prepared by the above-described procedure, using the (*P*)-$Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot(HO_2CCH_3)_2$ enantiomer as the starting product. $[\alpha]^{20}_D$ +167° (c 0.012, $CHCl_3$).

Synthesis of $Rh_2(C_4H_4NO_2)_2[(C_6H_4)P(C_6H_5)_2]_2$ (H−T) (2). To a solution of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot(HO_2CCH_3)_2$ (0.05 g, 0.05 mmol) in freshly distilled THF (25 mL) was slowly added $(CH_3)_3SiCl$ (27 μL, 0.20 mmol) in 5 mL of THF, and the mixture was stirred for 5 min. The resulting solution was transferred to a second flask containing succinimide (0.02 g, 0.20 mmol) and KOH (0.025 g, 0.44 mmol) in methanol (15 mL). The mixture was stirred at room temperature for 5 min. The ^{31}P NMR spectrum of the crude product showed the formation of two P-containing species **1** and **2**, in equal amounts. These two products were isolated by column chromatography (SiO_2−hexane), using ethyl acetate−hexane (3/1 mixture) as the eluent solvent. The H−T compound, **2**, is the first one eluted from the column.

Compound **2**. Yield: 30%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.20 (m, 2H), 1.45 (m, 2H), 1.78 (m, 2H), 2.08 (m, 2H), 6.52 (m, 4H), 6.68 (m, 2H), 6.92 (m, 10H), 7.18 (m, 2H), 7.28 (m, 6H), 7.52 (m, 4H). $^{31}P[^1H]$ NMR ($CDCl_3$, 300 MHz): δ 23.9 ($^1J_{Rh-P} = 171$ Hz, $^2J_{Rh-P} = -9$ Hz, $J_{Rh-Rh'} = 18$ Hz; values of J obtained from a simulated spectrum).

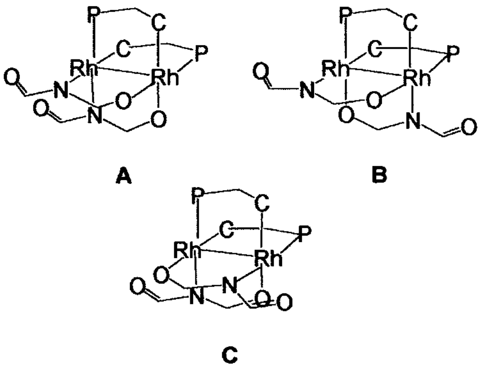
Synthesis of (*M*)-$Rh_2(C_4H_4NO_2)_2[(C_6H_4)P(C_6H_5)_2]_2$ (H−T) [(*M*)-2]. The reaction procedure was similar to that described above using the (*M*)-$Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot(HO_2CCH_3)_2$ enantiomer as the starting product. $[\alpha]^{20}_D$ −125° (c 0.012, $CHCl_3$).

Catalytic Experiments. Diazo compounds were prepared from the corresponding carboxylic acid by reaction with methyl chloroformate, followed by treatment with freshly prepared diazomethane.[8] All of the catalytic reactions were performed by dissolving the diazo compound (0.28 mmol) in dry CH_2Cl_2 (30 mL) under an argon atmosphere. To this solution was added the corresponding catalyst (0.003 g, 0.28×10^{-2} mmol; [substrate]/[Rh(II)-complex] = 100), and the mixture was stirred at room temperature until complete transformation of the diazo compound was observed by TLC chromatography. The solvent was evaporated, and the crude product was filtered through a short chromatography column to eliminate the catalyst. The yield of the reaction was calculated from the proton NMR.

The bicyclo[3.1.0]-hexan-2-one (**6**) was purified by HPLC chromatography, and the ee values were based on GC analysis.[9] The absolute stereochemistry of the cyclization product formed from the (*P*)-Rh(II) catalysts was determined as (1*R*,5*S*).[10]

X-ray Crystallography. A Siemens SMART CCD diffractometer was employed for data collection on crystals of compounds $\mathbf{1}\cdot(H_2O)(C_4H_5NO_2)$ (**3**) and $\mathbf{2}\cdot(H_2O)_2$ (**4**). Unit-cell dimensions were determined by a least squares fit of 50 reflections. The structures were solved by direct methods and refined on F^2 for all reflections using SHELXTL V 5.05.[11] In both cases, the positions of all non-hydrogen atoms were deduced from difference Fourier maps and refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions and refined riding on the carbon atom to which they are attached. The hydrogen atoms of the water molecules were ignored in both structures.

Chart 1



A B

C

Crystal Structure Determination of Complex $\mathbf{3}\cdot(CH_2Cl_2)$. Crystal data: $C_{49}H_{43}Cl_2O_7N_3P_2Rh_2$, MW = 1124.52, monoclinic, $a = 12.8114(8)$, $b = 19.5510(12)$, $c = 18.6265(12)$ Å, $\beta = 100.774(2)°$, $V = 4583.2(5)$ Å^3, $T = 296$ K, space group $P2_1/n$, $Z = 4$, μ(Mo Kα) = 0.963 mm^{-1}. Final conventional $R = 0.658$ for 13 797 "observed" reflections and 586 variables.

Crystal Structure Determination of Complex $\mathbf{4}\cdot(CH_2Cl_2)_2$. Crystal data: $C_{46}H_{40}Cl_4O_6N_2P_2Rh_2$, MW = 1125.37, monoclinic, $a = 10.0387(8)$, $b = 24.741(2)$, $c = 19.2080(17)$ Å, $\beta = 92.930(2)°$, $V = 4764.3(7)$ Å^3, $T = 296$ K, space group $P2_1/n$, $Z = 4$, μ(Mo Kα) = 1.033 mm^{-1}. Final conventional $R = 0.0713$ for 10 314 "observed" reflections and 559 variables.

Results and Discussion

Synthesis of 1 and 2. The thermal reaction of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2$ $(HO_2CCH_3)_2$ (racemic mixture) and 8 molar excess equiv of succinimide in refluxing toluene for several hours led to complex **1**, of formula $Rh_2(C_4H_4O_2N)_2[(C_6H_4)P(C_6H_5)_2]_2$, as the only reaction product. This compound crystallized as an adduct with one succinimide and one molecule of water (**3**). The ^{31}P NMR spectrum of this compound shows two signals of equal intensity coupled to the two rhodium nuclei, centered at 25.0 ($^1J_{Rh-P} = 178$ Hz; $^2J_{Rh-P} = 7$ Hz) and 14.7 ($^1J_{Rh-P'} = 146$ Hz; $^2J_{Rh-P'} = 8$ Hz) ppm. These data are consistent with a head-to-head arrangement of the bridging imidate ligands in the dinuclear unit. This assumption was confirmed by an X-ray crystal structure determination.

If $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2(HO_2CCH_3)_2$ (racemic mixture) in THF is reacted with $(CH_3)_3SiCl$, $Rh_2Cl_2[(C_6H_4)P(C_6H_5)_2]_2$ species can be generated in solution.[12] By addition of potassium succinimidate in the same solvent, a 1:1 mixture of **1** and a new species $Rh_2(C_4H_4O_2N)_2[(C_6H_4)P(C_6H_5)_2]_2$ (**2**) is formed. This new compound was better crystallized as a water adduct. An X-ray structure determination performed on this adduct, **4**, confirmed the formula $Rh_2(C_4H_4O_2N)_2[(C_6H_4)P(C_6H_5)_2]_2(H_2O)_2$ and also a symmetric (head-to-tail) arrangement of the succinimidate ligands on this compound.

Pure enantiomers (*M*)-**1** and (*P*)-**2** were obtained by the same procedure starting from the corresponding enantiomers of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2$.[1]

Up to three different isomers, A, B, and C, (Chart 1) could be expected from the thermal reaction of $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2$ and an excess of succinimide. However, the above results confirm that, in the experimental conditions used, only one compound **1** (**A**, Chart 1) is formed.

In $CDCl_3$ solution, compound **2** undergoes slow isomerization to produce **1**. This transformation, which was followed by ^{31}P NMR spectroscopy, is up to 80% complete after 48 h at 45 °C.

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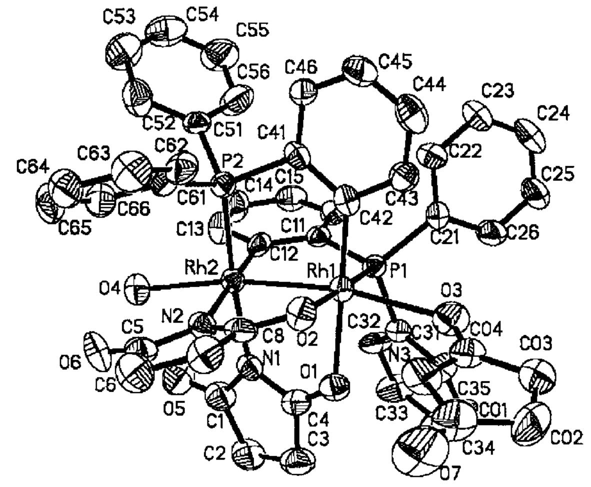


Figure 1. Molecular view of $Rh_2(C_4H_4NO_2)_2[(C_6H_4)P(C_6H_5)_2]_2(H_2O)(C_4H_5NO_2)$ (**3**), with the H atoms omitted for clarity. Selected bond distances (Å) and angles (deg) are Rh1−Rh2 2.5551(7), Rh1−C42 1.970(7), Rh1−P1 2.2052(16), Rh2−C12 1.997(6), Rh2−N1 2.119(5), C42−Rh1−O1 172.50(19), O2−Rh1−O3 90.00(16), and C12−Rh2−O4 90.9(2).

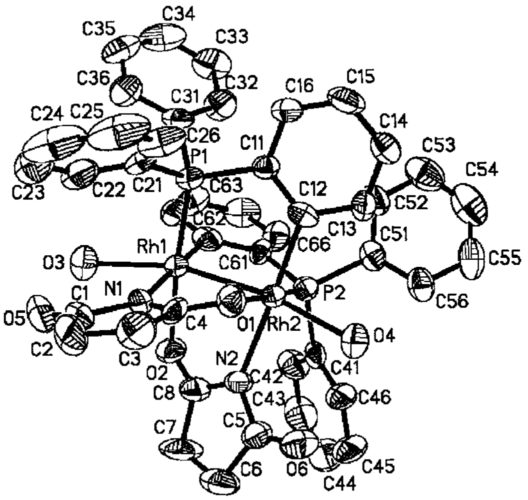


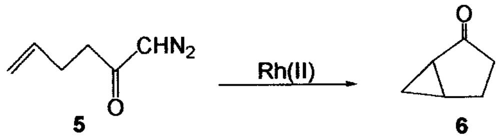
Figure 2. Molecular view of $Rh_2(C_4H_4NO_2)_2[(C_6H_4)P(C_6H_5)_2]_2{\cdot}2(H_2O)$ (**4**), with the H atoms omitted for clarity. Selected bond distances (Å) and angles (deg) are Rh1−Rh2 2.5386(10), Rh1−C62 2.003(9), Rh1−P1 2.2179(19), Rh2−C12 2.006(7), Rh2−P2 2.211(2), Rh2−N2 2.176(6), C62−Rh1−N1 177.0(3), O2−Rh1−O3 81.2(2), and C12−Rh2−O1 90.8(3).

The addition of an equimolar amount of free succinimide to compound **2** has no significant influence on the rate of isomerization. However, acetonitrile hastened this process; when a 40 molar excess of CH_3CN was added, compound **2** completely transformed to **1** in less than 15 h at the same temperature. It is remarkable that complete isomerization occurs very seldomly for this type of compound under the mild conditions used. Doyle and co-workers have found that the displacement of acetates from $Rh_2(O_2CCH_3)_4$, by certain amidate ligands, gave chiral dirhodium(II) *N*-acyl-2-oxoimidazolidine-4-carboxylate esters, $Rh_2(N{-}O)_4$. Three different isomers (2,2-cis),[4a] (3,1),[4a] and (4,0)[4b] have been structurally characterized. The (4,0) isomer has been isolated in up to 25% yield for short reaction times. In the reaction conditions used, refluxing a 10:1 chlorobenzene−benzonitrile mixture in the presence of free amide, the (4,0) isomer rapidly isomerizes (3−4 h), leading to an equilibrium mixture of (2,2-cis) and (3,1) geometries.[4b] To our knowledge, this is the only detailed report of isomerization in dirhodium(II) compounds. The presence of different types of ligands in $Rh_2(N{-}O)_4$ and $Rh_2(N{-}O)_2[(C_6H_4)P(C_6H_5)_2]_2$ compounds does not allow us to establish closer comparisons between both isomerization processes.

Structures of 3 and 4. Views of the structures of **3** and **4** are shown in Figures 1 and 2, respectively, together with important bond distances and angles.

In the structure of **3,** the two rhodium atoms are bridged by four ligands; two cisoid cyclometalated phosphines are in a head-to-tail arrangement, while the two succinimidate ligands are in a head-to-head configuration. This ligand distribution generates two different environments for the rhodium atoms. There is one molecule of succinimide coordinated through one oxygen atom to the less sterically hindered rhodium atom, and there is one molecule of water coordinated to the second rhodium. The Rh−Rh distance, 2.5551(7) Å, is slightly longer than the values reported for related dirhodium compounds with carboxylate ligands.[7,13] The Rh−O and Rh−N bonds trans to the carbon atoms are longer (2.181(4) and 2.178(5) Å) than those trans to the P atoms (2.145(4) and 2.119(5) Å), in agreement with the expected order of the trans influence of M−C and M−P. The average equatorial Rh−O bond distances in both compounds, **3** and **4**, are about 0.1 Å longer than those in the dirhodium(II) tetrakis imidazolidine compound.[4] The Rh−O bond distance involving the axial succinimide ligand is considerable longer (2.483(5) Å) than that for the molecule of water (2.284(4) Å).

Scheme 1



5 6

	Yield (%)	% ee
(*P*)-**1**	98	21 (1*R*,5*S*)
(*M*)-**2**	84	22 (1*S*,5*R*)
Rh_2(carboxamidates)[16]	50-94	3-23

The structure of **4** also contains two cyclometalated phosphines and two succinimidate ligands bridging both of the rhodium atoms in a head-to-tail configuration, resulting in a symmetric structure with each keto group of the imidate ligands protruding into an axial coordination site. This ligand distribution generates identical environments for the rhodium atoms that have a metal-to-metal bond distance (2.5386(10) Å) slightly shorter than that of compound **3**. Two molecules of water complete the octahedral coordination around the rhodium atoms. The Rh−O bonds are trans to a P atom, while the Rh−N bonds are trans to carbon. The observed Rh−O and Rh−N bond distances are very similar, in the range 2.16−2.17 Å. The two axial molecules of water have similar Rh−O bond distances, in the range 2.35−2.37 Å. In both compounds, the distances between the keto oxygen atoms and the oxygen of the axially coordinated molecule of water are relatively short (∼2.7 Å).

Catalysis. Compounds **1** and **2** were tested as catalysts in the transformation of 1-diazo-5-phenyl-2-pentanone; as reported for dirhodium(II) tetraacetate,[14] no C−H insertion product

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resulted, but addition to the aromatic ring was observed. Both Rh compounds were quite effective in the cyclopropanation of diazo compound **5**[15] to give **6** (98 and 84% yields, respectively, after 90 min of reaction at room temperature) (Scheme 1). The ability of the chiral (*P*)-**1** and (*M*)-**2** compounds to induce enantioselectivity was studied in the cyclopropanation of such a diazo compound, giving very similar ee values (∼22%). Chiral rhodium tetraamidate compounds have been reported to give similar ee values for the same diazo ketone.[16]

We have confirmed that, under the catalytic conditions, compound **2** did not undergo any detectable isomerization (less than 1%). Considering that the observed catalytic activities are very similar for **1** and **2**, the almost identical ee values found for both compounds indicate that the effect of the pending oxygen atom, at least in this particular case, is not catalytically relevant.

Conclusion

The new strategy described in the present paper to produce succinimidate derivatives $Rh_2(N{-}O)_2[(C_6H_4)P(C_6H_5)_2]_2$ that involves replacement of acetates by chlorines and further reaction with the deprotonated succinimide allows us to obtain isomers that are not stable in solution under the thermal reaction conditions. By this procedure, two compounds **1** and **2** have been prepared in ∼30% yield. It has been confirmed that the isomerization of **2** to **1** is accelerated by the presence of free acetonitrile. This observation represents one of the few examples of ligand rearrangement observed for dinuclear rhodium(II) compounds.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of complexes **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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