Stereoselective Synthesis and Catalytic Behavior of Rhodium(II) Compounds with Metalated Chiral Phospholanes as Ligands

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The reaction of $Rh_2(O_2CR)_4$ (R = CH_3, CF_3) with the chiral phosphine (2*R*,5*R*)-2,5-dimethyl-1-phenylphospholane (**1**) results in the formation of the mono-metalated compounds $Rh_2(O_2CR)_3$[PC*] (PC*H = (*2R,5R*)-2,5-dimethyl-1-phenylphospholane; R = CH_3 (**2**), CF_3 (**3**)) in high yield. The diastereoisomers $Rh_2(O_2CR)_2$[PC*]$_2$ (**(*P*)-4** and **(*M*)-6**) are formed in a 3:1 ratio by thermal reaction of **2** with phosphine **1**. However, the photochemical reaction of **2** with phosphine **1** in the presence of trifluoroacetic acid afforded compounds **(*P*)-5** and **(*M*)-7** in a 1:9 ratio. All these compounds, isolated as solvates with two molecules of RCO_2H, were tested in the catalytic transformation of α-diazo compounds, with **3** and **(*M*)-7** showing the highest selectivity.

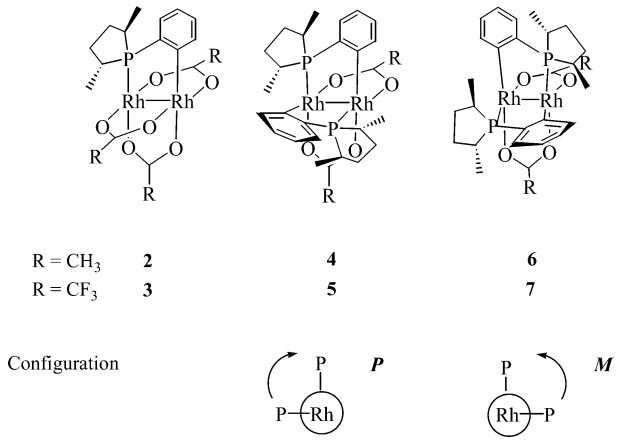
Introduction

Ortho metalation of arylphosphines is a well-known and often used reaction for the preparation of organometallic compounds.[1,2] Many catalysts of the general formula $Rh_2(O_2CR)_2(PC)_2$, PC representing metalated arylphosphines with head-to-tail configurations, are accessible by direct thermal reaction of the corresponding phosphine with dirhodium tetracarboxylate.[3−7] The inherent backbone chirality of these compounds has been exploited for enantioselective reactions, since the racemic mixture could be separated by standard resolution methods.[8,9]

Taking the previous results into consideration, it seemed of interest to explore the use of chiral phosphine ligands to produce new chiral metalated rhodium(II) catalysts. In this case the bis-cyclometalated compounds are formed as a mixture of two diastereoisomers, which could be readily isolated, while the mono-metalated compound is obtained as a pure enantiomer. Some preliminary studies have confirmed these expectations.[10]

We report here an improved synthetic method for the selective preparation of the mono-metalated compounds $Rh_2(O_2CR)_3$[PC*] (PC*H = (*2R,5R*)-2,5-dimethyl-1-phenylphospholane; R = CH_3 (**2**), CF_3 (**3**)) and the two bis-cyclometalated compounds $Rh_2(O_2CR)_2$[PC*]$_2$ (**4**−**7**) (Chart 1). Both types of catalysts have been tested in reactions involving inter- and intramolecular transformations of α-diazo compounds under different reaction conditions.

Chart 1



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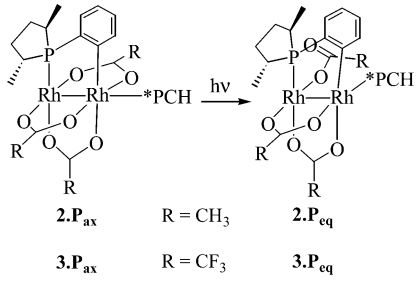
Scheme 1



Results and Discussion

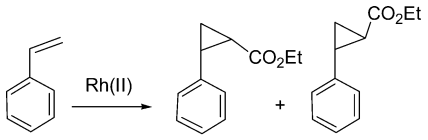
Recently we have found that after refluxing rhodium(II) acetate and the chiral phosphine (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (molar ratio 1:2.2), in a mixture of toluene and acetic acid (3:1) for 33 h, three compounds were formed in different yields.[10] These are $Rh_2(O_2CCH_3)_3$[PC*] (43%) and the two diastereoisomers $Rh_2(O_2CCH_3)_2$[PC*]$_2$ (23 and 13%).

We now report a different approach to prepare the target compounds. The synthesis of the mono-metalated compound $Rh_2(O_2CCH_3)_3$[PC*] (**2**) can be achieved in nearly quantitative yield by reducing the amount of phospholane and acetic acid used in the reaction. Compound **2** can be employed as starting material for the synthesis of $Rh_2(O_2CCF_3)_3$[PC*] (**3**), using carboxylate exchange reactions.[11] Compounds **2** and **3** were used to prepare the diastereoisomers $Rh_2(O_2CR)_2$[PC*]$_2$. The thermal and photochemical reactions, tested to induce the entrance of the second phospholane, were monitored by ^{31}P NMR spectroscopy.

Thermal Reaction. Compound **2** and phospholane **1** (1:1.1 molar ratio) reacted in a mixture of toluene and acetic acid (10:1) for 12 h, under reflux conditions, to form a mixture of the two diastereoisomers **(*P*)-4** and **(*M*)-6** in a ratio of about 3:1. Attempts to perform a similar reaction with compound **3** resulted in the formation of **(*P*)-5** and **(*M*)-7** in lower yields with extensive decomposition.

Photochemical Reaction. By adding an equimolar amount of **1** to a solution of **2** in C_6D_6, the phosphorus signal of compound **2**, at δ 37.4 ppm, practically disappeared to give two new resonances centered at 42.3 ppm ($^1J_{Rh-P}$ = 160 Hz) and −3.0 ppm ($^1J_{Rh-P}$ = 108 Hz), suggesting the formation of the adduct $Rh_2(O_2CCH_3)_3$[PC*]·PC*H (**2·P$_{ax}$**) in solution (Scheme 1). After irradiation of this sample for about 60 min, the ^{31}P NMR spectrum confirmed the formation of a new compound (δ 59.7 ppm, $^1J_{Rh-P}$ = 183 Hz; δ 35.4 ppm, $^1J_{Rh-P}$ = 140 Hz) with simultaneous decrease of the signals due to the adduct **2·P$_{ax}$**. This new intermediate compound was assigned the product structure **2·P$_{eq}$**, resulting from the rearrangement of the coordinated phospholane from the axial to the equatorial position. The observation of this signal with the corresponding chemical shift is diagnostic for the coordination of a phosphine in an equatorial position.[12] The reaction did not proceed further, and despite the addition of acetic acid to the sample, no significant amount of metalated products was observed.

Table 1. Asymmetric Cyclopropanation of Styrene



cat.	solvent	*T* (°C)	yield[a] (%)	**8**/**9**	% ee[b] **8**	% ee[b] **9**
		(1*R*,2*S*)/(1*S*,2*S*) Configuration[c]				
2	*n*-C_5H_{12}	36	58	31/69	17	9
3	CH_2Cl_2	40	66	30/70	20	6
3	*n*-C_5H_{12}	36	67	32/68	41	19
(*P*)-5	*n*-C_5H_{12}	36	46	30/70	22	23
(*M*)-6	CH_2Cl_2	40	40	32/68	13	27
		(1*S*,2*R*/1*R*,2*R*) Configuration[c]				
(*M*)-6	*n*-C_5H_{12}	36	35	35/65	<2	<3
(*M*)-7	CH_2Cl_2	25	40	40/60	32	30
(*M*)-7	CH_2Cl_2	40	90	38/62	43	41
(*M*)-7	*n*-C_5H_{12}	25[d]	57	30/70	22	35
(*M*)-7	*n*-C_5H_{12}	36	93	36/64	57	76

[a] Cyclopropanation yield based on diazo ester. [b] ee values calculated in this report were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-beta-CDX column. [c] Configuration assignment was based on the GC retention times.[19] [d] Rhodium compound is poorly soluble in pentane at room temperature.

Similar results were obtained when a mixture of **3** and **1** was treated in a similar way. However, upon addition of free trifluoroacetic acid to the solution of compound **3**, and standing at room temperature over an extended period of time, the bis-cyclometalated product **(*M*)-7** is almost exclusively formed (**(*M*)-7**:**(*P*)-5** = 9:1).

It is remarkable that the photochemical rearrangement of **2·P$_{ax}$** (or **3·P$_{ax}$**) to **2·P$_{eq}$** (or **3·P$_{eq}$**) is in all cases stereospecific, since only one set of signals is observed in the ^{31}P NMR spectrum, no matter what type of carboxylate group was used. Since the main product resulting from the intermediate species was **(*M*)-7**, we presume that the adduct to which these signals are assigned has the structure **2·P$_{eq}$** (or **3·P$_{eq}$**) depicted in Scheme 2. The axial to equatorial rearrangement is apparently reversible, since if a solution of **3·P$_{eq}$** in benzene solution was heated at 60 °C for less than 1 h, the adduct **3·P$_{ax}$** was detected in solution in substantial amounts.

By prolonged photochemical treatment (14 h) of **3·P$_{eq}$** in benzene solution at 40 °C, the cyclometalation was not as selective as it was at room temperature (see above) and the two diastereoisomers were formed in the ratio **(*M*)-7**:**(*P*)-5** = 4:1.

Exploratory Catalytic Studies. (a) Intermolecular Cyclopropanation. The reaction of ethyl diazoacetate with styrene was used as a model reaction to study the catalytic effectiveness, as well as the stereo- and enantioselectivity induced by the catalysts in the intermolecular cyclopropanation.

Mono- and bis-cyclometalated rhodium(II) compounds were used to study the influence of the ligands, the configuration around the active rhodium center, and the solvent polarity on their efficiency and selectivity in the cyclopropanation reaction. All of them, except **(*P*)-4**, gave rise to the cyclopropane diastereoisomers **8** and **9** with moderate to high yields (Table 1). The best results were obtained with diastereoisomer **(*M*)-7**, possessing

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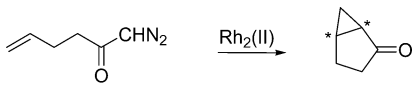
Table 2. Catalyst-Dependent Stereocontrol in the Cyclization of 10 in Refluxing Solvent



10 **11**

cat.	solvent	yield (%)[a]	% ee[b]	config[c]
2	*n*-C_5H_{12}	69	9	(1*R*,5*S*)
3	CH_2Cl_2	97	8	(1*S*,5*R*)
3	*n*-C_5H_{12}	74	14	(1*S*,5*R*)
(*P*)-5	*n*-C_5H_{12}	90	16	(1*S*,5*R*)
(*M*)-6	*n*-C_5H_{12}	75	62	(1*R*,5*S*)
(*M*)-7	*n*-C_5H_{12}	95	70	(1*R*,5*S*)

[a] Cyclopropanation yield based on diazo ketone. [b] ee values calculated in this report were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-beta-CDX column. [c] Configuration assignment was based on the GC retention times.[19]

trifluoroacetates as carboxylate ligands. In all cases the cis:trans ratio was about 30:70. This selectivity has not been observed for other bis-cyclometalated compounds, such as those having metalated triarylphosphines as ligands.[13] Furthermore, **(*M*)-7** was found to be also the most enantioselective catalyst. The effect of both the solvent and the temperature was studied in detail for this particular catalyst; the best selectivity was obtained in refluxing pentane. It should be mentioned that catalyst **(*M*)-7** induced the same configuration for the cyclopropanation products as the corresponding rhodium compounds obtained from triarylphosphines and the same *M* backbone chirality.[13]

The mono-metalated compounds were not thought to be promising candidates for enantioselective catalytic reactions. They have two different rhodium centers but only one, Rh(1), with the chiral periphery of the bridging metalated phospholane. The available results support that the other metal center, Rh(2), is more accessible for coordination. Thus, the reaction of **2** or **3** with phospholane **1** yielded selectively **2·P$_{ax}$** or **3·P$_{ax}$**, with the P atom linked to the Rh(2) metal center. By analogy, it could be expected that the diazo compound attached itself to the same axial position remote from the chiral metalated phospholane and, consequently, would induce low selectivity or no selectivity at all. Interestingly, catalyst **3** led to cyclopropane **8** with a 41% ee in refluxing pentane. The predominant configuration of the cyclopropane products for the mono-metalated compounds is the same as for the bis-cyclometalated compounds with *P* configuration and thus opposite to that of the compounds with *M* configuration.

(b) Intramolecular Cyclopropanation. For the intramolecular processes, 1-diazo-5-hexen-2-one (**10**)[14] was used as model substrate. All the catalysts, except **(*P*)-4**, were active in the cyclopropanation, giving the reaction product **11**, the highest yields being obtained with the trifluoroacetate derivatives (Table 2). As for the intermolecular processes, compounds with the *M* configuration were the most enantioselective catalysts. The ee value obtained with **(*M*)-7** was comparable to that already published for the most selective catalysts for the transformation of the diazo compound **10**. Thus, chiral salicylaldimine copper complexes[15] and bis-cyclometalated Rh(II) complexes[16] having metalated triarylphosphines as ligands led to **11** with up to 77% ee.

Interestingly, the cyclopropane product with the opposite configuration was obtained for each of the two mono-metalated catalysts. This behavior is not readily explicable and deserves further studies.

Conclusion

The present investigations have shown that, by modifying the reaction conditions, the dinuclear rhodium(II) complex $Rh_2(O_2CCH_3)_3$[PC*] (**2**) having one metalated chiral phospholane as a bridging ligand can be prepared from rhodium(II) acetate in nearly quantitative yield. Both **2** and **3**, the latter being obtained from **2** by exchange of the carboxylate groups, can be used to prepare the bis-cyclometalated diastereoisomers $Rh_2(O_2CCH_3)_2$[PC*]$_2$ (**4**−**7**), which possess either *P* or *M* as the dominant configuration, depending on whether the replacement of one bridging ligand is initiated thermally or photochemically. The photochemical reactions take place via the intermediates **2·P$_{eq}$** and **3·P$_{eq}$**, in which the added phospholane **P** occupies an equatorial position at the Rh(II) core. Exploratory catalytic studies revealed that for the model reaction of ethyl diazoacetate with styrene to give the diastereomeric cyclopropanes **8** and **9** the bis-cyclometaled compound **(*M*)-7**, possessing two trifluoroacetates as bridging ligands, is the best catalyst. Not only with **(*M*)-7** but also with other mono- and bis-cyclometalated complexes the ratio of **8** to **9** is about 30:70. This is noteworthy insofar as such selectivity has not been observed for related dinuclear rhodium(II) compounds having metalated triarylphosphines as bridging ligands. The diastereoisomer **(*M*)-7** proved to be also the most efficient enantioselective catalyst, giving rise in refluxing pentane to ee values for **8** and **9** of 57% and 76%, respectively. Moreover, compound **(*M*)-7** also turned out to be the best catalyst for the intramolecular cyclopropanation with 1-diazo-5-hexen-2-one (**10**) to afford the bicyclic ketone **11**. At the present stage, taking the yields and the ee values of the representative product into consideration, the general conclusion is that the catalytic efficiency of **(*M*)-7** is at least as good as that of other transition-metal catalysts used for the transformation of **10** to **11**. The question of whether further modifications of the coordination sphere around the dinuclear Rh(II) core would lead to even better results in the inter- as well as in the intramolecular cyclopropanation reactions is presently being studied in our laboratories.

Experimental Section

Commercially available $Rh_2(O_2CCH_3)_4$·2MeOH was purchased from Pressure Chemical Co. (2*R*,5*R*)-2,5-Dimethyl-1-phenylphospholane (**1**) was prepared according to literature procedures.[17] Analytical data for compounds **2**, **3**, **(*P*)-4**, **(*P*)-5**, **(*M*)-6**, and **(*M*)-7** were coincident with those previously

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reported for their enantiomers.[10] NMR spectra were recorded on a 400 MHz spectrometer, and chemical shifts are reported in ppm. The coupling constants (J) are in hertz (Hz). All the solvents were used in anhydrous form.

Catalytic Intermolecular Reactions. The reactions of ethyl diazoacetate with styrene were performed by slow addition (1.5 mL/h) of the solution of the diazo compound (81 μL, 0.8 mmol) in the solvent (5 mL) to a refluxing solution (20 mL) containing the rhodium(II) complex (1 mol %) and the styrene (230 μL, 2.0 mmol) in the same solvent. After the addition was finished, the reaction mixture was refluxed for an additional 2 h. The resulting solution was filtered at room temperature through a short plug of silica gel to remove the catalyst, and the solvent was evaporated in vacuo. The residue was analyzed by ^{1}H and ^{13}C NMR spectroscopy and by gas chromatography.

Catalytic Intramolecular Reactions. Diazo compound **10** was prepared from the corresponding acid by reaction with ethyl chloroformate, followed by treatment with freshly prepared diazomethane.[18] Catalytic reactions were performed by the addition of a solution of the diazo compound **10** (50 mg) in the solvent (5 mL) to a refluxing solution (10 mL) containing the rhodium(II) complex (molar ratio **10**:Rh(II) = 100:1) in the same solvent; the mixture was heated under reflux for 2 h. The workup procedure of the reaction mixture was similar to that mentioned above for the intermolecular processes.

Synthesis of $Rh_2(O_2CCH_3)_3(PC)\cdot 2CH_3CO_2H$ (2). A solution of $Rh_2(O_2CCH_3)_4\cdot$2MeOH (408 mg, 0.79 mmol) and **1** (129 mg, 0.67 mmol) in a mixture of toluene and acetic acid (65 mL, 10:1) were heated under reflux for 3.5 h. After the mixture was cooled, the solvent was evaporated in vacuo and the resulting blue solid dissolved in CH_2Cl_2 (2 mL). The solution was purified by chromatography on silica gel. Elution with CH_2Cl_2/acetone (1:1) produced a green fraction containing rhodium acetate, followed by a dark blue fraction containing compound **2**. The blue fraction was collected, and the solvent was evaporated. Recrystallization from CH_2Cl_2/pentane gave **2** as a blue solid. Yield: 390 mg (83%).^{1}H NMR ($CDCl_3$): 0.66 (dd, J_{PH} = 13.8, J_{HH} = 6.8, 3H, CH_3 ring), 1.03 (dd, J_{PH} = 15.6, J_{HH} = 6.9, 3H, CH_3 ring), 1.71 (s, 3H, CH_3 cis), 1.78 (s, 3H, CH_3 cis), 2.11 (s, 3H, CH_3 trans), 1.20−2.90 (m, 6H, CH_2, CH ring), 6.60−9.00 (m, 4H, C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): 35.9 (dd, $^1J_{RhP}$ = 152, $^2J_{RhP}$ = 3). Anal. Calcd for **2**·2CH_3COOH: C, 38.06; H, 4.79. Found: C, 38.25; H, 4.70.

Synthesis of $Rh_2(O_2CCF_3)_3(PC)\cdot 2CF_3CO_2H$ (3). A solution of compound **2** (300 mg, 0.43 mmol) in 10 mL of CF_3CO_2H/CH_2Cl_2 (4:1) was stirred for 10 h at room temperature. The solvent was evaporated. The resulting blue solid was dissolved in CH_2Cl_2 (2 mL) and then purified by chromatography on silica gel. Elution with CH_2Cl_2/acetone/CF_3CO_2H (100:100:0.1) produced a blue fraction from which the solvent was evaporated. Recrystallization from CH_2Cl_2/pentane gave **3** as a blue solid. Yield: 333 mg (80%). ^{1}H NMR ($CDCl_3$): 0.64 (dd, J_{PH} = 15.8, J_{HH} = 6.3, 3H, CH_3 ring), 1.26 (dd, J_{PH} = 16.6, J_{HH} = 6.9, 3H, CH_3 ring), 1.6−2.8 (m, 6H, CH_2, CH ring), 6.98−8.53 (m, 4H, C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): 36.4 (d, $^1J_{RhP}$ = 141 Hz). Anal. Calcd for **3**·2CF_3COOH: C, 27.40; H, 1.88. Found: C, 27.12; H, 1.99.

Synthesis of $Rh_2(O_2CCH_3)_2(PC)_2\cdot 2CH_3CO_2H$ ((*P*)-4 and (*M*)-6). A solution of compound **2** (100 mg, 0.14 mmol) and **1** (30.4 mg, 0.16 mmol) in a mixture of toluene and acetic acid (22 mL, 10:1) was heated under reflux for 12 h. After the mixture was cooled, the solvent was evaporated in vacuo and the resulting blue solid was dissolved in CH_2Cl_2 (2 mL). The solution was purified by chromatography on silica gel. Elution with CH_2Cl_2/diethyl ether/CH_3COOH (20:6:0.1) produced two close-running green fractions due to **(*M*)-6** and **(*P*)-4**, followed by a dark blue fraction due to **2**. From these green fractions, after recrystallization from CH_2Cl_2/pentane, blue solids of composition $Rh_2(O_2CCH_3)_2(PC)_2\cdot 2CH_3CO_2H$ (**(*P*)-4**; 65 mg, 55%) and (**(*M*)-6**; 24 mg, 20%) were obtained.

Data for **(*P*)-4** are as follows. ^{1}H NMR ($CDCl_3$): 0.33 (dd, J_{PH} = 14.9, J_{HH} = 7.1, 6H, CH_3 ring), 0.97 (dd, J_{PH} = 13.6, J_{HH} = 7.0, 6H, CH_3 ring), 1.2−2.8 (m, 12H, CH_2, CH ring), 1.98 (s, 3H, CH_3COO), 2.22 (s, 3H, CH_3COO), 6.84 (m, 2H, C_6H_4), 6.94 (m, 1H, C_6H_4), 7.90 (m, 1H, C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): 28.4 (AA′XX′ system). Anal. Calcd for **(*P*)-4**·2CH_3-$COOH$: C, 46.50; H, 5.61. Found: C, 46.89; H, 5.50.

Data for **(*M*)-6** are as follows. ^{1}H NMR ($CDCl_3$): 0.04 (dd, J_{PH} = 14.3, J_{HH} = 7.0, 6H, CH_3 ring), 1.21 (dd, J_{PH} = 15.5, J_{HH} = 7.0, 6H, CH_3 ring), 1.40−3.00 (m, 12H, CH_2, CH ring), 2.15−2.25 (s, 6H, CH_3COO), 6.70−7.52 (m, 8H, C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): 27.9 (AA′XX′ system). Anal. Calcd for **(*M*)-6**·2CH_3COOH: C, 46.50; H, 5.61. Found: C, 46.97; H, 5.20.

Synthesis of $Rh_2(O_2CCF_3)_2(PC)_2\cdot 2CF_3CO_2H$ ((*M*)-7). A solution of **2** (35 mg; 0.047 mmol), **1** (7.3 mg; 0.038 mmol), and trifluoroacetic acid (0.05 mL) in C_6D_6 (0.5 mL) was irradiated for 1 h and then stirred at room temperature for 10 days. The ^{31}P NMR spectrum of the resulting solution indicated the presence of the two bis-cyclometalated compounds **(*P*)-5** and **(*M*)-7** in a 10:1 ratio, some unreacted starting material **2**, and minor decomposition products. The solvent was evaporated in vacuo, and the resulting purple solid was dissolved in CH_2Cl_2 (1 mL) and purified by chromatography on silica gel. Elution with CH_2Cl_2/acetone/CF_3CO_2H (100:100:0.1) produced a blue-green fraction due to **(*M*)-7**. This fraction was collected, and the solvent was evaporated. Recrystallization from CH_2Cl_2/pentane gave **(*M*)-7** (34 mg, 65%) as a blue solid. ^{1}H NMR ($CDCl_3$): 0.04 (dd, J_{PH} = 15.5, J_{HH} = 7.0, 6H, CH_3 ring), 1.26 (dd, J_{PH} = 16.0, J_{HH} = 6.2, 6H, CH_3 ring), 0.80−2.50 (m, 12H, CH_2, CH ring), 6.74 (t, J = 7.7, 2H, C_6H_4), 6.86 (t, J = 7.4, 2H, C_6H_4), 6.98 (t, J = 7.5, 2H, C_6H_4), 7.58 (dd, J = 7.9, J = 3.6, 2H, C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$): 29.1 (AA′XX′ system). Anal. Calcd for **(*M*)-7**·2CF_3COOH: C, 36.87, H, 3.29. Found: C, 36.54, H, 3.51.

Synthesis of $Rh_2(O_2CCF_3)_2(PC)_2\cdot 2CF_3CO_2H$ ((*P*)-5). A solution of compound **(*P*)-4** (20 mg) in CF_3CO_2H/CH_2Cl_2 (10 mL, 4:1) was stirred for 5 h. The solvent was evaporated in vacuo. The resulting blue solid was dissolved in CH_2Cl_2 (1 mL) and then purified by chromatography on silica gel. Elution with CH_2Cl_2/acetone/CF_3CO_2H (100:100:0.1) gave a blue fraction from which the solvent was evaporated. Recrystallization from CH_2Cl_2/pentane gave **(*P*)-5** (14 mg, 70%) as a blue solid. ^{1}H NMR ($CDCl_3$): 0.28 (dd, J_{PH} = 15.4, J_{HH} = 7.2, 6H, CH_3 ring), 0.93 (dd, J_{PH} = 15.5, J_{HH} = 8.5, 6H, CH_3 ring), 1.4−3.00 (m, 12H, CH_2, CH ring), 6.85 (m, 2H, aromatics), 6.95 (m, 4H, aromatics), 7.56 (m, 2H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): 27.4 (AA′XX′ system). Anal. Calcd for **(*P*)-5**·2CF_3COOH: C, 36.87; H, 3.29. Found: C, 36.35; H, 3.63.

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(19) t_R values for compounds **8** and **9** (oven temperature 100 °C for 5 min and then 2 °C/min to 200 °C): *cis*-(1*S*,2*R*), 22.22 min; *cis*-(1*R*,2*S*), 22.56 min; *trans*-(1*S*,2*S*), 24.76 min; *trans*-(1*R*,2*R*), 24.98 min. t_R values for compound **11** (oven temperature 70 °C for 1 min, then 6 °C/min to 200 °C): (1*R*,5*S*), 7.42 min; (1*S*,5*R*), 8.02 min.