ortho-Metalated Dirhodium(II) Catalysts Immobilized on a Polymeric Cross-Linked Support by Copolymerization. Study of their Catalytic Activity in the Asymmetric Cyclopropanation of Styrene with Ethyl Diazoacetate

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Chiral *ortho*-metalated dirhodium(II) compounds containing the phosphine P(*p*-CH_2═$CHC_6H_4)_3$ have been efficiently immobilized by radical copolymerization with styrene and 1,4-divinylbenzene. Their catalytic activity has been tested in the cyclopropanation reaction of styrene with ethyl diazoacetate, achieving yields considerably higher that those obtained with the counterpart homogeneous catalysts, but having lower diastereo- and enantioselectivities. Immobilized catalysts anchored on the polystyrene (PS) by six positions have been shown to be more robust that those generated from compounds that have only three groups for anchoring.

Introduction

The heterogenization of chiral homogeneous catalysts is currently a field of increasing interest that has economical, toxicological, and environmental implications.[1] Entrapment, ionparing, and covalent binding are the three primary methods used to immobilize catalysts, covalent binding of a chiral catalyst on a support being the most widely used to obtain chiral heterogeneous catalysts.[1c] The physical and chemical properties of the organic or inorganic polymer, the method of immobilization, and the point of attachment to the catalyst affect the chiral metal center environment and, therefore, the intrinsic catalyst selectivities.[2] Thus, the major challenge of heterogenization lies in achieving yields and selectivities comparable to those of homogeneous catalysts and avoiding the degradation in enantioselectivity with the recycled catalyst.[1d]

The economy, availability, mechanical robustness, chemical inertness, and facile functionalization of cross-linked polystyrene (PS) led to its preference as a polymeric supports.[1c]

Chiral dirhodium(II) complexes have shown to be versatile catalysts to induce enantiocontrol in carbene transfer reactions.[3] Few examples in the literature report the immobilization of chiral dirhodium(II) catalysts and its use in asymmetric catalysis. Doyle, Bergbreiter, et al.[4a] and Doyle et al.[4b,c] reported the immobilization of different chiral dirhodium(II) carboxamidates on polyethylene-bound soluble, NovaSYn Tentagel(TG) hydroxy, or Merrifield resins functionalized with carboxamidate groups, through an interchange reaction of one carboxamidate group.[4] The immobilized catalysts were tested in the intermolecular cyclopropanation of styrene with menthyl-*d* diazoacetate[4a] or ethyl diazoacetate.[4b,c] The oligomer-bound dirhodium(II) catalyst provided considerable improvement through five runs, although only one catalyst immobilized on NovaSyn Tentagel(TG) hydroxy or Merrifield resins was able to provide virtually identical results for a second run but not a third try.[4b,c] High efficacy was demonstrated for intramolecular cyclopropanation and intramolecular C−H insertion and catalyst recovery. Davies et al.[5] have immobilized tetraprolinate dirhodium(II) catalysts on a pyridine-linked solid support by a simple strategy that combines the coordination of the pyridine group to one rhodium atom in its axial position and an encapsulation effect. The resulting dirhodium(II) catalysts have been shown to be very effective in the asymmetric cyclopropanation of styrene with methyl phenyldiazoacetate, as it recycled five times with virtually no loss in enantioselectivity.[5a,b] The authors have also studied the use of this strategy as an universal method for immobilization of all the standard chiral dirhodium(II) catalysts.[6]

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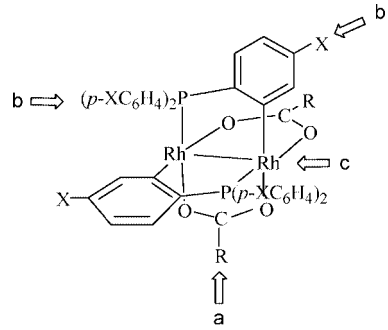
Scheme 1. Attachment Sites to Immobilize $Rh_2(O_2CR)_2(PC)_2$ on Cross-Linked Polystyrene



Chiral $Rh_2(O_2CR)_2(PC)_2$ [PC = *ortho*-metalated phosphine] have been reported in our group as enantioselective catalysts in the asymmetric cyclopropanation of styrene with ethyl diazoacetate.[3i,j,7] Furthermore, diastereoselectivities up to 90% were observed for ethyl *cis*-2-phenylcyclopropanecarboxylate introducing bulky *para*-substituents in the metalated phosphines.[8]

Three possible strategies could be considered when immobilizing these catalysts on a cross-linked polystyrene support, including (a) carboxylate ligands, (b) metalated phosphines, and (c) axial positions (Scheme 1).

In a previous paper[9] we have described the immobilization of $Rh_2(O_2CR)_2(PC)_2$ complexes through both carboxylate ligands by an interchange reaction with carboxyethylpolystyrene (strategy **a**). The catalysts were tested in the asymmetric cyclopropanation of styrene with ethyl diazoacetate. The yields were higher than those achieved with homogeneous 3-phenyl propionate counterparts or the standard trifluoroacetate derivatives, but diastereo- and enantioselectivities were lower in comparison to the standard catalysts. Some of them, however, have been shown to be very robust and yields, including diastereo- and enantioselectivities, remained steady for several cycles.

Here we present the synthesis and characterization of new *ortho*-metalated compounds, $Rh_2(O_2CR)_2(PC)_2$, containing *ortho*-metalated tris-styrylphosphine, $(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2$, and different carboxylate ligands (R = CF_3, CPh_3, $p\text{-}NO_2C_6H_4$, C_6F_5, and (L)-protos). The introduction of styryl groups in the phosphine allowed the immobilization of chiral dirhodium(II) compounds onto PS support by radical copolymerization with styrene and divinylbenzene (DVB).[1b,2] Their catalytic activity was tested with fresh and recycled catalysts for the standard asymmetric cyclopropanation of styrene with ethyl diazoacetate, using *n*-pentane as the solvent (Scheme 2), and the results were compared with the precursor homogeneous catalysts.

Results and Discussion

Dirhodium *ortho*-Metalated Compounds with the Phosphine P(*p*-CH_2=CHC_6H_4)$_3$. $Rh_2(O_2CMe)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]\cdot 2MeCO_2H$ (**4**) and $Rh_2(O_2CMe)_2[(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]_2\cdot 2MeCO_2H$ (**5**) head-to-tail compounds have been synthesized by standard methods.[10] These compounds were isolated as *P* and *M* enantiomers according to the procedure described in the literature.[3j] Chiral dirhodium complexes obtained by carboxylate interchange reactions are represented in Table 1. Using *N*-*p*-tolylsulfonyl-L-proline ((L)-protosH) as the bridging carboxylate ligand, (***M,L***) and (***P,L***) diastereoisomers were obtained.

Scheme 2. Catalyzed Cyclopropanation of Styrene with Ethyl Diazoacetate

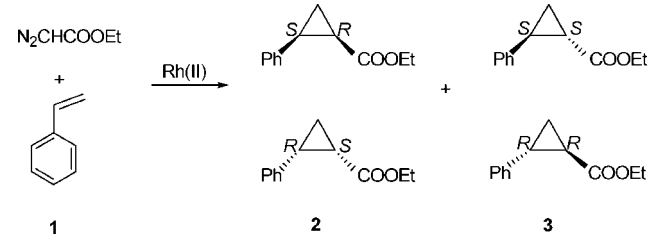
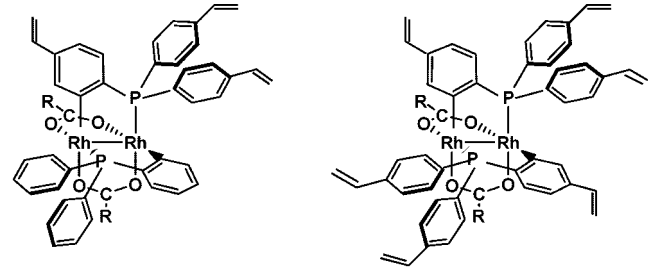


Table 1. Chiral Rh(II) Catalysts with *ortho*-Metalated Aryl Phosphine Ligands[a]



$Rh_2(O_2CR)_2(PC)(PC')$	R	$Rh_2(O_2CR)_2(PC')_2$
6(*M*)	CF_3	**11(*M*)**
7(*M*)	CPh_3	**12(*M*)**
8(*M*)	$p\text{-}NO_2C_6H_4$	**13(*M*)**
9(*M*)	C_6F_5	**14(*M*)**
10(*M,L*)	(L)-protos	**15(*M,L*)**
10(*P,L*)	(L)-protos	**15(*P,L*)**

[a] PC = $(C_6H_4)P(C_6H_5)_2$. PC′ = $(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2$.

The crystal structure for compound **4** (racemic mixture) has been determined. A view of the *P* configuration is shown in Figure 1 together with some representative bond distances and angles. The two rhodium atoms are bridged by four ligands: two acetate groups and two *cisoid ortho*-metalated phosphines, $(C_6H_4)P(C_6H_5)_2$ and $(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2$, in a head-to-tail arrangement. Each axial position is occupied by one oxygen atom from an acetic acid molecule. The value of the Rh−Rh distance, 2.4951(7) Å, falls within the range reported for dirhodium compounds of comparable structures.

Immobilization of 6(*M*)–15(*M*) Catalysts by Radical Copolymerization. Each chiral $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]$, **6(*M*)**−**10(*P,L*)**, and $Rh_2(O_2CR)_2[(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]_2$, **11(*M*)**−**15(*P,L*)**, compound has been quantitatively anchored on PS by radical copolymerization with styrene and divinylbenzene (DVB) using azoisobutyronitrile (AIBN) as a thermal radical initiator[1b,2] (Scheme 3). All the catalysts with *ortho*-metalated tris-styrylphosphines could also act as cross-linkers.

We have performed the immobilization of **6(*M*)** using different ratios of styrene:DVB and toluene:1-dodecanol as

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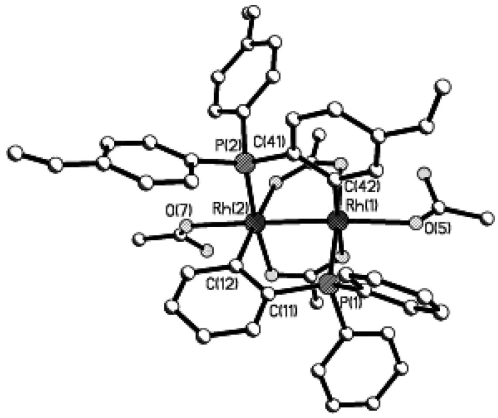
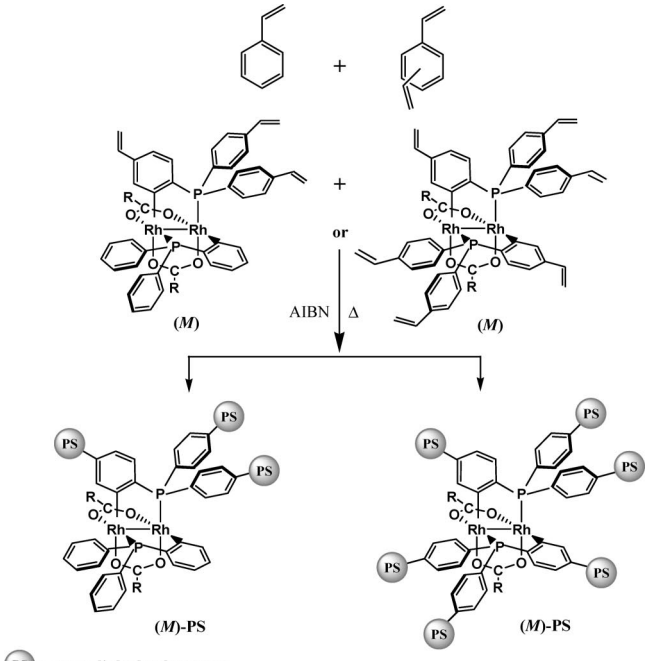


Figure 1. Molecular diagram for compound **4**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Rh1−Rh2 = 2.4951(7), Rh1−P1 = 2.2072(19), Rh1−C42 = 1.994(8), Rh2−P2 = 2.206(2), Rh2−C12 = 1.978(7), Rh2−O7 = 2.291(6). Selected angles (deg) are: O7−Rh2−Rh1 = 168.77(15), Rh2−Rh1−O5 = 166.64 (17), C12−Rh2−Rh1 = 96.9(2), C42−Rh1−Rh2 = 96.7(2).

porogens (Table SI.1) in order to study the influence on catalytic activity.[2] The obtained immobilized catalysts have been tested in the standard catalytic reaction. The best yields and diastereoselectivities for four cycles (Figures SI.1−5) have been reached when 0.029 mmol of **6(*M*)** was copolymerized with 185 mg of styrene and 185 mg of divinylbenzene in a mixture

Scheme 3. Immobilization of $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2]$-$[(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]$, 6(*M*)−10(*P,L*), and $Rh_2(O_2CR)_2[(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]_2$, 11(*M*)−15(*P,L*), by Radical Copolymerization[a]



R		
6(*M*)-PS	CF_3	**11(*M*)-PS**
7(*M*)-PS	CPh_3	**12(*M*)-PS**
8(*M*)-PS	*p*-$NO_2C_6H_4$	**13(*M*)-PS**
9(*M*)-PS	C_6F_5	**14(*M*)-PS**
10(*M,L*)-PS	(L)-protos	**15(*M,L*)-PS**
[a]**10(*P,L*)-PS**	(L)-protos	[a]**15(*P,L*)-PS**

[a] **10(*P,L*)-PS** and **15(*P,L*)-PS** were obtained from *P* enantiomers.

Table 2. Asymmetric Cyclopropanation of Styrene Catalyzed by $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]$ in *n*-Pentane as Solvent[a]

				% ee		configuration	
catalyst	R	yield %[b]	*cis*:*trans*[c]	**2**[d]	**3**[d]	**2**[e]	**3**[e]
6(*M*)	CF_3	34	40:60	88	88	1*S*, 2*R*	1*S*, 2*S*
7(*M*)	CPh_3	57	70:30	78	82	1*R*, 2*S*	1*R*, 2*R*
8(*M*)	*p*-$NO_2C_6H_4$	82	42:58	64	59	1*S*, 2*R*	1*S*, 2*S*
9(*M*)	C_6F_5	45	42:58	40	33	1*S*, 2*R*	1*S*, 2*S*

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), chiral catalyst (8 $\times 10^{-3}$ mmol), in refluxing *n*-pentane. [b] Cyclopropanation yield based on diazoacetate. [c] Determined by GC analysis and ^{1}H NMR. [d] ee values were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-beta-CDX column. [e] Configuration was determined by correlation of the sign of the rotation of polarized light with that of the known enantiomer.[11]

Table 3. Asymmetric Cyclopropanation of Styrene Catalyzed by $Rh_2(O_2CR)_2[(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]_2$ in *n*-Pentane as Solvent[a]

				% ee		configuration	
catalyst	R	yield %[b]	*cis*:*trans*[c]	**2**[d]	**3**[d]	**2**[e]	**3**[e]
11(*M*)	CF_3	34	47:53	88	84	1*S*, 2*R*	1*S*, 2*S*
12(*M*)	CPh_3	52	71:29	79	80	1*R*, 2*S*	1*R*, 2*R*
13(*M*)	*p*-$NO_2C_6H_4$	78	43:57	57	50	1*S*, 2*R*	1*S*, 2*S*
14(*M*)	C_6F_5	35	54:46	48	43	1*S*, 2*R*	1*S*, 2*S*

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), chiral catalyst (8 $\times$ 10^{-3} mmol), in refluxing *n*-pentane. [b] Cyclopropanation yield based on diazoacetate. [c] Determined by GC analysis and ^{1}H NMR. [d] ee values were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-beta-CDX column. [e] Configuration was determined by correlation of the sign of the rotation of polarized light with that of the known enantiomer.[11]

of 100 mg of toluene and 500 mg of 1-dodecanol. Subsequently, all the catalysts were immobilized according this procedure. Table SI.2 displays the rhodium, phosphorus, and carbon atomic percentages of all the immobilized catalysts.

From Homogeneous to Heterogeneous Catalysis. The two groups of homogeneous catalysts, $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]_2$, **6(*M*)−10(*P,L*)**, and $Rh_2(O_2CR)_2[(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]_2$, **11(*M*)−15(*P,L*)**, have been tested in catalysis. The results are displayed in Tables 2, 3, SI.3, and SI.4.

Each catalyst $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]$ and its counterpart $Rh_2(O_2CR)_2[(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]_2$ gave similar yields, reaching the highest values of 82% and 78% with **8(*M*)** and **13(*M*)**, respectively (R = *p*-$NO_2C_6H_4$).

However, some differences in the diastereocontrol between both groups of counterpart catalysts have been noticed. Catalysts with one *ortho*-metalated tris-styrylphosphine, $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]$, induced diastereocontrol for the *trans*-isomer. Only **7(*M*)**, with the bulkiest substituent in the carboxylate ligands, CPh_3, produced an inversion in the diastereocontrol, *cis*:*trans* ratio = 70:30. A related catalyst, $Rh_2(O_2CCPh_3)_2[(C_6H_4)P(C_6H_5)_2]_2$, gave a *cis:trans* ratio = 43:57.[3k] The presence of a second $(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2$ group, bulkier than $(C_6H_4)P(C_6H_5)_2$, in $Rh_2(O_2CR)_2[(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]_2$ induced a gradual change in the diastereocontrol toward the *cis*-isomer with the increasing of the R group size. **11(*M*)** and **13(*M*)** with less bulky substituents, R = CF_3 or *p*-$NO_2C_6H_4$, gave the *trans*-isomer in higher yield than the *cis*-isomer (Table 3). No diastereocontrol was achieved for **15(*P,L*)**.

No important differences in enantioselectivities were observed between either groups of counterpart catalysts. The highest

Table 4. First Cycle for the Asymmetric Cyclopropanation of Styrene Catalyzed by $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}PS\text{-}C_6H_3)P(p\text{-}PS\text{-}C_6H_4)_2]$ in *n*-Pentane as Solvent[a]

				% ee		configuration	
catalyst	R	yield %[b]	*cis*:*trans*[c]	**2**[d]	**3**[d]	**2**[e]	3
6(*M*)-PS	CF_3	93	45:55	58	28	1*S*, 2*R*	1*S*, 2*S*
7(*M*)-PS	CPh_3	88	65:35	57	56	1*R*, 2*S*	1*R*, 2*R*
8(*M*)-PS	$p\text{-}NO_2C_6H_4$	94	50:50	62	41	1*S*, 2*R*	1*S*, 2*S*
9(*M*)-PS	C_6F_5	92	47:53	15	9	1*S*, 2*R*	1*S*, 2*S*

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), amount (mg) of immobilized catalyst that corresponded to 0.01 mmol of chiral dirhodium(II) complex, in refluxing *n*-pentane. [b] Cyclopropanation yield based on diazoacetate. [c] Determined by GC analysis and ^1H NMR. [d] ee values were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-beta-CDX column. [e] Configuration was determined by correlation of the sign of the rotation of polarized light with that of the known enantiomer.[11]

Table 5. First Cycle for the Asymmetric Cyclopropanation of Styrene Catalyzed by $Rh_2(O_2CR)_2[(p\text{-}PS\text{-}C_6H_3)P(p\text{-}PS\text{-}C_6H_4)_2]_2$ in *n*-Pentane as Solvent[a]

				% ee		configuration	
catalyst	R	yield %[b]	*cis*:*trans*[c]	**2**[d]	**3**[d]	**2**[e]	**3**[e]
11(*M*)-PS	CF_3	89	56:44	63	27	1*S*, 2*R*	1*S*, 2*S*
12(*M*)-PS	CPh_3	86	66:34	60	59	1*R*, 2*S*	1*R*, 2*R*
13(*M*)-PS	$p\text{-}NO_2C_6H_4$	93	57:43	63	34	1*S*, 2*R*	1*S*, 2*S*
14(*M*)-PS	C_6F_5	88	54:46	28	3	1*S*, 2*R*	1*S*, 2*S*

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), amount (mg) of immobilized catalyst that corresponded to 0.01 mmol of chiral dirhodium (II) complex, in refluxing *n*-pentane. [b] Cyclopropanation yield based on diazoacetate. [c] Determined by GC analysis and ^1H NMR. [d] ee values were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-beta-CDX column. [e] Configuration was determined by correlation of the sign of the rotation of polarized light with that of the known enantiomer.[11]

enantiocontrol was achieved with catalysts that contain trifluoroacetate ligands, **6(*M*)** and **11(M)**, ee's up to 88% (1*S*, 2*R*) and up to 88% (1*S*, 2*S*). Catalysts **7(*M*)** and **12(*M*)**, with the bulkiest substituent in the carboxylate ligands, R = CPh_3, produced an inversion in the enantiocontrol for the *cis*-isomer (ee's up to 79% (1*R*, 2*S*) and the *trans*-isomer (ee's up to 82% (1*R*, 2*R*)). Catalyst $Rh_2(O_2CCPh_3)_2[(C_6H_4)P(C_6H_5)_2]_2$ also shows this inversion, ee's of 39% (1*R*, 2*S*) and 6% (1*R*, 2*R*).[3k]

The catalytic activity of all the immobilized catalysts was evaluated, and the results for the first cycle are displayed in Tables 4, 5, SI.5, and SI.6. These values were compared with those obtained with the counterpart homogeneous catalysts **6(*M*)–15(*P,L*)**.

Immobilized catalysts have provided exceptionally high yields, up to 94%, but they run lower diastereo- and enantiocontrol. This behavior has already been observed in other *ortho*-metalated dirhodium(II) compounds grafted through carboxylate ligands onto a cross-linked polystyrene resin.[9]

$Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][p\text{-}PS\text{-}(PC)]$ (*p*-PS-(PC) = *ortho*-metalated tris-styrylphosphine immobilized on a polymeric cross-linked support) catalysts with the ability to anchor on the PS support by three styryl groups in the copolymerization showed, in general, diastereocontrol for the *trans*-isomer, as did the counterpart homogeneous catalysts. **7(*M*)-PS** with bulky CPh_3 substituents, also run an inversion in the diastereo- and enantiocontrol as **7(*M*)**. All the $Rh_2(O_2CR)_2[p\text{-}PS\text{-}PC]_2$ catalysts, (**11(*M*)-PS−15(*P,L*)-PS**), with six anchoring sites on the PS, showed diastereocontrol for the *cis*-isomer (Tables 5 and SI.6).

7(*M*)-PS and **12(*M*)-PS**, R = CPh_3, provided the highest diastereocontrol and virtually identical catalytic results to the homogeneous counterparts.

Immobilized catalysts run enantioselectivities lower than the homogeneous counterparts. Only **8(*M*)-PS** and **13(*M*)-PS** (R = $p\text{-}NO_2C_6H_4$) gave similar enantiocontrol.

Steric factors provided by bulky groups in catalysts or by the support generated by copolymerization influenced the diastereo- and enantioselectivities. It can be assumed that these factors are also responsible for the decreasing in the diastereo- and enantiocontrol observed with immobilized catalysts.

After the first catalytic cycle, catalysts **6(*M*)-PS–15(*P,L*)** were easily recovered by filtration, centrifugation, or decantation and further washed with *n*-pentane. No leaching was observed during these procedures. The activity of these recycled catalysts has been tested. The yields, *cis:trans* ratios, and ee values were compared to those obtained with fresh catalysts.

7(*M*)-PS and **12(*M*)-PS** catalysts that run the highest diastereocontrol for the immobilized catalysts, with also high enantiocontrol, have been shown to be very robust. Figures 2 and 3 show yields, percentages, and ee for the *cis* and *trans* cyclopropane isomers obtained with recycled and reused catalysts.

A drop in the yield after the third cycle was observed for **7(*M*)-PS**, while **12(*M*)-PS** remained steady until cycle 10. Catalysts could be recovered and reused maintaining diastereo- and enantioselectivities for six cycles in the case of **7(*M*)-PS** and 10 with **12(*M*)-PS**. Considering that both catalysts gave virtually the same results for the first cycle, the robustness observed for **12(*M*)-PS** must be due to the catalyst's ability to be strongly immobilized and stabilized by the polymerization of the six styryl groups versus three in **7(*M*)-PS**.

Figures SI.3 and 6−14 display the behavior of recycled and reused **6(*M*)-PS**, **8(*M*)-PS−10(*L*)(*P*)-PS**, **11(*M*)-PS**, and **13(*M*)-PS−15(*L*)(*P*)-PS**. It is observed that yields decreased quicker than diastereo- and enantioselectivities with the number of cycles. The enantiocontrol for **6(*M*)-PS**, **8(*M*)-PS**, **11(*M*)-PS**, and **13(*M*)-PS** decreased smoothly with the number of cycles (Figure SI.15).

In all cases, catalysts $Rh_2(O_2CR)_2[(p\text{-}PS\text{-}(PC)]_2$ that could anchor on PS through six positions have been shown to be more robust than $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][p\text{-}PS\text{-}(PC)]$, which can only anchor in three possible points.

Conclusions

Catalysts $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]$ and $Rh_2(O_2CR)_2[(p\text{-}CH_2{=}CHC_6H_3)P(p\text{-}CH_2{=}CHC_6H_4)_2]_2$, which contain *ortho*-metalated tris-styrylphosphines, can be efficiently heterogenized by radical copolymerization with styrene and DVB. The tests of these immobilized catalysts in the asymmetric cyclopropanation of styrene with ethyl diazoacetate gave higher yields compared with those obtained with the counterpart homogeneous catalysts. Nevertheless, the diastereo- and enantioselectivities were, in general, lower. This behavior is summarized in Table 6, which displays the catalytic data obtained with homogeneous and heterogeneous catalysts containing triphenylacetate bridging ligands. Compounds $Rh_2(O_2CR)_2[(p\text{-}PS\text{-}(PC)]_2$, which could anchor through six positions on the PS, have been shown to be more robust that $Rh_2(O_2CR)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}PS\text{-}(PC)]$, which have only three points of anchorage. Yields and diastereo- and enantioselectivities are steady for 10 cycles with $Rh_2(O_2CCPh_3)_2[(p\text{-}PS\text{-}(PC)]_2$.

Experimental Section

General Considerations. Commercially available $Rh_2(O_2CMe)_4 \cdot (MeOH)_2$ was purchased from Pressure Chemical Co. CF_3CO_2H,

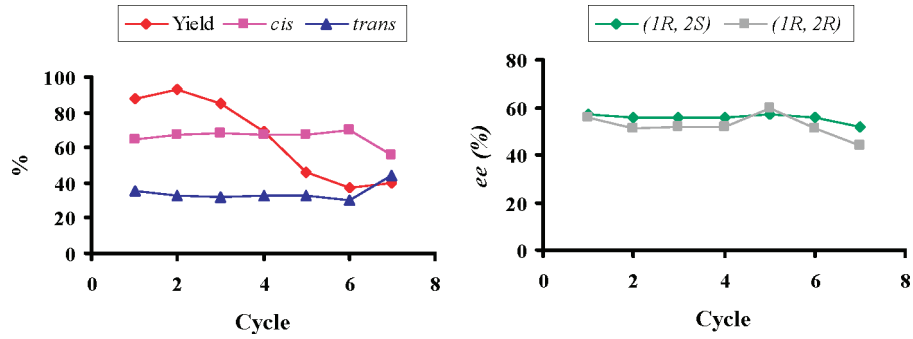


Figure 2. Variation of the yields, percentages, and ee of the *cis* and the *trans* cyclopropane isomers using recycled **7(*M*)-PS**, R = CPh_3, for seven cycles.

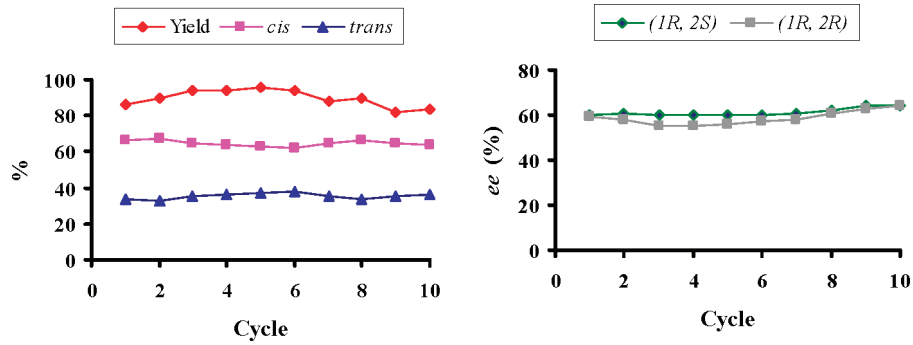


Figure 3. Variation of the yields, percentages, and ee of the *cis* and the *trans* cyclopropane isomers using recycled **12(*M*)-PS**, R = CPh_3, for 10 cycles.

Table 6. Catalytic Data Obtained Using Homogeneous and Immobilized Catalyst with Triphenylacetate Bridging Ligands

catalytic	homogeneous catalysts		immobilized catalysts (1st cycle)	
data	**7(*M*)**	**12(*M*)**	**7(*M*)-PS**	**12(*M*)-PS**
yield %	57	52	88	86
cis:trans ratio	70:30	71:29	65:35	66:34
% ee (1*R*, 2*S*)	88	88	57	60
% ee (1*R*, 2*R*)	88	84	56	59

Ph_3CCO_2H, $C_6F_5CO_2H$, *p*-$NO_2C_6H_4CO_2H$, styrene, divinylbenzene, azoisobutyronitrile (AIBN), and ethyl diazoacetate were used as purchased. All solvents were of analytical grade. *N*-*p*-Tolylsulfonyl-L-proline (ProtosH)[12] and P(*p*-CH_2=$CHC_6H_5)_3$[13] were synthesized according to the method described in the literature. Column chromatography was performed on silica gel (35–70 mesh). Solvent mixtures are volume/volume mixtures, unless otherwise specified. All reactions were carried out in oven-dried glassware under an argon atmosphere, although the isolated solids are air-stable.

Instrumentation. ^1H and $^{13}C\{^1H\}$ NMR (using the residual proton of $CDCl_3$ as reference), $^{19}F\{^1H\}$ NMR (with external CCl_3F as reference), and $^{31}P\{^1H\}$ NMR (with external H_3PO_4 as reference) spectra were recorded on a Bruker Avance 400 MHz spectrometer as solutions in $CDCl_3$ at 25 °C. Chemical shifts are reported in ppm. The coupling constants (*J*) are in hertz (Hz). Coupling constant values for AA′XX′ systems were obtained from simulated spectra. Elemental analyses were provided by Centro de Microanalisis Elemental, Universidad Complutense de Madrid. Rhodium:phosphorus:carbon ratios in the polymer were determined by energy-dispersive analysis of X-ray on a Philips XL-30 EDX scanning electron microscope with quantification performed using virtual standards. The operating voltage was 20 kV.

(12) Cupps, T. S.; Boutin, R. H.; Rapoport, H. P. *J. Org. Chem.* **1985**, *50*, 3972.

(13) Rabinowitz, R.; Marcus, R. *J. Org. Chem.* **1961**, *26*, 4157.

Synthesis of $Rh_2(O_2CMe)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_2$=$CHC_6H_3)P(p\text{-}CH_2$=$CHC_6H_4)_2]\cdot 2MeCO_2H$ (4). This compound was obtained by the standard method described in the literature.[10] Yield: 44%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.23 (m, 3H), 1.24 (m, 3H), 2.17 (s, 6H), 4.90 (d, J = 12 Hz, 1H), 5.18 (m, 3H), 5.64 (m, 2H), 6.10 (m, 1H), 6.47 (m, 1H), 6.56–6.81 (m, 11H), 6.91 (m, 5H), 7.12 (m, 1H), 7.29 (m, 5H), 7.53 (m, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 22.6 (s), 22.7,(s) 22.8 (d, J = 2 Hz), 113.0–145.0 (aromatic and olefinic), 165.3 (m, metalated C), 179.4 (s), 181.6 (d, J = 2 Hz), 181.6 (d, J = 2 Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 18.2 (dd, $^1J_{P\text{-}Rh}$ = 163 Hz, $^2J_{P\text{-}Rh}$ = 8 Hz), 19.2 (dd, $^1J_{P\text{-}Rh}$ = 162 Hz, $^2J_{P\text{-}Rh}$ = 8 Hz). Anal. Calcd (%) for $C_{50}H_{48}O_8P_2Rh_2$: C, 57.47; H, 4.31. Found: C, 57.08; H, 4.69.

X-Ray Crystal Structure Data for $Rh_2(O_2CMe)_2[(C_6H_4)P(C_6H_5)_2][(p\text{-}CH_2$=$CHC_6H_3)P(p\text{-}CH_2$=$CHC_6H_4)_2]\cdot 2MeCO_2H$ (4). $C_{50}H_{48}O_8P_2Rh_2$, triclinic, space group $P\bar{1}$, a = 10.1310(2), b = 12.6180(2), c = 19.3690(4) Å, α = 97.6920(8)°, β = 104.5790(10)°, γ = 90.7050(9)° V = 2371.98(8) Å^3, Z = 2, ρ_{calcd}=1.463 g cm^{-3}, crystal dimensions: 0.25 × 0.23 × 0.20 mm^3; Kappa K2K diffractometer; Cu Kα radiation, 293(2) K; 18 584 reflections, 6698 independent (μ = 6.688 mm^{-1}); refinement (on F^2) with SHELXTL (version 6.1), 565 parameters, 0 restraints, R_1 = 0.0638 ($I > 2\sigma$) and wR_2 (all data) = 0.1879, GOF = 1.077, max/min residual electron density: 1.194/−1.380 e Å^{-3}.

Synthesis of $Rh_2(O_2CMe)_2[(p\text{-}CH_2$=$CHC_6H_3)P(p\text{-}CH_2$=$CHC_6H_4)_2]_2\cdot 2\,MeCO_2H$ (5). This compound was obtained by the standard method described in the literature.[10]

Yield: 44%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.24 (s, 6H), 2.16 (s, 6H), 4.89 (d, J = 11 Hz 2H), 5.15 (m, 6H), 5.59 (m, 4H), 6.06 (m, 2H), 6.49–6.79 (m, 14H), 6.95 (m, 4H), 7.32 (m, 4H), 7.57 (m, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 21.8 (bs), 22.7 (d, J = 2 Hz), 114.0–145.0 (aromatic and olefinic), 165.2 (m, metalated C), 178.5 (bs), 181.7 (d, J = 3 Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 18.8 (AA′XX′ system, $^1J_{P\text{-}Rh}$

= 146 Hz, $^2J_{P\text{-}Rh}$ = −2 Hz, $^1J_{Rh\text{-}Rh}$ = 4 Hz). Anal. Calcd (%) for $C_{56}H_{54}O_8P_2Rh_2$: C, 59.89; H, 4.81. Found: C, 59.15; H, 4.77.

Synthesis of Enantiomerically Pure (*M*)-Rh$_2$(O$_2$CR)$_2$[(C$_6$H$_4$)P(C$_6$H$_5$)$_2$][(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$] and (*M*)-Rh$_2$(O$_2$CR)$_2$[(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$]$_2$ (R = CF$_3$, CPh$_3$, C$_6$F$_5$, *p*-NO$_2$C$_6$H$_4$) Compounds. The enantiomers **6**(*M*)–**9**(*M*) and **11**(*M*)–**14**(*M*) were obtained following the standard method described in the literature.[3j]

(*M*)-Rh$_2$(O$_2$CCF$_3$)$_2$[(C$_6$H$_4$)P(C$_6$H$_5$)$_2$][(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$] (6(*M*)). Yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.05 (d, J = 11 Hz, 1H), 5.32 (m, 3H), 5.75 (d, J = 12 Hz, 1H), 5.81 (d, J = 12 Hz, 1H), 6.18 (dd, J = 17 Hz, J = 11 Hz, 1H), 6.55–6.95 (m, 14H), 7.00–7.12 (m, 4H), 7.39 (m, 5H), 7.57 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 113.0–145.4 (aromatic, olefinic and CF_3), 161.1 (m, metalated C), 166.5 (q $^3J_{C\text{-}F}$ = 31 Hz). ^{19}F{^{1}H} NMR (376.2 MHz, $CDCl_3$, 298 K): δ −75.5 (s), −75.7 (s) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 17.1 (bd, $^1J_{P\text{-}Rh}$ = 171 Hz), 16.1 (bd, $^1J_{P\text{-}Rh}$ = 169 Hz) ppm. Anal. Calcd (%) for $C_{46}H_{34}F_6O_4P_2Rh_2$: C, 53.49; H, 3.30. Found: C, 52.78; H, 3.69.

(*M*)-Rh$_2$(O$_2$CCPh$_3$)$_2$[(C$_6$H$_4$)P(C$_6$H$_5$)$_2$][(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$] (7(*M*)). Yield: 46%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.20 (m, 2H), 5.27 (m, 2H), 5.62 (m, 2H), 5.87 (d, J = 17 Hz, 1H), 6.35–6.95 (m, 45H), 7.08 (m, 10H), 7.86 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 114.2−145.2 (aromatic, olefinic and CF_3), 164.1 (m, metalated C), 182.8 ppm (s). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ14.7 (d, $^1J_{P\text{-}Rh}$ = 163 Hz), 15.6 (d, $^1J_{P\text{-}Rh}$ = 161 Hz) ppm. Anal. Calcd (%) for $C_{82}H_{64}O_4P_2Rh_2$: C, 71.30; H 4.64. Found: C, 70.90; H 4.79.

(*M*)-Rh$_2$(O$_2$C(*p*-NO$_2$C$_6$H$_4$))$_2$[(C$_6$H$_4$)P(C$_6$H$_5$)$_2$][(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$] (8(*M*)). Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.05 (d, J = 12 Hz 2H), 5.35 (m, 3 H), 5.78 (d, J = 18 Hz 1H), 6.26 (m, 2H), 6.50–6.80 (m, 3H), 6.85 (m, 4H), 6.95–7.20 (m, 10H), 7.49 (m, 5H), 7.58 (m, 2H), 7.92 (m, 4H), 8.40 (m, 6H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 114.0−151.0 (aromatic and olefinic), 163.9 (m, metalated C), 171.9 (s), 174.3 (s) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K) : δ 19.4 (dd, $^1J_{P\text{-}Rh}$ = 163 Hz, $^2J_{P\text{-}Rh}$ = 6 Hz), 18.1 (dd, $^1J_{P\text{-}Rh}$ = 163 Hz, $^2J_{P\text{-}Rh}$ = 7 Hz) ppm. Anal. Calcd (%) for $C_{56}H_{42}N_2O_8P_2Rh_2$: C 59.05, H 3.69. Found: C, 58.68; H, 3.67.

(*M*)-Rh$_2$(O$_2$CC$_6$F$_5$)$_2$[(C$_6$H$_4$)P(C$_6$H$_5$)$_2$][(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$] (9(*M*)). Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.07 (d, J = 11 Hz, 1H), 5.23 (d, J = 11 Hz, 1H), 5.30 (d, J = 11 Hz, 1H), 5.41 (d, J = 18 Hz, 1H), 5.66 (d, J = 18 Hz, 1H), 5.60 (d, J = 18 Hz, 1H), 6.24 (dd, J = 18 Hz, J = 11 Hz, 1H), 6.57–6.85 (m, 13H), 7.01 (m, 2H), 7.07 (m, 2H), 7.22 (m, 6H), 7.50 (m, 2H), 7.57 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 113.0−145.0 (aromatic and olefinic), 161.4 (m, metalated C), 166.9 (b), 167.0 (b) ppm. ^{19}F{^{1}H} NMR (372.6 MHz, $CDCl_3$, 298 K): δ −173.3 (bt, J = 19 Hz, F_{meta}-C), −173.0 (bt, J = 19 Hz, F_{meta}-C), −163.7 (bt, J = 19 Hz, F_{para}-C), −163.2 (bt, J = 19 Hz, F_{para}-C), −149.8 (d, J = 20 Hz, F_{ortho}-C), −149.4 (d, J = 20 Hz, F_{ortho}-C) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 16.8 ($^1J_{P\text{-}Rh}$ = 164 Hz), 16.2 ($^1J_{P\text{-}Rh}$ = 163 Hz) ppm. Anal. Calcd (%) for $C_{56}H_{34}F_{10}O_4P_2Rh_2$: C, 54.72; H, 2.77. Found: C, 54.12; H, 2.72.

(*M*)-Rh$_2$(O$_2$CCF$_3$)$_2$[(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$]$_2$ (11(*M*)). Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.04 (d, J = 11 Hz, 2H), 5.30 (m, 6 H), 5.71 (d, J = 17 Hz, 2H), 5.80 (d, J = 17 Hz, 2H), 6.13 (dd, J = 18 Hz, J = 11 Hz, 2H), 6.48 (bs, 2H), 6.55–6.89 (m, 12H), 7.08 (m, 4H), 7.41 (m, 4H), 7.57 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 113.0–145.0 (aromatic, olefinic and CF_3), 160.2 (m, metalated C), 166.3 (q, J = 38 Hz) ppm . ^{19}F{^{1}H} NMR (376.2 MHz, $CDCl_3$, 298 K): δ −75.8 (s) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 14.8 (bd, J = 164 Hz) ppm. Anal. Calcd (%) for $C_{52}H_{40}F_6O_4P_2Rh_2$: C, 56.22; H 3.60. Found: C, 56.90; H, 3.72.

(*M*)-Rh$_2$(O$_2$CCPh$_3$)$_2$[(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$]$_2$ (12(*M*)). Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.18 (t, J = 11 Hz, 4H), 5.33 (d, J = 11 Hz, 2H), 5.64 (m, 4H), 5.88 (d, J = 18 Hz, 2H), 6.37 (m, 2H), 6.50–6.65 (m, 9H), 6.75 (m, 13H), 6.84 (m, 13H), 6.92 (m, 11H), 7.01 (d, J = 9 Hz, 2H), 7.09 (m, 6H), 7.86 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 114.8–145.1 (aromatic and olefinic), 162.2 (m, metalated C), 184.1 (s) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 15.5 (bd, J = 148 Hz) ppm. Anal. Calcd (%) for $C_{88}H_{70}O_4P_2Rh_2$: C, 72.43; H 4.80. Found: C, 71.90; H, 4.87.

(*M*)-Rh$_2$(O$_2$C(*p*-NO$_2$C$_6$H$_4$))$_2$[(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$]$_2$ (13(*M*)). Yield: 66%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.06 (m, 4H), 5.30 (m, 4H), 5.40 (d, J = 17 Hz, 2H), 5.74 (d, J = 18 Hz, 2H), 6.24 (m, 4H), 6.66 (m, 4H), 6.92 (m, 10H), 7.11 (d, J = 9 Hz, 4H), 7.50 (m, 6H), 7.89 (d, J = 9 Hz, 4H), 8.36 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 113.0−152.0 (aromatic and olefinic), 164.0 (m, metalated), 174.6 (s) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 18.7 (AA′XX′ system, $^1J_{P\text{-}Rh}$ = 170 Hz, $^2J_{P\text{-}Rh}$ = −4 Hz, $^1J_{Rh\text{-}Rh}$ = 8 Hz) ppm. Anal. Calcd (%) for $C_{62}H_{48}N_2O_8P_2Rh_2$: C, 61.18; H, 3.95. Found: C, 61.90; H, 4.10.

(*M*)-Rh$_2$(O$_2$CC$_6$F$_5$)$_2$[(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$]$_2$ (14(*M*)). Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 5.01 (d, J = 11 Hz, 2H), 5.28 (m, 6H), 5.69 (m, 4H), 6.17 (dd, J = 18 Hz, J = 11 Hz, 2H), 6.47–6.72 (m, 6H), 6.91 (m, 6H), 7.07 (m, 6H), 7.21 (m, 4H), 7.66 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 107.2–147.9 (aromatic and olefinic), 162.5 (m, metalated), 164.4 ppm (s). ^{19}F{^{1}H} NMR (372.6 MHz, $CDCl_3$, 298 K): δ −160.5 (m, F_{ortho}-C), −147.3 (m, F_{para}-C), −137.1 ppm (dt, J = 20 Hz, J = 6 Hz, F_{meta}-C). ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 17.9 ((AA′XX′ system, $^1J_{P\text{-}Rh}$ = 173 Hz, $^2J_{P\text{-}Rh}$ = −5 Hz, $^1J_{Rh\text{-}Rh}$ = 11 Hz) ppm. Anal. Calcd (%) for $C_{62}H_{40}F_{10}O_4P_2Rh_2$: C, 56.97; H, 3.06. Found: C, 56.23; H, 2.99.

Synthesis of (*M* or *P*)-Rh$_2$((L)-protos)$_2$[(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$]$_2$ and (*M* or *P*)-Rh$_2$((L)-protos)$_2$[(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$]$_2$ Diastereoisomers. The diastereoisomers **10**(*M,L*), **10**(*P,L*), **15**(*M,L*), and **15**(*P,L*) were obtained by standard methods described in the literature.[3j]

(*M*)-Rh$_2$((L)-protos)$_2$[(C$_6$H$_4$)P(C$_6$H$_5$)$_2$][(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$] (10(*M,L*)). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.97 (m, 6H), 2.31 (s, 6H), 2.46 (m, 2H), 2.84 (m, 2H), 3.17 (m, 2H), 4.20 (m, 2H), 5.02 (d, J = 11 Hz, 1H), 5.23 (m, 2H), 5.41 (d, J = 18 Hz, 1H), 5.73 (m, 2H), 6.19 (m, 1H), 6.61 (m, 3H), 6.76 (m, 12H), 6.99 (m, 6H), 7.13 (m, 4H), 7.33 (m, 4H), 7.75 (m, 6H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 21.4 (s), 24.4 (s), 29.5 (b), 49.0 (s), 63.2 (s), 113.0–145.0 (m, aromatic and olefinic), 165.3 (m, metalated C), 181.6 (s) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ 18.7 (bd, $^1J_{P\text{-}Rh}$ = 166 Hz), 19.6 (bd, $^1J_{P\text{-}Rh}$ = 162 Hz) ppm. Anal. Calcd (%) for $C_{66}H_{62}N_2O_8P_2S_2Rh_2$: C, 59.02; H, 4.62. Found: C, 58.83; H, 5.09.

(*P*)-Rh$_2$((L)-protos)$_2$[(C$_6$H$_4$)P(C$_6$H$_5$)$_2$][(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$] (10(*P,L*)). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.69 (m, 2H), 1.95 (m, 6H), 2.29 (bs, 6H), 2.90 (m, 2H), 3.57 (m, 2H), 4.25 (m, 2H), 4.93 (d, J = 11 Hz, 1H), 5.17 (dd, J = 11 Hz, J = 2 Hz 2H), 5.38 (d, J = 18 Hz, 1H), 5.67 (d, J = 18 Hz, 2H), 6.28 (m, 1H), 6.65 (m, 6H), 6.80 (m, 3H), 7.01 (m, 6H), 7.12 (m, 10H), 7.33 (m, 4H), 7.61 (m, 2H), 7.79 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 20.4 (s), 20.6 (s), 23.5 (s), 23.7 (s), 28.7 (s), 29.7 (s), 47.8 (s), 47.9 (s), 59.9 (s), 61.6 (s), 113.0–145.0 (m, aromatic and olefinic) 165.3 (m, metalated C), 180.4 (s), 180.6 (s) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$, 298 K): δ17.3 (dd, $^1J_{P\text{-}Rh}$ = 165 Hz, $^2J_{P\text{-}Rh}$ = 8 Hz), 17.9 (dd, $^1J_{P\text{-}Rh}$ = 171 Hz, $^2J_{P\text{-}Rh}$ = 7 Hz) ppm. Anal. Calcd (%) for $C_{66}H_{62}N_2O_8P_2S_2Rh_2$: C, 59.02; H, 4.62. Found: C, 58.70; H, 4.39.

(*M*)-Rh$_2$((L)-protos)$_2$[(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$]$_2$ (15(*M,L*)). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 2.31 (s, 6H), 2.81 (m, 2H), 3.12 (m, 10H), 4.16 (m, 2H), 4.98 (d, J = 12 Hz, 2H),

5.22 (dd, $J = 11$ Hz, $J = 2$ Hz, 4H), 5.36 (d, $J = 18$ Hz, 2H), 5.69 (m, 4H), 6.14 (m, 2H), 6.62 (m, 12H), 6.84 (m, 2H), 6.99 (m, 4H), 7.13 (m, 4H), 7.36 (m, 4H), 7.70 (m, 8H) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 21.3 (s), 24.3 (s), 29.4 (s), 49.0 (s), 63.2 (s), 113.0–145.0 (m, aromatic and olefinic), 165.3 (m, metalated), 181.5 (s) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ19.1 (bd, $^1J_{P\text{-}Rh} = 162$ Hz) ppm. Anal. Calcd (%) for $C_{72}H_{68}N_2O_8P_2S_2Rh_2$: C, 60.85; H, 4.79. Found: C, 58.75; H, 4.62.

(*P*)-Rh$_2$((L)-protos)$_2$[(*p*-CH$_2$=CHC$_6$H$_3$)P(*p*-CH$_2$=CHC$_6$H$_4$)$_2$]$_2$ (15(*P,L*)). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ1.77 (m, 2H), 2.04 (m, 4H), 2.28 (s, 6H), 3.30 (m, 2H), 3.60 (m, 2H), 3.98 (m, 2H), 4.33 (m, 2H), 4.96 (d, $J = 11$ Hz, 2H), 5.23 (m, 4H), 5.40 (d, $J = 17$ Hz, 2H), 5.70 (m, 4H), 6.20 (m, 2H), 6.56 (m, 2H), 6.69 (m, 4H), 6.82 (m, 2H), 6.99 (m, 4H), 7.07 (m, 10H), 7.28 (d, $J = 8$ Hz, 4H), 7.36 (m, 4H), 7.81 (d, $J = 8$ Hz, 4H) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 21.4 (s), 24.4 (s), 29.5 (s), 49.0 (s), 63.2 (s), 113.0–145.0 (m, aromatic and olefinic), 165.3 (m, metalated C), 181.6(s) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ18.5 (bd, $^1J_{P\text{-}Rh} = 164$ Hz) ppm. Anal. Calcd (%) for $C_{72}H_{68}N_2O_8P_2S_2Rh_2$: C, 60.85; H, 4.79. Found: C, 58.86; H, 4.99.

Immobilization of Catalysts. A 0.029 mmol amount of catalysts **6(*M*)–15(*P,L*)** was placed in a glass mold and solved in a mixture of 100 mg of toluene and 500 mg of 1-dodecanol (1:5 w/w). After the addition of 185 mg of styrene, 185 mg of divinylbenzene, and the initiator azoisobutyronitrile (AIBN) (1% total weight), the mixture was purged with argon. The closed mold was heated at 75 °C for 25 to 35 min, until the formation of the polymer was observed. The glass mold was broken, and the polymer was extracted with CH_2Cl_2 in a Soxhlet apparatus and dried.

Catalysts **6(*M*)-PS.a**, **b**, **d**, and **e** were obtained by immobilization of catalyst **6(*M*)** following the above procedure but using the amounts of styrene, divinylbencene, toluene, and 1-dodecanol displayed in Table SI.1.

Catalytic Intermolecular Cyclopropanation. The reactions of ethyl diazoacetate with styrene were performed by slow addition (1.5 mL/h) of the solution of the diazo compound (83 μL, 0.8 mmol) in *n*-pentane (5 mL) to a refluxing solution of *n*-pentane (15 mL) containing the amount of homogeneous or immobilized catalysts that corresponded to 1 mol % of dirhodium(II) complexes, and styrene (230 μL 2.0 mmol) in the same solvent. After complete addition, the reaction mixture was stirred at reflux for 2 h with homogeneous catalysts or 12 h in the case of immobilized catalysts and cooled to room temperature. The resulting solution was filtered through a short plug of silica to remove the homogeneous catalyst or separated from the immobilized catalyst by decantation. In both cases, the solvent was evaporated under reduced pressure.

The immobilized catalysts have been recovered by decantation, washed with *n*-pentane, and reused following the above procedure.

In both conditions, the yield of the reaction was calculated by ^{1}H spectroscopy and the enantiopurities of the products were calculated by chiral gas chromatography (oven temperature 100 °C for 5 min, then 2 °C/min to 200 °C). t_R: *cis*-1*S*,2*R*, 22.22 min; *cis*-1*R*,2*S*, 22.56 min; *trans*-1*R*,2*R*, 24.76 min; *trans*-1*S*,2*S*, 24.98 min.

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Supporting Information Available: Composition of the mixture for the radical copolymerization of compounds, atomic percentages of rhodium, phosphorus and carbon of all the immobilized catalysts and variation of the yields of cyclopropanes, percentages and ee of the *cis*- and the *trans*-isomers using recovered and reused catalysts (Figures SI.1−15 and Tables SI.1−6) are included. Crystallographic data of compound **4** in CIF format. This material is available free of charge via the Internet at http:/pubs.acs.org.

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