Immobilized Chiral *ortho*-Metalated Dirhodium(II) Compounds as Catalysts in the Asymmetric Cyclopropanation of Styrene with Ethyl Diazoacetate

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Immobilization of *ortho*-metalated dirhodium(II) compounds has been achieved by a carboxylate interchange reaction between (*M*)-Rh_2(L-protos)$_2$[(*p*-XC_6H_3)P(*p*-XC_6H_4)$_2$]$_2$ diastereoisomers and carboxyethylpolystyrene polymer (**PS**-$C_6H_4(CH_2)_2CO_2H$). The immobilized chiral catalysts have been tested in the standard reaction of asymmetric cyclopropanation of styrene with ethyl diazoacetate, giving higher yields than homogeneous chiral trifluoroacetate derivatives, but their diastereo- and enantioselectivities were lower. Some of the immobilized catalysts have proved to be very robust. The catalytic behavior of (*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2$[(*p*-$XC_6H_3$)P(*p*-$XC_6H_5$)$_2$]$_2$ compounds has been studied as a model for the immobilized catalysts.

Introduction

The immobilization of transition-metal complexes on solid supports and their use as catalysts in synthesis have environmentally benign and economic implications.[1] Nowadays, their use in asymmetric catalysis implies a challenge for the synthetic chemist.[2] Hetereogenization of homogeneous catalysts allows the combination of the advantages of homogeneous and heterogeneous systems. However, the immobilized catalysts yield low selectivities, lower than those obtained in homogeneous conditions. Furthermore, it is necessary to consider other problems, such as the search for methodologies for immobilization and the quantitative recovery of the catalysts and their physical degradation.[1d] In theory, it is assumed that similar results to those obtained with homogeneous catalysts can be reached if the immobilized ones conserve similar metal center environments. 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 selectivity.[3]

The design of the chiral catalysts to induce enantiocontrol in carbene transfer reactions is a subject of interest,[4] copper and rhodium chiral catalysts[4d,5,6] being the most versatile among them.

Enantioselective catalysis with chiral dirhodium(II) compounds of the general formula $Rh_2(O_2CR)_2(PC)_2$ [PC = *ortho*-metalated phosphine] has been reported in our group.[6i−j,7] Enantioselectivities up to 91% and up to 87%, for ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylate, were reached in the asymmetric cyclopropanation of styrene with ethyl diazoacetate.[7] Moreover, introducing bulky *para*-substituents in the metalated phosphines resulted in diastereoselectivities up to 90% for ethyl *cis*-2-phenylcyclopropanecarboxylate.[8]

There are few examples in the literature that report the immobilization of chiral dirhodium(II) catalyst and their use in asymmetric cyclopropanation reactions. Doyle et al.[9a−c] reported the immobilization of different chiral dirhodium(II) carboxamidates on NovaSyn Tentagel (TG) hydroxy resin or Merrifield resins functionalized with carboxamidate groups, via an interchange reaction. These immobilized catalysts have been tested in asymmetric intra- and intermolecular cyclopropanation and

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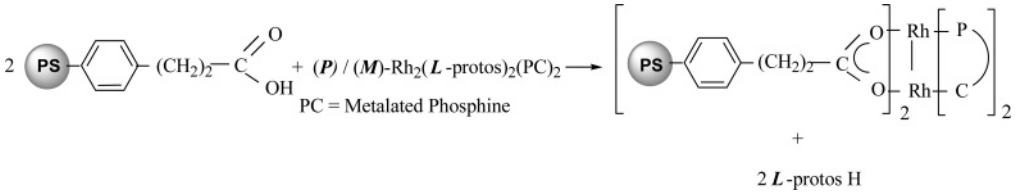
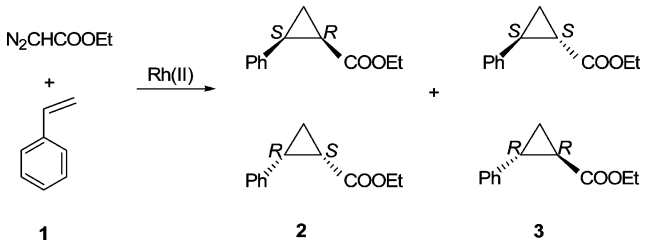
Scheme 1. General Procedure to Immobilize Chiral *ortho*-Metalated Dirhodium(II) Compounds



Scheme 2. Catalyzed Cyclopropanation of Styrene with Ethyl Diazoacetate



intramolecular C−H insertion reactions.[9] They were shown to have more diastereo- and enantiocontrol than the homogeneous counterparts in the standard intermolecular cyclopropanation of styrene with ethyl diazoacetate. After catalyst recovery and reuse, only one was able to provide virtually identical results for a second run but not for a third.[9a] Previously, Doyle, Bergbreiter, et al.[9d] used oligomer-bound dirhodium(II) 2-pyrrolidone-5(*S*)-carboxylate catalyst in the intermolecular cyclopropanation of styrene with menthyl-*d* diazoacetate. The catalyst provided considerable improvement through five runs with a major decrease of the diastereoselection after run 2. High enantioselection was observed in intramolecular cyclopropanation and intramolecular C−H insertion reactions. Davies et al.[10] have immobilized tetraprolinate dirhodium(II) catalysts on a pyridine-linked solid support by a simple strategy that combines the coordination of pyridine to one rhodium atom in its axial position and an encapsulation effect. The resulting dirhodium(II) catalysts are very effective for the cyclopropanation of styrene with methyl phenyldiazoacetate. Under optimized conditions, they can be recycled five times with virtually no loss in enantioselectivity. The authors have also studied the use of this strategy as a universal method for immobilization of all the standard chiral dirhodium(II) catalysts.[11]

In this paper we present the first example of immobilization of chiral $Rh_2(O_2CR)_2(PC)_2$ compounds on cross-linked polystyrene resin (**PS**) by an exchange reaction of carboxylate ligands between the complexes and carboxyethylpolystyrene (**PS**-$C_6H_4(CH_2)_2CO_2H$) (Scheme 1). The catalytic activity with fresh and recycled catalysts has been tested for the standard asymmetric cyclopropanation of styrene with ethyl diazoacetate (Scheme 2).

Results and Discussion

Immobilization of Chiral *ortho*-Metalated Dirhodium(II) Compounds. $Rh_2(O_2CR)_2(PC)_2$ compounds that contain two *ortho*-metalated aryl phosphines and two carboxylates as bridging ligands show fast and quantitative interchange of both carboxylate ligands by other bridging ligands.[12] The use of carboxyethylpolystyrene permits the grafting of chiral *ortho*-metalated dirhodium(II) compounds on a cross-linked polystyrene resin (**PS**). This reaction was performed by stirring the carboxyethylpolystyrene polymer and (*M*)-Rh_2(L-protos)$_2$[(*p*-XC_6H_3)P(*p*-XC_6H_4)$_2$]$_2$ (X = H (**4**), F (**5**), Cl (**6**), Br (**7**), CF_3 (**8**), Me (**9**), ^{t}Bu (**10**), $SiMe_3$ (**11**)) diastereoisomers in CH_2Cl_2 at room temperature for 24 h or by refluxing in toluene for 1 h (Scheme 3). The resulting purple-red solids were filtered and washed with CH_2Cl_2. The filtered liquid was colorless in all cases, and no leaching of the immobilized complexes, (*M*)-Rh_2-($O_2C(CH_2)_2C_6H_4$-**PS**)$_2$[(*p*-XC_6H_3)P(*p*-XC_6H_4)$_2$]$_2$ (X = H (**12**), F (**13**), Cl (**14**), Br (**15**), CF_3 (**16**), Me (**17**), ^{t}Bu (**18**), $SiMe_3$ (**19**)), was observed during the whole process. No leaching was also observed when more polar solvents, acetone or methanol, were used in the washing procedure.

The quantitative analysis of the L-protosH obtained by substitution of both L-protos carboxylates in the homogeneous catalysts (**4**−**11**) (Scheme 3) confirmed that the reaction was essentially complete when all the immobilized catalysts (**12**−**19**) were grafted by the two *cis* positions (see Experimental Section).

Two aspects of the immobilization have been evaluated: the reaction conditions and the catalysts loading on the cross-linked polymer; both have a significant influence on the catalytic reaction selectivity. Catalyst **19** was prepared in CH_2Cl_2 at room temperature for 24 h or in refluxing toluene for 1 h. The catalytic results using fresh and recycled immobilized catalyst **19** are displayed in Table 1. Different loadings of homogeneous catalyst **6**, 0.005 (a), 0.01 (b), and 0.02 (c) mmol on 100 mg of carboxyethylpolystyrene giving **14**, were tested in catalysis. The catalytic results are displayed in Table 2.

The best results in diastereo- and enantioselectivities were achieved by the catalyst prepared at room temperature. But, even though the best yields were achieved with the lowest loading, the best diastereo- and enantioselectivities for the nine cycles were reached with 0.01 mmol of catalyst per 100 mg of polymer. Higher loadings (c) did not improve the results.

All the catalyst were grafted by stirring 0.01 mmol of the precursors **4**−**11** and 100 mg of carboxypolystyrene in CH_2Cl_2 at room temperature for 24 h. Table 3 displays the phosphorus and carbon analysis of the immobilized catalysts.

Racemic mixtures of (*M*) and (*P*)-$Rh_2(O_2CMe)_2$[(*p*-XC_6H_3)P(*p*-XC_6H_4)$_2$]$_2$·2$MeCO_2H$ (X = H, F, Cl, Br, CF_3, Me, ^{t}Bu, $SiMe_3$) have been obtained by standard methods.[14] The reaction with *N*-*p*-tolylsulfonyl-L-proline (L-protosH) allows separation by chromatography of (*M*)- or (*P*)-Rh_2(L-protos)$_2$[(*p*-XC_6H_3)P(*p*-XC_6H_4)$_2$]$_2$ (X = H (**4**), F (**5**), Cl (**6**), Br (**7**), CF_3 (**8**), Me (**9**), ^{t}Bu (**10**), $SiMe_3$ (**11**)) diastereoisomers as intermediates. Further reaction with a nonchiral carboxylic acid gave *M* or *P* enantiomers.[6i]

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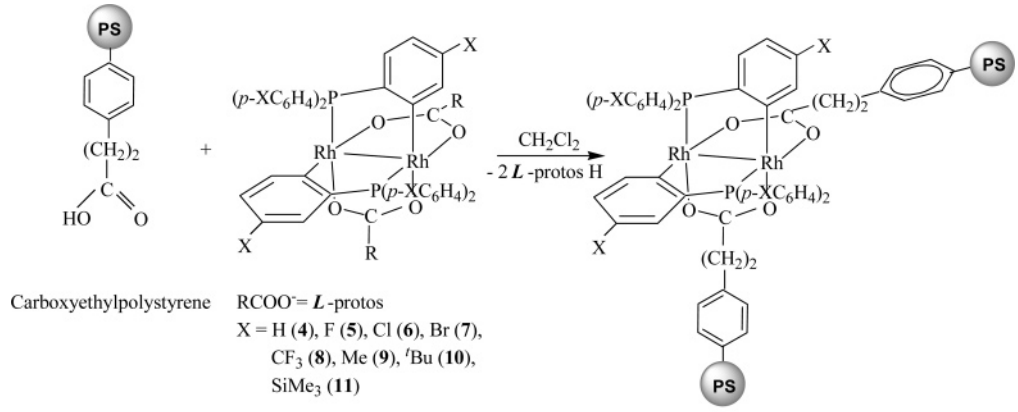
Scheme 3. Synthesis of Immobilized Chiral *ortho*-Metalated Dirhodium(II) Compounds 12−19



Carboxyethylpolystyrene RCOO⁻= ***L***-protos

X = H (**4**), F (**5**), Cl (**6**), Br (**7**), CF_3 (**8**), Me (**9**), ^{t}Bu (**10**), $SiMe_3$ (**11**)

X = H (**12**), F (**13**), Cl (**14**), Br(**15**) CF_3 (**16**), Me (**17**), ^{t}Bu (**18**), $SiMe_3$ (**19**)

Table 1. Asymmetric Cyclopropanation of Styrene Catalyzed by 19[a]

	yield, %[b]		*cis*:*trans*[c]		ee, %[d] **2** (1*S*, 2*R*)[e]		ee, % **3** (1*R*, 2*R*)	
cycle	**19**[f]	**19**[g]	**19**[f]	**19**[g]	**19**[f]	**19**[g]	**19**[f]	**19**[g]
1	79	75	69:31	66:34	56	49	12	16
2	69	69	69:31	64:36	56	46	10	14
3	60	55	66:34	61:39	57	40	8	11
4	51	15	58:42	55:45	53	25	9	7

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), amount (mg) of immobilized catalyst that corresponded to 1 mol % of chiral dirhodium(II) complex 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.[13] [f]Catalyst immobilized in CH_2Cl_2 at room temperature. [g]Catalyst immobilized in refluxing toluene.

Table 2. Asymmetric Cyclopropanation of Styrene Catalyzed by 14 with Different Loadings on the Cross-Linked Polymer[a]

	yield, %[b]			*cis*:*trans*[c]			ee, %[d] **2** (1*S*, 2*R*)[e]			ee, %[d] **3** (1*S*, 2*S*)[e]		
cycle	a	b	c	a	b	c	a	b	c	a	b	c
1	93	94	94	44:56	41:59	43:57	47	52	36	58	61	52
2	93	94	93	43:57	42:58	46:54	47	52	35	59	62	50
3	84	93	93	43:57	42:58	47:53	44	51	37	59	63	52
4	81	91	84	45:55	43:57	46:54	42	52	37	57	63	52
5	90	89	83	43:57	41:59	46:54	45	52	25	59	65	43
6	95	89	85	44:56	42:58	47:53	46	52	30	59	65	47
7	93	89	87	43:57	43:57	47:53	45	51	29	60	65	47
8	88	84	85	43:57	43:57	46:54	45	45	22	59	65	42
9	88	62	65	41:59	42:58	46:54	46	43	3	61	61	22

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), amount (mg) of immobilized catalyst that corresponded to 1 mol % of chiral dirhodium(II) complex 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.[13]

Catalytic Experiments. Catalytic activity of **12**−**19** was evaluated, and the results for the first cycle are displayed in Table 4.

These values were compared with those obtained when the catalytic reaction was performed in homogeneous conditions using the counterpart (*M*)-3-phenylpropionate derivatives, $Rh_2(O_2C(CH_2)_2C_6H_5)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]_2$ (X = H (**20**), F (**21**), Cl (**22**), Br (**23**), CF_3 (**24**), Me (**25**), ^{t}Bu (**26**), $SiMe_3$ (**27**)),

Table 3. Phosphorus and Carbon Analysis of Immobilized Catalysts

catalyst	X	%P	%C
12	H	0.50	84.84
13	F	0.62	83.91
14	Cl	0.64	82.90
15	Br	0.54	80.49
16	CF_3	0.46	82.19
17	Me	0.63	84.17
18	^{t}Bu	0.57	84.41
19	$SiMe_3$	0.40	83.87

Table 4. First Cycle in the Asymmetric Cyclopropanation of Styrene Catalyzed by (*M*)-$Rh_2(O_2C(CH_2)_2C_6H_4\text{-}PS)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]_2$ in *n*-Pentane as Solvent[a]

				% ee		configuration	
catalyst	X	yield, %[b]	*cis*:*trans*[c]	**2**[d]	**3**[d]	**2**[e]	**3**[e]
12	H	82	42:58	57	66	1*S*, 2*R*	1*S*, 2*S*
13	F	89	39:61	48	65	1*S*, 2*R*	1*S*, 2*S*
14	Cl	94	41:59	52	61	1*S*, 2*R*	1*S*, 2*S*
15	Br	92	47:53	34	51	1*S*, 2*R*	1*S*, 2*S*
16	CF_3	89	39:61	46	66	1*S*, 2*R*	1*S*, 2*S*
17	Me	87	45:55	66	70	1*S*, 2*R*	1*S*, 2*S*
18	^{t}Bu	85	68:32	56	15	1*S*, 2*R*	1*R*, 2*R*
19	$SiMe_3$	79	69:31	56	12	1*S*, 2*R*	1*R*, 2*R*

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), amount (mg) of immobilized catalyst that corresponded to 1 mol % of chiral dirhodium(II) complex 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.[13]

Table 5, or the standard (*M*)-trifluoroacetate derivatives, $Rh_2(O_2CCF_3)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]_2$ (X = H (**28**), F (**29**), Cl (**30**), Br (**31**), CF_3 (**32**), Me (**33**), ^{t}Bu (**34**), $SiMe_3$ (**35**)), Table 6.

All the immobilized catalysts, with an average yield of 87%, have provided higher yields than when using the homogeneous counterparts **20**−**27** or the standard catalyst **28**−**35**. The low yields observed for the homogeneous catalysts **20**−**27** can be attributed to their low stability that was observed during the catalytic process. The "$-C_6H_4(CH)_2CO_2^-$" groups bonded to the polystyrene stabilize these dirhodium(II) catalysts.

Catalysts **12**−**17** showed diastereocontrol for the *trans* isomer, while those with bulky *para*-substituents in metalated phosphines, **18** and **19**, did so for the *cis* isomer. The same trend was observed when the catalytic reaction was performed under homogeneous conditions with the counterpart 3-phenylpropionate derivatives, **20**−**27**. A slightly lower diastereocontrol was observed with homogeneous catalysts with bulky *para*-substit-

Table 5. Asymmetric Cyclopropanation of Styrene Catalyzed by (*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2$ [(*p*-XC_6H_3)P(*p*-$XC_6H_4)_2]_2$ in *n*-Pentane as Solvent[a]

				% ee		configuration	
catalyst	X	yield, %[b]	*cis*:*trans*[c]	**2**[d]	**3**[d]	**2**[e]	**3**[e]
20	H	25	33:67	31	41	1*S*, 2*R*	1*S*, 2*S*
21	F	22	38:62	42	37	1*S*, 2*R*	1*S*, 2*S*
22	Cl	71	38:62	55	62	1*S*, 2*R*	1*S*, 2*S*
23	Br	57	41:39	58	43	1*S*, 2*R*	1*S*, 2*S*
24	CF_3	67	31:69	36	63	1*S*, 2*R*	1*S*, 2*S*
25	Me	15	40:60	49	16	1*S*, 2*R*	1*S*, 2*S*
26	^{t}Bu	12	60:40	27	16	1*S*, 2*R*	1*R*, 2*R*
27	$SiMe_3$	43	63:47	42	28	1*S*, 2*R*	1*R*, 2*R*

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), chiral catalyst (8×10^{-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.[13]

Table 6. Asymmetric Cyclopropanation of Styrene Catalyzed by (*M*)-$Rh_2(O_2CCF_3)_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]_2$ in *n*-Pentane as Solvent[a]

				% ee		configuration	
catalyst	X	yield, %[b]	*cis*:*trans*[c]	**2**[d]	**3**[d]	**2**[e]	**3**[e]
28[f]	H	55	48:52	91	87	1*S*, 2*R*	1*S*, 2*S*
29[g]	F	77	47:53	74	74	1*S*, 2*R*	1*S*, 2*S*
30	Cl	52	41:59	84	85	1*S*, 2*R*	1*S*, 2*S*
31[h]	Br	80	53:47	84	81	1*S*, 2*R*	1*S*, 2*S*
32	CF_3	56	32:68	84	88	1*S*, 2*R*	1*S*, 2*S*
33[f]	Me	40	61:39	87	75	1*S*, 2*R*	1*S*, 2*S*
34[h]	^{t}Bu	46	83:17	81	3	1*S*, 2*R*	1*S*, 2*S*
35[h]	$SiMe_3$	39	90:10	91	7	1*S*, 2*R*	1*S*, 2*S*

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), chiral catalyst (8×10^{-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.[13] [f] See ref 7. [g]See ref 15. [h] See ref 8.

uents, **26** and **27**, versus the equivalent immobilized catalysts, **18** and **19**. Meanwhile the other homogeneous catalysts, **20**−**25**, yielded a slightly better diastereocontrol. An inversion in the diastereocontrol was observed with catalysts when X = Br (**15**, **23**) or Me (**17**, **25**) versus the trifluoroacetate complexes (**31**, **33**). The high diastereselectivity for the *cis* isomer observed with homogeneous catalysts, **34** (X = ^{t}Bu) and **35** (X = $SiMe_3$), was partially reduced when the trifluoroacetate ligands were substituted by 3-phenylpropionates or carboxyethylpolystyrene. *cis:trans* ratios of 83:17 (**34**) and 90:10 (**35**), respectively, versus 60:40 (**26**), 63:47, (**27**), 68:32 (**18**), and 69:31 (**19**), were achieved.

The standard chiral dirhodium(II) compounds, $Rh_2(O_2CCF_3)_2(PC)_2$, have been reported by our group as some of the most enantioselective catalysts in the asymmetric cyclopropanation of styrene with ethyl diazoacetate.[6j,7,8] Homogeneous trifluoroacetate catalysts, **28**−**35**, result in, at least for *cis* isomer **2**, a high enantiocontrol for the catalytic reaction, but a drop in enantioselectivity was obtained with the homogeneous 3-phenylpropionate, **20**−**27**, or the immobilized, **12**−**19**, catalysts. Inversion for the *trans*-isomer (1*R*, 2*R*) was observed using catalysts with bulky *para*-substituents, **18**, **19**, **26**, and **27**. The homogeneous trifluoroacetate derivatives, **34** and **35**, gave low enantioselectivities for the *trans* isomer (1*S*, 2*S*). The variable low enantiocontrol observed with the homogeneous 3-phenylpropionate derivatives, **20**−**27**, versus the immobilized catalysts **12**−**19**, suggested a lower stability of these homogeneous catalysts.

The grafted catalysts, **12**−**19**, gave higher yields but lower diastereo- and enantioselectivities than those observed with the standard homogeneous trifluoroacetate derivatives. In the immobilization, the substitution of $CF_3CO_2^-$ by (**PS**)-$C_6H_4(CH_2)_2CO_2^-$ or $C_6H_5(CH_2)_2CO_2^-$ ligands in the catalysts did not modify the symmetry environment around the catalytic metal center, but introduced important electronic effects due to the presence of less electron-withdrawing groups, "$-C_6H_4(CH_2)_2CO_2^-$". The polymer in which the catalysts were grafted is far off the chiral center and would not give additional steric effects. No large differences in diastereoselectivity were observed in the catalytic behavior when it was compared to the results obtained using the immobilized or the counterpart homogeneous catalysts. These could be used as models to study the diastereo- and enantiocontrol run with immobilized catalyts. Furthermore, the carboxyethylpolystyrene ligands stabilized the dirhodium(II) compounds. Taking into account that *ortho*-metalated dirhodium(II) compounds with bridging trifluoroacetate ligands have shown to give high enantioselectivities for this catalytic reaction,[6j,7,8] electronic factors seem to be most important. The substitution of $CF_3CO_2^-$ for less electron-withdrawing ligands, "$-C_6H_4(CH_2)_2CO_2^-$", did not favor the catalytic reaction. The design of new carboxystyrene resins like (**PS**)-$C_6H_4(CF_2)_2CO_2H$ could graft *ortho*-metalated dirhodium(II) catalysts with high enantiocontrol for the studied catalytic reaction.

One of the major challenges in heterogeneous asymmetric catalysis lies in avoiding degradation in enantioselectivity with recycled catalysts.[10b] Compounds **12**−**19** have been easily recovered by filtration, centrifugation, or decantation and further washed with *n*-pentane. No leaching was observed during these procedures. The activity of the recycled catalysts has been tested. The yields, *cis:trans* ratios, and ee values were compared to those obtained with fresh catalyst.

Catalysts with electron-withdrawing *para*-substituents in the metalated phosphines **13**−**16** appeared to be robust. With **14**, X = Cl, the cyclopropane yield (94−89%) remained steady over 7 cycles and the *cis:trans* ratio over 9 cycles, and it could be recycled seven times without a drop in the enantioselectivity (Figure 1). Catalysts **16**, X = CF_3, maintained the yield, *cis:trans* ratio, and both ee's over 7 cycles, Figure SI.1. In the case of catalyst **13**, X = F, yields of 89−84% were obtained in the first 4 cycles, the *cis:trans* ratio changed in cycle 9, and both ee's remained steady for 7 cycles, Figure SI.2. Using **15**, X = Br, high yields (92−88%) were maintained in the first 4 cycles and the diastereoselectivities 6 cycles, and the enantioselectivies increased moderately in cycles 5 and 6, Figure SI.3.

17, X = Me, also behaved as a robust catalyst; the yield was maintained over 5 cycles with a slight increase in cycles 2 and 3. The diastereo- and enantioselectivities remained unchanged over 8 cycles, Figure 2.

Catalyst **12**, X = H, could be recovered and reused for only 3 cycles. The yield gradually decreased and the diastereo- and enantioselectivies increased slightly from the first to the third cycle, Figure 3. When using catalysts with bulky *para*-substituents in the metalated phosphines, a decrease in yield was observed from cycle 1 to 5 with **18**, and from cycle 1 to 4 with **19**. The diastereoselectivity was maintained until cycle 3 with **18** and the enantioselectivities until cycle 4, Figure 4. In the case of **19**, only the two first cycles conserved the diastereoselectivity and the enantioselectivities for 4 cycles, Figure SI.4. Those catalysts underwent faster degradation than **13**−**17** under the reaction conditions.

Considering that all catalysts have been supported in the same cross-linked polystyrene resin, the different degradation observed

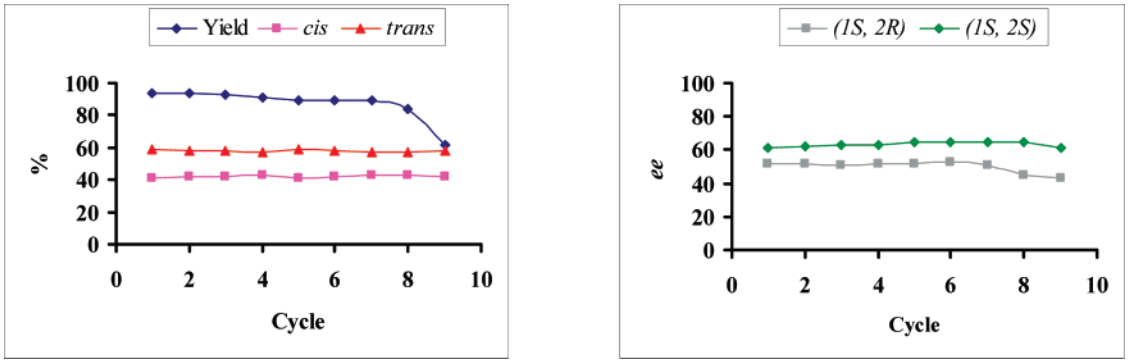


Figure 1. Variation of the yields, percentages, and ee's of the *cis*- and *trans*-cyclopropane isomers using recycled **14** (X = Cl) for 9 cycles.

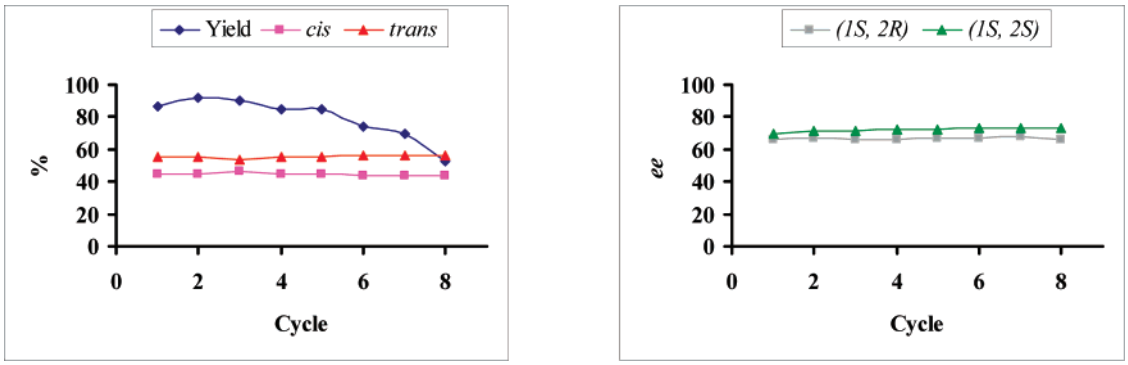


Figure 2. Variation of the yields, percentages, and ee's of the *cis*- and *trans*-cyclopropane isomers using recycled **17** (X = Me) for 8 cycles.

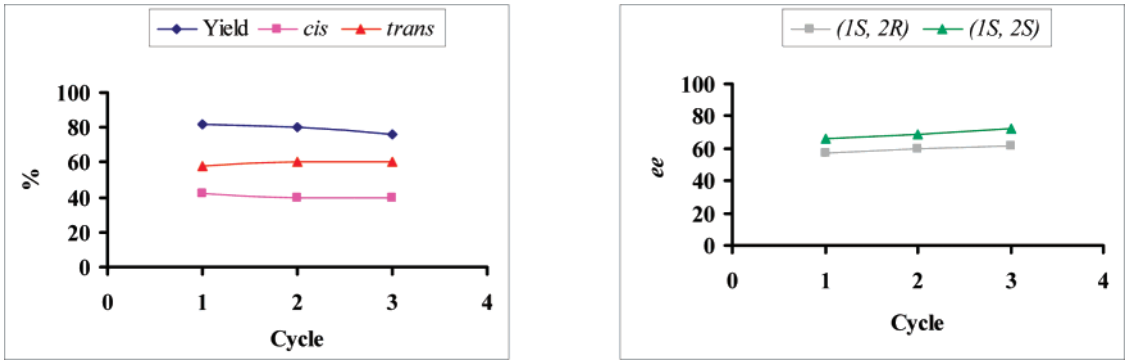


Figure 3. Variation of the yields, percentages, and ee's of the *cis*- and *trans*-cyclopropane isomers using recycled **12** (X = H) for 3 cycles.

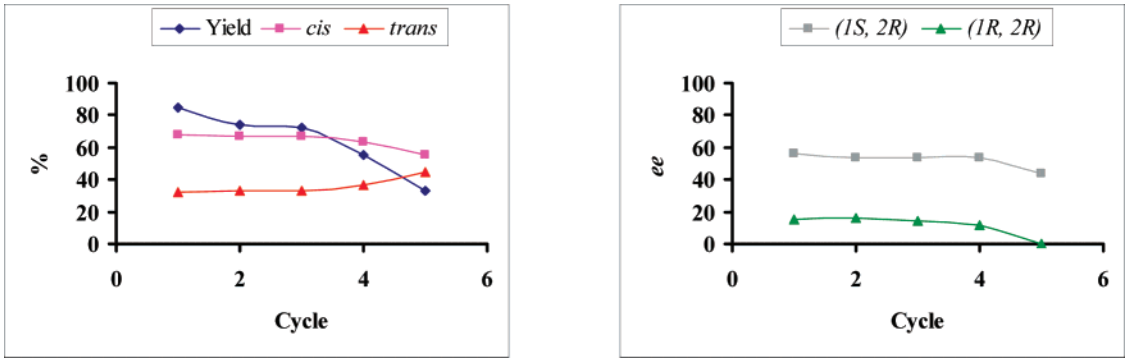


Figure 4. Variation of the yields, percentages, and ee's of the *cis*- and *trans*-cyclopropane isomers using recycled **18** (X = ^{t}Bu) for 5 cycles.

for the recycled catalysts can be attributed mainly to the stability during the catalytic reaction of the grafted chiral dirhodium(II) compounds. Electron-withdrawing F, Cl, Br, and CF_3 and donor Me *para*-substituents in the *ortho*-metalated phosphines stabilized the catalysts, avoiding a quick degradation, but other donor or bulky substituents, H, ^{t}Bu, and $SiMe_3$, did not.

Conclusions

The interchange reactions of carboxylates have proved to be a good method to quantitatively immobilize chiral *ortho*-metalated dirhodium(II) compounds on a cross-linked polystyrene resin. The tests of immobilized catalysts in the asymmetric

cyclopropanation of styrene with ethyl diazoacetate gave higher yields compared to those obtained with the standard homogeneous trifluoroacetate derivatives; nevertheless, the diastereo- and enantioselectivities were generally lower. These differences can be attributed to electronic effects due to the substitution of $CF_3CO_2^-$ ligands by "$-C_6H_4(CH_2)_2CO_2^-$" groups. Catalysts with electron-withdrawing, F, Cl, Br, and CF_3, or Me *para*-substituents in the metalated phosphines have shown to be very robust; the yields and diastereo- and enantioselectivities are steady for many cycles.

Experimental Section

General Considerations. Commercially available $Rh_2(O_2CMe)_4 \cdot (MeOH)_2$ was purchased from Pressure Chemical Co. P(*p*-$XC_6H_4)_3$ (X = H, F, Cl, CF_3, Me, ^{t}Bu, CF_3CO_2H, $C_6H_5(CH_2)_2CO_2H$, styrene, and ethyl diazoacetate were used as purchased. Carboxyethylpolystyrene was 100−200 mesh, 1% cross-linked, and purchased from Aldrich (typical loading: 0.8−1.5 mmol·g^{-1}). All solvents were of analytical grade. *N*-*p*-tolylsulfonyl-L-proline (L-ProtosH),[16] (*M*)-Rh_2(L-protos)$_2$[(*p*-XC_6H_3)P(*p*-$C_6H_5)_2]_2$ (X = H, F, Me, ^{t}Bu) diastereoisomers,[6j] (*M*)-$Rh_2(O_2CCF_3)_2$[(*p*-XC_6H_3)P(*p*-$C_6H_5)_2]_2$ (X = H, F, Br, Me, ^{t}Bu, $SiMe_3$) enantiomers,[6j,7,8b] and P(*p*-$XC_6H_4)_3$ (X = Br, $SiMe_3$)[17] were synthesized according to the method described in the literature. Column chromatography was performed on silica gel (35−70 mesh). Solvent mixtures were volume/volume mixtures, unless specified otherwise. All reactions were carried out in oven-dried glassware under an argon atmosphere, although the isolated solids were air-stable.

Instrumentation. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 25 °C in $CDCl_3$ unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent peaks. ^{31}P spectra were referenced to an external H_3PO_4 sample. Chemical shifts are reported in ppm and coupling constants (*J*) in hertz. Coupling constants for AA′XX′ spectra are from simulated spectra. Elemental analyses were provided by Centro de Microanalisis Elemental, Universidad Complutense de Madrid. Phosphorus and carbon analyses of the immobilized catalysts were provided by Organisch-Chemisches Institut der Universität Heidelberg The ee values were based on GC analysis with a 2,3-di-*O*-acetyl 6-*O*-*tert*-butyldimethylsilyl beta CDX column.

Synthesis of (*M*)-Rh_2(L-protos)$_2$[(*p*-XC_6H_3)P(*p*-$XC_6H_5)_2]_2$ Diastereoisomers. The (*M*)-Rh_2(L-protos)$_2$)[(*p*-XC_6H_3)P(*p*-$XC_6H_5)_2]_2$ diastereoisomers were obtained by standard methods described in the literature.[6j]

(*M*)-Rh_2(L-protos)$_2$[(*p*-ClC_6H_3)P(*p*-$ClC_6H_4)_2]_2$, 6. Yield: 68%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.42−0.62 (m, 2H); 0.79−0.93 (m, 2H); 0.96−1.14 (m, 4H); 2.47 (bs, 6H); 2.77−2.92 (m, 2H); 3.10−3.29 (m, 2H); 4.12−4.26 (m, 2H); 6.62 (t, J = 8.3 Hz, 2H); 6.69−6.97 (m, 8H); 7.10−7.19 (m, 8H); 7.29−7.41 (m, 4H); 7.61−7.72 ppm (m, 8H). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 21.4 (s); 24.4 (s); 29.6 (s); 48.5 (s); 63.0 (s); 111.5−143.6 (aromatic); 168.1 (m, $C_{(metalated)}$); 181.2 ppm (bs). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 298 K): δ 20.6 ppm (bd, J = 169 Hz). Anal. Calcd (%) for $C_{60}H_{50}Cl_6N_2O_8P_2Rh_2S_2$: C, 48.95; H, 3.40. Found: C, 48.38; H, 3.22.

(*M*)-Rh_2(L-protos)$_2$[(*p*-BrC_6H_3)P(*p*-$BrC_6H_4)_2]_2$, 7. Yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.50−0.66 (m, 2H); 0.80−0.92 (m, 2H); 1.00−1.20 (m, 4H); 2.34 (bs, 6H); 2.78−2.94 (m, 2H); 3.14−3.31 (m, 2H); 4.20 (bs, 2H); 6.46−6.66 (m, 6H); 6.84−7.01 (m, 4H); 7.16 (d, J = 8.0 Hz, 4H); 7.20−7.30 (m, 4H); 7.45−7.63 (m, 8H); 7.72 ppm (d, J = 8.1 Hz, 4H). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 21.4 (s); 24.36 (s); 29.7 (s); 48.92 (s); 63.1 (s); 124.4−143.4 (aromatic); 168.3 (m, $C_{(metalated)}$); 181.2 ppm (bs). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 298 K): δ 21.0 ppm (bd, J = 167 Hz). Anal. Calcd (%) for $C_{60}H_{50}Br_6N_2O_8P_2Rh_2S_2$: C, 41.45; H, 2.88. Found: C, 41.22, H, 3.04.

(*M*)-Rh_2(L-protos)$_2$[(*p*-$CF_3C_6H_3$)P(*p*-$CF_3C_6H_4)_2]_2$, 8. Yield: 64%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.56−0.69 (m, 2H); 0.82−0.94 (m, 2H); 0.96−1.08 (m, 4H); 2.66 (bs, 6H); 2.75−2.85 (m, 2H); 3.10−3.21 (m, 2H); 4.10 (bs, 2H); 6.51−6.57 (m, 4H); 6.62−6.71 (m, 6H); 6.78 (t, J = 8 Hz, 4H); 7.06 (t, J = 8 Hz, 4H); 7.16 (d, J = 8 Hz, 4H); 7.60−7.70 (m, 4H) 7.71 ppm (d, J = 8 Hz, 4H). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 20.4 (s); 23.3 (s); 30.0 (s); 48.0 (s); 62.2 (s); 108.1−142.2 (aromatic); 167.6 (m, $C_{(metalated)}$); 181.2 ppm (bs). ^{19}F{^{1}H} NMR (282.2 MHz, $CDCl_3$, 298 K): δ −110.45 (s); −111.36 (s); −111.80 ppm (s). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 298 K): δ 18.5 ppm (bd, J = 167 Hz). Anal. Calcd (%) for $C_{66}H_{50}F_{18}N_2O_8P_2Rh_2S_2$: C, 47.45; H, 3.00. Found: C 48.12; H, 2.78.

(*M*)-Rh_2(L-protos)$_2$[(*p*-$Me_3SiC_6H_3$)P(*p*-$Me_3SiC_6H_4)_2]_2$, 11. Yield: 58%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ −0.01 (s, 18H); 0.18 (s, 18H); 0.19 (s, 18H); 0.80−0.90 (m, 4H); 1.00.1.10 (m, 4H); 2.31 (bs, 6H); 2.71−2.80 (m, 2H); 3.16−3.25 (m, 2H); 4.16−4.20 (m, 2H); 6.40 (dd, J = 8, J = 9 Hz, 2H); 6.64 (dd, J = 8, J = 10 Hz, 4H); 6.83−6.88 (m, 2H); 7.08−7.13 (m, 8H); 7.49−7.53 (m, 4H); 7.65−7.72 ppm (m, 8H). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ −1.2 (s); −1.1 (s); 21.4 (s); 24.8 (s); 29.4 (s); 48.8 (s); 63.2 (s); 125.3−147.5 (aromatic); 164.5 (m, $C_{(metalated)}$); 181.3 ppm (bs). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 298 K): δ 19.7 ppm (bd, J = 166 Hz). Anal. Calcd (%) for $C_{78}H_{104}N_2O_8P_2Rh_2Si_6S_2$: C, 55.19; H, 6.13. Found: C, 54.53; H, 6.30.

Synthesis of Enantiomerically Pure $Rh_2(O_2C(CH_2)_2C_6H_5)_2$[(*p*-$XC_6H_3$)P(*p*-$XC_6H_4)_2]_2$ and $Rh_2(O_2CCF_3)_2$[(*p*-XC_6H_3)P(*p*-$XC_6H_4)_2]_2$ Compounds. The enantiomerically pure compounds as 3-phenylpropionate and trifluoroacetate derivatives have been obtained following the procedures described in the literature.[5h,i,7]

(*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2$[($C_6H_4$)P($C_6H_5)_2]_2$, 20. Yield: 71%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.68 (t, J = 7 Hz, 4H); 2.98 (t, J = 7 Hz, 4H); 6.58−6.65 (m, 4H); 6.77−6.81 (m, 2H); 6.86−6.91 (m, 4H); 6.96−7.00 (m, 4H); 7.05−7.10 (m, 6H); 7.18−7.22 (m, 4H); 7.25−7.40(m, 10H); 7.64−7.69 ppm (m, 4H). ^{13}C-{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 31.3 (s); 37.6 (s); 120.9−145.8 (aromatic); 182.9 ppm (bs). ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$, 298 K): δ 18.8 ppm (bd, $^1J_{P-Rh}$ = 130 Hz). Anal. Calcd (%) for **20**·2$C_6H_5(CH_2)_2CO_2H$, $C_{72}H_{66}O_8P_2Rh_2$: C, 65.16; H, 4.98. Found: C, 64.7; H, 5.24.

(*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2$[(*p*-$FC_6H_3$)P(*p*-$FC_6H_4)_2]_2$, 21. The product is so soluble in the normal solvents that it cannot be precipitated and has been characterized only by spectroscopy methods. Yield: 62%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.78 (t, J = 7 Hz, 4H); 3.03 (t, J = 7 Hz, 4H); 6.56−6.62 (m, 4H); 6.68−6.78 (m, 4H); 6.81−6.86 (m, 4H); 6.96−7.02 (m, 6H); 7.22−7.36 (m, 10H); 7.48−7.57 ppm (m, 4H). ^{13}C{^{1}H} NMR (75.4 MHz): δ 31.3 (s); 37.7 (s); 109.8−165.0 (aromatic); 169.5 (m, $C_{(metalated)}$); 183.5 ppm (d, J = 3 Hz). ^{19}F{^{1}H} NMR (282.2 MHz, $CDCl_3$, 298 K): δ −112.50 (s); −113.0 (s); −113.6 ppm (s). ^{31}P-{^{1}H} NMR (121.4 MHz, $CDCl_3$, 298 K): δ 19.8 ppm (AA′XX′ system, $^1J_{P-Rh}$ = 171 Hz, $^2J_{P-Rh}$ = −9 Hz, $^1J_{Rh-Rh}$ = 20 Hz).

(*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2$[(*p*-$ClC_6H_3$)P(*p*-$ClC_6H_4)_2]_2$, 22. Yield: 68%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.84 (t, J = 7 Hz, 4H); 3.09 (t, J = 7 Hz, 4H); 6.61−6.67 (m, 4H); 6.82−6.85 (m, 4H); 6.97−7.01 (m, 4H); 7.11−7.16 (m, 6H); 7.26−7.37 (m, 10H); 7.45−7.52 ppm (m, 4H). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ 31.2 (s); 37.7 (s); 122.1−142.7 (aromatic); 167.5 (m, $C_{(metalated)}$); 183.6 ppm (d, J = 2 Hz). ^{31}P{^{1}H} NMR (121.4 MHz,

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$CDCl_3$, 298 K): δ 20.2 ppm (dd, $^1J_{P-Rh}$ = 169 Hz, $^2J_{P-Rh}$ = 7 Hz). Anal. Calcd (%) for **22**·$2C_6H_5(CH_2)_2CO_2H$, $C_{72}H_{60}Cl_6O_8P_2Rh_2$: C, 56.36; H, 3.91. Found: C, 56.46; H, 4.27.

(*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2[(p\text{-}BrC_6H_3)P(p\text{-}BrC_6H_4)_2]_2$, 23. Yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.84 (t, J = 7 Hz, 4H); 3.09 (t, J = 7 Hz, 4H); 6.45−6.48 (m, 2H); 6.54−6.61 (m, 4H); 6.97−7.01 (m, 8H); 7.19−7.22 (m, 4H); 7.25−7.32 (m, 10H); 7.44−7.47 ppm (m, 4H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 31.9 (s); 37.7 (s); 124.0−144.0 (aromatic); 168.0 (m, $C_{(metalated)}$); 183.7 ppm (d, J = 2 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 298 K): δ 20.6 ppm (dd, $^1J_{P-Rh}$ = 169 Hz, $^2J_{P-Rh}$ = 7 Hz). Anal. Calcd (%) for **23**·$2C_6H_5(CH_2)_2CO_2H$, $C_{72}H_{60}Br_6O_8P_2Rh_2$: C, 48.01; H, 3.33. Found: C, 47.83; H, 3.90.

(*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2[(p\text{-}F_3CC_6H_3)P(p\text{-}CF_3C_6H_4)_2]_2$, 24. Yield: 71%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.76 (t, J = 8 Hz, 4H); 3.03 (t, J = 8 Hz, 4H); 6.53−6.58 (m, 4H); 6.68−6.72 (m, 4H); 6.79−6.83 (m, 4H); 6.94−6.98 (m, 8H); 7.24−7.34 (m, 8H); 7.45−7.52 ppm (m, 4H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 30.3 (s); 36.7 (s); 108.3−141.0 (aromatic); 168.4 (m, $C_{(metalated)}$); 182.3 ppm (d, J = 2 Hz). $^{19}F\{^1H\}$ NMR (282.2 MHz, $CDCl_3$, 298 K): δ −63.4 (s); −63.9 (s) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 298 K): δ 18.7 (bd, J = 163 Hz). Anal. Calcd (%) for **24**·$2C_6H_5(CH_2)_2CO_2H$, $C_{78}H_{60}F_{18}O_8P_2Rh_2$: C, 53.98; H, 3.46. Found: C, 54.53; H, 3.60.

(*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2[(p\text{-}MeC_6H_3)P(p\text{-}MeC_6H_4)_2]_2$, 25. Yield: 69%. Spectroscopy data: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.85 (s, 6H); 2.29 (s, 6H); 2.30 (s, 6H); 2.78 (t, ^1J = 8 Hz, 4H); 3.10 (t, ^1J = 8 Hz, 4H); 6.53−6.56 (m, 4H); 6.73−6.77 (m, 6H); 6.85−6.87 (m, 4H); 6.94−6.96 (m, 4H); 7.09−7.12 (m, 6H); 7.17−7.22 (m, 4H); 7.55−7.60 ppm (m, 4H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 21.2 (s); 21.3 (s); 21.8 (s); 31.3 (s); 37.7 (s); 122.0−142.4 (aromatic); 165.3 (m, $C_{(metalated)}$); 182.6 ppm (d, J = 2 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 298 K): δ 17.4 ppm (AA′XX′ system, $^1J_{P-Rh}$ = 168 Hz, $^2J_{P-Rh}$ = −4 Hz, $^1J_{Rh-Rh}$ = 8 Hz). Anal. Calcd (%) for **25**·$2C_6H_5(CH_2)_2CO_2H$, $C_{78}H_{78}O_8P_2Rh_2$: C, 66.38; H, 5.53. Found: C, 65.85; H, 5.56.

(*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2[(p\text{-}^tBuC_6H_3)P(p\text{-}^tBuC_6H_4)_2]_2$, 26. Yield: 75%.^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 1.03 (s, 9H), 1.20 (s, 9H); 1.26 (s, 9H); 2.81 (t, J = 7 Hz, 4H); 3.12 (t, J = 7 Hz, 4H); 6.38−6.44 (m, 2H); 6.78−6.84 (m, 6H); 6.92−6.95 (m, 4H); 7.06−7.13 (m, 6H); 7.25−7.39 (m, 10H); 7.48−7.54 ppm (m, 4H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 31.0 (s); 31.1 (s); 31.2 (s); 37.0 (s); 119.0−152.0 (aromatic); 164.1 (m, $C_{(metalated)}$); 182.6 ppm (d, J = 2 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 298 K): 17.0 ppm (AA′XX′ system, $^1J_{P-Rh}$ = 170 Hz, $^2J_{P-Rh}$ = −8 Hz, $^1J_{Rh-Rh}$ = 19 Hz). Anal. Calcd (%) for **26**·$2C_6H_5(CH_2)_2CO_2H$, $C_{96}H_{114}O_8P_2Rh_2$: C, 69.31; H, 6.86. Found: C, 68.92; H, 6.80.

(*M*)-$Rh_2(O_2C(CH_2)_2C_6H_5)_2[(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2]_2$, 27. Yield: 68%.^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.00 (s, 9H); 0.01 (s, 9H); 0.14 (s, 9H); 2.80 (t, J = 8 Hz, 4H); 3.09 (t, J = 8 Hz, 4H); 6.38−6.42 (m, 2H); 6.73−6.80 (m, 6H); 6.90−6.96 (m, 6H); 7.01−7.06 (m, 4H); 7.12−7.25 (m, 10H); 7.49−7.55 ppm (m, 4H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ −1.40 (s); −1.17 (s); −1.02 (s); 31.2 (s); 36.9 (s); 124.0−148.0 (aromatic); 163.8 (m, $C_{(metalated)}$); 182.9 ppm (bs). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 298 K): δ 18.8 ppm (bd, $^1J_{P-Rh}$ = 166 Hz). Anal. Calcd (%) for **27**·$2C_6H_5(CH_2)_2CO_2H$, $C_{90}H_{114}O_8P_2Rh_2Si_6$: C, 61.43; H, 6.48. Found: C, 60.90; H, 6.80.

(*M*)-$Rh_2(O_2CCF_3)_2[(p\text{-}ClC_6H_3)P(p\text{-}ClC_6H_4)_2]_2$, 30. Yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 6.49 (bs, 2H); 6.59 (dd, J = 8, J = 9 Hz, 2H); 6.70 (dd, J = 8, J = 10 Hz, 4H); 6.88 (td, J = 2, J = 8 Hz, 2H); 7.17 (dd, J = 2, J = 8 Hz, 4H); 7.34−7.40 (m, 4H); 7.44−7.51 ppm (m, 4H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 123.1 (bs); 127.9 (bd, J = 45 Hz); 128.4 (t, J = 10 Hz); 133.5 (d, J = 10 Hz); 134.0 (bs); 134.5 (d, J = 11 Hz); 136.0 (bs); 137.5 (m); 142.2 (bd, J = 77 Hz); 163.3 (m, $C_{(metalated)}$); 166.8 ppm (q, J = 38 Hz). $^{19}F\{^1H\}$ NMR (282.2 MHz, $CDCl_3$, 298 K): δ −75.75 ppm (s). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 298 K): δ 18.4 ppm (bd, J = 166 Hz). Anal. Calcd (%) for $C_{40}H_{22}Cl_6F_6O_4P_2Rh_2$: C, 41.34; H, 1.90. Found: C, 42.14; H, 2.25.

(*M*)-$Rh_2(O_2CCF_3)_2[(p\text{-}CF_3C_6H_3)P(p\text{-}CF_3C_6H_4)_2]_2$, 32. Yield: 88%. ^{1}H NMR (300 MHz, CDCl3, 298 K): δ 6.27 (bs, 2H); 6.54−6.68 (m, 4H); 6.68−6.79 (m, 4H); 6.86 (dd, J = 8, J = 8 Hz, 4H); 7.06 (dd, J = 8, J = 8 Hz, 4H); 7.46−7.63 ppm (m, 4H). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 110.4 (dd, J = 10, J = 20 Hz); 115.3 (m); 124.4 (m); 125.8 (d, J = 49 Hz); 134.6 (m); 135.45 (m); 140.2 (d, J = 78 Hz); 160.0−166.0 ppm (multiplets overlaping). $^{19}F\{^1H\}$ NMR (282.2 MHz, $CDCl_3$, 298 K): δ −110.07 (s); −109.83 (s); −108.72 (s); −75.47 ppm (s). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 298 K): δ 17.7 ppm (bd, J = 170 Hz). Anal. Calcd (%) for $C_{46}H_{22}F_{24}O_4P_2Rh_2$: C, 40.53; H, 1.62. Found: C, 41.34; H, 2.14.

Immobilization of Catalysts. A suspension of 100 mg of carboxyethylpolystyrene in a solution of 0.005, 0.01, or 0.02 mmol of diastereoisomers (*M*)-Rh_2(L-protos)$_2[(p\text{-}XC_6H_3)P(p\text{-}XC_6H_4)_2]_2$ (X = H (**4**), F (**5**), Cl (**6**), Br (**7**), CF_3 (**8**), Me (**9**), ^{t}Bu (**10**), $SiMe_3$ (**11**)) was gently stirred for 24 h in CH_2Cl_2 at room temperature or heated in refluxing toluene for 1 h. The color of the resin changed from white to red-purple. After filtration of the solvent, the solid that corresponded to the immobilized catalyst, (*M*)-$Rh_2(CO_2\text{-}(CH_2)_2\text{-}C_6H_4\text{-}$**PS**$)_2[(p\text{-}XC_6H_3)P(p\text{-}C_6H_5)_2]_2$ (X = H (**12**), F (**13**), Cl (**14**), Br (**15**), CF_3 (**16**), Me (**17**), ^{t}Bu (**18**), $SiMe_3$ (**19**)) was washed four times in CH_2Cl_2 and dried under vacuum. No color was observed in the filtered liquid and subsequent washes.

Quantitative analysis of the L-protosH obtained during the immobilization process was performed by ^{1}H NMR spectroscopy. The integration of the methyl signal in L-protosH at 2.4 ppm and the quantitative comparison with the methyl signal at 4.0 of a 2-methoxynaphthalene sample indicated that 2 mol of L-protosH per mol of catalyst have been liberated during the immobilization process. It can be concluded that catalysts **12**−**19** have been grafted by the two *cis* positions.

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 immobilized or homogeneous 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 12 h in the case of immobilized and homogeneous 3-phenylpropionate catalysts, or 2 h with homogeneous tiflouroacetate catalysts, and cooled to room temperature. The resulting solution was separated from the immobilized catalyst by decantation or filtered through a short plug of silica to remove the homogeneous catalyst. 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 all cases 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: Variation of the cyclopropane yields, percentages, and ee of the *cis* and *trans* isomers using fresh and recovered catalysts **13**, **15**, **16**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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