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Enantio- and Diastereocontrol in Intermolecular Cyclopropanation Reaction of Styrene Catalyzed by Dirhodium(II) Complexes with Bulky *ortho*-Metalated Aryl Phosphines: Catalysis in Water as Solvent. Study of a (+)-Nonlinear Effect

Francisco Estevan, Julio Lloret, Mercedes Sanaú, and Mª Angeles Úbeda*

Departamento de Química Inorgánica, Facultad de Química, Universitat de Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

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Enantiomerically pure dirhodium(II) complexes with *ortho*-metalated *para*-substituted aryl phosphines have been shown to lead to an enantio- and diastereoselective cyclopropanation of styrene with ethyl diazoacetate. Enantioselectivities up to 91% and diastereoselectivities up to 90% are observed for ethyl *cis*-2-phenylcyclopropanecarboxylate. High enantio- and diastereoselectivities are observed for the synthesis of ethyl *cis*-2-phenylcyclopropanecarboxylate using water as solvent. Additionally, a (+)-nonlinear effect, (+)-NLE, has been observed and studied in the asymmetric catalytic reaction developed in *n*-pentane.

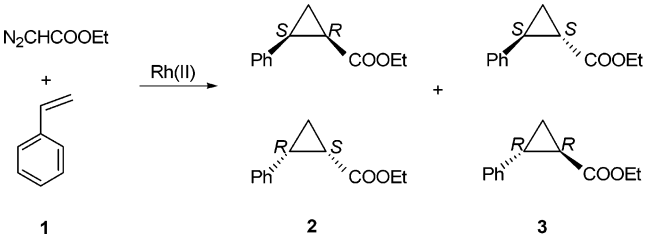
Introduction

The design of chiral catalysts to induce enantiocontrol in carbene transfer reactions is presently a subject of interest.[1−5] The intermolecular cyclopropanation reaction of styrene, **1**, with ethyl diazoacetate is frequently used as a model reaction to measure the stereo- and enantioselectivity of new catalysts (Scheme 1).

Chiral copper catalysts,[6−10] especially those with bis-oxazoline ligands, have been found to induce the highest levels of enantiocontrol. Enantioselectivities up to 99% for ethyl 2-phenylcyclopropanecarboxylates have been obtained in the cyclopropanation of styrene. Ruthenium catalysts have also produced a high level of enantiocontrol in the cyclopropanation of olefins,[11] but their carbenoids are less reactive than those derived from copper catalysts.

Chiral dirhodium(II) catalysts do not provide, in general, high selectivities in the intermolecular cyclopropanation reaction of styrene.[12] Dirhodium(II) catalysts of general formula $Rh_2(O_2CR)_2(PC)_2$, containing two *ortho*-metalated aryl phosphines (PC) in a head to tail arrangement,[13] have backbone chirality and can be isolated as pure enantiomers by conventional resolution methods.[14,15] Our group has reported some of these dirhodium(II) catalysts as the most enantioselective among dirhodium(II) catalysts, giving enantioselectivities up to 91% and up to 87%, for ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylate, respectively.[15] However, the diastereoselectivities obtained are about 60:40 or less.

Scheme 1. Catalyzed Cyclopropanation of Styrene



According to the transition state model proposed for the cyclopropanation reaction of styrene catalyzed by enantiomers of $Rh_2(O_2CR)_2(PC)_2$,[15] the presence of bulky substituents on the metalated ring might improve the diastereocontrol of the catalyst. To probe this hypothesis, we have studied some dirhodium(II) catalysts with different substituents in the *para* positions of the aryl groups. Preliminary results show that diastereoselectivities up to 90% can be achieved for ethyl *cis*-2-phenylcyclopropanecarboxylate.[16]

Water is an inexpensive and environmentally benign solvent that can be advantageous sometimes.[17−21] There are few examples in the literature that study the cyclopropanation reaction in water as solvent. Nishiyama et al.,[22] using aqueous/

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* To whom correspondence should be addressed. E-mail: angeles.ubeda@uv.es. Fax: (34)963544322.

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organic biphasic media and a chiral ruthenium catalyst, have obtained high enantiomeric excesses, up to 96−97%, and high *trans:cis* diastereoselectivities, up to 97:3. Using nonchiral dirhodium(II) carboxylates, Charette et al.[23] observed that the yields were highly dependent on the nature of the carboxylate, with the highest yields, up to 72%, corresponding to hydrophobic catalysts and a *trans:cis* ratio of 62:38. The authors also performed the cyclopropanation reaction in water using the chiral ruthenium(II) compound reported by Nishiyama with high enantio- and diastereoselectivity. Recently, Afonso et al.[24,25] have used water as an efficient solvent in the intramolecular C−H insertion of diazo substrates and $Rh_2(O_2CCH_3)_4$ as catalyst, which was recycled and reused up to 11 times.

The cyclopropanation of styrene catalyzed by chiral dirhodium complexes in water as solvent has never been reported. The high enantio- and diastereoselectivies reached in the catalytic reaction with the enantiomerically pure $Rh_2(O_2CCF_3)_2[(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2]_2$ prompted us to study its catalytic behavior in aqueous medium.

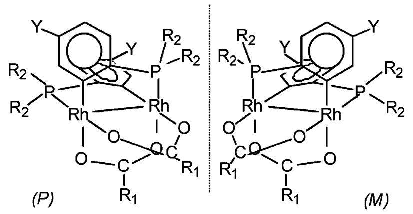
The nonlinear effects (NLEs) in asymmetric catalysis were first described quantitatively by Kagan and Agamy et al. in 1986.[26,27] Reactions that present (+)-NLEs are very attractive in asymmetric catalysis, since starting from an optically impure catalyst it is possible to obtain products with higher enantiopurity than that expected from the catalyst's optical purity.[28,29] This represents an amplification of the chirality.

Recently, Zinic et al.[30] have reported the first example of a (+)-NLE in the cyclopropanation of styrene with ethyl diazoacetate catalyzed by a chiral Cu(I)−bisoxazoline complex. The (+)-NLE was explained by the possible formation of a catalytically inactive heterochiral *meso*-complex.

In this paper, we present the first study of (+)-NLE in chiral dirhodium(II) compounds observed when in the cyclopropanation reaction of styrene developed in *n*-pentane the enantiomerically pure catalyst (*M*)-$Rh_2(O_2CCF_3)_2[(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2]_2$ is progressively contaminated by (*P*)-$Rh_2(O_2CCF_3)_2[(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2]_2$.

Results and Discussion

Dirhodium *ortho*-Metalated Compounds. $Rh_2(O_2CMe)_2[(p\text{-}XC_6H_4)P(p\text{-}XC_6H_5)_2]_2\cdot 2MeCO_2H$ compounds that contain different groups at the *para* position of all the aryl groups of the phosphine, X = Br, **4**, X = Me_3Si, **5**, X = Et_3Si, **6**, X = Ph_3Si, **7**, X = H,[13] **8**, X = Me_3C,[15] **9**, have been obtained by standard methods[31] or according to the method reported in each case. These compounds have been resolved as their enantiomers, *P* and *M*, as trifluoroacetate derivatives, according to the procedure described in the literature.[14,15]



Catalyst	Phosphine Ar$_3$P (Ar)	R$_1$	R$_2$	Y
10(*M*)	-C_6H_5	CF_3	-C_6H_5	H
11(*M*)	*p*-BrC_6H_4	CF_3	*p*-Br-C_6H_4	Br
12(*M*)	*p*-Me_3C-C_6H_4	CF_3	*p*-Me_3C-C_6H_4	Me_3C
13(*M*)	*p*-Me_3Si-C_6H_4	CF_3	*p*-Me_3Si-C_6H_4	Me_3Si
14(*M*)	*p*-Et_3Si-C_6H_4	CF_3	*p*-Et_3Si-C_6H_4	Et_3Si
15(*M*)	*p*-Ph_3Si-C_6H_4	CF_3	*p*-Ph_3Si-C_6H_4	Ph_3Si

Figure 1. Rh(II) catalysts with *ortho*-metalated aryl phosphine ligands.

The chiral dirhodium complexes used as catalysts in this study are represented in Figure 1. All of them present circular dichroism that is related with the conformation of the complex (Figure 2 and SI 2−4).

Crystal structures for complexes **5** and **7** (racemic mixtures) are shown in Figures 3 and 4, respectively, together with some representative bond distances and angles. In both structures, the two rhodium atoms are bridged by four ligands: two acetate groups and two *cisoid* cyclometalated phosphines, $(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2$ or $(p\text{-}Ph_3SiC_6H_3)P(p\text{-}Ph_3SiC_5H_4)_2$, in a head to tail arrangement. In compound **5**, each axial position is occupied by an oxygen atom of one acetic acid molecule, completing the slightly distorted octahedral coordination around the rhodium atom. In the case of compound **7**, these axial positions are occupied by ethyl acetate molecules. The crystals of **7** did not diffract well, presumably because of the phenyl-ring disorder. The value of the Rh−Rh distance, 2.5116(6) Å, in compound **5** falls within the range reported for dirhodium compounds of comparable structures, whereas the value of 2.683(2) Å observed in compound **7** is one of the largest Rh−Rh distances for this type of compound.

Asymmetric Catalysis. In *n*-Pentane as Solvent. Catalysts **11(*M*)**−**15(*M*)**, Figure 1, have been tested in the cyclopropanation of styrene with ethyl diazoacetate using *n*-pentane as solvent and following the procedure described in the Experimental Section. The results are presented in Table 1. Previously reported values for catalyst **10(*M*)**[15] are also included for comparison.

The diastereoselectivities and the yields are very affected by the substituents in the aryl groups of the metalated phosphine in the catalysts. An increase of the diastereoselectivity is observed with the size of the substituent from the H to Me_3Si, H < Br < Me_3C < Me_3Si, **10(*M*)**−**13(*M*)**, reaching a *cis:trans* ratio of 90:10. Catalysts with bulkier substituents, Et_3Si or Ph_3Si, **14(*M*)** and **15(*M*)**, respectively, gave low diastereoselectivities. The enantioselectivities increase for the *cis* isomer (1*S*, 2*R*) and decrease for the *trans* isomer (1*S*, 2*S*) from catalysts **10(*M*)** to **13(*M*)**. Low enantioselectivities are obtained with catalysts **14(*M*)** and **15(*M*)**; in both cases the ee for the *trans* isomer, **3**, corresponds to the (1*R*, 2*R*) enantiomer, with an

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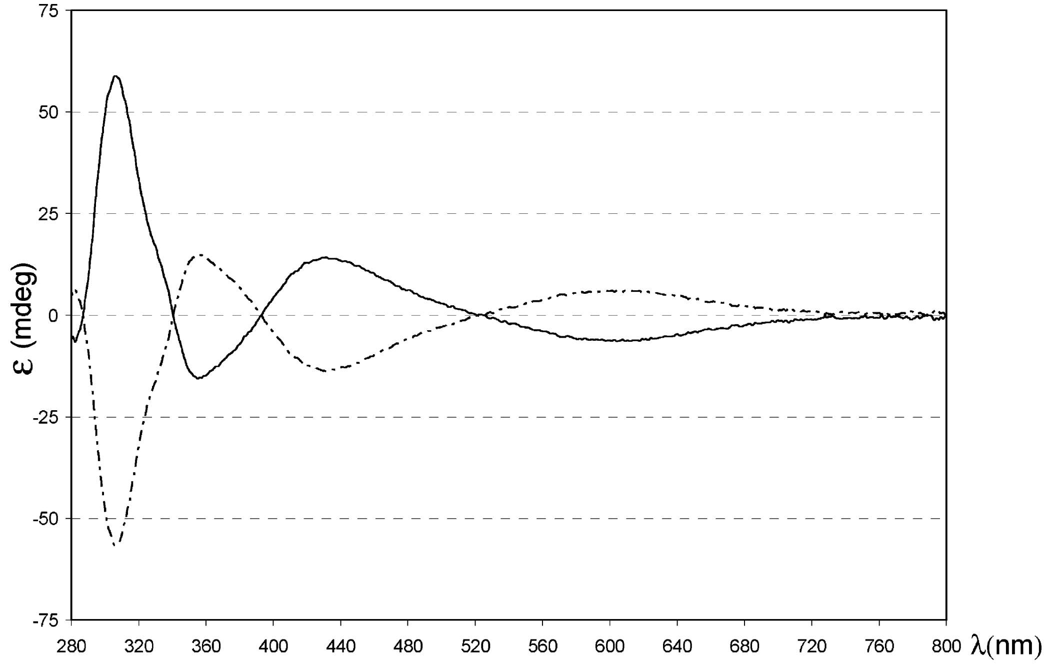


Figure 2. CD spectra of enantiomers **13(*M*)** (solid curve) and **13(*P*)** (dashed curve). 5 × 10^{-5} M in $CDCl_3$.

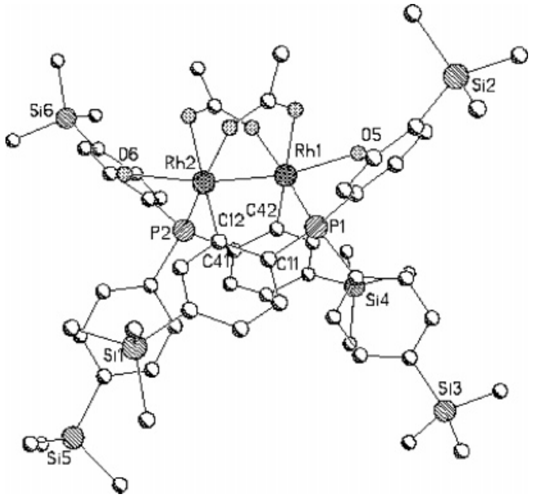


Figure 3. Molecular diagram for $Rh_2(O_2CMe)_2[(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2]_2\cdot 2MeCO_2H$, **5**. Hydrogen atoms are omitted for clarity. Only the oxygen atoms bonded to rhodium and corresponding to the $MeCO_2H$ axial molecules have been drawn. Selected bond distances (Å) are: Rh1−R2 = 2.5116(6), Rh1−P1 = 2.2019(16), Rh1−C42 = 2.005(6), Rh2−P2 = 2.2078(17), Rh2−C12 = 2.004(6), Rh2−O6 = 2.326(4). Selected angles (°) are: O6−Rh2−Rh1 = 170.21(12), C12−Rh2−Rh1 = 97.05(2), C42−Rh1−Rh2 = 97.42(19), O5−Rh1−Rh2 = 167.87(13), P1−Rh1−Rh2 = 88.59(5), P2−Rh2−Rh1 = 87.92(5).

inversion of the enantioselectivity. Catalyst **15(*M*)** shows the highest yield for this catalytic reaction.

The best diastereo- and enantioselectivities are reached when the catalyst contains *p*-Me_3Si substituents in the metalated phosphine, **13(*M*)**. A *cis:trans* ratio of 90:10 and an ee of 91% for the (1*S*, 2*R*) isomer, obtained in 39% yield, are observed.

Catalyst **15(*M*)**, very insoluble in *n*-pentane, has been recovered and used for a second catalytic cycle. The results showed high yield, poor diastereoselectivity, and a decrease in the enantioselectivity, Table 1.

The observed high enantio- and diastereoselectivities for **2** with catalysts **12(*M*)** and **13(*M*)** can be rationalized on the basis of the model depicted in Figure 5. For *M*-catalysts, the nonmetalated aryl groups of the phosphine and also the metalated aryl group with bulky substituents limit the possible orientations of the coordinated carbene. As a result, the orientation A_1 in Figure 5, placing the ester group of the carbene at the less sterically demanding quadrant in the neighborhood of the carboxylate ligands, will be favored compared to the opposite orientation, B_1. The high enantiocontrol observed for these *ortho*-metalated dirhodium(II) catalysts has previously been attributed[15,16] to a discrimination between the cyclopropanation pathways resulting from intermediates A_1 and B_1. With the introduction of relatively bulky substituents in the phosphines, the approaching of the olefin will be restricted to intermediates A_2 and A_3, Figure 5. The steps $A_1 \rightarrow A_2$ and $A_1 \rightarrow A_3$ are no longer equally favored. In the $A_1 \rightarrow A_3$ step,

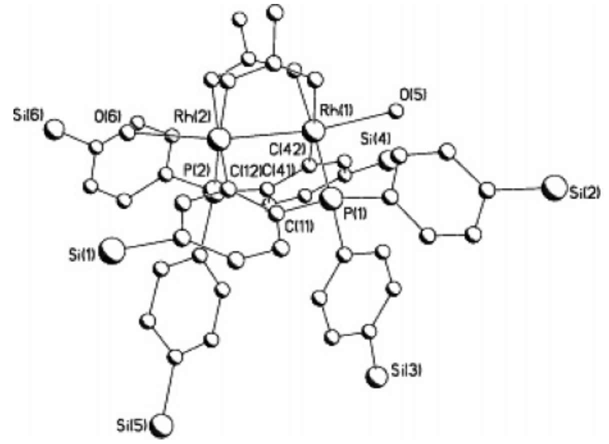


Figure 4. Schematic molecular diagram for $Rh_2(O_2CMe)_2[(p\text{-}Ph_3SiC_6H_3)P(p\text{-}Ph_3SiC_6H_4)_2]_2\cdot 2MeCO_2Et$, **7**. All the phenyl groups concerning $SiPh_3$ moieties have been omitted for clarity, together with the hydrogen atoms. Only the oxygen atoms bonded to rhodium and corresponding to the $MeCO_2Et$ axial molecules have been drawn. Selected bond distances (Å) are: Rh1−Rh2 = 2.683(2), Rh1−P1 = 2.274(4), Rh1−C42 = 1.955(13), Rh2−P2 = 2.1410(3), Rh2−C12 = 2.052(14), Rh2−O6 = 2.444(10). Selected angles (°) are: O6−Rh2−Rh1 = 168.9(2), C12−Rh2−Rh1 = 101.0(4), C42−Rh1−Rh2 = 102.4(5), O5−Rh1−Rh2 = 171.6 (4), P1−Rh1−Rh2 = 84.80(12), P2−Rh2−Rh1 = 83.65(12).

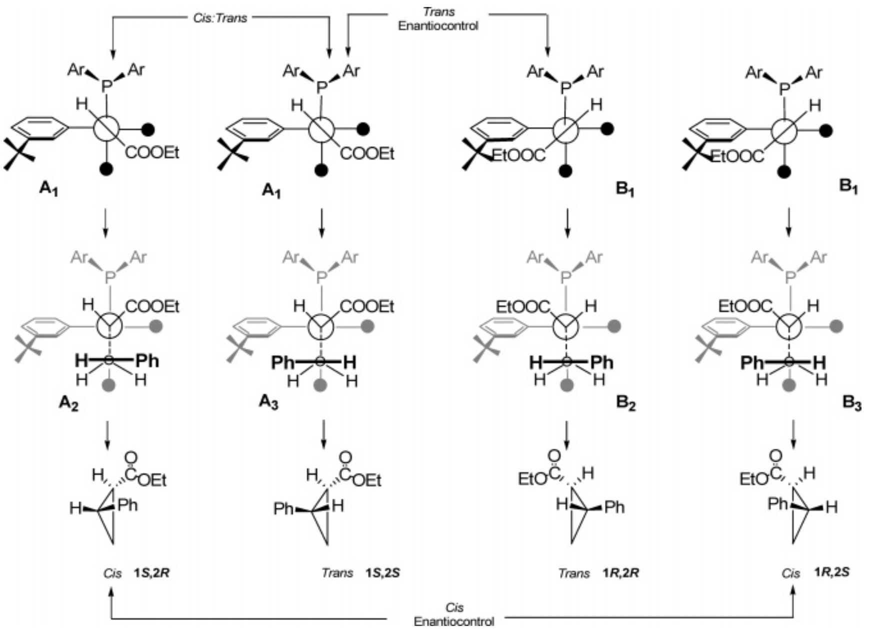


Figure 5. Projection of coordinated carbene on a (*M*)-dirhodium complex along the Rh−Rh axis. Model for the cyclopropanation of styrene.

Table 1. Asymmetric Cyclopropanation of Styrene Catalyzed by (*M*)-Enantiomers in *n*-Pentane as Solvent[a]

			% ee		configuration	
catalyst	yield, %[b]	*cis*:*trans*[c]	**2**[d]	**3**[d]	**2**[e]	**3**[e]
10(*M*)	55	48:52	91	87	1*S*, 2*R*	1*S*, 2*S*
11(*M*)[f]	80	53:47	84	81	1*S*, 2*R*	1*S*, 2*S*
12(*M*)[f]	46	83:17	81	3	1*S*, 2*R*	1*S*, 2*S*
13(*M*)[f]	39	90:10	91	7	1*S*, 2*R*	1*S*, 2*S*
14(*M*)	11	68:32	51	9	1*S*, 2*R*	1*R*, 2*R*
15(*M*)	85	52:48	26	26	1*S*, 2*R*	1*R*, 2*R*
15(*M*)[g]	92	52:48	12	17	1*S*, 2*R*	1*R*, 2*R*

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), and 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.[41] [f] See ref 16. [g] Second cycle.

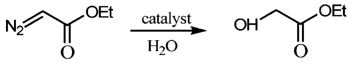
a repulsive interaction between the phenyl ring of the approaching olefin and the substituents on the metalated ring occurs at a certain moment of the process. This discrimination can explain the increasing diastereoselectivity with the bulkiness of the phosphine substituent, from H to Me_3Si.

The transition state data proposed by Davies et al.[32] allowed us to carry out a simple molecular modeling study that supports this model.[33]

There is not a clear explanation for the low enantioselectivities and the inversion of the configuration observed in *trans* isomer **3** when catalysts with substituents bulkier than Me_3Si in the phosphines are used. We can suppose that it is due to steric factors. The intermediates A_2 and B_2, with less interaction between the bulky substituents and the phenyl group of the styrene, offer the best orientation to produce the cyclopropanation products.

In Water as Solvent. The catalytic cyclopropanation of the styrene developed in water has a biphasic nature. Charette et al.[23] consider that in this reaction the hydrophobic catalyst is into the styrene layer, and at the same time, the ethyl diazoacetate, quite soluble in water, slowly diffuses into this layer. The catalytic reaction occurs in the organic layer.

Scheme 2. O-H Insertion Reaction



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The use of amphiphilic compounds in water produces a micellar system that appears to be homogeneous because of the formation of colloidal size aggregates; however, the absorbed reactants are in a microheterogeneous two-phase system. The micellar effect can produce an acceleration or inhibition of one chemical reaction performed in an aqueous medium. Micellar-forming surfactants have been considered in some two-phase systems better phase transfer reagents than short-chain amphiphiles.[34]

The catalyst **13(*M*)** produced a highly diastereo- and enantioselective cyclopropanation of styrene with ethyl diazoacetate in *n*-pentane. These results prompted us to study its catalytic reactivity in water as reaction medium to improve the reaction yield. The catalytic reactions were performed at room temperature using different addition times of the ethyl diazoacetate neat or dissolved in 3 mL of water. The results are presented in Table 2.

When the reaction is performed under aqueous conditions, *cis*- and *trans*-(EtOOC)(H)C=C(H)(COOEt), **16**, was formed as well as the O−H insertion adduct **17**,[35] Scheme 2. When 83 μL of ethyl diazoacetate was dissolved in 6 mL of water, 40% of the alcohol was formed within 2 h. The percentages of the byproducts, **16** and **17**, are also included in Table 2.

When the catalytic reaction was run in water, the yields obtained are higher than in *n*-pentane, up to 61% versus 39% (Table 2, entries 1−3). The *cis*:*trans* ratio dropped to 71:29 instead of 90:10 obtained in *n*-pentane, and the ee of 90% (1*S*, 2*R*) was comparable, being higher for enantiomer (1*S*, 2*S*), 43%

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Table 2. Asymmetric Cyclopropanation of Styrene Catalyzed by 13(*M*) in Water as Solvent[a]

entry	H_2O,[b] mL	addition time (min)	surfactant	yield, %[c]	*cis*:*trans*[d]	ee 2[e,f] 1*S*, 2*R*	ee 3[e,f] 1*S*, 2*S*	**16**,[g] %	**17**,[g] %
1	3	120		50	69:31	80	30	6	44
2	3	60		61	66:33	80	30	9	30
3	3	5		57	71:29	90	43	5	38
4		<1		10	80:20	85	21	65	25
5	3	60	SDS	44	69:31	70	8	16	40
6	3	5	SDS	57	82:18	91	33	14	29
7		<1	SDS	8	75:25	89	30	62	30
8	3	60	Cetyl[h]	41	70:30	79	34	11	48
9	3	5	Cetyl[h]	40	75:25	85	18	26	34
10		<1	Cetyl[h]	12	86:14	90	25	45	43

[a] Styrene (2 mmol), ethyl diazoacetate (0.8 mmol), and chiral catalyst (8×10^{-3} mmol), room temperature. [b] mL of water added to 83 μL of ethyl diazoacetate. [c] Cyclopropanation yield based on diazoacetate. [d] Determined by GC analysis and ^{1}H NMR. [e] ee values were based on GC analysis with a 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldimethylsilyl-beta-CDX column. [f] Configuration was determined by correlation of the sign of the rotation of polarized light with that of the known enantiomer.[41] [g] Determined by ^{1}H NMR. [h] Cetyltrimethylammonium hydrogen sulfate.

versus 7% (Table 2, entry 3). The competing OH insertion is favored; the alcohol, **17**, was obtained with yields up to 44% (Table 2, entry 1).

The diastereoselectivity increased until 80% in *cis* isomer when neat ethyl diazoacetate was quickly added (Table 2, entry 4). The ee for isomer (1*S*, 2*R*) was kept high, 80%, but a decrease was observed for isomer (1*S*, 2*S*), 21%. The yield dropped to 10% because of the formation of the dimer in a higher yield, 60%.

The catalytic reaction has also been studied under micellar conditions by adding a surfactant to the aqueous medium. The anionic surfactant sodium dodecyl sulfate, SDS, or the cationic cetyltrimethylammonium hydrogen sulfate was tested. The results are included in Table 2, entries 5−10.

The best diastereoselectivity, *cis*:*trans* ratio of 86:14, was achieved using cetylmethylammonium hydrogen sulfate as surfactant and with a quick addition of pure ethyl diazoacetate. The ee for isomer (1*S*, 2*R*) was 90%. The yield is only 12% (Table 2, entry 10). Using SDS, a *cis*:*trans* ratio of 82:18 with good ee for (1*S*, 2*R*), 91%, and a yield of 57% were obtained (Table 2, entry 6). The use of surfactants led us to improve the diastereoselectivity of the catalytic reaction, 86:14 versus 90:10, reached in *n*-pentane as solvent.

High ee for enantiomer (1*S*, 2*R*) was observed using water as solvent or in aqueous micellar conditions (Table 2, entries 3, 6, and 10). These values were comparable with those obtained when the catalytic reaction was performed in *n*-pentane.

Using surfactants, a slight increase in the dimer formation, **16**, was observed (Table 2, entries 5, 6, 8, and 9). The surfactants were good phase transfer reagents and allowed a better diffusion of the ethyl diazoacetate from the water to the organic phase, favoring the dimer formation.

The catalytic cyclopropanation of styrene in water or in micellar conditions gives better yields and is faster than in *n*-pentane. The reaction was run at room temperature, and the increase of the temperature did not favor the reaction.

(+)-NLE. We have studied the variation of the enantioselectivity for the *cis* isomer, (1*S*, 2*R*), when pure enantiomer **13(*M*)** was progressively contaminated with the enantiomer **13(*P*)**. The reactions were run in CH_2Cl_2 and *n*-pentane as solvents.

The results represented in Figure 6 show a plot of ee (%) obtained for (1*S*, 2*R*) versus the enantiomeric purity of **13(*M*)** going from 100 to 0% (racemate). When the catalytic reaction was run in CH_2Cl_2, a straight line was observed as expected. The ee for (1*S*, 2*R*) decreased in a linear fashion until 0, values corresponding to the use of the racemate as catalyst. When the solvent used was *n*-pentane, a concave curve was observed. This result represents a situation where values of the ee for (1*S*, 2*R*) were higher than those predicted, and consequently we have a (+)-NLE.

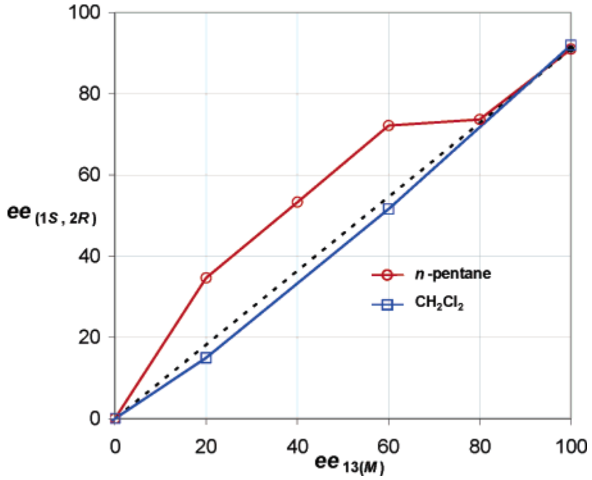

Figure 6. Plot of the $ee_{(1S,\ 2R)}$ (%) versus the enantiomeric purity of **13(*M*)** (%).

The **13(*M*)**:**13(*P*)** mixtures in *n*-pentane containing more than 10% of **13(*P*)** produced precipitates that were not observed in CH_2Cl_2, Figure 7.

The solid obtained in a mixture containing 70% **13(*M*)** and 30% **13(*P*)** ($ee_{13(M)} = 40$) was filtered and used as catalyst in a cyclopropanation reaction of styrene developed in CH_2Cl_2; the ee for the isomer (1*S*, 2*R*) was 1%. The solid behaved as an asymmetric inactive catalyst. The filtered liquid was evaporated until dryness, and the solid obtained was also tested in the reaction, now giving 85% ee and favoring the (1*S*, 2*R*) isomer.

The basic condition for the appearance of NLE was summarized by Kagan,[36] saying that "the generation of diastereomeric species is the key feature that gives deviation from linearity". In our case, we can considerer the competitive formation of an unreactive precipitate containing equal amounts of each antipode. This effect is known as the "reservoir effect".[26]

When **13(*M*)** and **13(*P*)** were mixed in a 90:10 ratio, no precipitate was observed in *n*-pentane, Figure 7. The representative point for the $ee_{1S,2R}$ in Figure 6 follows the linearity; the (+)-NLE was observed only for higher ratios in **13(*P*)**.

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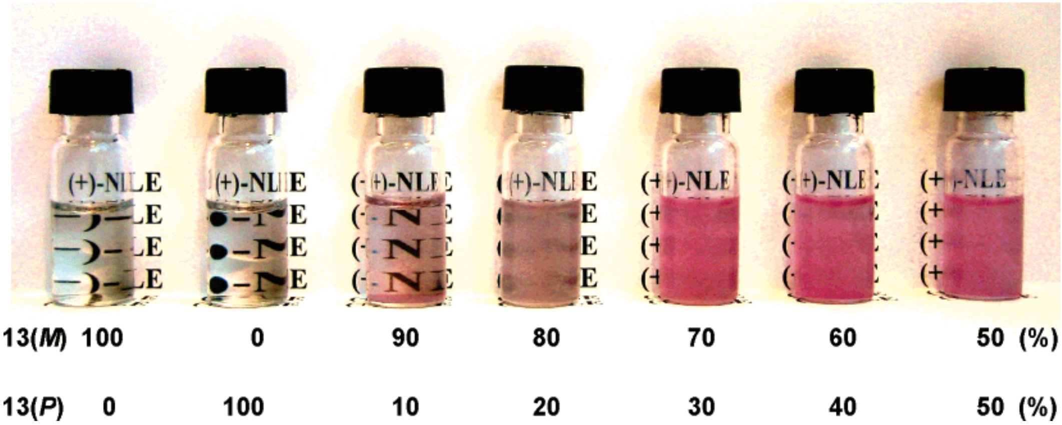

Figure 7. Formation of a precipitate with various **13(*M*)**:**13(*P*)** ratios.

Conclusions

The results indicate that *ortho*-metalated dirhodium(II) compounds with aryl phosphines containing bulky *para*-substituents can produce high diastereo- and enantioselectivities in the intermolecular cyclopropanation of styrene. The diastereoselectivities reached for ethyl-*cis*-2-arylcyclopropanecarboxylate clearly exceed those previously observed with other dirhodium(II) catalysts for this particular model reaction. With substituents bulkier than Me_3Si, a lack of diastereo- and enantioselectivities is observed.

The results also indicate that the asymmetric cyclopropanation of styrene using chiral dirhodium(II) catalyts and water as solvent is possible with good results. Diastereo- and enantioselectivities comparable to those obtained in *n*-pentane are reached when in the presence of (***M***)-$Rh_2(O_2CCF_3)_2[(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2]_2$ as catalyst the catalytic reaction is performed in aqueous micellar conditions.

The (+)-NLE observed for the (1*S*, 2*R*) isomer in the cyclopropanation reaction of styrene using as catalyst (*M*)-$Rh_2(O_2CCF_3)_2[(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2]_2$ progressively contaminated by the enantiomer *P* shows that the catalyst does not need to be 100% enantiomerically pure to reach high ee.

Experimental Section

General Considerations. Commercially available $Rh_2(O_2CMe)_4\cdot(MeOH)_2$ was purchased from Pressure Chemical Co. $P(C_6H_5)_3$, $P(p\text{-}Me_3CC_6H_4)_3$, CF_3CO_2H, styrene, and ethyl diazoacetate were used as purchased. All solvents were of analytical grade. *N*-*p*-Tolylsulfonyl-L-proline (ProtosH),[37] $Rh_2(O_2CMe)_2[(C_6H_4)P(C_6H_5)_2]_2$ $2MeCO_2H$,[13] (*M*)-$Rh_2(O_2CCF_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot 2CF_3CO_2H$, $Rh_2(O_2Me)_2[p\text{-}Me_3CC_6H_3)P(p\text{-}Me_3CC_6H_4)_2]_2\cdot 2MeCO_2H$, (*M*)-$Rh_2(O_2CCF_3)_2[p\text{-}Me_3CC_6H_3)P(p\text{-}Me_3CC_6H_4)_2]_2\cdot 2H_2O$,[15] $P(p\text{-}BrC_6H_4)_3$, $P(p\text{-}Me_3SiC_6H_4)_3$, $P(p\text{-}Et_3SiC_6H_4)_3$, and $P(p\text{-}Ph_3SiC_6H_4)_3$[38−40] 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 specified otherwise. All reactions were carried out in oven-dried glassware under argon atmosphere, although the isolated solids are air-stable.

Instrumentation. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at 25 °C in $CDCl_3$ unless otherwise indicated. ^1H 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 (Hz). Elemental analyses were provided by Centro de Microanalisis Elemental, Universidad Complutense de Madrid. Circular dichroism were measured on a JASCO J-810 spectropolarimeter. The ee values were based on GC analysis with a 2,3-di-*O*-acetyl 6-*O*-*tert*-butyldimethylsilyl beta CDX column.

Synthesis of $Rh_2(O_2CMe)_2(PC)_2\cdot 2MeCO_2H$ Compounds. The $Rh_2(O_2CMe)_2(PC)_2\cdot 2MeCO_2H$ compounds were obtained by standard methods described in the literature.[13]

$Rh_2(O_2CMe)_2[(p\text{-}BrC_6H_3)P(p\text{-}BrC_6H_4)_2]\cdot 2MeCO_2H$ (4). Yield: 70%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.30 (s, 6H), 2.22 (s, 6H), 6.47 (m,2H), 6.61 (m, 4H), 6.98 (d, $J = 8$ Hz, 2H), 7.31 (m, 4H), 7.50 (m, 4H), 7.55 (m, 4H), 7.65 (m, 2H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): 22.48 (s, CH_3), 22.77 (s, CH_3), 124.77 (s), 124.93 (s), 130.10 (d, $J = 37$ Hz), 130.86 (s), 131.00 (s), 132.03 (d, $J = 12$ Hz), 133.57 (s), 133.77 (s), 134.80 (s), 135.18 (s), 135.33 (s), 140.74 (d, $J = 16$ Hz), 143.36 (d, $J = 75$ Hz), 168.22 (m, metalated C), 180.84 (s), 182.25 (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 21.8 ppm (d, $J = 163$ Hz). Anal. Calcd (%) for $C_{44}H_{36}Br_6O_8P_2Rh_2$: C 36.19, H 3.14. Found: C 36.57, H 3.23.

$Rh_2(O_2CMe)_2[(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2]\cdot 2MeCO_2H$ (5). Yield: 65%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ −0.03 (s, 18H), 0.20 (s, 18H), 0.24 (s, 18H), 1.15 (s, 6H), 2.11 (s, 6H), 6.38 (dd, $J = 10$ Hz, $J = 7$ Hz, 2H), 6.82 (m, 6H), 7.08 (d, $J = 5$ Hz, 2H), 7.17 (m, 4H), 7.51 (m, 4H), 7.61 (m, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): −1.39 (s), −1.20 (s), −1.15 (s), 22.46 (bs, CH_3), 125.93 (d, $J = 9$ Hz), 131.87 (s), 132.21 (s), 132.73 (d, $J = 8$ Hz), 133.53 (d, $J = 10$ Hz), 133.89 (d, $J = 45$ Hz), 139.96 (s), 140.72 (s), 141.42 (s), 143.04 (d, $J = 15$ Hz), 146.72 (d, $J = 73$ Hz), 163.64 (m, metalated C), 189.85 (s), 181.39 (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 19.07 ppm (AA′XX′ system). Anal. Calcd (%) for $C_{62}H_{90}O_8P_2Rh_2Si_6$: C, 53.59; H, 6.38. Found: C, 52.80; H, 6.54.

Single crystals of **5** suitable for X-ray diffraction methods were obtained by crystallization in a CH_2Cl_2−hexane−acetic acid mixture.

$Rh_2(O_2CMe)_2[(p\text{-}Et_3SiC_6H_3)P(p\text{-}Et_3SiC_6H_4)_2]\cdot 2MeCO_2H$ (6). Yield: 85%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.82 (m, 36H), 0.96 (m, 54H), 1.28 (s, 6H), 2.13 (s, 6H), 6.69 (m, 4H), 7.12 (m, 4H), 7.49 (m, 10H), 7.63 (m, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): 3.30 (s, CH_3), 3.32 (s, CH_3), 3.55 (s, CH_3), 7.40 (s, CH_2), 7.48 (s, CH_2), 7.69 (s, CH_2), 22.30 (s, CH_3), 22.89 (d, $J = 3$ Hz), 126.78 (d, $J = 8$ Hz), 130.97 (d, $J = 9$ Hz), 131.48 (d, $J = 2$ Hz), 132.94 (d, $J = 47$ Hz), 134.09 (d, $J = 11$ Hz), 134.65 (d, $J = 45$ Hz), 137.42 (d, $J = 2$ Hz), 137.91 (d, $J = 2$ Hz), 138.32

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(d, $J = 2$ Hz), 142.66 (d, $J = 2$ Hz), 143.41 (d, $J = 15$ Hz), 147.75 (d, $J = 72$ Hz), 163.67 (m, metalated C), 179.13 (s, CO_2), 181.21 (d, $J = 2$ Hz, CO_2). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 17.8 ppm (AA′XX′ system). Anal. Calcd (%) for $C_{80}H_{126}O_8P_2Rh_2Si_6$: C, 58.16; H, 7.6. Found: C, 57.65; H, 7.8.

$Rh_2(O_2CMe)_2[(p\text{-}Ph_3SiC_6H_3)P(p\text{-}Ph_3SiC_6H_4)_2]\cdot 2MeCO_2H$ (7). Yield: 52%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.44 (s, 6H), 1.86 (s, 6H), 6.50 (m, 2H), 6.60 (m, 4H), 6.83 (m, 2H), 6.95 (d, $J = 7$ Hz, 4H), 7.14 (m, 28H), 7.31 (m, 28H), 7.41 (m, 32H), 7.54 (m, 12H), 7.78 (m, 2H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): 21.8 (s, CH_3), 24.0 (s, CH_3), 124.7 (s), 124.9 (s), 130.2 (d, $J = 37$ Hz), 130.9 (s), 131.0 (s), 132.0 (d, $J = 12$ Hz), 133.6 (s), 133.8 (s), 134.8 (s), 135.2 (s), 135.6 (s), 140.7 (d, $J = 16$ Hz), 143.4 (d, $J = 75$ Hz), 168.2 (m, metalated C), 180.8 (s), 182.3 (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 14.7 ppm (bd, $^1J_{Rh-P} = 143$ Hz). Anal. Calcd (%) for $C_{152}H_{126}O_8P_2Rh_2Si_6$: C, 72.54; H, 5.01. Found: C, 71.94; H, 5.08.

Single crystals of **7** suitable for X-ray diffraction methods were obtained by crystallization in an ethyl acetate−hexane mixture.

Synthesis of Enantiomerically Pure $Rh_2(O_2CCF_3)_2(PC)_2$ Compounds. The enantiomerically pure compounds as trifluoroacetate derivatives have been obtained following the procedure described in the literature.[14,15]

$Rh_2(O_2CCF_3)_2[(p\text{-}BrC_6H_3)P(p\text{-}BrC_6H_4)_2]$ (11(*M*)). Yield: 20%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.55(m, 2H), 6.65 (m, 6H), 7.10 (m, 2H), 7.35 (m, 4H), 7.45 (m, 4H), 7.55 (m, 4H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 114.78 (q, $J = 289$ Hz), 125.35 (d, $J = 4$ Hz), 125.91 (d, $J = 12$ Hz), 127.95 (s), 128.43 (s), 131.46 (t, $J = 10$ Hz), 133.71 (d, $J = 9$ Hz), 134.20 (s), 134.68 (d, $J = 10$ Hz), 140.80 (m), 142.81 (d, $J = 77$ Hz), 164.40 (m, metalated C), 166.86 (q, $J = 39$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 18.8 ppm (bd $^1J_{P-Rh} = 167$ Hz).$^{19}F\{^1H\}$ NMR (376.0 MHz, $CDCl_3$, 298 K): −76.4 ppm (s, CF_3). Anal. Calcd (%) for $C_{40}H_{22}Br_6F_6O_4P_2Rh_2$: C, 33.63; H, 1.54. Found: C, 32.82; H, 1.46.

$Rh_2(O_2CCF_3)_2[(p\text{-}Me_3SiC_6H_3)P(p\text{-}Me_3SiC_6H_4)_2]$ (13(*M*) and 13(*P*)). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ −0.01 (s, 9H), 0.21 (s, 9H), 0.24 (s, 9H), 6.42 (dd, $J = 10$ Hz, $J = 8$ Hz, 2H), 6.84 (m, 4H), 6.93 (m, 4H), 7.23 (m, 4H), 7.49 (m, 8H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): −1.48 (s), −1.27 (s), 114.90 (q, $J = 288$ Hz), 124.20 (d, $J = 38$ Hz), 126.94 (d, $J = 8$ Hz), 127.64 (d, $J = 10$ Hz), 130.95 (s), 131.60 (s), 132.71 (m), 141.84 (d, $J = 18$ Hz), 142.90 (d, $J = 9$ Hz), 146.35 (d, $J = 74$ Hz), 159.80 (m, metalated C), 166.00 (q, $J = 39$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 15.47 ppm (bd, $J = 162$ Hz). $^{19}F\{^1H\}$ NMR (376.0 MHz, $CDCl_3$, 298 K): −75.22 ppm (s, CF_3).

13(*M*). Yield: 32%. Anal. Calcd (%) for $C_{58}H_{76}F_6O_4P_2Rh_2Si_6$: C, 50.02; H, 5.48. Found: C, 50.32; H, 5.64.

13(*P*). Yield: 25%. Anal. Calcd (%) for $C_{58}H_{76}F_6O_4P_2Rh_2Si_6$: C, 50.02; H, 5.48. Found: C, 49.99; H, 5.55.

$Rh_2(O_2CCF_3)_2[(p\text{-}Et_3SiC_6H_3)P(p\text{-}Et_3SiC_6H_4)_2]$ (14(*M*)). The product is so soluble in the normal solvents that it cannot be precipitated and has only been characterized by spectroscopy methods. Yield: 19%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.65 (m, 18H), 0.87 (m, 27H), 6.23 (dd, $J = 10$ Hz, $J = 8$ Hz, 2H), 6.65 (dd, $J = 11$ Hz, $J = 8$ Hz, 4H), 6.82 (dd, $J = 6$ Hz, $J = 1$ Hz, 2H), 7.00 (m, 4H), 7.17 (m, 4H), 7.35 (m, 6H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 2.23 (bs, CH_3), 2.41 (s), 6.28 (s), 6.38 (s), 6.57 (s), 114.19 (q, $J = 288$ Hz), 126.74 (d, $J = 8$ Hz), 129.42 (d, $J = 38$ Hz), 131.05 (d, $J = 4$ Hz), 131.50 (d $J = 4$ Hz), 132.09 (d, $J = 47$ Hz), 132.10 (d, $J = 23$ Hz), 132.08 (d, $J = 5$ Hz), 132.54 (d, $J = 10$ Hz), 138.00 (s), 138.90 (s), 141.70 (d, $J = 15$ Hz); 144.97 (d, $J = 72$ Hz), 159.59 (m, metalated C) 165.20 (q, $J = 37$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 14.60 ppm (bd, $J = 162$ Hz). $^{19}F\{^1H\}$ NMR (376.0 MHz, $CDCl_3$, 298 K): −77.2 ppm (s, CF_3).

$Rh_2(O_2CCF_3)_2[(p\text{-}Ph_3SiC_6H_3)P(p\text{-}Ph_3SiC_6H_4Si)_2]$ (15(*M*)). Yield: 37%. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 6.80 (d, $J = 6$ Hz, 4H), 7.02 (m, 6H)), 7.20 (m, 22H), 7.36 (m, 22H), 7.41 (m, 30H), 7.52 (m, 26H), 7.63 (d, $J = 6$ Hz, 2H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 115.43 (q, $J = 287$ Hz), 127.85 (s), 127.95 (s), 129.53 (s), 129.72 (d, $J = 6$ Hz), 131.82 (d, $J = 8$ Hz), 133.22 (d, $J = 7$ Hz), 133.40 (s), 133.64 (s), 135.08 (d, $J = 10$ Hz), 135.75 (m), 136.10 (s), 136.35 (s), 143.90 (d, $J = 68$ Hz), 161.20 (m, metalated C) 166.47 (q, $J = 36$ Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ 14.82 ppm (bd, $J = 146$ Hz). $^{19}F\{^1H\}$ NMR (376.0 MHz, $CDCl_3$, 298 K): −75.47 (s, CF_3). Anal. Calcd (%) for $C_{148}H_{112}F_6O_4P_2Rh_2Si_6$: C, 70.98; H, 4,48. Found: C, 70.56; H, 4.69.

Catalytic Intermolecular Cyclopropanation. In *n*-Pentane as Solvent. 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 pentane (5 mL) to a refluxing solution of *n*-pentane (15 mL) containing the dirhodium(II) complex (1 mol %) and styrene (230 μL 2.0 mmol) in the same solvent. After complete addition, the reaction mixture was stirred at reflux for 2 h and cooled to room temperature. The resulting solution was filtered through a short plug of silica to remove the catalyst, and the solvent was evaporated under reduced pressure.

In Water as Solvent. Different solutions of diazoacetate (83 μL)−water (Table 2) were added to a mixture of the dirhodium(II) complex (1 mol %) and styrene (230 μL) in water (3 mL) at room temperature. After the addition the reaction was stirred for half an hour. The solution was treated with a saturated solution of NaCl (5 mL) and extracted with ethyl ether (4 × 5 mL). The organic layer was dried over Na_2SO_4, filtered, and dried under reduced pressure.

In both cases the yield of the reaction was calculated by ^1H and ^{13}C NMR 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.

(+)-NLE. Each catalyst (12.4 mg, 8.3×10^{-3} mmol) was prepared mixing **13(*M*)** and **13(*P*)** enantiomers in the ratio indicated in each experiment. All the catalytic reactions were performed as indicated for *n*-pentane solvent in the Experimental Section.

X-ray Crystallographic Study. X-ray crystal structure data for compound 5: $C_{58}H_{86}O_8P_2Si_6Rh_2\cdot 2H_2O$, triclinic, space group $P\bar{1}$, $a = 15.0100(2)$ Å, $b = 15.8590(10)$ Å, $c = 16.2240(2)$ Å, $\alpha = 106.0690(6)°$, $\beta = 92.0150(7)°$, $\gamma = 94.9480(6)°$, $V = 3690.26(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.216$ g cm^{-3}, crystal dimensions 0.27 × 0.25 × 0.23 mm^3; Kappa CCD 2000 diffractometer; Cu Kα radiation, 293(2) K; 16 847 reflections, 13 141 independent ($\mu = 5.305$ mm^{-1}); refinement (on F^2) with SHELXTL-NT (version 6.1), 686 parameters, 0 restraint, $R_1 = 0.0951$ ($I > 2\sigma$) and wR_2 (all data) = 0.2540, GOF = 1.140. CCDC 242554.

X-ray crystal structure data for compound 7: $C_{156}H_{136}O_8P_2Si_6Rh_2$, monoclinic, space group $C2/c$, $a = 45.216(9)$ Å, $b = 31.596(6)$ Å, $c = 25.500(5)$ Å, $\beta = 122.17(3)°$, $V = 30837(11)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.109$ g cm^{-3}, crystal dimensions 0.28 × 0.25 × 0.23 mm^3; Kappa CCD diffractometer; Mo Kα radiation, 293(2) K; 44 109 reflections, 12 069 independent ($\mu = 0.332$ mm^{-1}); refinement (on F^2) with SHELXTL-NT (version 6.1), 1422 parameters, 2264 restraints, $R_1 = 0.1226$ ($I > 2\sigma$) and wR_2 (all data) = 0.3394, GOF = 1.397. There is a very high thermal motion associated with some degree of disorder over two sites in some of the phenyl rings, as commonly observed in phenyl ring substituents on Ph_3Si ligands.

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Supporting Information Available: A simple molecular modeling study for the intermediates A_2 and A_3 on the model depicted in Figure 5 and circular dichroism graphics for compounds **10(*M*)**, **11(*M*)**, **13(*M*)−15(*M*)**, **10(*P*)**, and **13(*P*)**. Crystallographic data of compounds **5** and **7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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