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Asymmetric inter- and intramolecular cyclopropanations of alkenes catalyzed by rhodium D_4-porphyrin: a comparison of rhodium- and ruthenium-centred catalysts

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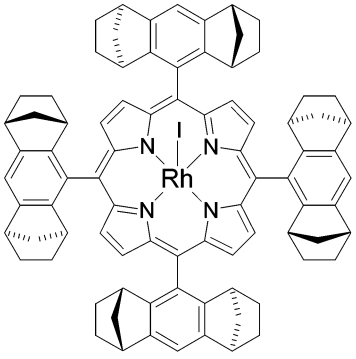
Abstract—Iodo-(5,10,15,20-tetrakis(1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl)porphyrinatorhodium(III), designated as [Rh(P*)(I)], was prepared and its catalytic activity in the asymmetric cyclopropanation of alkenes with ethyl diazoacetate (EDA) was examined. High catalyst turnovers (TON $>10^3$) and moderate enantioselectivities (up to 68% ee) were observed. However, the obtained *trans*/*cis* ratios are low. Competition experiments revealed that electron-donating substituents on styrene accelerate the cyclopropanations. The $\log(k_X/k_H)$ versus σ^+ plot for substituted styrenes exhibits a good linearity with a small negative ρ^+ value (–0.14). [Rh(P*)(I)] is also active in the intramolecular cyclopropanation of allyl diazoacetates. A comparison between rhodium and ruthenium porphyrin complexes was made.

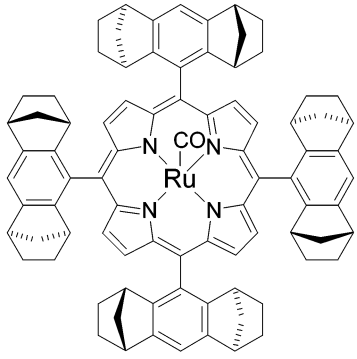
1. Introduction

Because of the utility of cyclopropanes as building blocks for the construction of organic molecules, there has been much interest in the synthesis of chiral cyclopropanes from achiral starting materials.[1] Chiral metal complexes, particularly those of copper(I) and rhodium(II), have been widely used as catalysts for asymmetric cyclopropanations.[2,3] In general, metalloporphyrins provide robust catalysts for group- and atom-transfer reactions[4] and the use of metalloporphyrins to catalyze alkene cyclopropanations has made important advances in recent years.[5–8]

The catalytic activity of rhodium porphyrins toward carbene transfer reactions was first reported by Callots.[5a,b] Subsequently, Kodadek and co-workers reported the asymmetric version of alkene cyclopropanations with chiral rhodium porphyrin catalysts.[6a,c] While thousands



[Rh(P*)(I)]



[Ru(P*)(CO)]

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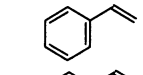
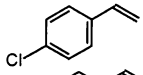
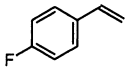
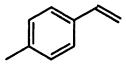
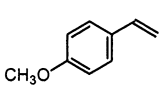
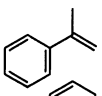
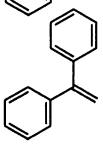
of turnovers of the cyclopropane products can be obtained, the enantioselectivity is generally poor. For example, the cyclopropanation of styrene with the iodorhodium(III) catalysts containing the 'chiral wall'[6a] and 'chiral fortress'[6c] porphyrins produce *cis*-cyclopropyl ester in 10 and 15% ee, respectively. Recently, Che and Berkessel independently reported that high ee values (up to 90%) of *trans*-cyclopropyl ester can be obtained with the [Ru(P*)(CO)] catalyst.[7a,c] It is therefore of interest to prepare the rhodium(III) complex with the D_4 porphyrin ligand and compare its performance with that of [Ru(P*)(CO)]. Herein, we report our findings on the use of [Rh(P*)(I)] in intermolecular and intramolecular cyclopropanation.

2. Results and discussion

The D_4-porphyrin, H_2P^*, was synthesized according to the literature procedure.[9] The rhodium catalyst [Rh^{III}(P*)I] used in this work was prepared from tetracarbonylbis(μ-chloro)dirhodium in 37% yield. Asymmetric cyclopropanation of various styrenes with EDA were performed in CH_2Cl_2 at 40°C in the presence of [Rh(P*)(I)]. The results are summarized in Table 1. Similar to other rhodium porphyrin systems, all the turnovers with [Rh(P*)(I)] are >1000. For styrene the ee of the *trans*- and *cis*-cyclopropyl esters are 61 and 36%, respectively, which are much higher than those obtained with Kodadek's catalyst, though a lower *trans*/*cis* ratio of 1:1.5 was obtained.[6a,c] The results using [Ru(P*)(CO)] as catalyst for comparison are summarized in Table 1. In contrast to the high *trans*/*cis* ratios and high ee values for *trans*-isomers produced by [Ru(P*)(CO)], reactions with [Rh(P*)(I)] have lower *trans*/*cis* ratios and low ee values for *trans*-cyclopropane products. However, [Rh(P*)(I)] gave a significant amount of *cis*-isomer with higher ee than that obtained with [Ru(P*)(CO)] catalyst. Another important observation is that the absolute configuration of the major enantiomers in the Rh porphyrin-catalyzed reactions (*trans*-(1*S*,2*S*) and *cis*-(1*S*,2*R*)), are the same as those from Ru porphyrin-catalyzed reactions. All other styrene derivatives gave similar observations.

To find out more about the active intermediate in the reaction, the relative rates of cyclopropanation of substituted styrenes using [Rh(P*)(I)] with EDA were determined through competition experiments. The reaction was enhanced by electron-donating groups but retarded by electron-withdrawing groups. A Hammett plot of $\log(k_X/k_H)$ versus $\sigma(+)$ is shown in Fig. 1. Good $\sigma(+)$ correlation is obtained with a very small ρ^+ of

Table 1. Comparative yields and enantioselectivities of [Rh(P*)(I)]- and [Ru(P*)(CO)]-catalyzed intermolecular cyclopropanation of alkenes

Substrate	[Rh(P*)(I)]				[Ru(P*)(CO)][a]			
	Yield (%)	*trans*/*cis*	ee (%)		Yield (%)	*trans*/*cis*	ee (%)	
			trans	*cis*			*trans*	*cis*
	66	1.5	61[b] (1*S*,2*S*)	36[b] (1*S*,2*R*)	83	17.8	86 (1*S*,2*S*)	4 (1*S*,2*R*)
	81	1.2	62[c] (1*S*,2*S*)	20[c] (1*S*,2*R*)	66	23.1	90 (1*S*,2*S*)	4 (1*S*,2*R*)
	72	0.9	62[d](1*S*,2*S*)	33[d] (1*S*,2*R*)	–	–	–	–
	71	1.2	49[b] (1*S*,2*S*)	42[b] (1*S*,2*R*)	78	18.0	81 (1*S*,2*S*)	9 (1*S*,2*R*)
	83	1.6	68[b] (1*S*,2*S*)	44[b] (1*S*,2*R*)	61	15.3	85 (1*S*,2*S*)	8 (1*S*,2*R*)
	75	1.0	46[d]	46[d]	69	3.0	87	35
	78	–	32[b]		76	–	81	

[a]Results for [Ru(P*)(CO)] have been reported previously.[7b] [b]Determined by chiral HPLC (Daicel OJ). [c]Determined by GC-MS after conversion to the L-menthyl ester. [d]Determined by Chiral GC (Cyclodex B, 25m).

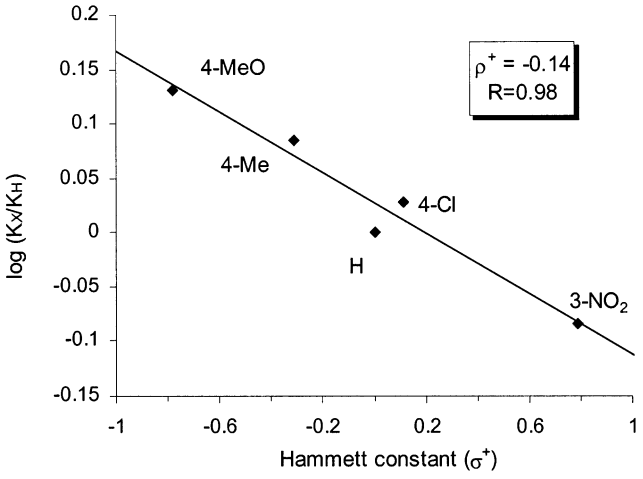


Figure 1. Log(k_X/k_H) versus σ^+ plot for [Rh(P*)(I)]-catalyzed cyclopropanation of substituted styrenes with EDA.

–0.14. This value is lower than that of [Ru(P*)(CO)] (–0.44)[7b] and much lower than that of copper(I) terpyridine (–0.79)[10] and copper(I) tris(pyrazolyl) borate (–0.85)[11] reported previously. The negative value supports formation of an electrophilic metal–carbene complex intermediate with a small positive charge build-up at the benzylic carbon in the transition state. This may also indicate an early transition state compared with other catalytic systems.

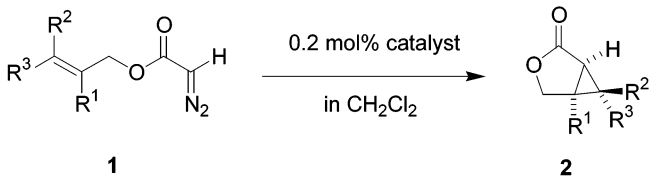
Recently, we reported the first metalloporphyrin-catalyzed intramolecular cyclopropanation of alkenes using [Ru(P*)(CO)].[7b] Using [Rh(P*)(I)], we studied similar catalytic reactions and the results are shown in Table 2 (see Scheme 1). Most of the substrates were smoothly converted to the corresponding lactones in moderate to good yields, with no detectable side products by ^{1}H NMR and GC–MS analyses of the crude reaction mixture after removal of the solvent. At least several hundred turnovers of the cyclopropane product were obtained in each case. However, only moderate enantioselectivities were observed. The best enantioselectivity comes from allylic acetates **1c** and **1j**, which gave 49 and 48% ee, respectively. Nonetheless, these results indicate that the catalytic system reported here could be extended to the cyclization of unsaturated diazoacetates in which the double bond is mono-, di-, and tri-substituted with alkyl and aryl groups. The results using [Ru(P*)(CO)] as catalyst are included in Table 2. A very interesting aspect when comparing [Rh(P*)(I)] and [Ru(P*)(CO)] is that the former smoothly converts α-substituted diazoacetates to the corresponding lactones in good yields and with moderate enantioselectivities, while there is no reaction with [Ru(P*)(CO)] even when the reaction was carried at 40°C. Also, lower stereochemical induction was observed for allylic acetate **1d** with both catalysts. The product *cis*:*trans* ratios are 2.8 and 0.75 with [Rh(P*)(I)] and [Ru(P*)(CO)], respectively, which might indicate the formation of an intermediate which can lead to loss of stereochemistry.

Catalyst [Ru(P*)(CO)] induced good yield and high enantioselectivity in the catalytic intramolecular cyclopropanation of **1g** (77% yield and 85% ee). However, its activity and enantioselectivity dropped dramatically in reactions with diazoacetates bearing a methyl or ethyl group at the R^3 position (**1e**,**f**). Another important finding is that with **1g**, [Ru(P*)(CO)] gave the opposite enantiomer as the major product when compared with [Rh(P*)(I)]. In fact, if we compare the absolute configuration of the products formed from different allylic acetates, some dependence of the steric influences of the olefinic substituents on the absolute configuration of the bicyclic lactones has been found. The absolute configuration of lactones **2a** formed from allylic acetate **1a** with [Rh(P*)(I)] and [Ru(P*)(CO)] catalysts are both

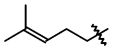
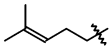
Table 2. Comparative yields and enantioselectivities of [Rh(P*)(I)]- and [Ru(P*)(CO)]-catalyzed intramolecular cyclopropanation of **1a–j**

Allylic diazoacetate **1**	Cyclopropane **2**	[Rh(P*)(I)]		[Ru(P*)(CO)][a]	
		Yield (%)	Ee (%)[b,c]	Yield (%)	Ee (%)[b,c]
a	**a**	23	20 (1*R*,5*S*)	48	24 (1*R*,5*S*)
b	**b**	79	24 (1*R*,5*S*)	nd[d]	–
c	**c**	59	49 (1*R*,5*S*)[e]	nd[d]	–
d	**d**	31	31 (1*S*,5*R*)	18	22 (1*S*,5*R*)
	g	11	11 (1*R*,5*S*)	24	57 (1*S*,5*R*)
e	**e**	33	24 (1*R*,5*S*)	67	28 (1*S*,5*R*)
f	**f**	78	25 (1*R*,5*S*)[e]	63	22 (1*S*,5*R*)[e]
g	**g**	84	20 (1*R*,5*S*)[e]	77	85 (1*S*,5*R*)[e]
h	**h**	81	37 (1*R*,5*S*)	65	36 (1*R*,5*S*)
i	**i**	89	12 (1*R*,5*S*)	82	18 (1*R*,5*S*)
j	**j**	65	48 (1*R*,5*S*)	85	30 (1*R*,5*S*)

[a] Some of the results for [Ru(P*)(CO)] have been reported previously.[7b]
[b] Enantiomeric excesses were determined by a chiral GC column: Chiraldex G-TA, 30 m.
[c] Absolute configurations were assigned by comparing the elution orders of enantiomers reported by Doyle.[13]
[d] Not determined.
[e] Absolute configurations were assigned by comparing the elution orders with those of a similar allylic diazoacetate.



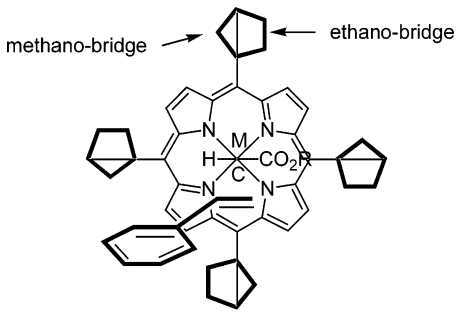
1 2

	R^1	R^2	R^3
a	H	H	H
b	Me	H	H
c	Ph	H	H
d	H	Ph	H
e	H	H	Me
f	H	H	Et
g	H	H	Ph
h	H	Me	Me
i	H	Me	
j	H		Me

Scheme 1.

(1*R*,5*S*) whereas for allylic acetates having substituents at R^2 (**1d**), the absolute configuration of lactones are both (1*S*,5*R*). For allylic acetates with substituents at both R^2 and R^3 (**1h–j**), both [Rh(P*)(I)] and [Ru(P*)(CO)] gave lactone products with the (1*R*,5*S*) configuration only. However, the absolute configuration of lactones formed from allylic acetates having substituent at R^3 (**1e–g**) have opposite configuration when [Rh(P*)(I)] and [Ru(P*)(CO)] were used. For example, with a Ph group at the R^3 position (**1g**), the configuration of the lactone formed from [Ru(P*)(CO)] and [Rh(P*)(I)] are (1*S*,5*R*) and (1*R*,5*S*), respectively.

The mechanism of the rhodium porphyrin-catalyzed cyclopropanation has been studied by Kodadek and co-workers.[6b,e] An intermediate complex observed at –40°C, identified as the diazonium ion adduct was found to be inactive in the cyclopropanation. Although the mechanism is still elusive, a Rh porphyrin carbene complex had been proposed as the active intermediate[6b,e] though such a species has never been isolated or properly characterized. However, X-ray crystal structures of chiral Ru(II)–[7b] and Os(II)–porphyrin carbene complexes[5e] were recently reported. If we assume that the Rh(III)– and Ru(II)–porphyrin catalysts react with EDA in the intermolecular cyclopropanation reactions to form active metallocarbene intermediates with similar structures, the alkene should approach the active metallocarbene complexes from either the *si* or *re* face as represented by **3** and **4**, respectively (which are viewed along the M–C bond axis of the presumed metallocarbene). In these two cases, the C–H bond of the metallocarbene bisects the N–Rh–N angle. The enantioselectivity of the intermolecular alkene cyclopropanation is determined by the interaction between the chiral porphyrin ligand and the substituents on the alkene as it approaches the metallocarbene center in the transition state. In **3**, the reacting double bond approaches the carbene from the less hindered *re* face of the rhodium carbene moiety. On the other hand, the reacting double bond approaches the carbene from the more hindered *si* face of the rhodium carbene in **4**. If the orientations of the double bond with respect to the face of the catalyst are the same in **3** and **4**, these two spatial arrangements necessarily lead to the formation of enantiomeric cyclopropyl lactones. Furthermore, based on the intermolecular cyclopropanation



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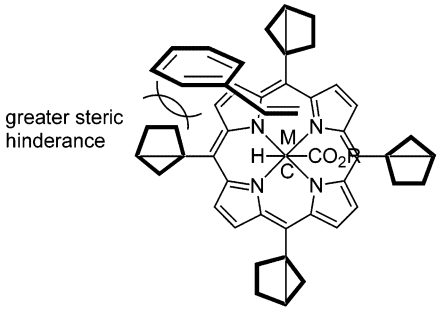

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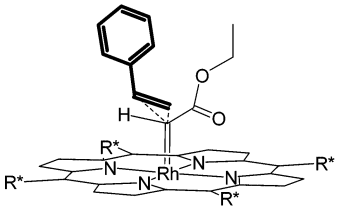
results, the observed enantioselectivity and stereoselectivity of the Rh–porphyrin-catalyzed reactions is consistent with the alkene approach trajectories depicted in representations **5** and **6**. In both cases, the alkene approaches the carbene in a perpendicular fashion. These proposals are consistent with the mechanism previously proposed.[6b,e]



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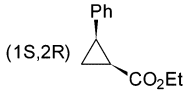

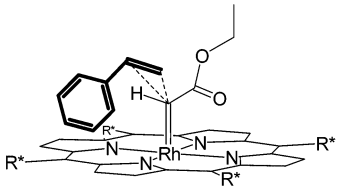

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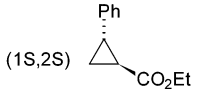
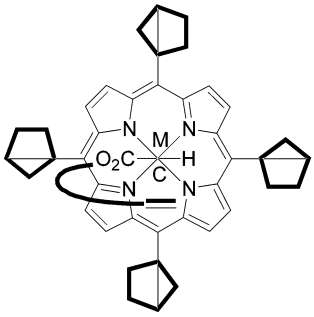


In intramolecular cyclopropanation, if allylic acetate **1** reacts with metalloporphyrin to form active metallocarbene intermediates, there should be two possible configurations **7** and **8**. In **7**, the reacting double bond approaches the carbene from the less hindered *re* face of the rhodium carbene bond. On the other hand, the reacting double bond approaches the carbene from the more hindered *si* face of the rhodium carbene bond in **8**. If the orientations of the double bond with respect to the face of the catalyst are the same in **7** and **8**, these two spatial arrangements necessarily lead to the formation of enantiomeric cyclopropyl lactones.

According to the intramolecular cyclopropanation results, we propose that the selectivities for allylic cyclopropanations observed with catalyst [Rh(P*)(I)] are consistent with the alkene approach trajectories depicted in representations **9** and **10**. In these two representations, the carbon–carbon double bond of the substrate approaches to the carbene centre perpendicular to the metal carbene bond. For *cis*-disubstituted and trisubstituted allylic diazoacetates, configuration **9** should be favored, as the interaction of the R^2 group with the catalyst face is very pronounced in **10**. *trans*-Disubstituted allylic diazoacetates should favor **10** because interactions of the R^1 and R^3 groups with the catalyst face are most pronounced in **9**. For ruthenium–porphyrin-catalyzed reactions, the absolute configurations of the products obtained are the same with rhodium–porphyrin catalyst except for *trans*-disubstituted allylic diazoacetates. Since the enantioselectivities observed with this class of substrates are low, we do not want to speculate about the mechanism of the reaction at the moment. Work studying the mechanism of the ruthenium porphyrin-catalyzed cyclopropanation reaction is now underway.



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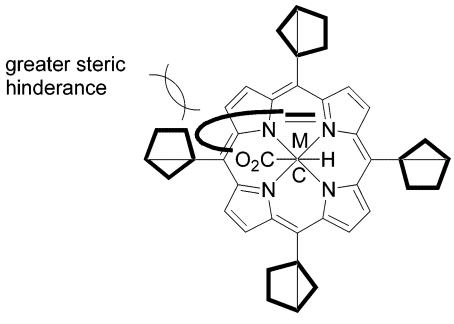

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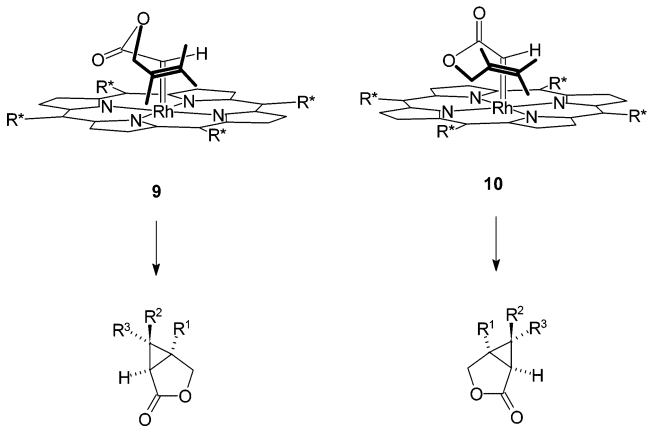

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3. Conclusion

The intermolecular cyclopropanations catalyzed by [Rh(P*)(I)] proceed in good yields with moderate to good enantioselectivities. Moderate enantioselectivities were observed for intramolecular cyclopropanation of allylic diazoacetate using [Rh(P*)(I)] as catalysts. The reactivities of the Ru and Rh catalysts using the same chiral D_4 porphyrin are quite different. The metal-dependant 'switch' in enantioselectivity for the *trans*-allyl diazoacetate indicates that the catalysts might react through a different mechanism.

4. Experimental

4.1. Materials

Tetracarbonylbis(μ-chloro) dirhodium and ethyl diazoacetate were purchased from Strem and Aldrich, respectively. H_2P^* was prepared according to the literature method.[9] Alkenes are purified by either vacuum distillation or chromatography just prior to use. Allylic and homoallylic diazoacetates were prepared according to the literature procedure.[12]

4.2. Preparation of [Rh(P*)I]

A mixture of H_2P^* (50 mg), tetracarbonylbis(μ-chloro) dirhodium (50 mg) and anhydrous sodium carbonate (100 mg) in decalin (20 ml) was heated under reflux under an inert atmosphere for 2 days. An orange fraction was obtained by column chromatography with CH_2Cl_2 as eluent. To the concentrated solution, iodine (50 mg) was added. The mixture was stirred at room temperature for 6 h. Removal of the solvent gave a brown solid, which was washed and purified by column chromatography with toluene as the eluent. A red orange solid characterized as Rh(P*)I was obtained in 37% yield. +ve FAB MS: m/z cluster at 1371(M^+), 1244(M^+–I); UV–vis/CH_2Cl_2 λ_{max} (log ε): 526(18), 412(94), 374(35), 296(39); IR (KBr): 2959.9, 2920.1, 2867.7, 1701.03, 1295.6, 1015.71; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05–1.50 (m, 32H), 1.75–1.96 (m, 16H), 2.62–2.65 (m, 3H), 2.72–2.75 (m, 2H), 2.88–2.91 (m, 3H), 3.49–3.62 (m, 8H), 7.35 (s, 4H), 8.63–8.78 (m, 8H). Anal. calcd for $C_{84}H_{76}N_4RhI{\cdot}2H_2O{\cdot}CH_3CN$: C, 71.31; H, 5.78; N, 4.83. Found: C, 71.45; H, 6.10; N, 4.72%.

4.3. General procedure for catalytic cyclopropanation

A typical procedure is given for the reaction of styrene with EDA in the presence of [Rh(P*)(I)] (catalyst:EDA:substrate = 1:2000:10000). The reaction was carried out under nitrogen. A solution of [Rh(P*)(I)] (2 mg, 2.45 μmol) and styrene (2.65 g, 25.4 mmol) in dichloromethane (10 ml) was stirred at ambient temperature for 30 min. To the mixture was added EDA (0.58 g, 5.08 mmol) dropwise with the aid of a syringe pump over a period of 8 h and the mixture was stirred for a further period of ca.12 h. The *trans*/*cis* ratio was determined by GC–MS after purification by flash column chromatography (15:1 hexane:Et_2O as eluent).

4.4. General procedure for cyclopropanation of allylic diazoacetates in the presence of [Ru(P*)(CO)]

A solution of the allylic diazoacetate (0.25 mmol) in anhydrous CH_2Cl_2 (6 mL) was added dropwise to a stirred solution of catalyst [Ru(P*)(CO)] (0.2 mol%) in CH_2Cl_2 (1.5 mL) at room temperature. During this time the initial red-orange color of the reaction solution imparted by [Ru(P*)(CO)] catalysts become brown. After addition was complete, the reaction mixture was then stirred for about 15 h under a nitrogen atmosphere. The crude product was purified by flash chromatography eluting with hexane/ Et_2O mixtures. GC–MS and NMR analyses were performed to characterize the product.

4.5. General procedure for cyclopropanation of allylic diazoacetates in the presence of [Rh(P*)(I)]

A solution of the diazoacetate (0.25 mmol) in anhydrous CH_2Cl_2 (6 mL) was added dropwise to a well-stirred solution of Rh(P*)(I) catalyst (0.2 mol%) in CH_2Cl_2 (1.5 mL) at 40°C. Over this time the initial light brown color of the Rh(P*)(I) catalysts often turned dark brown. After addition was complete, the reaction mixture was then stirred for about 15 h under a nitrogen atmosphere. The crude product was purified by flash chromatography eluting with hexane/Et_2O mixtures. GC–MS and ^{1}H NMR analyses were performed to characterize the product.

4.6. Ee analysis and comparison of absolute configurations of intramolecular cyclopropanation products

4.6.1. (1α,5α)-3-Oxabicyclo[3.1.0]hexan-2-one, 1a. Enantiomer separation was carried out on a 30 m Chiraldex G-TA column operated at 80°C for 2 min and then programmed to 150°C at 1°C/min: 50.8 min for the (1*R*,5*S*) enantiomer, 54.8 min for the (1*S*,5*R*) enantiomer.

4.6.2. (1α)-5α-Methyl-3-oxabicyclo[3.1.0]hexan-2-one, 1b. Enantiomer separation was carried out on a 30 m Chiraldex G-TA column operated at 110°C: 44.6 min for the (1*S*,5*R*) enantiomer, 45.8 min for the (1*R*,5*S*) enantiomer.

4.6.3. (1α)-5α-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one, 1c. Enantiomer separation on a 30 m Chiraldex G-TA column operated at 125°C: 243.6 min and 251.7 min for two enantiomers.

4.6.4. (1α,5α)-6α-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one, 1d. The two diastereomers were separated by column chromatography on silica gel using hexane/ Et_2O (1:1). Enantiomeric excess for each diastereomer was determined using a 30 m Chiraldex G-TA column operated at 150°C: (i) for *trans* isomer: 88.3 min for the (1*S*,5*R*) enantiomer, 96.6 min for the (1*R*,5*S*) enantiomer; for *cis* isomer: 86.4 min and 92.1 min for the two enantiomers.

4.6.5. (1α,5α)-6β-Methyl-3-oxabicyclo[3.1.0]hexan-2-one, 1e. Enantiomer separation was carried out on a 30 m Chiraldex G-TA column operated at 120°C: 35.1 min and 36.3 min for the two enantiomers.

4.6.6. (1α,5α)-6β-Ethyl-3-oxabicyclo[3.1.0]hexan-2-one, 1f. Enantiomer separation was carried out on a 30 m Chiraldex G-TA column operated at 140°C: 20.1 min and 21.5 min for two enantiomers; 11 and 6% ee, respectively; ^{1}H NMR (300 MHz) δ 4.41 (dd, 1H), 4.15 (d, 1H), 2.30–2.18 (comp, 2H), 1.48–1.38 (m, 2H), 1.12–1.05 (m, 3H).

4.6.7. (1α,5α)-6β-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one, 1g. Enantiomer separation was carried out on a 30 m Chiraldex G-TA column operated at 150°C: 91.15 min for the (1*S*,5*R*) enantiomer and 99.7 min for the (1*R*,5*S*) enantiomer.

4.6.8. (1α,5α)-6,6-Dimethyl-3-oxabicyclo[3.1.0]hexan-2-one, 1h. Enantiomer separation was carried out on a 30 m Chiraldex G-TA column operated at 120°C: 16.6 min for the (1*S*,5*R*) enantiomer, 21.4 min for the (1*R*,5*S*) enantiomer.

4.6.9. (1α,5α)-6α-Methyl-6β-(4-methyl-3-penten-1-yl)-3-oxabicyclo[3.1.0]hexan-2-one, 1i. Enantiomer separation was carried out on a 30 m Chiraldex G-TA column operated at 150°C: 62.4 min for the (1*S*,5*R*) enantiomer and 67.9 min for the (1*R*,5*S*) enantiomer.

4.6.10. (1α,5α)-6β-Methyl-6α-(4-methyl-3-penten-1-yl)-3-oxabicyclo[3.1.0]hexan-2-one, 1j. Enantiomer separation was carried out on a 30 m Chiraldex G-TA column operated at 150°C: 59.3 min for the (1*S*,5*R*) enantiomer and 63.8 min for the (1*R*,5*S*) enantiomer.

4.7. General procedure for competition reactions

To a two-necked round-bottomed flask were added [Rh(P*)I] (0.05 mol%), styrene (2.5 mmol) and substituted styrene (2.5 mmol) in dichloromethane (2 ml) under nitrogen. The solution was stirred at ambient temperature for 30 min. Ethyl diazoacetate (1 mmol) in dichloromethane (1 ml) was added dropwise to the reaction mixture. The mixture was allowed to stir for 12 h at room temperature. The ratios of the resulting cyclopropanes were determined by GC analysis.

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