Highly Enantioselective Intermolecular Cyclopropanation Catalyzed by Dirhodium(II) Tetrakis[3(*S*)-phthalimido-2-piperidinonate]: Solvent Dependency of the Enantioselection

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Abstract: The enantioselectivity in cyclopropanations catalyzed by dirhodium(II) tetrakis[3(*S*)-phthalimido-2-piperidinonate] has been found to be substantially improved by employing ether as the rarely used solvent. Cyclopropanations of styrenes or 1,1-disubstituted alkenes with 2,4-dimethyl-3-pentyl diazoacetate in ether are promoted by this catalyst to afford the corresponding cyclopropane products in the highest levels of enantioselectivity (up to 98% ee) reported to date for the dirhodium(II)-catalyzed intermolecular cyclopropanation reactions.

Since the pioneering work of Nozaki and Noyori[1] with chiral salicylaldiminatocopper(II) complexes as cyclopropanation catalysts in 1966, the development of a catalytic, asymmetric cyclopropanation of prochiral alkenes with diazoacetates has been the subject of intensive studies in the field of asymmetric synthesis.[2] Consequently, an enormous amount of effort has been focused on the design, synthesis, and evaluation of asymmetric cyclopropanation catalysts, wherein cobalt,[3] copper,[4-10] ruthenium,[11,12] and rhodium[13-19] complexes of rationally designed chiral ligands have recently been devised. Of these catalysts, chiral copper(I) catalysts bearing C_2-symmetric nitrogen ligands[9,20] such as semicorrin[5] and bis(oxazoline)[6-8] ligands originally developed by Pfaltz,[5] Masamune,[6] and Evans[7] have proven to be by far the most successful for asymmetric cyclopropanations of various alkenes with chiral or even achiral diazoacetates (up to 99% ee), while the bis(oxazolinyl)pyridine-ruthenium(II) complex of Nishiyama[11] has been demonstrated to provide an exceptionally high order of *trans*-selectivities as well as similarly high enantioselectivities in cyclopropanation of 1-alkenes as the foregoing copper(I) catalysts. With respect to chiral dirhodium(II) catalysts, the dirhodium(II) carboxamidate complexes pioneered by Doyle[13] have proven to be the catalysts of choice for intramolecular enantioselective cyclopropanations of diazoacetates and diazoacetamides,[14] but less effective for intermolecular counterparts,[15] while the dirhodium(II) prolinate complexes initially developed by McKervey[16] have been demonstrated by Davies[17] to be uniquely suited to enantioselective and diastereoselective intermolecular cyclopropanation of selected alkenes with vinyldiazoacetates as the substitute for diazoacetates.

Our efforts in this area led to the development of dirhodium(II) tetrakis[3(*S*)-phthalimido-2-piperidinonate], Rh_2[(*S*)-PTPI]$_4$, the dirhodium(II) core of which is surrounded by four bridging amide ligands with two oxygen and two nitrogen donor atoms bound to each octahedral rhodium in a *cis* configuration as shown in Figure 1.[21] The efficacy of this catalyst was demonstrated by cyclopropanation of styrenes with *d*-menthyl diazoacetate in up to 90% de, wherein the stereochemical outcome was rationalized by evaluating an asymmetric environment at the rhodium(II) carbene center featured by the two protruding phthalimido walls. However, the enantioselective version with achiral diazoacetates resulted in modest enantioselectivities. Herein, we wish to report that this goal has been achieved by employing ether as the rarely used solvent, thereby giving the cyclopropane products in the highest levels of enantioselectivity (up to 98% ee) reported to date for the dirhodium(II)-catalyzed intermolecular cyclopropanation reactions.

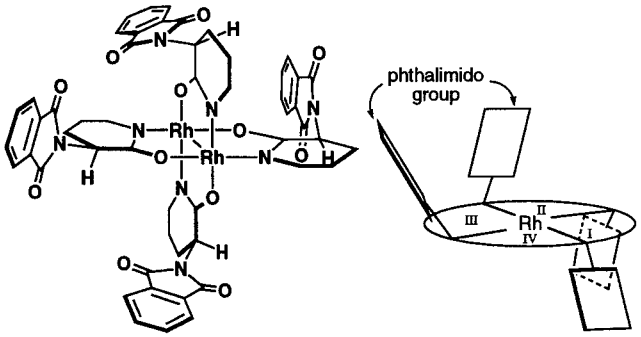
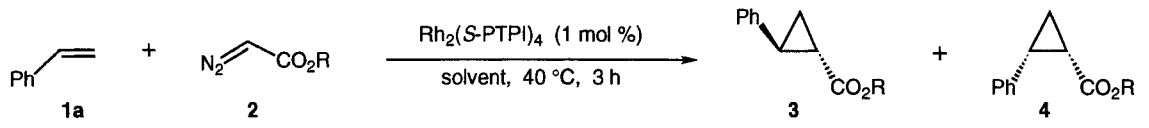


Figure 1. Schematic representation of Rh_2(*S*-PTPI)$_4$

In order to realize highly enantioselective cyclopropanation, we explored the effects of solvent on the enantioselectivity through cyclopropanation of styrene (**1a**) with 2,4-dimethyl-3-pentyl diazoacetate (**2a**), based on the previous studies with CH_2Cl_2.[21] Some representative results are presented in Table 1. To our delightful surprise, the use of ethereal solvents such as ether, THF, and DME was found to provide a mixture of *trans*- and *cis*-cyclopropane products **3a** and **4a** in high enantioselectivities (entries 5, 9, and 10), wherein ether exhibited the highest selectivity (up to 98% ee) reported to date for the dirhodium(II)-catalyzed intermolecular cyclopropanation reactions (entry 5). In contrast, the conventionally used solvents such as CH_2Cl_2, $(CH_2Cl)_2$, and $CHCl_3$ displayed poor to modest enantioselectivities (entries 1-3), while the use of benzene resulted in just high enantioselectivities (entry 4). The composite results demonstrate that solvent effects on enantioselectivity are dramatic while the diastereoselectivity is modest and virtually unaltered in all cases. It should be noted that ethereal solvents have been rarely used in this type of reactions.[22] While the beneficial effects of ether have yet to be elucidated, it is also worthy of note that a major improvement in enantioselectivity could be observed with the ethyl, *t*-butyl, and dicyclohexylmethyl diazoacetates (**2b-d**) by switching the reaction solvent from CH_2Cl_2 to ether (entries 6-8).[23] Following the general trend in this field, a steady increase in enantioselectivity was observed on increasing the steric bulk of the ester alkyl group, and the value obtained using **2a** was found to be by far the highest. As a closely related precedent, it is of particular interest to note that Davies and co-workers have recently reported that the enantioselectivity in cyclopropanation with vinyldiazoacetates or methyl phenyldiazoacetate catalyzed by dirhodium(II) tetrakis[*N*-(4-dodecylphenylsulfonyl)-(*S*)-prolinate] could be significantly enhanced by changing the solvent from CH_2Cl_2 to pentane.[17,18]

With the optimized conditions for enantioselective cyclopropanation developed, we next turned our attention to an applicability of the present protocol to other alkenes than styrene (**1a**), and the results are summarized in Table 2. As is evident from the table, it has now been demonstrated that Rh_2[(*S*)-PTPI]$_4$-catalyzed cyclopropanation featured by the combinational use of 2,4-dimethyl-3-pentyl diazoacetate (**2a**) as a carbene source and ether as a solvent can be successfully extended to a variety of alkenes including *p*-substituted styrenes **1b** and **1c**, (*E*)-1-

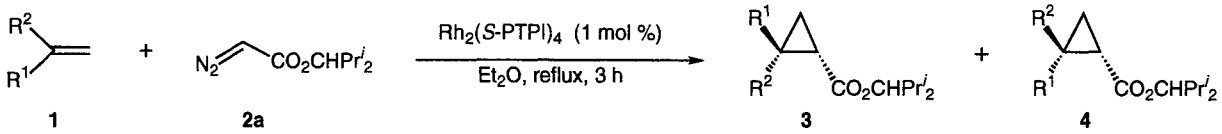
Table 1. Effects of Solvent and Ester Group on Enantioselectivities in Rh_2(*S*-PTPI)$_4$-Catalyzed Cyclopropanation of Styrene with Diazoacetates[a]



		diazoacetate **2**		*trans*-cyclopropane **3**				*cis*-cyclopropane **4**			
entry	solvent		R		% yield		% ee[b]		% yield		% ee[b]
1	CH_2Cl_2	**2a**	$CHPr^i_2$	**3a**	54		49	**4a**	19		63
2	$(CH_2Cl)_2$	**2a**	$CHPr^i_2$	**3a**	46		42	**4a**	20		59
3	$CHCl_3$	**2a**	$CHPr^i_2$	**3a**	47		7	**4a**	28		22
4	benzene	**2a**	$CHPr^i_2$	**3a**	29		79	**4a**	15		76
5	Et_2O	**2a**	$CHPr^i_2$	**3a**	54		98	**4a**	19		96
6	Et_2O	**2b**	Et	**3b**	36	(31)[c]	51 (17)[c]	**4b**	27	(19)[c]	49 (28)[c]
7	Et_2O	**2c**	Bu^t	**3c**	33	(36)[c]	68 (43)[c]	**4c**	32	(33)[c]	66 (41)[c]
8	Et_2O	**2d**	$CH(c\text{-}C_6H_{11})_2$	**3d**	45	(46)[c]	90 (43)[c]	**4d**	19	(16)[c]	90 (41)[c]
9	THF	**2a**	$CHPr^i_2$	**3a**	30		79	**4a**	12		82
10	DME	**2a**	$CHPr^i_2$	**3a**	47		79	**4a**	19		81

[a] All reactions were carried out as previously described (ref. 21). For absolute configuration of the product; see ref. 24. [b] Determined by HPLC (Daicel Chiralcel OJ) after conversion into the corresponding alcohol. [c] The values in parentheses were obtained with CH_2Cl_2 as a solvent

Table 2. Enantioselective Cyclopropanation of Terminal Alkenes in Et_2O[a]



	alkene **1**			*trans*-cyclopropane **3**				*cis*-cyclopropane **4**			
entry		R^1	R^2		% yield	% ee	config[b]		% yield	% ee	config[b]
1	**1b**	*p*-$MeOC_6H_4$	H	**3e**	40	95[c]	1*S*, 2*S*	**4e**	21	97[c]	1*S*, 2*R*
2	**1c**	*p*-ClC_6H_4	H	**3f**	30	98[d]	1*S*, 2*S*	**4f**	28	98[d]	1*S*, 2*R*
3	**1d**	(*E*)-PhCH=CH	H	**3g**	26	96[e]	1*S*, 2*S*	**4g**	29	98[e]	1*S*, 2*R*
4	**1e**	*n*-C_6H_{13}	H	**3h**	37	89[f]	1*S*, 2*S*	**4h**	15	82[f]	1*S*, 2*R*
5	**1f**	Ph	Ph	**3i**	77	95[c]	1*S*				
6	**1g**	Ph	Me	**3j**	43	94[c]	1*S*, 2*S*	**4j**	37	95[c]	1*S*, 2*R*
7[g]	**1h**	Me	Me	**3k**	34	95[h]	1*S*				

[a] Reactions were performed as previously described (ref. 21), unless otherwise stated. [b] For determination, see ref. 24. [c] Determined by HPLC (Daicel Chiralcel OJ or OD) after LAH reduction. [d] Determined by HPLC (Daicel Chiralcel OD) after LAH reduction and acetylation. [e] Determined by HPLC (Daicel Chiralcel OJ) after ozonolysis followed by reductive workup and benzoylation. [f] Determined by ^1H NMR analysis of the corresponding methyl ester in the presence of Eu(hfc)$_3$ for **3h** and (*R*)-MTPA ester of the corresponding alcohol for **4h**. [g] The reaction was carried out in a sealed tube. [h] Determined by HPLC (Daicel Chiralcel OD) after LAH reduction and (*R*)-MTPA esterification

phenylbutadiene (**1d**), 1-octene (**1e**), 1,1-diphenylethylene (**1f**), α-methylstyrene (**1g**), and 2-methylpropene (**1h**). It should be noted that exceedingly high levels of enantioselectivity comparable to those obtained with the foregoing copper(I) catalysts could be attained in all cases except for the case of 1-octene (entry 4). It is of particular interest that virtually similar enantioselectivities were observed with *trans*- and *cis*-cyclopropane products in every case where they were possible except for the case of 1-octene, while the *trans*/*cis* selectivities were generally modest. The preferred absolute stereochemistry at C1 of the cyclopropane products is *S* in all cases[24] as predicted based on the operational model previously proposed.[21] While electronic change on the benzene ring of styrenes **1** had a minimal effect (entries 1 and 2), a slight drop in enantioselectivity observed with 1-octene suggested that the electronic nature of alkenes might be one of the critical factors responsible for high degree of asymmetric induction in the concerted nonsynchronous cyclopropanation generally accepted.[31]

Finally, it must be stated that the present protocol could not be applied to cyclopropanation of *cis*- or *trans*-β-methylstyrene, with less than 5% of cyclopropane products being observed. The limited substrate compatibility, however, may support our operational model,[21] wherein the alkene approaches the rhodium(II) carbene in a parallel orientation[5,9b,11,15b] shown in **A** rather than in a perpendicular orientation[32] shown in **B** relative to the rhodium(II)-carbon axis in the transition state (Figure 2). According to this model, 1,2-disubstituted alkenes are sluggish substrates because one of the alkene substituents in **A** would suffer severe steric interactions with the face of the rhodium(II) carbene complex.[22]

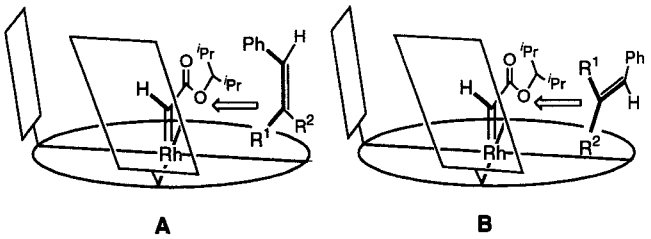


Figure 2. The parallel and perpendicular approaches of the alkene to the rhodium(II) carbene intermediate

In summary, we have realized an exceptionally high order of enantioselectivity in cyclopropanation catalyzed by $Rh_2[(S)\text{-PTPI}]_4$, albeit with the limited substrates (styrenes, (*E*)-1-phenylbutadiene, and 1,1-disubstituted alkenes), wherein the combinational use of 2,4-dimethyl-3-pentyl diazoacetate (**2a**) as a carbene source and ether as a solvent has proven to be crucial to our success. The modification of this catalyst to resolve the critical problem of diastereocontrol is currently in progress.

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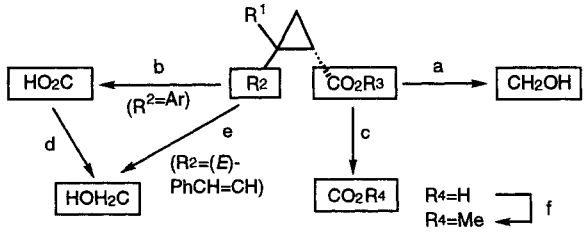
(23) The solvent effect was also observed with *d*-menthyl diazoacetate. The diastereomeric excess was enhanced to 93% in ether from

89% in CH_2Cl_2 for the *trans*-isomer and to 88% in ether from 83% in CH_2Cl_2 for the *cis*-isomer.

(24) Absolute configurations of the products were determined by comparison of the sign of optical rotation after conversion into known compounds. **3a-d** and **4a-d** were converted to (+)-(1*S*,2*S*)- and (+)-(1*S*,2*R*)-2-phenylcyclopropanemethanol,[7a,25] respectively *via* a in Scheme 1. **3e** was converted to (+)-(1*S*,2*S*)-1,2-cyclopropanedicarboxylic acid[26] *via* b and c. Both **4e** and **4g** were converted to (-)-(1*S*,5*R*)-3-oxabicyclo[3.1.0]hexan-2-one[27] *via* b, d, and c for **4e** and *via* e and c for **4g**. **3f** and **4f** were converted to (+)-(1*S*,2*S*)- and (+)-(1*S*,2*R*)-2-phenylcyclopropanemethanol, respectively *via* a followed by dechlorination using Na, *t*-BuOH in THF. **3g** was converted to (+)-(1*S*,2*S*)-methyl 2-hydroxymethylcyclopropanecarboxylate[28] *via* e, c, and f. **3h** and **4h** were converted to (+)-(1*S*,2*S*)- and (+)-(1*S*,2*R*)-2-*n*-hexylcyclopropanecarboxylic acid,[4a] respectively *via* c. **3i** was converted to (+)-(1*S*)-2,2-diphenylcyclopropanemethanol[29] *via* a. **3j** was converted, after epimerization at C1 of **3j**, to (-)-(1*S*,2*R*)-1-methyl-1,2-cyclopropanedicarboxlic acid[30] *via* b and c. **4j** was converted to (+)-(1*R*,2*S*)-1-methyl-1,2-cyclopropanedicarboxlic acid[30] *via* b and c. **3k** was converted to (+)-(1*S*)-2,2-dimethylcyclopropanecarboxylic acid[7a] *via* c.



(a) $LiAlH_4$, THF. (b) $RuCl_3$, $NaIO_4$, CCl_4-CH_3CN-H_2O. (c) KOH, MeOH. (d) BH_3-THF. (e) O_3, MeOH, then $NaBH_4$. (f) CH_2N_2, Et_2O

Scheme 1

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(32) A perpendicular approach has been proposed originally by Callot[33] and later by Kodadek to explain the shape selectivity observed in rhodium(III) porphyrin-catalyzed cyclopropanation.[31c] Recently, Davies and co-workers have also invoked this approach to rationalize the results that vinylcarbenoids typically fail to react with *trans*-alkenes but exhibit high reactivity toward *cis*-alkenes.[17c]

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