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D_2-Symmetric Dirhodium Catalyst Derived from a 1,2,2-Triarylcyclopropanecarboxylate Ligand: Design, Synthesis and Application

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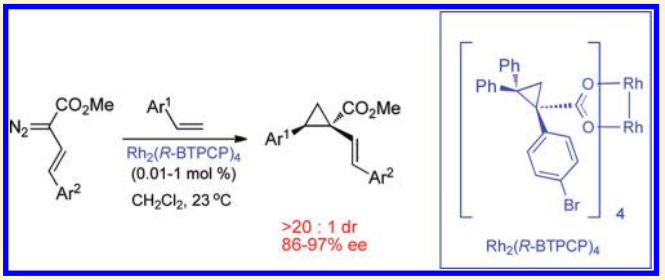
Supporting Information

ABSTRACT: Dirhodium tetrakis-(*R*)-(1-(4-bromophenyl)-2,2-diphenylcyclopropanecarboxylate) (Rh_2(*R*-BTPCP)$_4$) was found to be an effective chiral catalyst for enantioselective reactions of aryl- and styryldiazoacetates. Highly enantioselective cyclopropanations, tandem cyclopropanation/Cope rearrangements and a combined C−H functionalization/Cope rearrangement were achieved using Rh_2(*R*-BTPCP)$_4$ as catalyst. The advantages of Rh_2(*R*-BTPCP)$_4$ include its ease of synthesis, its tolerance to the size of the ester group in the styryldiazoacetates, and its compatibility with dichloromethane as solvent. Computational studies suggest that the catalyst adopts a D_2-symmetric arrangement, but when the carbenoid binds to the catalyst, two of the *p*-bromophenyl groups on the ligands rotate outward to make room for the carbenoid and the approach of the substrate to the carbenoid.



INTRODUCTION

Dirhodium catalysts have played a prominent role in the metal-catalyzed reactions of diazo compounds.[1] Over the past few decades, great effort has been made to prepare various chiral dirhodium tetracarboxylate and dirhodium tetracarboxamidate catalysts.[2,3] Our group has studied a series of prolinate-based dirhodium catalysts, such as Rh_2(*S*-DOSP)$_4$ (**1**, Figure 1),[3f] and examined their capacity to induce high asymmetric induction in the reactions of donor/acceptor carbenoids.[1a] The asymmetric induction in these catalyzed reactions is sensitive to solvent and substrate structure.[3f] High asymmetric induction with Rh_2(*S*-DOSP)$_4$ as catalyst requires the use of a methyl ester as the acceptor group in the carbenoid and nonpolar solvents such as hydrocarbons.[3f] Although our effort to solve these limitations has led to the development of other promising catalysts, such as the phthalimidocarboxylate Rh_2(*S*-PTAD)$_4$ (**2**)[4] and the bridged dicarboxylate catalyst, Rh_2(*S*-biTISP)$_2$ (**3**),[5] the relatively tedious synthetic routes to these catalysts erode their overall appeal. Therefore, the development of both synthetically accessible and highly selective chiral dirhodium catalysts remains highly desirable. Herein, we report the concise synthesis of a novel catalyst, Rh_2(*R*-BTPCP)$_4$ (**4**), and its application in highly enantioselective transformations of donor/acceptor carbenoids.

Over the past few years, we have developed several novel enantioselective reactions of donor/acceptor carbenoids, such as cyclopropanation,[3f,4−6] formal [4 + 3] cycloaddition,[7] C−H functionalization,[1a] and ylide transformations.[8] These reactions have been used in total synthesis[9] and as enabling technologies in medicinal chemistry programs.[7,10] We have become intrigued with the possibility of using the new asymmetric transformations to enable the design of new chiral catalysts. Indeed, the inspiration for the development of Rh_2(*S*-PTAD)$_4$, a related catalyst to Hashimoto's catalyst Rh_2(*S*-PTTL)$_4$ (**5**),[3e] came from the discovery that donor/acceptor carbenoids undergo enantioselective C−H functionalization of adamantane.[4] Donor/acceptor carbenoids are also capable of generating highly substituted cyclopropanes with high enantioselectivity.[3f,4−6,11] We decided to explore whether the resulting cyclopropanecarboxylic acids would be useful ligands for dirhodium catalysts. The cyclopropane ring would be expected to limit the possible conformations of the ligands and in this way we would hope to address the limitations observed with the Rh_2(*S*-DOSP)$_4$ catalyst.[3f]

RESULTS AND DISCUSSION

To evaluate the utility of cyclopropanecarboxylate catalysts, the 1,2-diphenylcyclopropanecarboxylate complex **8**, Rh_2(*R*-DPCP)$_4$, was prepared (Scheme 1). Rh_2(*R*-DOSP)$_4$-catalyzed enantioselective cyclopropanation of styrene **6** with methyl phenyldiazoacetate **7**, afforded the diarylcyclopropanecarboxylate in 81% yield, >20: 1 dr and 91% *ee*,[6] which was further enriched to >99% *ee* by recrystallization. A sequential hydrolysis and recrystallization provided the diphenylcyclopropanecarboxylic acid in 60% yield and >99% *ee*. Finally, ligand exchange with sodium rhodium carbonate in refluxing water gave **8** in 65% yield.

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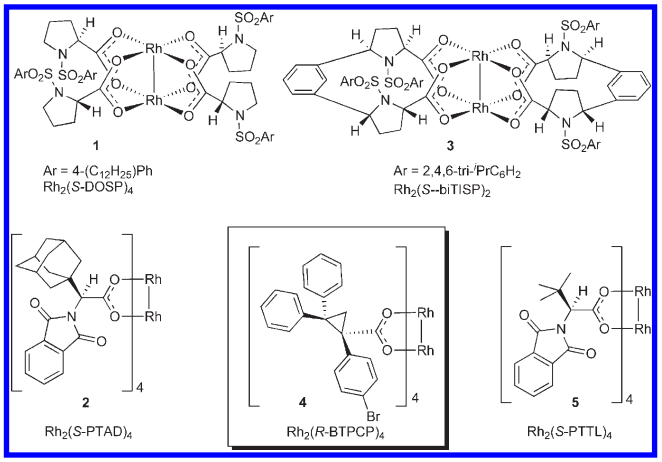
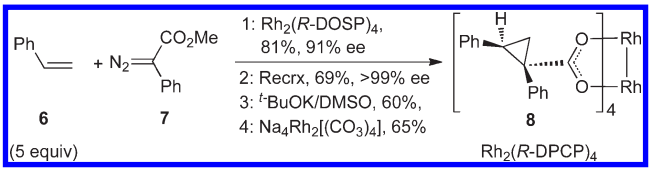
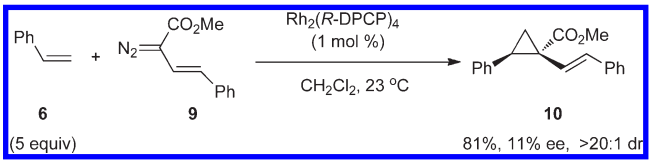


Figure 1. Chiral dirhodium catalysts.

Scheme 1. Synthesis of $Rh_2(R\text{-DPCP})_4$



Scheme 2. Evaluation of $Rh_2(R\text{-DPCP})_4$



The selectivity of $Rh_2(R\text{-DPCP})_4$ was evaluated in the standard cyclopropanation reaction between styrene **6** and styryldiazoacetate **9** using dichloromethane as solvent (Scheme 2). The styrylcyclopropane **10** was formed in 81% yield and with high diastereoselectivity (>20: 1 dr), which is typical for the cyclopropanation chemistry of donor/acceptor carbenoids. However, the asymmetric induction exhibited by $Rh_2(R\text{-DPCP})_4$ was only 11% *ee*.

At this stage, we re-examined what might be required for an effective cyclopropanecarboxylate ligand. Even though the cyclopropanecarboxylate in **8** has two stereogenic centers, the two phenyl rings are on the opposite side of the ring to the carboxylate. Therefore, the phenyl rings are not likely to display a major chiral influence on the catalyst nor are they likely to limit conformational mobility of the ligands. To overcome this issue, we decided to make a ligand with an additional phenyl ring *syn*- to the carboxylate. The triarylcyclopropanecarboxylate, was prepared from $Rh_2(R\text{-DOSP})_4$ catalyzed cyclopropanation reactions between 1,1-diphenylethylene (**11**) and *para*-bromophenyl diazoacetate **12** (Scheme 3). As previously established, this type of cyclopropanation proceeds with very high enantioselectivity.[6,11] The cyclopropane ester was converted to the corresponding carboxylic acid by ^{t}BuOK in dimethyl sulfoxide without erosion of enantioselectivity and was enriched to 99% ee after recrystallization.

Scheme 3. Synthesis of $Rh_2(R\text{-BTPCP})_4$

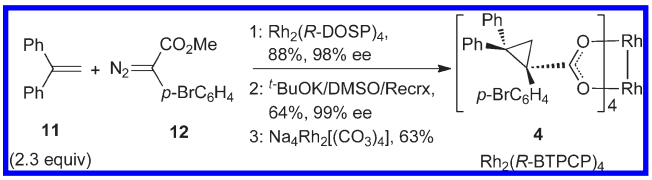
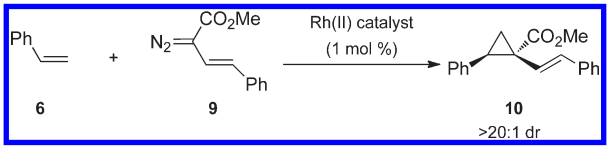


Table 1. Initial Evaluation of $Rh_2(R\text{-BTPCP})_4$- and $Rh_2(R\text{-DOSP})_4$-Catalyzed Cyclopropanation[a]



				$Rh_2(R\text{-BTPCP})_4$		$Rh_2(R\text{-DOSP})_4$	
entry	solvent	temp. (°C)	time (h)	yield (%)	*ee* (%)	yield (%)	*ee* (%)
1	pentane	23	1.5	82	84[b]	85	92
2	CH_2Cl_2	23	1.5	86	91	80	81
3	CH_2Cl_2	0	2.0	72	92[c]	81	84
4	CH_2Cl_2	−78	12	71	91	78	87
5[d]	CH_2Cl_2	23	24	77	92	69	81
6[e]	CH_2Cl_2	23	60	46	92	38	81

[a] Standard conditions: **9** (0.4 mmol) was added to a solution of Rh(II) catalyst and styrene (2.0 mmol) under argon over 1 h. Reported yields were obtained after chromatographic purification. dr was determined by ^{1}H NMR prior to chromatography, and *ee* was determined by chiral HPLC. Absolute configuration of **10** was assigned according to previous studies.[3f] [b] −89% *ee* was obtained when $Rh_2(S\text{-BTPCP})_4$ was used. [c] $Rh_2(S\text{-BTPCP})_4$ was used. [d] 0.1 mol % catalyst. [e] 0.01 mol % catalyst.

Standard ligand exchange conditions generated $Rh_2(R\text{-BTPCP})_4$ (**4**) in 63% yield as a green solid.

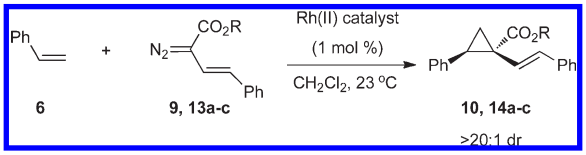
With $Rh_2(R\text{-BTPCP})_4$ in hand, its efficiency was examined in the standard reaction between the styryldiazoacetate **9** and styrene **6**. The influence of the syn-phenyl group in the ligand was dramatic as the reaction in dichloromethane at 23 °C generated the cyclopropane **10** in 91% *ee*, which is better than the same reaction catalyzed by $Rh_2(R\text{-DOSP})_4$ (81% *ee*), (Table 1, entry 2). Further experiments comparing $Rh_2(R\text{-BTPCP})_4$ and $Rh_2(R\text{-DOSP})_4$ are summarized in Table 1. Temperature did not influence the enantioselectivity of the $Rh_2(R\text{-BTPCP})_4$-catalyzed reaction between **9** and styrene **6** as **10** was produced in 91% *ee* over a reaction temperature range from 23 to −78 °C (Table 1, entries 2, 4). Furthermore, decreasing the catalyst loading from 1 to 0.01 mol % did not alter the enantioselectivity (Table 1, entries 5, 6),[12] but the reaction did not go to completion at the 0.01 mol % catalyst loading.

High asymmetric induction with $Rh_2(S\text{-DOSP})_4$ can only be obtained when the electron-withdrawing group is a methyl ester.[3f] Even changing the methyl ester to a *tert*-butyl ester caused a dramatic drop in the enantioselectivity. Therefore, a study was undertaken to determine how $Rh_2(R\text{-BTPCP})_4$-catalyzed reactions responded to the size of the ester (Table 2). $Rh_2(R\text{-BTPCP})_4$ exhibited good tolerance to ester size, and the

enantioselectivity actually improved on increasing the ester size from methyl to *tert*-butyl (Table 2, entries 1−4, from 91% *ee* to 95% *ee*). In contrast, hindered esters were confirmed to have a detrimental effect on asymmetric induction with Rh_2(*R*-DOSP)$_4$, leading to a steady drop in enantioselectivity from 81% *ee* to 16% *ee* (Table 2, entries, 5−8).

To probe the generality of this catalyst in enantioselective cyclopropanation with donor/acceptor carbenoid intermediates, various combinations of aryl- or vinyldiazoacetates with terminal alkenes were evaluated. The results for representative vinyldiazoacetates and terminal alkenes are summarized in Table 3.

Table 2. Effect of Ester Size on Asymmetric Cyclopropanation[a]

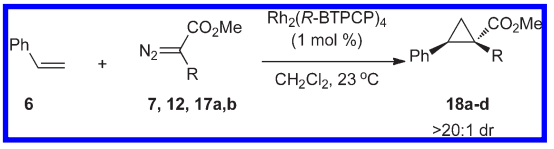


entry	starting material	R	catalyst	product	yield (%)	ee (%)
1	**9**	Me	Rh_2(*R*-BTPCP)$_4$	**10**	86	91
2	**13a**	Et	Rh_2(*R*-BTPCP)$_4$	**14a**	88	93
3	**13b**	^{i}-Pr	Rh_2(*R*-BTPCP)$_4$	**14b**	89	96
4	**13c**	^{t}-Bu	Rh_2(*R*-BTPCP)$_4$	**14c**	87	95
5	**9**	Me	Rh_2(*R*-DOSP)$_4$	**10**	80	81
6	**13a**	Et	Rh_2(*R*-DOSP)$_4$	**14a**	84	75
7	**13b**	^{i}-Pr	Rh_2(*R*-DOSP)$_4$	**14b**	82	55
8	**13c**	^{t}Bu	Rh_2(*R*-DOSP)$_4$	**14c**	80	16

[a] Standard conditions: Diazo compound (0.4 mmol) was added to a solution of Rh(II) catalyst and styrene (2.0 mmol) in dichloromethane under argon over 1 h. Reported yields were obtained after chromatographic purification. dr was determined by ^{1}H NMR prior to chromatography, and *ee* was determined by chiral HPLC.

All the reactions proceeded smoothly in dichloromethane, affording the corresponding cyclopropanes **16a-k** with high diastereo- and enantioselectivity with yields ranging from 59% to 94%. Carbenoid precursors with electron-donating substituents on the donor group (Table 3, entry 11) resulted in higher asymmetric induction than those having electron-withdrawing substituents on the donor group (Table 3, entries 9, 10). Electron-deficient alkenes gave better enantioselectivity than electron-rich alkenes. An optimum system is *para*-trifluoromethylstyrene and its reaction with styryldiazoacetate **9**, produced the cyclopropane **16a** in 97% *ee* (Table 3, entry 1). In contrast, the reaction with *para*-methoxystyrene produced the corresponding cyclopropane **16e** in 83% *ee* at room temperature, but this could be improved to 93% *ee* when the reaction was conducted at −40 °C (Table 3, entry 5). Inclusion of an *ortho* substituent on the styrene had little influence on the enantioselectivity, as reaction of *ortho*-methylstyrene and methyl

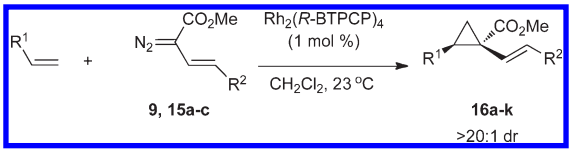
Table 4. Rh_2(*R*-BTPCP)$_4$-Catalyzed Asymmetric Cyclopropanation with Aryldiazoacetates[a]



entry	starting material	R	product	yield (%)	*ee* (%)
1	**7**	Ph	**18a**	82	83
2	**12**	*p*-BrC_6H_4	**18b**	80	85
3	**17a**	*p*-MeOC_6H_4	**18c**	74	91
4	**17b**	*p*-$CF_3C_6H_4$	**18d**	86	89

[a] Standard conditions: Diazo compound (0.4 mmol) was added to a solution of Rh(II) catalyst and styrene (2.0 mmol) in dichloromethane under argon over 1 h. Reported yields were obtained after chromatographic purification. dr was determined by ^{1}H NMR prior to chromatography, and *ee* was determined by chiral HPLC. Absolute configuration of the products was assigned according to previous studies.[6]

Table 3. Rh_2(*R*-BTPCP)$_4$-Catalyzed Asymmetric Cyclopropanation with Styryldiazoacetates[a]



entry	R^1	diazo compound	R^2	product	yield (%)	*ee* (%)
1	*p*-$CF_3C_6H_4$	**9**	Ph	**16a**	87	97
2	*p*-$NO_2C_6H_4$	**9**	Ph	**16b**	92	95
3	*p*-ClC_6H_4	**9**	Ph	**16c**	86	95
4	3,4-diClC_6H_3	**9**	Ph	**16d**	88	93
5	*p*-MeOC_6H_4	**9**	Ph	**16e**	94	84(93)[b]
6	*o*-$CH_3C_6H_4$	**9**	Ph	**16f**	88	93
7	*o*-$MeO_2CC_6H_4$	**9**	Ph	**16g**	59	89
8	$H_3C(CH_2)_3$	**9**	Ph	**16h**	60	90[c]
9	Ph	**15a**	*p*-ClC_6H_4	**16i**	82	90
10	Ph	**15c**	3,4-diClC_6H_3	**16j**	79	86
11	Ph	**15d**	3,4-di$MeOC_6H_3$	**16k**	70	−93[d]

[a] Standard conditions: Diazo compound (0.4 mmol) was added to a solution of Rh(II) catalyst and styrene (2.0 mmol) in dichloromethane under argon over 1 h. Reported yields were obtained after chromatographic purification. dr was determined by ^{1}H NMR prior to chromatography, and *ee* was determined by chiral HPLC. [b] Reaction was conducted at −40 °C. [c] dr >10:1. [d] Rh_2(*S*-BTPCP)$_4$ was used as catalyst.

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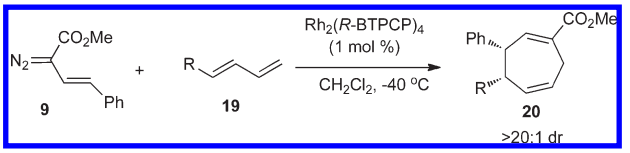
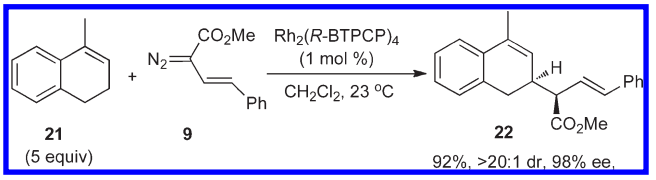
Table 5. Rh_2(*R*-BTPCP)$_4$ Catalyzed Tandem Cyclopropanation/Cope Rearrangement[a]



entry	starting diene	R	product	yield (%)	*ee* (%)
1	**19a**	Ph	**20a**	56	87
2	**19b**	*p*-$CF_3C_6H_4$	**20b**	71	91
3	**19c**	*p*-$MeOC_6H_4$	**20c**	60	89

[a] Standard conditions: Diazo compound (0.4 mmol) was added to a solution of Rh(II) catalyst and styrene (2.0 mmol) in dichloromethane at −40 °C under argon over 1 h. Reported yields were obtained after chromatographic purification. dr was determined by ^{1}H NMR prior to chromatography, and *ee* was determined by chiral HPLC. Absolute configuration of the products was assigned according to previous studies.[7a]

Scheme 4. Combined C−H Cope/Retro-Cope Reaction[a]



2-vinylbenzoate with the styryldiazoacetate **9** provided the cyclopropanes **16f** and **16g** in 93% *ee* and 89% *ee*, respectively (Table 3, entries 6, 7). Unactivated alkenes are also suitable substrates as 1-hexene (Table 3, entry 8) gave the cyclopropane **16h** in 60% yield and 90% *ee*.

The cyclopropanation reactions of representative aryldiazoacetates are summarized in Table 4. The reactions generated the cyclopropanes **18a**−**d** in high yield and stereoselectivity (>20:1 dr, 83−91% *ee*), with *p*-methoxyphenyl derivative **17a** giving the highest enantioselectivity (91% *ee*). These results are similar to the reported results for the Rh_2(*S*-DOSP)$_4$-catalyzed cyclopropanations of aryldiazoacetates in hexane as solvent.[6]

Encouraged by the cyclopropanation results, we decided to investigate the scope of the catalyst further by looking at more elaborate reactions of vinyldiazoacetates. When vinyldiazoacetates react with dienes, a formal [4 + 3] cycloaddition occurs by a tandem cyclopropanation/Cope rearrangement.[7] The Rh_2(*R*-BTPCP)$_4$-catalyzed reactions of styryldiazoacetate **9** with dienes **19** gave rise to the cycloheptadienes **20** in 56−71% yield and the enantioselectivity was 87−91% *ee*. As is typical of this transformation,[7] **20** were formed as single diastereomers.

In recent years, vinyldiazoacetates have been shown to be broadly useful in a range of C−H functionalization reactions.[1a] An example is the formal C−H functionalization of dihydronaphthalene **21** to form **22**.[13] This reaction proceeds by a sequence involving a combined C−H functionalization/Cope rearrangement followed by a reverse Cope rearrangement. When this reaction was catalyzed by Rh_2(*R*-BTPCP)$_4$, the product **22** was formed in 92% yield as a single diastereomer and in 98% ee (Scheme 4).[13] This result compares favorably to the Rh_2(*S*-DOSP)$_4$-catalyzed formation of **22** with hexane as solvent.

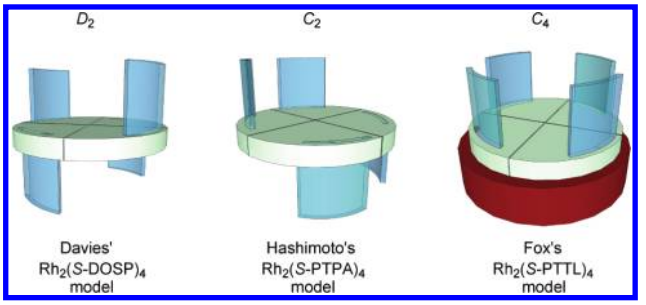


Figure 2. Three distinct ligand orientations used to rationalize enantioselectivity in dirhodium carboxylate-catalyzed reactions.

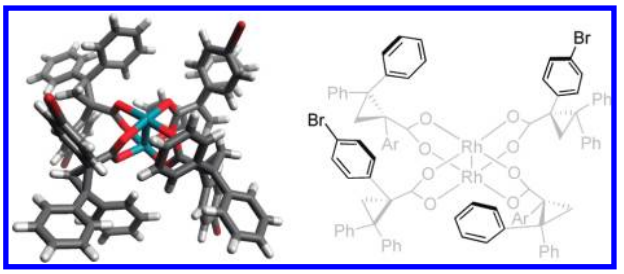


Figure 3. X-ray crystal structure of Rh_2(*R*-BTPCP)$_4$ (axial ligands omitted for clarity).

Even though dirhodium tetracarboxylates contain two potentially reactive rhodium sites and four identical ligands of C_1 symmetry, they are capable of very high asymmetric induction.[2a] Previously, this feature was explained by envisioning the dirhodium tetracarboxylates in conformations of higher symmetry than the ligands themselves. For Rh_2(*S*-DOSP)$_4$-catalyzed reactions, we proposed the catalyst to preferentially exist in a D_2 symmetric "up-down-up-down" conformation, providing identical C_2 symmetric binding sites at both rhodium faces of the catalyst (Figure 2).[3f] Hashimoto rationalized the selectivity of his phthalimido amino acid derived catalysts by proposing a C_2 symmetric "up-up-down-down" arrangement for the catalyst.[3e] More recently, Fox reported that the *tert*-butyl catalyst Rh_2(*S*-PTTL)$_4$, the most broadly used of Hashimoto's catalysts, exists in an "all-up" distorted C_4 conformation.[3h,i] According to this model, the bulky *tert*-butyl groups are necessary to limit reactivity to only one of the Rh faces of the catalyst, whereas a distorted C_4 symmetric chiral crown-like ligand arrangement guides the facial selectivity at the open Rh-face. Recently, other groups have reported X-ray structures of related catalysts to Rh_2(*S*-PTTL)$_4$, and all these catalysts adopt an "all-up" C_4 conformation.[3j,k,m,n] Because Rh_2(*R*-BTPCP)$_4$ is structurally quite different from the other above-mentioned chiral dirhodium tetracarboxylate catalysts, a study to determine what made it such an effective chiral catalyst was undertaken.

A single crystal X-ray diffraction analysis of Rh_2(*R*-BTPCP)$_4$ provided valuable insights into the catalyst geometry. In the X-ray structure, the large chiral ligands of Rh_2(*R*-BTPCP)$_4$ are organized in an overall D_2 symmetric arrangement, forming identical rectangular orthogonal (approximately 8.5 × 10.5 Å) binding cavities of C_2 symmetry at the two catalytically active axial termini of the rhodium dimer (Figure 3).

Rh_2(*R*-BTPCP)$_4$ and Rh_2(*S*-PTTL)$_4$ have different overall symmetry, D_2 and distorted C_4, respectively, but they possess a related rectangular binding cavity at the reactive axial positions

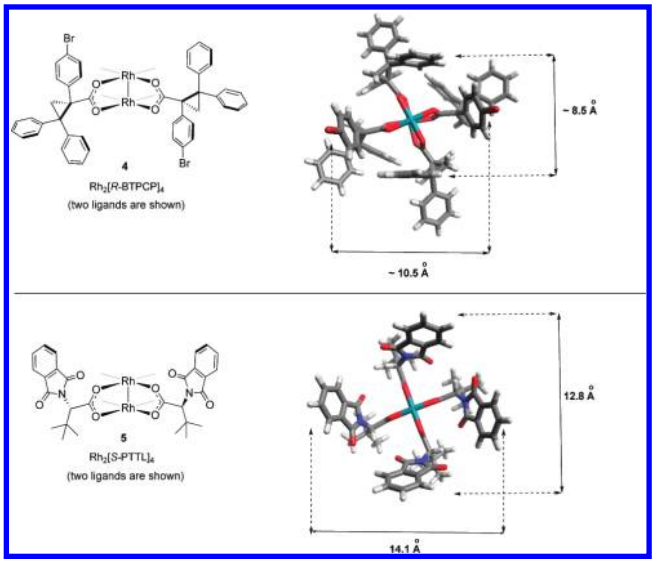


Figure 4. Catalytically active sites of Rh_2(*R*-BTPCP)$_4$ (X-ray) and Rh_2(*S*-PTTL)$_4$ (calculated structure).

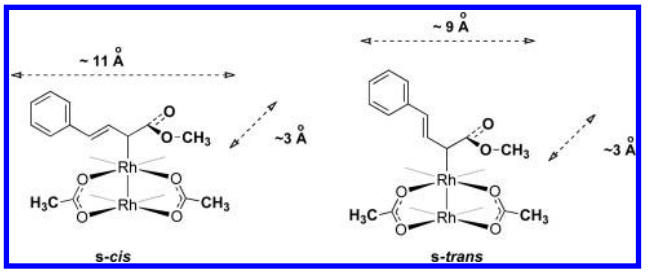


Figure 5. DFT model of s-cis and s-trans carbene conformers.

(Figure 4). The rectangular biding cavity for Rh_2(*R*-BTPCP)$_4$ (8.5 × 10.5 Å) is significantly smaller than the cavity for Rh_2(*S*-PTTL)$_4$ (12.8 × 14.1 Å). Furthermore, both Rh faces of Rh_2(*R*-BTPCP)$_4$ have identical binding cavities of C_2 symmetry. However, for Rh_2(*S*-PTTL)$_4$ only one Rh face has the rectangular binding cavity, whereas the other face is considered to be blocked by the *tert*-butyl groups. According to the Rh_2(*S*-PTTL)$_4$ model proposed by Fox,[3h,i] a carbene would align with the wide dimension of the catalyst leaving the *Si* face open for the attack because of the wider gap between two of the ligands. To test if the same model could be utilized to explain the stereochemical outcome of Rh_2(*R*-BTPCP)$_4$-catalyzed transformations, a computational analysis of the catalyst-carbene complex was conducted.

Traditional computational approaches to analyze dirhodium carbene complexes have tended to rely on the X-ray structure of the catalyst in combination with DFT optimized geometries of the carbenoid with a simplified, achiral, catalyst model.[3j,m,14] Although such analysis may provide preliminary insights into the catalyst selectivity, more precise studies accounting for interactions between the carbene and ligands, as well as ligand mobility in these systems would give a much better understanding of the role of the chiral catalyst. In fact, our preliminary DFT calculations[15−17] on the simplified model of the dirhodium-(tetracarboxylate)-carbene complex (Figure 5) demonstrates the importance of such studies. A comparison of the DFT optimized geometries, given in Figure 5, with the reported size of the catalyst binding cavity (Figure 4) reveals that even the shortest

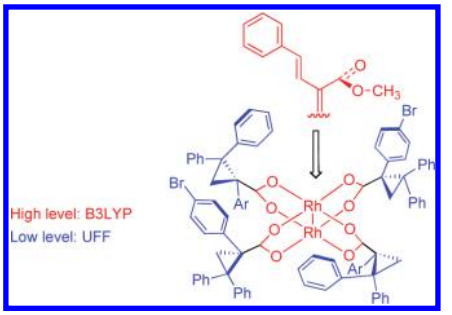


Figure 6. ONIOM partitioning of Rh_2(*R*-BTPCP)$_4$-carbene complex.

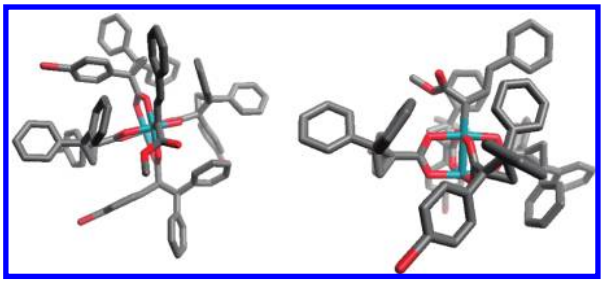


Figure 7. Lowest-energy conformation of s-trans carbene, top view (left) and side view (right). Hydrogen atoms were omitted for clarity.

s-trans carbenoid conformation would not fit into the tight environment (the dimensions shown on Figures 4 and 5 were measured from atomic centers and do not account for atomic radii) of the Rh_2(*R*-BTPCP)$_4$ catalyst.

Performing DFT calculations on the complete rhodium carbene complex (approximately 200 atoms) would be impractical unless very small basis sets were used,[3i] and these may not give a realistic representation of the complex. Therefore, we employ an alternative ONIOM approach[18] to study the carbenoid reaction. A two-layer ONIOM (QM:MM) method used in these studies divides the whole system into two subsystems (denoted "model" and "real" layers) and treat them at the best possible level of theory. The ONIOM partitioning of the catalyst-carbene system that was used is shown in Figure 6. In these studies the B3LYP[15−17] and UFF[19] methods were used for the calculations of the "model" (in red) and "real" (in blue) layers, respectively. Such partition provided an accurate description for the central rhodium carboxylate-carbene complex and accounted for the steric influence of the surrounding ligands.

Our computational results support the importance of the steric environment within the catalyst. Thus even the best matching combination of the shortest s-trans carbene aligned with the widest dimension of the orthogonal binding cavity caused steric repulsions significant enough to rotate two *para*-bromophenyl groups in either conrotary or disrotary directions. A similar result was obtained when the s-trans carbene was aligned with the shortest catalyst dimension; this time the phenyl groups rotated in a similar way. Overall, we were able to locate sixteen distinct minima on the potential energy surface corresponding to different conformations of the s-trans carbene with Rh_2(*R*-BTPCP)$_4$. The lowest energy conformation, separated from the closest one by ΔE = 1.8 kcal/mol is depicted in Figure 7. In this conformer two ligands rotated in a conrotary fashion to minimize steric interactions with the carbene, whereas the other two ligands remained in the upward position to reduce steric

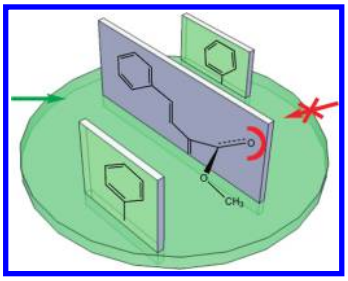


Figure 8. Predictive stereochemical model for Rh_2(*R*-BTPCP)$_4$-catalyzed transformation.

repulsions with the neighboring ligands. This arrangement resulted in a C_2 symmetric environment at the carbene site cavity containing two phenyl rings and two *para*-bromophenyl groups. One of the rings is blocking the donor group (aryl, styryl) while the other one is positioned next to the acceptor group (ester). The same ligand conformation having the s-cis carbene geometry was found to be 2.5 kcal/mol higher.

On the basis of the computational data summarized above, we propose a stereochemical model that explains the selectivity observed in Rh_2(*R*-BTPCP)$_4$ catalyzed transformations (Figure 8). It is well established that the substrate approaches donor/acceptor-substituted rhodium-carbenoids over the donor group.[17a] The ester group aligns perpendicular to the carbene plane, and blocks attack on its side. When the substrate approaches over the donor group, the *Re*-face is blocked by the aryl ring of the ligand leaving the *Si*-face open for the attack. This model predicts correctly the observed absolute configuration of the products.

CONCLUSION

In conclusion, we have developed dirhodium tetrakis-triarylcyclopropanecarboxylates as a new class of chiral catalysts with a relatively rigid and easily tunable backbone. The efficiency and selectivity of this catalyst has been demonstrated in a variety of highly diastereo- and enantioselective reactions of donor/acceptor carbenoids. The computational analysis allowed us to propose a stereochemical model to explain selectivity of the new catalyst. This analysis illustrates the importance of considering the conformational mobility of the ligands once the carbene is bound to the catalyst.

ASSOCIATED CONTENT

Supporting Information. Synthetic details, computational details, X-ray crystallographic data, and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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