Rhodium-Stabilized Diarylcarbenes Behaving as Donor/Acceptor Carbenes

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ABSTRACT Rhodium-stabilized diaryl carbenes typically generated from diaryldiazomethanes have been generally classified as donor/donor carbenes. This combined computational and experimental study demonstrates that diarylcarbenes display reactivity characteristics that are more reminiscent of donor/acceptor carbenes. When the reactions are carried out with chiral dirhodium catalysts, Rh$_2$(*S*-PTAD)$_4$ and Rh$_2$(*S*-NTTL)$_4$, highly enantioselective and diastereoselective cyclopropanations can be achieved, forming 1,1,2-triarylcyclopropanes. The reason for this behavior is because the two rings are unable to align in the plane of the rhodium carbene at the same time. The aryl ring aligned in the plane of the carbene behaves as a donor group, whereas, the aryl ring aligned orthogonally behaves as an acceptor group.

Introduction

Transition metal carbenes are capable of a wide range of synthetically useful reactions. The vast majority of the early work in this field was conducted using acceptor and acceptor/acceptor carbenes.[1] More recently, it was discovered that donor/acceptor carbenes have attenuated reactivity, and are still very reactive due to the presence of the acceptor group, but with greatly improved selectivity due to the presence of the donor group.[2] These carbene intermediates are especially valuable for intermolecular reactions.[3] Cyclopropanation reactions with these carbenes are routinely highly diastereoselective[4] and they undergo intermolecular C—H functionalization with exquisite site selectivity.[5] A wide range of chiral dirhodium catalysts induce highly enantioselective reactions with this type of carbene.[6] Recent efforts have focused on developing other types of carbene intermediates that are capable of similar levels of selectivity to the traditional donor/acceptor carbenes. A system that has drawn recent interest is diarylcarbenes, which has been classified as donor/donor carbene.[7] They are effective in a variety of intramolecular reactions, including some highly enantioselective processes. So far, however, examples of intermolecular cyclopropanations of these carbenes are limited to symmetrical diarylcarbenes,[8] except for one example,[9] and as far as we are aware, no enantioselective versions are known.

Computational[10] and X-ray crystallographic[9, 11] studies have revealed a distinctive feature of rhodium-stabilized donor/acceptor carbenes with regards to the alignment of the two substituents on the carbene (Figure 1A). As illustrated in structure **1** the donor group lies virtually in the same plane as the rhodium carbene bond, whereas the acceptor group is orthogonal. This arrangement influences the approach of the alkene during the cyclopropanation: the π–π interaction between the aryl group of styrene and the donor group of the carbene drives the diastereoselectivity of the reaction, as illustrated in structure **2**, which is a model of the transition state for the styrene cyclopropanation.[10b] This would lead to the formation of cyclopropane **3** as the major diastereomer. Consistent with this concept, one of the most distinctive features of the metal-stabilized donor/acceptor carbenes is the high levels of diastereoselectivity observed in their cyclopropanation reactions, often >20:1 d.r.[12]

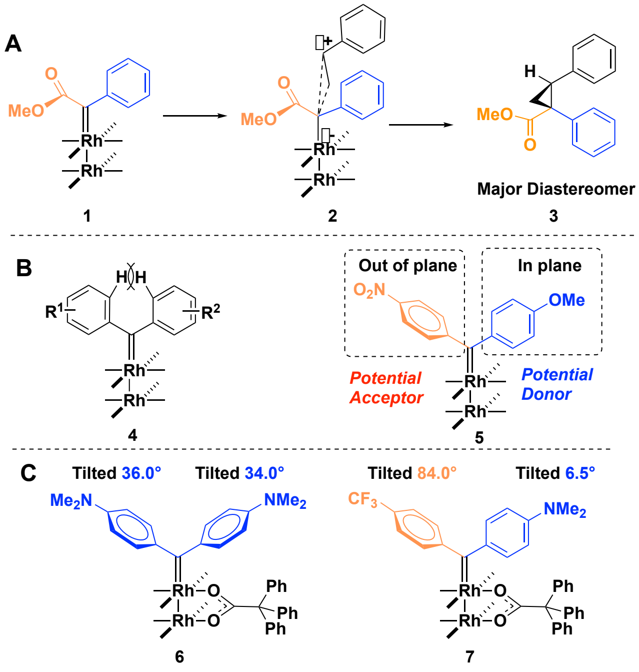


Figure 1. Diarylcarbenes as donor/acceptor carbenes.

On the basis of this model, we became intrigued by the possibility that diarylcarbenes **4**, which would be intuitively considered as donor/donor carbenes, could have a reactivity profile similar to donor/acceptor carbenes (Figure 1B). The premise is that both aryl groups would not be able to align in the same plane as the rhodium carbene at the same time, and one of the rings will be tilted out of the plane and will only weakly interact with the empty π-orbital of carbene, i.e., will act as an acceptor group. Further details are outlined in the supporting information(S70). This feature of the diarylcarbene should be even more pronounced if one of the aryl groups had an electron-withdrawing substituent and the other had an electron-donating substituent as illustrated for structure **5**. This basic hypothesis behind our study is in line with the latest findings by Fürstner and coworkers who isolated dirhodium complexes of diarylcarbenes and characterized them by X-ray crystallography (Figure 1C).[9] They have shown that in the bis-p-*N,N*-dimethylamino-phenylcarbene complex **6**, both aryl rings are tilted out of the plane of the rhodium carbene bond by 34.0° and 36.0°. However, in the case of p-(*N,N*-dimethylamino)phenyl-p-(trifluoromethyl)phenyl-carbene **7**, the ring with the donor group is tilted only 6.5° out of the plane, whereas the electron-deficient ring is titled by 84.0°, more in line with the basic hypothesis behind our study. Furthermore, it was shown that **7** reacted with *p*-methoxystyrene to form a cyclopropane in a diastereoselective manner but the product epimerized during attempted purification by chromatography.[9]

This work consists of both computational and experimental studies to determine what would be required for diaryl carbenes to behave like donor/acceptor carbenes. We examined seven diaryl carbenes derived from the diaryldiazomethanes **8a-g** (Figure 2). The first is the parent diphenyldiazomethane (**8a**). The next three would examine the effect of an acceptor group (p-NO_2) (**8b**), a donor group (-OMe) (**8c**), and both an acceptor and a donor group on the rings (**8d**). Fürstner found the cyclopropane generated from **7** epimerized during chromatography, presumably because the *N,N*-dimethylamino group is too strong a donor group and would favor cyclopropane ring-opening/ring-closing reaction *via* zwitterionic intermediates. Therefore, we used a methoxy group as the donor group, still a reasonable donor but not as strong as the *N,N*-dimethylamino group. As our central tenet relies on the two aryl groups being unable to exist in the same plane as the carbene at the same time, we also examined three *o*-chloro derivatives (**8e-g**) to see if this group would further disfavor the co-planarity of the two aryl rings.

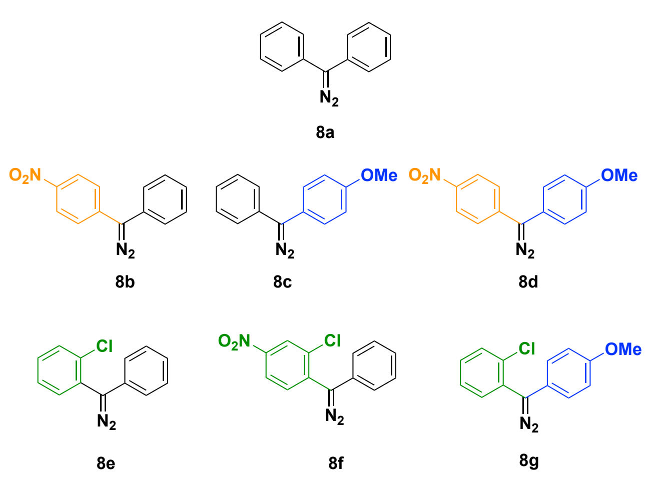
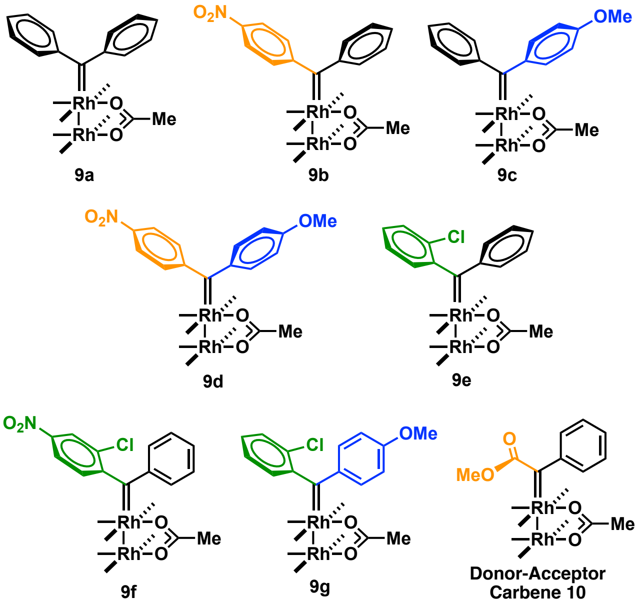


Figure 2. Diarylcarbene precursors.

Computational Studies

At the first stage, we computationally challenged our central hypothesis about the alignments of the aryl groups and determined what functionality on the diarylcarbenes would be most suitable to enhance donor/acceptor like characteristics. For this purpose, we have calculated structures of the (tetraacetate)-dirhodium carbene intermediates and the following cyclopropanation transition states. The calculations were conducted at the B3LYP level of density functional theory[13] with the D3BJ dispersion corrections[14] using Gaussian09 program[15], and the 6-31(d,p) basis set for the main group elements, and the Lanl2dz basis sets and associated Hay-Wadt effective core potential for rhodium atoms.[16] The solvent effect was incorporated into calculations (including the geometry optimization) at the PCM level of theory by using dichloromethane as a solvent.[17]

The computed structures of the rhodium bound carbenes (**9a-g**) derived from **8a-g** are shown in Figure 3. As a reference point, the computed structure of the classic donor/acceptor carbene **10** derived from methyl phenyldiazo acetate is also included. In **10**, the phenyl ring is tilted only 7.3° out of the plane and the ester group is 88.9° out of the plane, showing the typical structural characteristic of a rhodium bound donor/acceptor carbene. Due to the steric repulsion, both the aryl rings of the diarylcarbenes **4** cannot be in the same plane as the dirhodium carbene. In the case of the parent system **9a**, both aryl rings are tilted equally by 36.3°. This is in close agreement



	Substituents on Aryl Rings		Torsion Angle for Electron-poor or Hindered Aryl Ring (°)	Torsion Angle for Electron-rich Aryl Ring (°)
9a	H	H	35.9	36.0
9b	4-NO_2	H	45.6	31.2
9c	H	4-OMe	41.0	28.6
9d	4-NO_2	4-OMe	49.2	25.2
9e	2-Cl	H	59.8	23.8
9f	2-Cl, 4-NO_2	H	81.7	8.6
9g	2-Cl	4-OMe	77.0	6.7
10	H	H	88.9	7.3

Figure 3. Computational analysis of the tilting angle of the aryl rings of rhodium acetate bound diarylcarbenes

to the tilt observed in the crystallographic structures of related symmetrical diaryl carbene complexes.[9] This result indicates that both aryl groups would have similar characteristics, and would not correspond to the concept of one ring aligning nearly in the plane of the rhodium carbene and behave as a donor group and the other as the acceptor group.

The situation is different with the substituted diaryl carbenes. In the case of the substituted systems **9b-d**, both rings are tilted, but the more electron-rich ring tilts the least. In the case of **9d**, the ring with the *p*-nitrophenyl ring is tilted 49.2°, whereas the *p*-methoxyphenyl ring is tilted 25.2°. The steric effect on the distortion angle was studied next, and in structures **9e-g** an *ortho*-chloro substituent was introduced to increase the bulkiness of the electron-poor aryl ring. As seen in Figure 3, the presence of this Cl atom greatly enhances the tilting angle. In the case of **9f**, the aryl ring with an *o*-chloro and a *p*-nitro group is tilted 81.7°, but the phenyl group is tilted only 8.6°. Similarly, in **9g**, the *o*-chloro substituted ring is tilted 77.0° whereas the *p*-methoxyphenyl ring is tilted only 6.7°. Thus, even though both rings are tilted to some extent, by having the right combination of steric and electronic effects, it is possible to design rhodium diarylcarbene intermediates where there is considerable difference in how the two rings align.

As seen in Figure 4, the more electron-rich ring of the studied donor/donor carbenes preferentially aligns close to the same plane as the rhodium carbene, which is a consequence of stronger interaction of the ring's occupied π-orbital with the carbene's empty π-orbital. In order to evaluate further this effect, we also examined the canonical lowest occupied molecular orbital (LUMO) of the rhodium carbenes. In the case of donor-acceptor carbene **10**, derived from methyl phenyldiazoacetate, the LUMO shows considerable delocalization into the aryl ring and very little into the ester (Figure 4). Particularly interesting is the observation that there is considerably more delocalization into the aryl rings than into back bonding to the rhodium, which emphasizes a significant π (ring) - π(carbene) interaction, similar in the free carbene. In contrast, with the diphenylcarbene complex **9a**, the delocalization occurs equally into both rings, suggesting the carbene will be stabilized but would not have the distinctive features of a donor/acceptor carbene. When the two rings are differentiated, as in **9f** and **9g**, then the delocalization occurs mainly into the more electron-donating ring with very little electron density in the sterically constrained or electron-deficient ring. The orbital distribution in **9f** and **9g** is more similar to a classic donor/acceptor carbene **10** than a donor/donor carbene. So, it would be reasonable to expect these carbenes to exhibit a reactivity profile similar to what is observed with a classic donor/acceptor carbene.

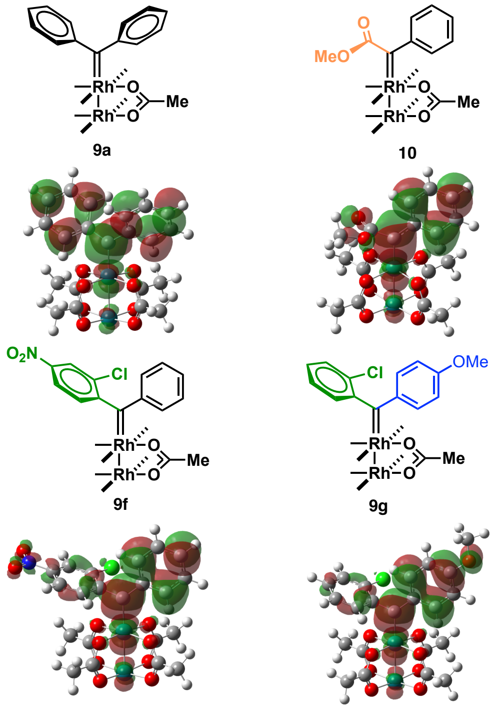
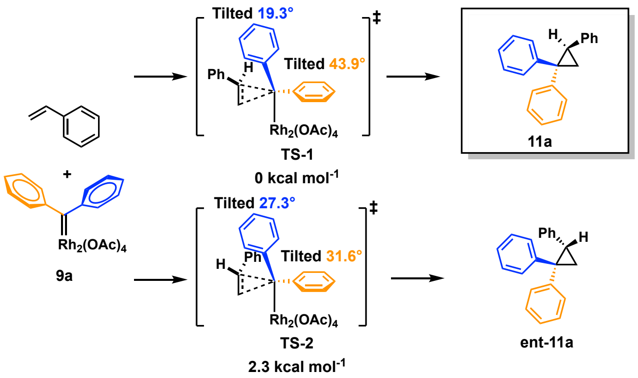


Figure 4. LUMO orbitals of the representative diarylcarbenes **9a**, **9f** and **9g** and donor/acceptor carbene **10.**

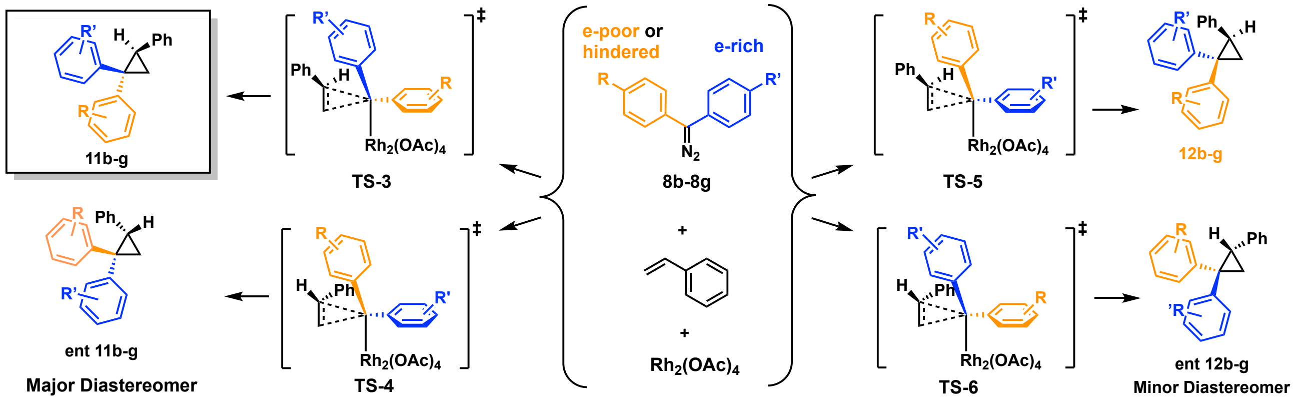
Thus, the calculations of the diarylcarbene complexes **9b-d** established that the more electron-rich rings are more closely aligned in the plane with the rhodium carbene bond but still both rings are twisted out of the plane, although this is less pronounced in the case of the *o*-chloro substrates **9e-g**. At this point, we were intrigued whether the donor/acceptor characteristic might be even more pronounced in the transition state during cyclopropanation. Therefore, we also investigated the transition states of the cyclopropanation of styrene. In addition, we analyzed the located transition states to predict the likely diastereoselectivity of the cyclopropanation with the various diarylcarbenes.

We first evaluated the cyclopropanation TS for the diphenylcarbene **9a** (Scheme 1). We found that even though both rings are equally tilted in the carbene complex, at the transition state aryl rings are unequally tilted, by 19.3° and 43.9° for **TS-1** and 27.3° and 31.6° for **TS-2**, respectively, in some degree similar to that of a donor/accepter carbene (Scheme 1). In **TS-1**, the attack of the styrene occurs over the ring which is closer to the plane of the rhodium carbene bond. This structural motif is reminiscent to that in the preferred TS for the donor/acceptor carbene, where attack occurs over the donor group. We also analyzed **TS-2**, where the styrene approached over the aryl ring that is more orthogonal to the rhodium carbene plane. The energy difference between these two transition states is 2.3 kcal mol^{-1} favoring **TS-1**, with styrene approaching over the less tilted aryl ring. Assuming the attack of the styrene occurs from the front face of the carbene, as illustrated in **TS-1** and **TS-2**, then these transition states would generate **11a** and **ent-11a**, the two enantiomers of the cyclopropane product. If a chiral catalyst is used, which can

Scheme 1. Computational analysis of the transition state for cyclopropanation with diphenylcarbene.



Scheme 2. Computational analysis of the transition state for cyclopropanation with diarylcarbenes 9b-g.



	Substituents R	R'	TS-3	TS-4 -1)a	TS-5	TS-6	Smallest -1) and Calculated d.r.b		The Lowest TSc,d Torsion Angle Aryl Ring/Aryl Ring (°)	The 2nd Lowest TSc,d Torsion Angle Aryl Ring/Aryl Ring (°)
8b	4-NO_2	H	0.0/0.0	5.9/4.7	1.7/1.7	3.7/1.9	1.7/1.7	16:1	48.2 (2.6) / 17.3 (-13.9)	18.4 (-27.2) / 45.6 (14.4)
8c	H	4-OMe	0.0/0.0	5.1/3.8	2.0/1.8	4.7/3.7	2.0/1.8	19:1	41.9 (0.9) / 21.2 (-7.4)	21.2 (-19.8) / 41.6 (13.0)
8d	4-NO_2	4-OMe	0.0/0.0	7.5/6.0	4.1/4.0	4.8/3.6	4.8/3.6	>50:1	46.0 (-3.2) / 20.0 (-5.2)	34.0 (-15.2) / 26.5 (1.3)
8e	2-Cl	H	0.0/0.0	6.2/6.4	2.6/2.0	5.2/4.7	2.6/2.0	30:1	53.7 (-6.1) / 20.0 (-3.8)	27.6 (-32.2) / 50.5 (26.7)
8f	2-Cl, 4-NO_2	H	0.0/0.0	9.3/8.0	4.8/3.2	5.0/3.4	4.8/3.2	>50:1	56.9 (-24.8) / 18.4 (9.8)	32.6 (-49.1) / 46.8 (38.2)
8g	2-Cl	4-OMe	0.0/0.0	6.8/5.4	3.7/2.8	5.9/4.6	3.7/2.8	>50:1	51.5 (-25.5) / 21.8 (15.1)	33.0 (-44.0) / 43.0 (36.3)

The styrene is shown approaching from the front face of the carbene. a. The relative enthalpy and Gibbs free energies are shown as $\Delta H/\Delta G$; b. diastereomeric ratio is calculated based on the Gibbs free energies (calculated at 25°C and 1 atm); c. Distortion angle of the electron-poor or hindered aryl ring is presented in orange and the electron-rich aryl ring is presented in blue; d. Deviation from its carbene is shown in parenthesis.

distinguish from front face and back face attack of the carbene, then this analysis leads to the conclusions that asymmetric inductions could be possible in the cyclopropanation with diphenyl carbene. This would be an interesting outcome because the carbene site does not become a stereogenic center during the cyclopropanation and the asymmetric induction is possible simply because one of the phenyl rings of the diphenylcarbene behaves as a donor group and the other adopts an orthogonal position blocking the approach of the substrate.

The transition states for the six substituted diarylcarbene intermediates **8b-g** were also examined as summarized in Scheme 2. The full details of these calculations are given in the supplementary information. Calculations were conducted for attack of the styrene occurring over either the electron-rich or the electron-deficient aryl ring, leading to four possible transition states **TS-3**, **TS-4**, **TS-5** and **TS-6**. The more stable transition state in each of six substituted diarylcarbene case, **TS-3**, has the substrate approaching over the electron-rich aryl ring, which is structurally similar to the donor group in the donor/acceptor carbenes. The energy differences between the calculated transition states gives a prediction for the levels of diastereoselectivity for each substrate. The smallest free energy difference is 1.7 kcal mol^{-1} for the *p*-nitrodiphenylcarbene **8b**, which would lead to a predicted diastereomeric ratio of **11b** to **12b** of about 16:1 dr. Most notable is the energy differences for **9d**, **9f** and **9g** (~3 kcal mol^{-1}), which predicts the cyclopropanation will proceed with >50:1 d.r. In all cases, a significant change in the amount of tilting of the aryl rings occurred by going from the rhodium carbene complex to the transition state for cyclopropanation. In these TSs, one of the aryl rings is tilted to be out of plane similar to the behavior of an acceptor group in donor-acceptor carbenes. In the preferred lower energy transition state **TS-3** the torsion angle for the titling of the aryl rings is relatively similar for all the diarylcarbenes **9b-g**. The electron-rich arene is tilted 17-22° and the electron-deficient arene is tilted 41-57°. Therefore, if a chiral catalyst was used, capable of distinguishing between attacks at the front face versus the back face of the rhodium carbene, then the cyclopropanation could proceed with high levels of both enantio- and diastereoselectivity. Thus, computational analyses have predicted that diarylcarbenes could have some of the distinctive characteristics of donor/acceptor carbenes.

Synthetic Studies

To further challenge our prediction and validate the computational data we experimentally studied the stereoselectivity of the cyclopropanation of styrene with the diaryldiazomethanes **8a-g.** We examined the reactions with both the achiral dirhodium tetraacetate catalyst and some of the chiral catalysts that have been developed for donor/acceptor carbene reactions. A complete study on a range of catalysts is described in the SI (Table S1). From this study three chiral catalysts, Rh_2(*S*-DOSP)$_4$, Rh_2(*S*-PTAD)$_4$ and Rh_2(*S*-NTTL)$_4$ were identified as the most promising for this study (Figure 5).

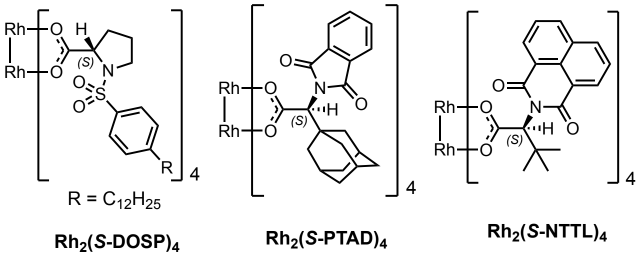
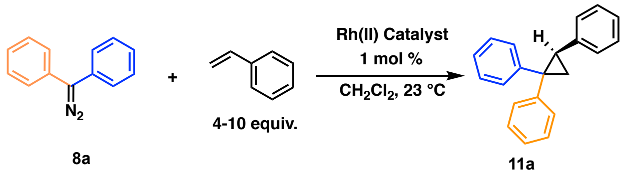


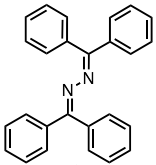
Figure 5. Chiral Dirhodium Catalysts.

The first system that was examined is the reaction with diphenyldiazomethane **8a** (Scheme 3). The rhodium-catalyzed reaction of **8a** with styrene to form the cyclopropane **11a** went in relatively low yield unless a large excess of styrene (10 equiv) was used as a trapping agent. A major side product was the formation of the azine **13**, which is a known side product of diarylcarbene reactions.[7g,8d] This suggests that the carbene is not reacting very quickly with the styrene allowing time for the carbene to react with additional diaryldiazomethane, which is added slowly *via* inverse addition. Rh_2(*S*-DOSP)$_4$ catalyst gave relatively low levels of enantioselectivity but this was expected because Rh_2(*S*-DOSP)$_4$ tends to give high enantioselectivity only with donor/acceptor carbenes in which the acceptor group is a methyl ester,[18] and where the acceptor and donor groups are in orthogonal planes. Furthermore, the reaction needed to be carried out in dichloromethane because of the solubility of the diaryldiazomethane; other solvents were also tested (Table S2), but it is known that Rh_2(*S*-DOSP)$_4$ performs best in hydrocarbon solvents (Table S2).[19] In contrast, both Rh_2(*S*-NTTL)$_4$ and Rh_2(*S*-PTAD)$_4$ generated **11a** with very high enantioselectivity (92-93% ee). This result is highly significant because if the aryl rings were not differentially tilted, the two faces of the carbene would be identical and no asymmetric induction would be expected.

Scheme 3. Diphenyldiazomethane cyclopropanation



catalyst	styrene equiv.	yield, %	ee, %[a]
$Rh_2(OAc)_4$	4	21	–
Rh_2(*S*-DOSP)$_4$	4	23	18
Rh_2(*S*-NTTL)$_4$	4	36	93
Rh_2(*S*-NTTL)$_4$	10	86	93
Rh_2(*S*-PTAD)$_4$	4	65	92
Rh_2(*S*-PTAD)$_4$	10	88	92



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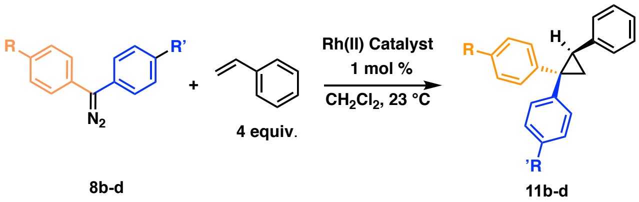
a. ee % was determined using chiral HPLC analysis.

The cyclopropanation with the diaryldiazomethanes **8b-d**, with donor and/or acceptor groups was then examined (Scheme 4). In general, these reactions proceed in better yields than the reaction of diphenyldiazomethane, especially when a strong acceptor group was present, with **8e-g** requiring 10 equiv of styrene. The cyclopropanations with the *p*-nitro derivative **8b** and the *p*-methoxy derivative **8c** gave variable diastereoselectivity (1.2-12:1 for **8b** and 8-20:1 for **8c**), which is reasonably consistent with the predicted values of 16:1 and 19:1, respectively for the $Rh_2(OAc)_4$ catalyzed reactions. As expected, the Rh_2(*S*-DOSP)$_4$- catalyzed reactions gave poor enantioselectivity but the Rh_2(*S*-PTAD)$_4$ and Rh_2(*S*-NTTL)$_4$- catalyzed reactions were highly enantioselective. The most impressive result was the Rh_2(*S*-PTAD)$_4$- catalyzed reaction with **8c**, which generated the cyclopropane **11c** in 66% yield, 20:1 d.r. and 97% ee. When the diaryldiazomethane contained both a donor and an acceptor group, as in **8d**, the reactions is high yielding and highly diastereoselective, in good agreement with the computationally predicted result. The Rh_2(*S*-PTAD)$_4$- catalyzed reaction with **8d** generated the cyclopropane **11d** in 88% yield, >50:1 d.r. and 92% ee. The choice of the methoxy group as the donor group was also validated because there was no evidence of a change in the diastereomeric ratio after chromatography. The absolute and relative configuration of cyclopropane **11a** and **11c** were confirmed by X-ray crystallographic data, and the other cyclopropane products were tentatively assigned by analogy.

Scheme 4. Cyclopropanation with 8b-d.

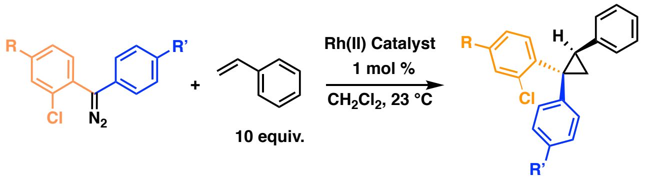


	R	R'	Catalyst	yield, %	d.r.[a]	ee, %
11b	4-NO_2	H	Rh_2(*S*-DOSP)$_4$	62	12:1	18
11b	4-NO_2	H	Rh_2(*S*-NTTL)$_4$	82	1.2:1	87
11b	4-NO_2	H	Rh_2(*S*-PTAD)$_4$	90	2:1	92
11c	H	4-OMe	Rh_2(*S*-DOSP)$_4$	36	10:1	25
11c	H	4-OMe	Rh_2(*S*-NTTL)$_4$	60	8:1	98
11c	H	4-OMe	Rh_2(*S*-PTAD)$_4$	66	20:1	97
11d	4-NO_2	4-OMe	Rh_2(*S*-NTTL)$_4$	90	>50:1	87
11d	4-NO_2	4-OMe	Rh_2(*S*-PTAD)$_4$	88	>50:1	92

a. d.r. was determined by crude NMR analysis.

The next series of substrates that were examined were the *o*-chloro-substituted diaryldiazomethane **8e-g** (Scheme 5). These were anticipated to be exceptional substrates because the sterically hindered ring is severely tilted, whereas the second ring has very little tilting. All three substrates gave rise to the cyclopropanes, **11e-g** with exceptionally high diastereo-control (>50:1 d.r.), in good agreement with the predicted results. However, the enantioselectivity of the reactions were variable. The Rh_2(*S*-PTAD)$_4$-catalyzed reaction of **8e**, having just the *o*-chloro substituent was very effective forming **11e** in 91% yield and 85% ee. The aryldiazomethane **11f** with an additional nitro group was formed in high yields (88-89% yield), but the level of enantioselectivity for **11f** was relatively low (20-57% ee). The reaction with the *p*-methoxy derivative **8g**, did not go in as high yield, presumably because the carbene is not sufficiently electrophilic. However, the Rh_2(*S*-PTAD)$_4$ reaction does proceed with high enantioselectivity, forming **11g** in 93% ee.

Scheme 5. Cyclopropanation with 8e-g.



8e-g

11e-g

	R	R'	Catalyst	yield, %	d.r.	ee, %
11e	H	H	Rh_2(*S*-NTTL)$_4$	72	>50:1	82
11e	H	H	Rh_2(*S*-PTAD)$_4$	91	>50:1	85
11f	4-NO_2	H	Rh_2(*S*-NTTL)$_4$	88	>50:1	57
11f	4-NO_2	H	Rh_2(*S*-PTAD)$_4$	89	>50:1	22
11g	H	4-OMe	Rh_2(*S*-NTTL)$_4$	34	>50:1	92
11g	H	4-OMe	Rh_2(*S*-PTAD)$_4$	56	>50:1	93

Conclusion

The above-presented studies reveal that the carbenes derived from diaryldiazomethanes have many of the characteristics of donor/acceptor carbenes. We demonstrated an orthogonal approach to donor/acceptor carbenes by utilizing steric and electronic effects of substituents on a diaryl carbene system. The cyclopropanations are highly diastereoselective, which is a distinctive feature for donor/acceptor carbenes. When the chiral catalysts Rh_2(*S*-PTAD)$_4$ or Rh_2(*S*-NTTL)$_4$ are used, the reactions can be highly enantioselective, even in the case of the symmetrical diphenyldiazomethane. By emphasizing the difference between the two rings with appropriately positioned donor/acceptor or sterically interfering groups, the donor/acceptor characteristic can be enhanced. These studies set the foundation to the concept that diaryldiazomethanes have an unexpected range of intermolecular reactions because they behave more like donor/acceptor carbenes rather than donor/donor carbenes.

ASSOCIATED CONTENT

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.
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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Full experimental data for the compounds described in the paper (PDF) and X-ray crystallographic data (CIF) for compounds **11a** (CCDC 1988247), and **11c** (CCDC 1988251).

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Conflict of Interest. HMLD is a named inventor on a patent entitled, Dirhodium Catalyst Compositions and Synthetic Processes Related Thereto (US 8,974,428, issued March 10, 2015). The other authors have no competing financial interests.

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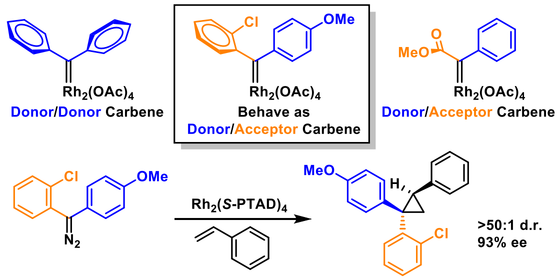
TOC graphic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