

Mini Review

Catalyst selection for metal carbene transformations

Daren J. Timmons, Michael P. Doyle *

Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA

Received 28 July 2000; accepted 7 September 2000

Abstract

Recent work has led to a greater understanding of the unique catalytic capabilities of chiral dirhodium(II) carboxamidates. High levels of product control, especially enantioselectivity, can be achieved with these catalysts in a wide variety of metal carbene transformations. Catalyst selection is the key to these applications that include addition, insertion, and ylide processes. Often two chiral dirhodium(II) carboxamidate catalysts applied to the same substrate provide exceptional selectivity, but for different products. © 2001 Published by Elsevier Science B.V.

Keywords: Dirhodium(II) carboxamidates; Metal carbene; Asymmetric catalysis; Diazo compound; Cyclopropanation; Insertion

The effectiveness of dirhodium(II) catalysts for a diversity of reactions with diazo compounds is well established [1–5]. Although a wide variety of catalysts are available for metal carbene transformations, dirhodium(II) carboxamidate catalysts offer distinct advantages for reaction selectivity [1,3]. For example, they are the most universally applicable to enantioselective metal carbene transformations of diazoacetates [2]. During the last few years, new dirhodium(II) carboxamidate catalysts have been developed, and the range of their usefulness has expanded [6–9]. Also, the uniqueness of each catalyst is becoming better understood. The chemo-, regio-, diastereo-, and enantioselectivity brought about by specific catalysts can be radically different, but it is now possible to select the best catalyst for a specific transformation. This review is intended to provide an overview of these catalysts to facilitate and simplify catalyst selection.

The dirhodium(II) carboxamidates utilized in our laboratories all have the same basic framework. Four bridging carboxamidate ligands arranged around a dirhodium core reflect the well-known paddlewheel structural motif (Fig. 1). The two rhodium atoms are generally considered to be singly bonded having the

electronic configuration $\sigma^2\pi^4\delta^2\delta^*\pi^*4$ [10]. The most selective catalysts have the ligands arranged such that each rhodium atom is bound to two nitrogen atoms *cis* to each other and two oxygen atoms *cis* to each other (Fig. 2): the '*cis*-2,2' configuration [11]. It is possible to form the '3,1' and the '4,0' ligand arrangements with certain carboxamidates, but the selectivity of these dirhodium(II) compounds in metal carbene transforma-

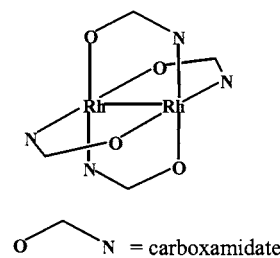


Fig. 1. Paddlewheel structural motif for dirhodium(II) carboxamidates.

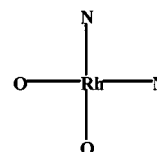


Fig. 2. The '*cis*-2,2' configuration for dirhodium(II) carboxamidates.

* Corresponding author. Fax: +1-520-6264815.

E-mail address: mdoyle@u.arizona.edu (M.P. Doyle).

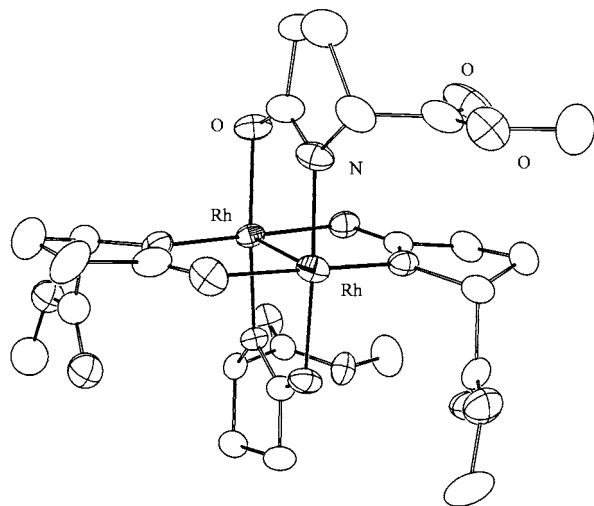


Fig. 3. Thermal ellipsoid plot of $\text{Rh}_2(5R\text{-MEPY})_4$. Hydrogen atoms have been omitted for clarity.

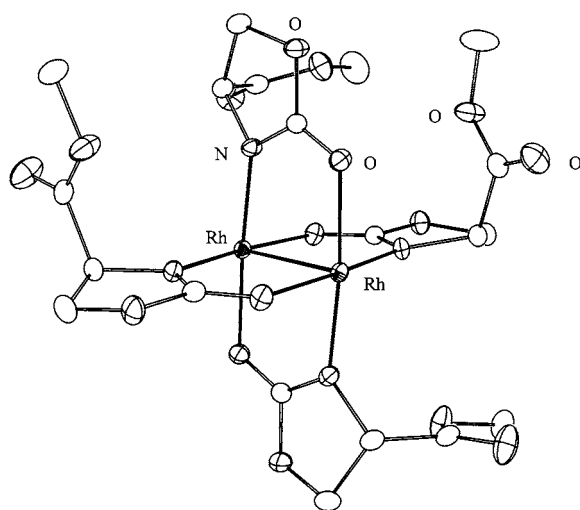


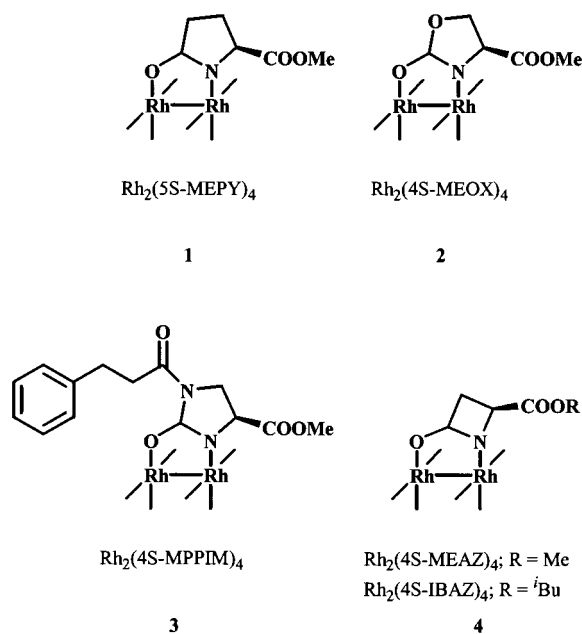
Fig. 4. Thermal ellipsoid plot of $\text{Rh}_2(4S\text{-MEOX})_4$. Hydrogen atoms have been omitted for clarity.

tions is low [6,12]. The ‘*trans*-2,2’ structural arrangement has not been observed in the preparation of dirhodium(II) carboxamidates.

A typical preparation for these catalysts involves heating to reflux a mixture of rhodium acetate and, normally, an equivalent excess of the carboxamidine ligand in chlorobenzene. The process is semi-automated by fitting the reaction flask with a Soxhlet extractor containing sodium bicarbonate to trap the acetic acid generated during the reaction and drive the equilibrium to product. Dirhodium(II) carboxamidate formation is followed by HPLC, and the complex is conveniently purified by column chromatography on a reverse-phase support.

Chiral catalysts with carboxamidate ligands have been prepared in four classes: 2-oxapyrrolidine-5-car-

boxylates (**1**) [13,14], 2-oxaaxazoline-4-carboxylates (**2**) [15,16], *N*-acyl-2-oxaimidazolidine-4-carboxylates (**3**) [6,17], and 2-oxaazetididine-4-carboxylates (**4**) [7,9]. Only the *S*-configuration is shown in **1–4**, but the *R*-configured dirhodium(II) carboxamidates have been prepared in most cases. Well over 30 of these carboxamidate catalysts have been synthesized and tested in our laboratories, but we will describe the reactivity and selectivity of only a few. Each ligand contains an ester group at the chiral center alpha to nitrogen. Alkyl groups at the same site, especially isopropyl and benzyl [13], are significantly less effective in enantiocontrol and actual product control than the ester functionality, and results with a carboxamide were disappointing [18]. When the ligands are attached to the dirhodium core, the ester functionality protrudes over the axial coordination sites forming a chiral environment around each rhodium atom.



More than 12 different chiral catalysts have been determined by X-ray crystallography [6,7,13,15–18]. Thermal ellipsoid plots are shown for $\text{Rh}_2(5R\text{-MEPY})_4$ (Fig. 3), $\text{Rh}_2(4S\text{-MEOX})_4$ (Fig. 4), $\text{Rh}_2(4S\text{-MPPIM})_4$ (Fig. 5), and $\text{Rh}_2(4S\text{-BNAZ})_4$ (Fig. 6). Noteworthy is the rigidity of the ligand framework around the dirhodium axis; this allows consistently reproducible results in catalyst applications without observable solvent effects or non-linear behavior [19]. One can also see from Fig. 5 that dipolar constraints, which force the *N*-acyl carbonyl group to be *trans* to the rhodium ligated oxygen atom from the same MPPIM ligand, allow the *N*-acyl group to have a substantial impact on the chiral environment.

The structural parameters for these dirhodium(II) compounds are indicative, to a first approximation, of

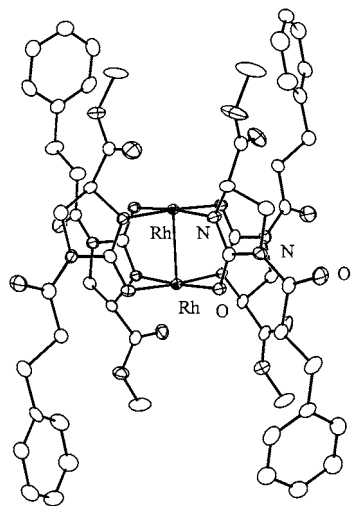


Fig. 5. Thermal ellipsoid plot of $\text{Rh}_2(4S\text{-MPPIM})_4$. Hydrogen atoms have been omitted for clarity.

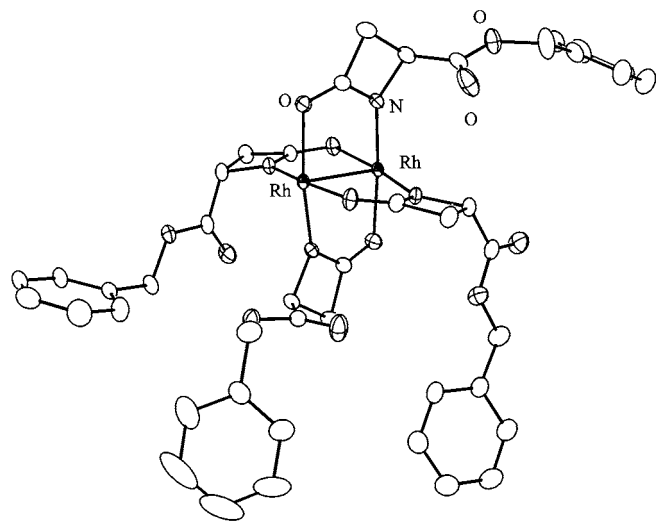
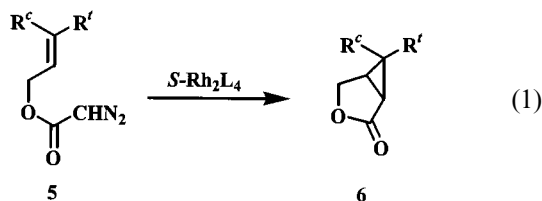


Fig. 6. Thermal ellipsoid plot of $\text{Rh}_2(4S\text{-BNAZ})_4$. Hydrogen atoms have been omitted for clarity.

the electronic effects of the ligands. For **1**, **2** and **3**, the Rh–Rh bond distance only varies between 2.445 and 2.477 Å [11]. The Rh–Rh bond distance in **4** ($\text{Rh}_2(4S\text{-BNAZ})_4$, $\text{R} = \text{CH}_2\text{Ph}$) is strikingly longer at 2.5331 Å [7]. The origin of this lengthening of the Rh–Rh single

bond resides with the four-membered azacycle. The geometric constraints of this ligand type do not allow the donor orbitals of both the nitrogen and oxygen atoms to simultaneously maximize their overlap with the rhodium-based orbitals. The five-membered azacycles have a better geometric match with the optimal Rh–Rh bond distance and allow for better ligand–metal orbital overlap. The longer Rh–Rh bond distance in $\text{Rh}_2(4S\text{-BNAZ})_4$, and presumably the other class **4** compounds, causes an increase in their electrophilicity; these catalysts show increased reactivity toward diazo substrates.

The exceptional ability of these catalysts to influence enantiocontrol has been demonstrated in a broad selection of metal carbene transformations. Those presented here will exemplify the contrasting behavior of chiral dirhodium(II) carboxamidate catalysts towards specific applications. As a first example, consider the intramolecular cyclopropanation reaction of allylic diazoacetates (Eq. (1)). Normally these reactions can be performed effectively and with high enantioselectivity using the $\text{Rh}_2(\text{MEPY})_4$ catalyst [17]. The *S*-configured catalyst produces (1*R*,5*S*)-**6**, whereas the *R*-configured catalyst forms (1*S*,5*R*)-**6**. All *cis*-disubstituted systems produce cyclopropane products in $\geq 94\%$ ee (e.g. $\text{R}^c = \text{Ph}$, Et, ^{*i*}Pr, ^{*i*}Bu, Bu_3Sn , I), but the *trans*-disubstituted systems gives lower % ee values for the cyclopropane products. This is rectified by mechanistic analysis of the factors that influence enantiocontrol, and through such analysis $\text{Rh}_2(4S\text{-MPPIM})_4$ was found to substantially improve enantiocontrol (Table 1) [20].

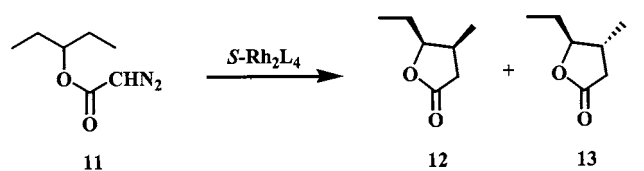
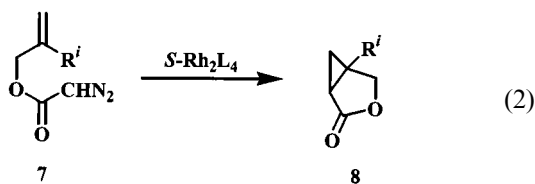


An even more dramatic effect could be found with methallyl diazoacetate and its analogs (Eq. (2)). Here, $\text{Rh}_2(4S\text{-MPPIM})_4$ influenced sufficiently the conformational preferences of the reacting metal carbene to effect high enantiocontrol (Table 1) [21]. Of special interest is the comparative effectiveness of a chiral bis-oxazoline-ligated copper(I) catalyst (87% ee for **8a** and 82% ee for **8b**).

Table 1

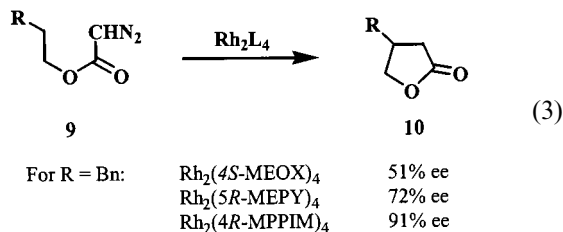
Influence of chiral catalysts in enantiocontrol in intramolecular cyclopropanation reactions of allylic diazoacetates

Diazo compound	R^t	R^c	R^t	% ee with	
				$\text{Rh}_2(5S\text{-MEPY})_4$	$\text{Rh}_2(4S\text{-MPPIM})_4$
5a	^{<i>n</i>} Pr	H	H	85	95
5b	P	H	H	68	96
7a	H	H	Me	7	89
7b	H	H	^{<i>n</i>} Bu	35	93



$\text{Rh}_2(4S\text{-MEOX})_4$	69(98% ee)	31(92% ee)
$\text{Rh}_2(5S\text{-MEPY})_4$	78(98% ee)	22(71% ee)
$\text{Rh}_2(4S\text{-MPPIM})_4$	97(99% ee)	3

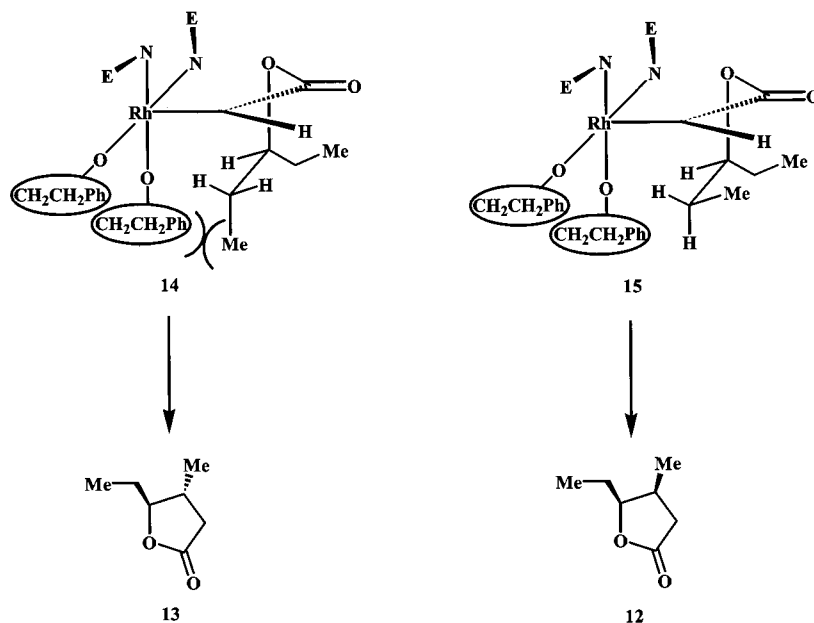
The advantages of $\text{Rh}_2(\text{MPPIM})_4$ can be further demonstrated in the formation of γ -butyrolactones (Eq. (3)). Intramolecular C–H insertion reactions of diazoacetates with dirhodium(II) carboxamidates are highly regioselective and form only the γ -lactone [22]. The *R*-configured catalysts give *R*-**10** while the *S*-configured catalysts give *S*-**10**. Moderate levels of enantiocontrol were obtained with $\text{Rh}_2(\text{MEPY})_4$ and $\text{Rh}_2(\text{MEOX})_4$, but use of $\text{Rh}_2(\text{MPPIM})_4$ resulted in high enantioselectivity for *R* = benzyl in Eq. (3) [23]. Even more striking results can be seen for diastereocontrol in C–H insertion reactions of 3-pentyl diazoacetate (Eq. (4)) [20] which is only one example of many in which diastereoselectivity is significantly enhanced with the use of $\text{Rh}_2(\text{MPPIM})_4$ [24–26].



The enhanced enantioselectivity observed for $\text{Rh}_2(\text{MPPIM})_4$, **3**, can be understood by the projection of Scheme 1. The *N*-3-phenylpropanoyl group of *S*-**3** has a substantial impact on the orientation of the alkyl

group on the carbene moiety. If the methyl group is close to the catalyst face (**14**) the product will be the *trans*-isomer (**13**). However, a high energy transition state results from the close contact of the alkyl chain with the *N*-acyl group. The conformer that positions the alkyl chain away from the *N*-acyl group (**15**) will greatly minimize *N*-acyl contact resulting in a lower energy transition state, and consequently, high diastereoselectivity for the *cis*-isomer (**12**).

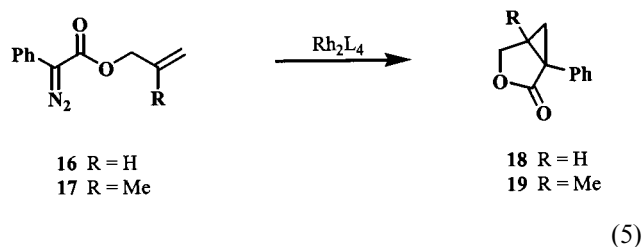
Although chiral dirhodium(II) carboxamidates are effective in the decomposition of diazoacetates and diazoacetamides [27], they have been found to be unreactive towards vinyl- and phenyldiazoacetates, as well as with β -carbonyl derivatives such as diazomalones. Recently we have established that $\text{Rh}_2(\text{MEAZ})_4$, **4a**, and $\text{Rh}_2(\text{IBAZ})_4$, **4b**, are effective in the cyclopropanation of dimethyl diazomalone as well as intramolecular cyclopropanation reactions of vinyl- and phenyldiazoesters [8]. The long Rh–Rh bond distance in these catalysts signals their increased reactivity. The structurally stable and well-defined chiral environment around each rhodium atom makes high enantiocontrol possible. While dimethyl diazomalone does not react with styrene in the presence of $\text{Rh}_2(\text{MEPY})_4$, the cyclo-



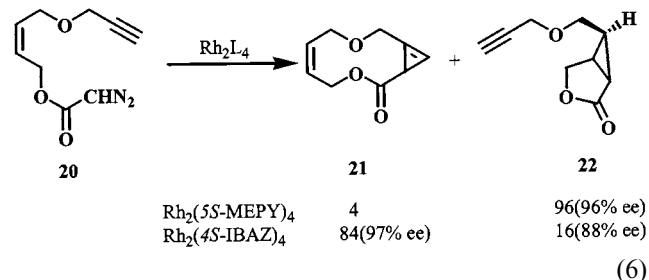
Scheme 1.

propane product is formed in 97% yield (44% ee) when the reaction is conducted with $\text{Rh}_2(4S\text{-MEAZ})_4$. The highest reported enantiomeric excess for diazomalonate reactions comes from this same transformation but using the *p*-CF₃-substituted styrene (50% ee).

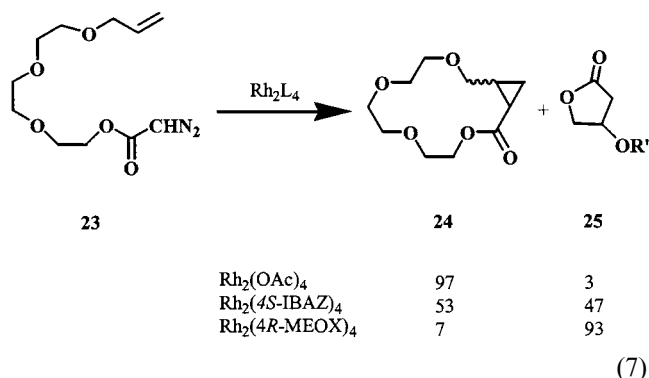
A high level of enantiocontrol can be effected by using $\text{Rh}_2(\text{MEAZ})_4$ in the intramolecular cyclopropanation of phenyldiazoacetates [8]. In the decomposition of allyl phenyldiazoacetate (**16**) and methallyl phenyldiazoacetate (**17**) both $\text{Rh}_2(\text{IBAZ})_4$, and $\text{Rh}_2(\text{MEAZ})_4$ provide high product yields of **18** and **19**, but $\text{Rh}_2(\text{MEAZ})_4$ provides the highest % ee in both cases (Eq. (5)). For comparison, use of $\text{Rh}_2(S\text{-DOSP})_4$ (DOSP = *N*-(arylphenylsulfonyl)proline), aryl = *p*-CH₃(CH₂)₁₁-C₆H₄, results in comparable yields but greatly reduced enantioselectivity [28,29]. Results are shown in Table 2. The less reactive carboxamidate catalysts $\text{Rh}_2(\text{MEPY})_4$, $\text{Rh}_2(\text{MEOX})_4$ and $\text{Rh}_2(\text{MPPIM})_4$ gave low yields and < 5% ee.



Not only do the azetidine-ligated series of catalysts (**4**) have increased reactivity, but they can have a very different chemoselectivity related to **1–3**. The competing processes of cyclopropanation and cyclopropanation in the decomposition of **20** by different catalysts give evidence of the differences (Eq. (6)) [30]. Use of the less reactive $\text{Rh}_2(5S\text{-MEPY})_4$ resulted in almost exclusively the cyclopropanation product **22** with 96% ee. However, when the more reactive $\text{Rh}_2(4S\text{-IBAZ})_4$ was employed, a high selectivity for the cyclopropanation product **21** was revealed. Enantioselectivity remained high with 97% ee for **21** and 88% ee for **22**. With $\text{Rh}_2(S\text{-DOSP})_4$, the cyclopropanation product was formed in a 96:4 ratio but with very low enantioselectivity ($\leq 20\%$ ee).



Both C–H insertion and cyclopropanation reactions catalyzed by dirhodium(II) carboxamidates have been shown to occur in high yield and high selectivity and a competitive reaction between the two is shown in Eq. (7) [31]. A diazoacetate linked through three ethylene glycol units (**23**) is decomposed by dirhodium(II) catalysts to give a mixture of the cyclopropane addition product (**24**) and the C–H insertion product (**25**). Highly reactive dirhodium(II) acetate yields almost exclusively the addition product (**24**). A near 50:50 mixture is obtained with $\text{Rh}_2(4S\text{-IBAZ})_4$, and the product distribution reverses almost completely for $\text{Rh}_2(4R\text{-MEOX})_4$ which gives primarily the C–H insertion product (**25**). Yield, diastereo- and enantioselectivity were independent of the catalyst employed. In this example, the more reactive catalysts favor the macrocyclic addition product while the less reactive catalysts give the C–H insertion product. This trend is also seen in several other examples [31].



Along a different vein, we have recently reported that $\text{Rh}_2(\text{MEOX})_4$ can be effective in the formation of ylide-derived products [32]. The diazo decomposition of **26** leads to a mixture of an ylide rearrangement product (**27**) and a cyclopropane product. Use of $\text{Rh}_2(\text{OAc})_4$ gives a 73:27 ratio of **27** to cyclopropane, while use of $\text{Rh}_2(\text{MEOX})_4$ gives mainly ylide product (89:11). Diastereoselectivity is dramatically different between $\text{Rh}_2(\text{OAc})_4$ and $\text{Rh}_2(\text{MEOX})_4$ (Eq. (8)). The *erythro*-isomer (**27E**) is the primary product from the reaction with $\text{Rh}_2(\text{OAc})_4$, while the *threo*-isomer (**27T**) is highly favored when $\text{Rh}_2(\text{MEOX})_4$ is used. A very high level of enantiocontrol is obtained using either the *S* or the *R* isomer of $\text{Rh}_2(\text{MEOX})_4$, and both diastereoselectivity and enantioselectivity results indicate that the [2,3]-sig-

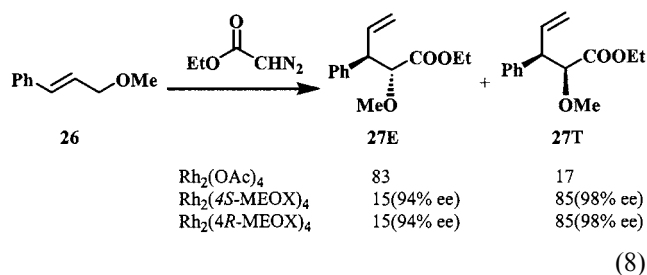
Table 2
Influence of chiral catalysts in enantiocontrol in intramolecular cyclopropanation reactions of phenol allylic diazoacetates

Catalyst	% ee of	
	18, R = H	19, R = Me
$\text{Rh}_2(4S\text{-MEAZ})_4^a$	68	84
$\text{Rh}_2(S\text{-DOSP})_4^b$	36	51

^a In CH₂Cl₂.

^b In pentane.

matropic rearrangement occurs through a metal-associated ylide intermediate. The possibility of chiral induction for other ylide-generated products remains an exciting area of advancement for dirhodium(II) carboxamidates. Hashimoto has provided similarly spectacular results for carbonyl ylide reactions [33].



Because direct comparisons between catalysts have not been reported for many catalysts of metal carbene transformations, we have not been able to report their relative advantages. We have, however, reported some data from the use of dirhodium(II) carboxylates whose chiral ligand was a sulfonylprolinate [28,29] where advantages appear to reside in reactions of phenyldiazoacetates and styryldiazoacetates. Copper catalysts have been employed for intermolecular cyclopropanation reactions [1,2], but the scope of their applications is limited. Katsuki has reported a series of chiral cobalt and ruthenium catalysts and their directed applicabilities for intermolecular cyclopropanation reactions [34–36]. Nishiyama was the originator of the chiral pybox-ruthenium(II) catalysts for cyclopropanation [21,37], but these catalysts do not affect C–H insertion reactions. In contrast, chiral dirhodium(II) carboxamidates do not offer exceptional diastereocontrol in intermolecular cyclopropanation reactions [38,39].

As has been shown in this review, high levels of product control can be achieved in cyclopropanation, cyclopropanation, macrocycle formation, C–H insertion and ylide rearrangements in a wide variety of systems with the use of dirhodium(II) carboxamidate catalysts. While no one catalyst is sufficient, utilizing a small arsenal of dirhodium(II) carboxamidates can provide excellent results. We are now able to choose a catalyst that will provide optimum results. The examples provided here offer good catalyst selection criteria.

Acknowledgements

We gratefully acknowledge the financial support of the National Science Foundation and the National Institutes of Health (Grant GM 46503) for this research.

References

- [1] M.P. Doyle, M.A. McKerver, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*, Wiley, New York, 1998.
- [2] (a) M.P. Doyle, D.C. Forbes, *Chem. Rev.* 98 (1998) 911. (b) M.P. Doyle, *Enantiomer* 4 (1999) 621. (c) M.P. Doyle, M.N. Protopopova, *Tetrahedron* 54 (1998) 7917.
- [3] (a) A. Padwa, D.J. Austin, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1797. (b) A. Padwa, K.E. Krumpke, *Tetrahedron* 48 (1992) 5385.
- [4] (a) T. Ye, M.A. McKerver, *Chem. Rev.* 94 (1994) 1091. (b) M.P. Doyle, M.A. McKerver, *J. Chem. Soc. Chem. Commun.* (1997) 983.
- [5] D.J. Miller, C.J. Moody, *Tetrahedron* 51 (1995) 10811.
- [6] M.P. Doyle, Q.-L. Zhou, C.E. Raab, G.H.P. Roos, S.H. Simonsen, V. Lynch, *Inorg. Chem.* 35 (1996) 6064.
- [7] M.P. Doyle, Q.-L. Zhou, S.H. Simonsen, V. Lynch, *Synlett* (1996) 697.
- [8] M.P. Doyle, S.B. Davies, W. Hu, *Org. Lett.* 2 (2000) 1145.
- [9] M.P. Doyle, S.B. Davies, W. Hu, *J. Chem. Soc. Chem. Commun.* (2000) 867.
- [10] F.A. Cotton, R.A. Walton, *Multiple Bonds between Metal Atoms*, 2nd ed., Clarendon Press, Oxford, 1993, p. 431.
- [11] M.P. Doyle, Chapter 7, in: R.D. Adams, F.A. Cotton (Eds.), *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, VCH Publishers, New York, 1998.
- [12] M.P. Doyle, C.E. Raab, G.H.P. Roos, V. Lynch, S.H. Simonsen, *Inorg. Chim. Acta* 266 (1997) 13.
- [13] M.P. Doyle, W.R. Winchester, J.A.A. Hoorn, V. Lynch, S.H. Simonsen, R. Ghosh, *J. Am. Chem. Soc.* 115 (1993) 9968.
- [14] M.P. Doyle, W.R. Winchester, M.N. Protopopova, A.P. Kazala, L.J. Westrum, *Org. Synth.* 73 (1996) 13.
- [15] M.P. Doyle, W.R. Winchester, M.N. Protopopova, P. Müller, G. Bernardinelli, D.G. Ene, S. Motallebi, *Helv. Chim. Acta* 76 (1993) 2227.
- [16] M.P. Doyle, A.B. Dyatkin, M.N. Protopopova, C.I. Yang, C.S. Miertschin, W.R. Winchester, S.H. Simonsen, V. Lynch, R. Ghosh, *Recueil Trav. Chim. Pays-Bas* 114 (1995) 5763.
- [17] M.P. Doyle, R.E. Austin, A.S. Bailey, M.P. Dwyer, A.B. Dyatkin, A.V. Kalinin, M.M.Y. Kwan, S. Liras, C.J. Oalman, R.J. Pieters, M.N. Protopopova, C.E. Raab, G.H.P. Roos, Q.-L. Zhou, S.F. Martin, *J. Am. Chem. Soc.* 117 (1995) 5763.
- [18] M.P. Doyle, W.R. Winchester, S.H. Simonsen, R. Ghosh, *Inorg. Chim. Acta* 220 (1994) 193.
- [19] M.P. Doyle, Q.-L. Zhou, C. Charnsangavej, M.A. Longoria, *Tetrahedron Lett.* 37 (1996) 4129.
- [20] M.P. Doyle, Q.-L. Zhou, A.B. Dyatkin, D.A. Ruppert, *Tetrahedron Lett.* 36 (1995) 7579.
- [21] M.P. Doyle, C.S. Peterson, Q.-L. Zhou, H. Nishiyama, *J. Chem. Soc. Chem. Commun.* (1997) 211.
- [22] M.P. Doyle, A. van Oeveren, L.J. Westrum, M.N. Protopopova, T.W. Clayton, Jr., *J. Am. Chem. Soc.* 113 (1991) 8982.
- [23] J.W. Bode, M.P. Doyle, M.N. Protopopova, Q.-L. Zhou, *J. Org. Chem.* 61 (1996) 9146.
- [24] M.P. Doyle, A.B. Dyatkin, G.H.P. Roos, F. Canas, D.A. Pierson, A. van Basten, P. Müller, P. Polleux, *J. Am. Chem. Soc.* 116 (1994) 4507.
- [25] M.P. Doyle, A.V. Kalinin, D.G. Ene, *J. Am. Chem. Soc.* 118 (1996) 8837.
- [26] M.P. Doyle, J.S. Tedrow, A.B. Dyatkin, C.J. Spaans, D.G. Ene, *J. Org. Chem.* 64 (1999) 8907.
- [27] M.P. Doyle, R.E. Austin, A.S. Bailey, M.P. Dwyer, A.B. Dyatkin, A.V. Kalinin, M.M.Y. Kwan, S. Liras, C.J. Oalman, R.J. Pieters, M.N. Protopopova, C.E. Raab, G.H.P. Roos, Q.-L. Zhou, S.F. Martin, *J. Am. Chem. Soc.* 117 (1995) 5763.

- [28] H.W.L. Davies, B.D. Doan, *J. Org. Chem.* 64 (1999) 8501.
- [29] For reviews of the effectiveness of chiral dirhodium(II) carboxylates with styryldiazoacetates in cyclopropanation reactions see: (a) H.M.L. Davies, *Aldrichim. Acta* (1997) 107, (b) H.M.L. Davies, *Eur. J. Org. Chem.* (1999) 2459.
- [30] M.P. Doyle, D.G. Ene, C.S. Peterson, V. Lynch, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 700.
- [31] M.P. Doyle, W. Hu, *Tetrahedron Lett.* 41 (2000) 6265.
- [32] M.P. Doyle, D.C. Forbes, M.M. Vasbinder, C.S. Peterson, *J. Am. Chem. Soc.* 120 (1998) 7653.
- [33] S. Kitagaki, M. Anada, O. Kataoka, K. Matsuno, C. Umeda, N. Watanabe, S. Hashimoto, *J. Am. Chem. Soc.* 121 (1999) 1417.
- [34] T. Fukuda, T. Katsuki, *Tetrahedron Lett.* 38 (1997) 3443.
- [35] T. Uchida, R. Irie, T. Katsuki, *Tetrahedron* 56 (2000) 3501.
- [36] T. Niimi, T. Uchida, R. Irie, T. Katsuki, *Tetrahedron Lett.* 41 (2000) 3647.
- [37] H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki, K. Itoh, *Bull. Chem. Soc. Jpn.* 68 (1995) 1247.
- [38] S. Kitagaki, H. Matsuda, N. Watanabe, S. Hashimoto, *Synlett.* (1997) 1171.
- [39] P. Müller, C. Baud, D. Ene, S. Motallebi, M.P. Doyle, B.D. Brandes, A.B. Dyatkin, M.M. See, *Helv. Chim. Acta* 78 (1995) 459.