DOI: 10.1002/ejic.200800944

Metal-Catalyzed Olefin Cyclopropanation with Ethyl Diazoacetate: Control of the Diastereoselectivity

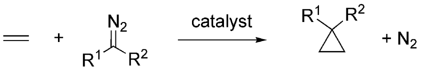
Ana Caballero,[a] Auxiliadora Prieto,[b] M. Mar Díaz-Requejo,*[a] and Pedro J. Pérez*[a]

Keywords: Carbenes / Cyclopropanation / Diastereoselectivity / Olefins / Transition metals

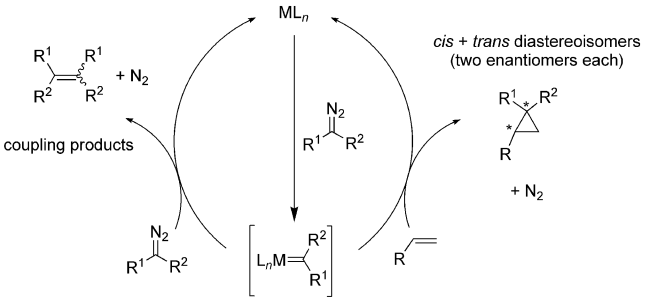
The control of the *cis/trans* diastereoselectivity by catalyst design in the olefin cyclopropanation reaction with ethyl diazoacetate is reviewed. Catalysts based on ruthenium, copper, rhodium, iron, osmium and cobalt are discussed. The degree of stereocontrol achieved for styrene and related aryl-containing olefins is higher than that for terminal alkenes with no aryl substituents.

Introduction

Cyclopropanes are versatile molecules with many potential applications in organic chemistry.[1] Among the known methods to prepare them, the formal addition of a carbene group from a diazo compound to an unsaturated double bond [Equation (1)] has been exhaustively developed in the last decades.[2,3] Although such a process was initially induced either thermally or photochemically, further use of transition-metal catalysts allowed exerting a certain control in the selectivity of this reaction. This is a key issue in this transformation, in which different products and isomers can be formed. Scheme 1 shows the catalytic cycle of a typical olefin cyclopropanation reaction, in which an olefin reacts with a diazo compound in the presence of a given catalyst. Substituted olefins lead to the formation of two diastereoisomers, *cis* and *trans* (assuming that the substituents of the diazo compound are different), each of them corresponding to a mixture of two enantiomers. It is also worth mentioning that, in most cases, the catalyst also induces the catalytic coupling of the diazo compound, a undesired reaction that diminishes the yields of cyclopropanes. This is a process in which chemo-, diastereo- and enantioselectivity are variables that affect the products obtained at the end of the reaction. Chemoselectivity is intended as the [cyclopropanes]/[coupling products] ratio, the formation of the latter not being desirable. Diastereoselectivity is described by the relative amounts of the *cis* and *trans* isomers, in the so-called diastereomeric ratio (*dr*, *cis/trans*). Finally, the enantioselectivity is given by the ratio of each enantiomer in each diastereoisomer: a different *ee* value is usually observed for the *cis* and *trans* diastereomers.[3] Those selectivities depend exclusively on the nature of the catalyst; therefore, catalyst design is crucial when pursuing a certain diastereo- or enantiomer.



(1)



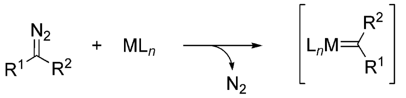
Scheme 1. Olefin cyclopropanation reaction with diazo compounds.

It is well-established that this transformation (Scheme 1) occurs through the intermediacy of a transient metallocarbene species [Equation (2)] formed by the interaction of the catalyst precursor and the diazo compound.[2,4] Those species are electrophilic in nature, their reaction with the nucleophiles in the reaction medium (olefin, diazo compound) being then favoured. Usually, reaction with a second molecule of diazo compound takes place readily, leading to the undesired coupling products. However, a common technique employed in this area is the slow addition of the diazo compound into a solution of the catalyst and the olefin.

---

[a] Laboratorio de Catálisis Homogénea, Departamento de Química y Ciencia de los Materiales, Unidad Asociada al CSIC, Campus de El Carmen s/n, Universidad de Huelva,
21007 Huelva, Spain
Fax: +34-959219942
E-mail: perez@dqcm.uhu.es
[b] Departamento de Ingeniería Química, Química Física y Química Orgánica, Campus de El Carmen s/n, Universidad de Huelva,
21007 Huelva, Spain

In this way, most of the catalysts display good values of chemoselectivity toward cyclopropanes, and the control of the chemoselectivity is not difficult with this methodology. On the other hand, since the first report by Nozaki[5] of the asymmetric, metal-catalyzed cyclopropanation of an olefin, a number of systems have been reported[2,3] to induce such transformations, which have enabled the nearly quantitative (>99%) as well as completely enantioselective (>99:1) cyclopropanation of many double bonds.



(2)

However, the control of the diastereoselection, i.e., the *cis*/*trans* ratio, has been more difficult to accomplish. For some time it was supposed that such control was inaccessible, on the basis of the idea that the interaction between the metallocarbene and the olefin takes place at a distance far enough from the pocket generated by the ligands around the metal centre (Figure 1). Because of this, the effect of the catalyst structure on the *cis*/*trans* ratio was only observable in a few, highly elaborated catalysts. Nevertheless, in the last decade a number of systems have been described to induce large excesses of either *cis* or *trans* cyclopropanes. This shows that the appropriate selection of ligands and the metal could have some influence in the *cis*/*trans* ratio. Other variables are the nature of the diazo compound and the olefin. The substituents at the diazo functionality affect the reaction as a result of both their electronic and steric properties. Diazo compounds with one or two substituents different from hydrogen, with different electronic nature (electron-withdrawing or electron-donating), with very bulky groups or with chiral groups have been employed in the olefin cyclopropanation reaction.[2,3] In order to compare the sole effect of the catalyst structure in the cyclopropanation reaction, we have focussed exclusively on those systems using ethyl diazoacetate (EDA), N_2CHCO_2Et, as the carbene source. This diazo compound is quite convenient from a synthetic point of view, since it is quite stable, can be purchased from several sources and it is employed at the

Ana Caballero (1976) graduated in Chemistry at the Universidad de Sevilla (1999) and obtained her Ph.D. from the Universidad de Huelva (2004) with Prof. Pedro J. Pérez. Later she moved to the Laboratoire de Chemie de la Coordination (CNRS, Toulouse) for a postdoctoral stay with Dr. Sylviane Sabo-Etienne. After two years, she obtained (in 2007) her current position at the Universidad de Huelva within the "Ramon y Cajal" Programme. Her research interests are focussed on the development of late transition-metal catalyst for the transformation of hydrocarbons by using diazo compounds or borane reagents as functionalization reagents.

Auxiliadora Prieto (1975) graduated in Chemistry at the Universidad de Sevilla (1998) and obtained her Ph.D. from the Universidad de Sevilla (2003) with Prof. Rosario Fernández and Dr. Jose M^a Lassaletta. A postdoctoral stay followed at the Center for Catalysis- University of Aarhus (Denmark) with Prof. Karl A. Jorgensen. Since 2005 she is enrolled at the Universidad de Huelva with a junior lectureship in organic chemistry. She is currently interested in the development of chiral ligands with potential application in homogeneous catalysis.

M. Mar Díaz-Requejo (1971) graduated in Chemistry at the Universidad de Sevilla (1994) and obtained her Ph.D. from the Universidad de Huelva in 2000 with Prof. Pedro J. Pérez. She joined Prof. Brookhart's group at the University of North Carolina, Chapel Hill (USA) for a postdoctoral stay between 2001–2003. That year, she enrolled in the "Ramón y Cajal" Programme in Spain. She has recently become Lecturer of Inorganic Chemistry. Her current research work is related to the development of group-11-metal-based catalysts for the functionalization of C–H bonds by carbene and nitrene transfer reactions.

Pedro J. Pérez (1965) graduated in Chemistry in 1987 in Sevilla. He received his Ph.D. degree in Chemistry (1991) in the Universidad de Sevilla, under the direction of Prof. Ernesto Carmona. As a Fulbright Scholar, he then joined Prof. Brookhart's group at UNC-Chapel Hill (USA), where he started the research related to the use of copper-based catalysts for diazo decomposition. In 1993 he moved to a new university founded in Huelva, as an Assistant Professor (1993–1995), later becoming Lecturer (1995) and finally Professor of Inorganic Chemistry (2005). The general research interest of his group is related to the development of late-transition-metal complexes for their use as catalysts in transformations with low reactive substrates. He is also responsible of the Homogeneous Catalysis Laboratory, an Associate Unit to the Spanish National Council of Research (CSIC) [http://www.catalysisatuhu.com].

industrial level. Probably this explains why most of the work related to olefin cyclopropanation has been performed with EDA. A survey in literature databases shows that the number of contributions based on the use of this diazo compound is nine times those with *tert*-butyl diazoacetate and thirty times those with 2-phenyldiazoacetate. However, we wish to remark that the use of these diazo reagents have usually provided high *cis*/*trans* ratios, the effect of the metal being secondary. Therefore, we have not considered them in this contribution, which focuses on the effect of the metal catalyst on the *dr* values.

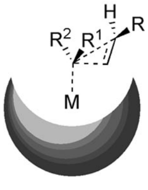
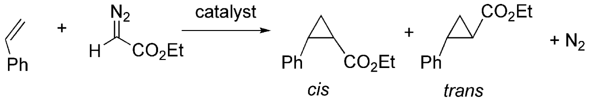


Figure 1. The metallocarbene–olefin interaction. Dashed lines represent breaking or forming bonds.

Most of the work described in the literature is based on the use of styrene as the model olefin [Equation (3)]. For the sake of comparison of the capabilities of a given catalyst to exert any effect on the diastereoselectivity of the cyclopropanation reaction, this is quite a convenient substrate: the use of di- or trisubstituted olefins would substantially alter the geometry of the above transition state. In this contribution, the current state of the art in the olefin cyclopropanation reaction with ethyl diazoacetate is presented from the perspective of the control of the *cis*/*trans* diastereoselectivity. In many cases, styrene is the preferred substrate, although other olefins, particularly 2,5-dimethyl-2,4-diene or terminal alkenes will also be presented. It is well known that the *trans* diastereoisomer is thermodynamically preferred. This is in accord with a vast number of catalytic systems described to induce a certain excess of this isomer. Because of this, in this account we will only consider those catalytic systems that provide a high excess of one of the cyclopropanes.

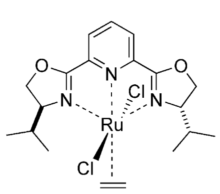


(3)

Cyclopropanation of Styrene with Ethyl Diazoacetate

Ruthenium-Based Catalysts

In 1994, Nishiyama[6] reported the use of ruthenium complex **1** containing the pybox ligand as a very efficient catalyst for the asymmetric styrene cyclopropanation reaction, with a 8:92 respective distribution of the *cis* and *trans* cyclopropanes. This and related Ru–pybox systems have provided both high diastereo- (toward *trans*) and enantioselectivity with styrene as the olefin.



1

(8:92)

Further studies on the use of ruthenium complexes as catalysts for this transformation were developed by using porphyrin ligands. Simultaneous, independent work by Berkessel,[7] Simonneoux[8] and Che[9] showed the capabilities of Ru(porphyrin)(CO) complexes to catalyze, with a manifest excess of the *trans* isomer, the reaction of styrene and EDA. Complexes **2** or **3** were reported to afford *cis*/*trans* mixtures of 4:96 and 2:98, respectively, the R* groups being polycyclic substituents. Porphyrins with simple substituents such as ethyl (in **4**) or phenyl (in **5**) also induced high *trans* selectivity. It is worth mentioning that the porphyrin skeleton has been employed as the core for a dendritic structure, the corresponding ruthenium carbonyl derivative **6** being also a good catalyst (Figure 2).[9c]

In addition to pybox or porphyrin ligands, a series of complexes containing Schiff bases have also been reported to exert a certain degree of diastereocontrol toward the *trans* cyclopropane. Thus, the tetradentate N_2O_2 ligand when coordinated to the Ru centre in an α-*cis* fashion **7** originated[10] a 2:98 *dr*. Other pyridine-diimine[11] **8** or salen[12] **9** derivatives also directed toward this isomer, although to a lower extend. In situ generated catalytic species using $RuCl_2(PPh_3)_3$ and the phosphane-containing P,N,N ligands (**10**) produced a 3:97 mixture of isomers (Figure 3).[13]

Several groups have focussed on the design of heterogeneous systems based on the immobilization of some of the already discussed soluble catalysts. In all cases, the diastereoselection observed in the homogeneous system is maintained in the heterogeneous counterpart. Thus, polymer-supported complexes of ruthenium-containing porphyrin ligands have been reported to effectively catalyze this transformation (9:91 *dr*).[14] Mayoral et al. have described the use of pyridinebis(oxazoline)-containing ruthenium complexes anchored to a solid support (*trans* isomer in the range 90–94%).[15] Such covalent interaction has been achieved either by grafting or by polymerization. Finally, work by Kühn and co-workers[16] has shown that $Cp^*Ru(PPh_3)_2Cl$ can be grafted on mesoporous aluminosilicates and employed as a heterogeneous catalyst that yields a 8:92 *dr*.

The control of the diastereoselectivity toward the formation of the *cis* isomer in the reaction of styrene and EDA was first reported by Katsuki,[17a] in a seminal work pub-

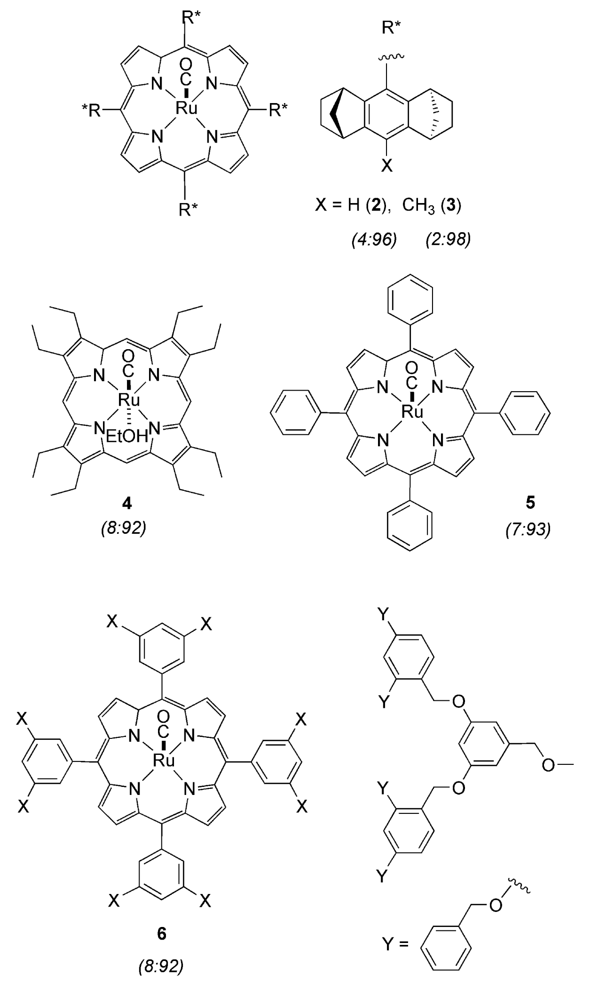


Figure 2. Ru-based catalysts for styrene cyclopropanation with EDA with *trans* diastereoselection.

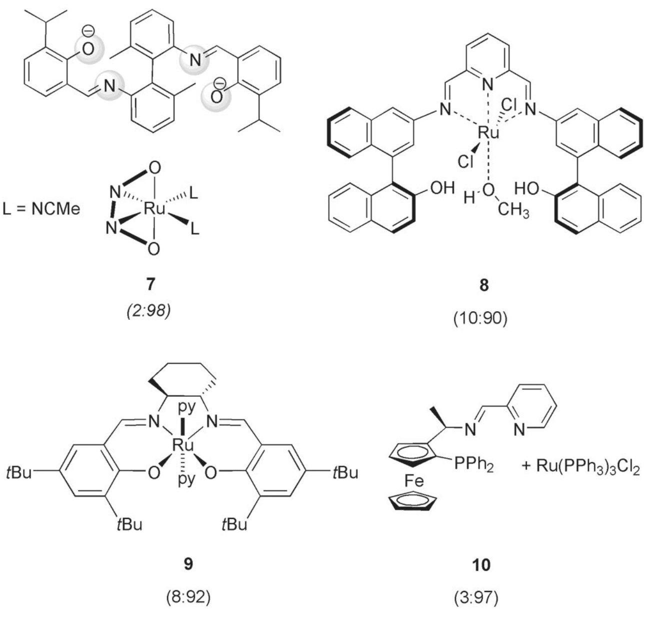


Figure 3. More Ru-based catalysts for styrene cyclopropanation with EDA with *trans* diastereoselection.

lished in 2000, after previous work with the bulkier *tert*-butyl diazoacetate.[17b] The (salen)Ru(NO)$^+$ complex **11** catalyzed the former transformation with high *cis* diastereoselection (93:7, *dr*), although in low yield (33%) and under irradiation. Later, Mezzetti[18] described the catalytic properties of cationic, five-coordinate complexes **12** and **13** with a tetradentate PNNP ligand that led to the nearly exclusive formation of the *cis* isomer. Finally, it is also worth mentioning the use of ferrocenyl-based diphosphane ligands that also provided an excess of the *cis* isomer when added to solutions of Ru(dmso)Cl$_2$ to in situ generate the catalytically active species (Figure 4).[19]

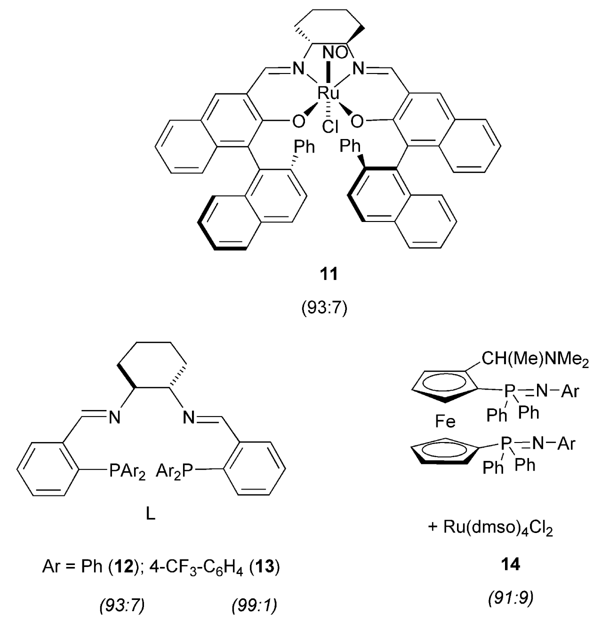
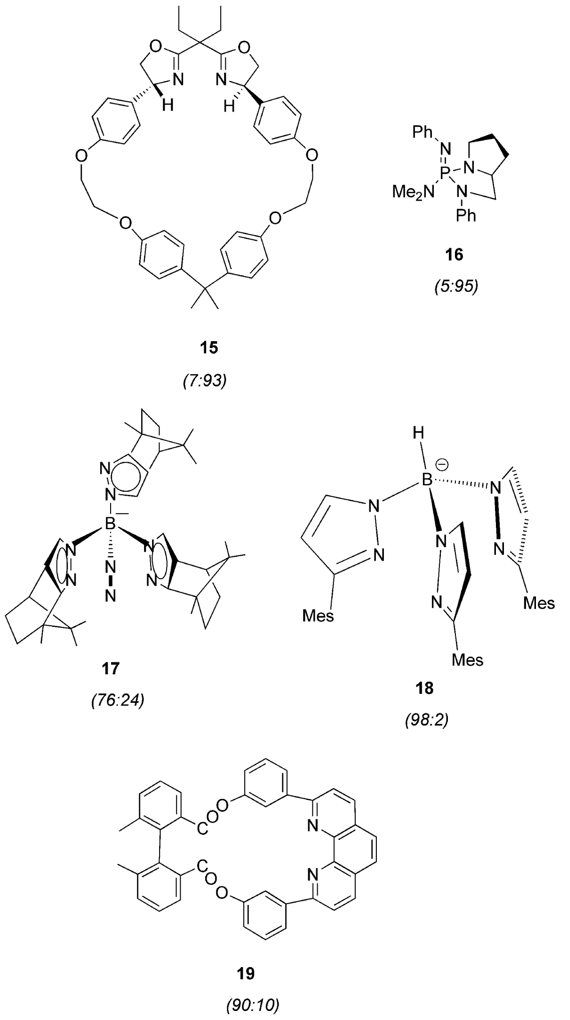


Figure 4. Ru-based catalysts for styrene cyclopropanation with EDA with *cis* diastereoselection.

Copper-Based Catalysts

In spite of the number of copper-based catalysts reported for this transformation, very few are capable of inducing a certain degree of diastereoselectivity. Only a couple of examples are known to promote a significant excess of the *trans* isomer. Sunjic[20] described the use of supramolecular Cu^{I} complexes such as **15** for the asymmetric cyclopropanation of styrene, which provided a 7:93, *cis*/*trans* mixture of cyclopropanes. Catalyst **16**, in situ generated from CuOTf and iminodiazaphospholidine and with a stereogenic phosphorus centre, has also been reported to produce the *trans* isomer in large excess (5:95).[21] In the case of the *cis* isomer, seminal work by Brunner et al. included a copper complex[22] with an optically active tetrakis(pyrazolylborate) ligand **17** that induced a 76:24, *cis*/*trans* mixture. Further work with tris(pyrazolylborate) ligands led to Pérez and coworkers[23] to find that the hydrotris(3-mesitylpyrazolyl)borate ligand **18** efficiently catalyzed this transformation (98% yield), affording a 98:2, *cis*/*trans* mixture of cyclopropanes.

A third example was given by Benaglia,[24] describing the use of phenanthroline-containing macrocycles **19** that afforded a 90:10 ratio of products (Figure 5).



15 (7:93)

16 (5:95)

17 (76:24)

18 (98:2)

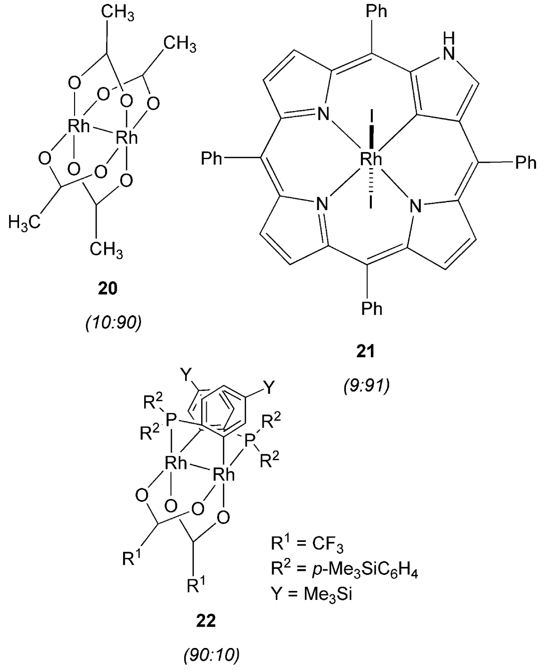
19 (90:10)

Figure 5. Cu-based catalysts for styrene cyclopropanation with EDA with large diastereoselection (*cis*/*trans*).

Rhodium-Based Catalysts

With no doubt, rhodium has been the metal of choice for most of the work carried out with the aim of transferring a carbene group from a diazo compound to organic substrates.[2,3] In contrast with the excellent results obtained regarding enantiomeric excesses in the cyclopropanation of styrene with EDA, very few examples of high diastereomeric excess are known with this metal. Doyle[25] described the use of several complexes derived from plain dirhodium tetraacetate as catalysts for this transformation along with a series of diazoacetates with bulky substituents. In some cases, very high stereoselectivities were observed for elaborated diazo compounds; however, the simple $Rh_2(OAc)_4$ (**20**) only gave a moderate 38:62 *cis*/*trans* diastereoselection. Interestingly, later work by Yadav with the same catalyst but operating with an ionic liquid as the reaction medium led to a 10:90 mixture of cyclopropanes.[26] Another rhodium-based catalyst that favours the formation of the *trans* isomer contains an *N*-confused porphyrin ligand **21**: Furuta reported a 9:91 distribution of isomers for this transformation with this Rh^{III} catalyst.[27]

We are only aware of one catalytic system based on rhodium to induce a large excess of the *cis* isomer in the reaction of styrene and EDA. The catalyst possesses the typical Rh^{II} dimeric structure with several *ortho*-metalated arylphosphane ligands and was employed by Lahuerta, Ubeda and co-workers[28] to afford a 90:10 *cis*/*trans* ratio of cyclopropanes (complexes **22**, Figure 6).



20 (10:90)

21 (9:91)

$R^1 = CF_3$
$R^2 = p\text{-}Me_3SiC_6H_4$
$Y = Me_3Si$

22 (90:10)

Figure 6. Rh-based catalysts for styrene cyclopropanation with EDA with large diastereoselection (*cis*/*trans*).

Catalysts Based on Iron, Osmium and Cobalt

Iron complexes with porphyrin ligands have been reported to induce a high *trans* diastereoselection. Kodadek, Woo and co-workers[29] reported such behaviour for several Fe^{II} porphyrin complexes. Fe(TPP) (**23**, [TPP = tetrakis(tetraphenylporphyrin)] induced a 10:90 *dr*. The addition of one equivalent of cobaltocene relative to Fe induced, in several cases, the enhancement of the catalytic activity as well as the *trans* stereoselectivity. Related iron complexes **24** where later reported by Woo[30] to reach a 95% yield of the *trans* isomer. More recently, Che described the use of the Halterman iron porphyrin **25** and cobaltocene to reach a 4:96 mixture of cyclopropanes.[31] On the other hand, there are no examples of iron catalysts to induce the formation of the *cis* cyclopropanes in high yield. It is only worth mentioning the work by Hossain[32] with $[CpFe(CO)_2(thf)]BF_4$ (**26**) that afforded mixtures with the 60:40 *dr*.

The use of osmium-based catalyst is reduced to one system, also reported by Woo,[33] and with structures similar to those of the iron analogues. The OsTTP core **27** was found to react with EDA to yield an isolable osmium–carbene complex. In addition, the catalytic reaction with EDA and styrene led to the formation of a 9:91 *cis*/*trans* mixture.

Two different types of catalyst based on cobalt have been described to induce large diastereoselection. Katsuki[34] described the use of the salen-containing cobalt complex **28** to induce a 99:1 *cis*/*trans* mixture of cyclopropanes. The second family of catalysts has been reported by Zhang et al.[35] and contain a porphyrin ligand with substituents slightly different from those reported with other metals. The use of catalysts **29** have led to the observation of large *trans* excesses as high as 98%, with 0.5 equiv. of 4-(dimethylaminopyridine) (DMAP) as an additive. In the absence of DMAP, both yield and diastereoselectivity were significantly decreased (Figure 7).

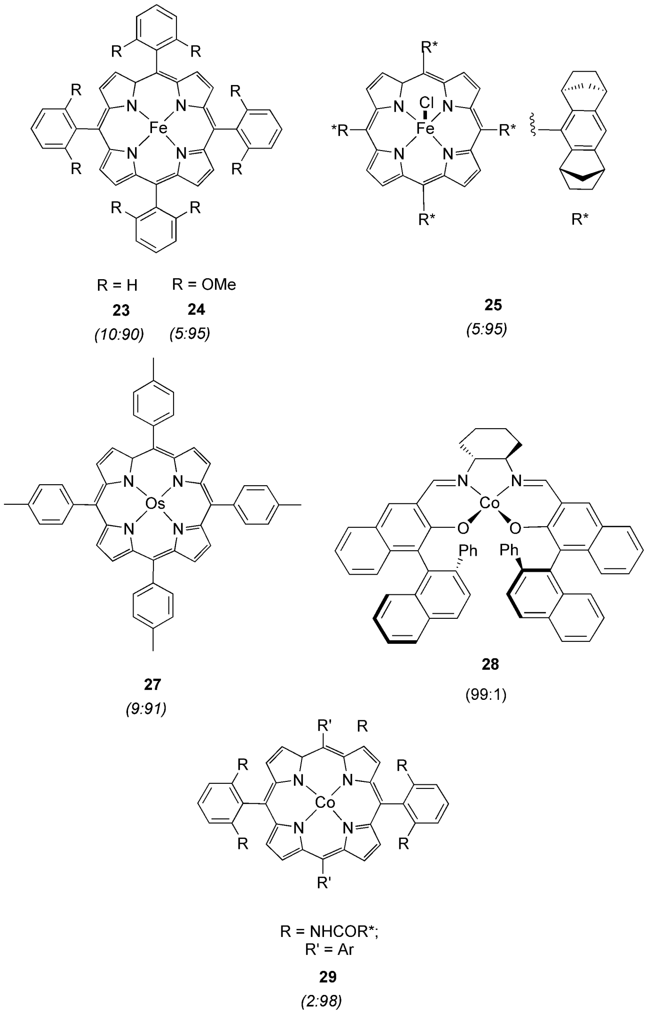
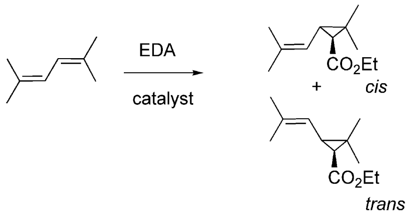


Figure 7. Catalysts based in Fe, Os or Co inducing high diastereoselection (*cis*/*trans*).

Cyclopropanation of Aliphatic Olefins with Ethyl Diazoacetate

As mentioned above, styrene has been extensively employed as the model substrate for the metal-catalyzed olefin cyclopropanation reaction with diazo compounds. However, the most interesting substrate from an industrial point of view is 2,5-dimethyl-2,4-hexadiene, since it constitutes the starting material for the synthesis of chrysanthemate derivatives employed as pesticides[2,3] [Equation (4)]. Therefore, alkenes containing alkyl groups instead of aryl substituents can model, to a certain extent, the behaviour expected for the corresponding diene. Very few examples of high diastereoselection have been reported for olefins with no aryl substituents. Table 1 shows all those catalytic systems for which at least a 3:1 ratio of the *cis* or *trans* isomers has been obtained by using ethyl diazoacetate as the carbene source.



(4)

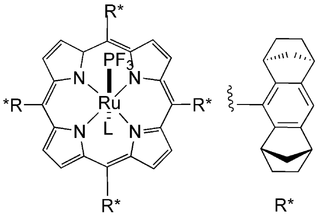
Table 1. Metal-catalyzed alkene cyclopropanation with EDA with significant diastereomeric excesses.

Catalyst	Olefin	*dr*[a]	Yield	Ref.
30	1-octene	1:99	42	[7b]
8	1-heptene	17:83	45	[11]
9	1-pentene	19:81	20	[12]
[**13**RuCl]SbF$_6$	1-octene	85:15	66	[18c]
14 + Ru(dmso)$_4$Cl$_2$	1-hexene	84:16	88	[19]
18Cu	1-hexene	77:23	84	[23b]
18Cu	1-octene	75:25	80	[23b]
[**12**RuCl] + TlPF$_6$	2,5-dimethyl-2,4-hexadiene	94:6	18	[18a]
18Cu	2,5-dimethyl-2,4-hexadiene	78:22	78	[23b]
31	2,5-dimethyl-2,4-hexadiene	76:24	84	[36]

[a] Diastereomeric ratio, *cis*/*trans*.

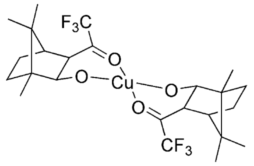
For terminal aliphatic alkenes, only one example is known to provide nearly complete diastereoselection toward the *trans* cyclopropane. It was reported by Berkessel with the Ru-based catalyst **30**. Unfortunately, yields were moderate, a fact that is also observed in other cases with these olefins, in which the reactivity is lower than that of styrene. Orientation to *cis*-cyclopropanes is yet unknown to reach values higher than 85%: this is the maximum value reached as reported by Mezzetti with a cationic catalyst containing ligand **13**.

The situation does not vary with 2,5-dimethyl-2,4-hexadiene as the olefin. In this case, selectivity toward the *trans* isomer is not reported in high excess, although it is quite probable that some of the systems shown in the previous section, exclusively focussed toward styrene, could provide significant values of diastereoselectivities when applied to this diene. Mezzetti and co-workers found that the complex [**12**RuCl], in the presence of TlPF$_6$, catalyzed the reaction of EDA and the diene to give a 94:6 *cis*/*trans* mixture of diastereoisomers, although in low yield. Other copper systems, on tris(pyrazolylborate) ligands **18** or Cu(facam)$_2$ (**31**), led to mixtures of ca. 3:1, favouring the *cis* isomer, with better yields than those for the ruthenium case.



L = MeCN

30



31

Future Development

We can conclude that control of diastereoselectivity in the olefin cyclopropanation reaction is far from being complete. In the case of styrene and related aryl-containing olefins, high *cis* or *trans* selectivities have been achieved, but in a reduced number of systems. The situation is worse for terminal alkenes with no aryl groups as substituents, for which no high *cis* stereocontrol has yet been achieved, and only one case with large *trans* selectivity is known (and with moderate yield). Therefore, the design of very active, diastereoselective catalysts for the olefin cyclopropanation reaction with diazo compounds remains a challenge, to a certain degree. The ultimate catalyst to pursue, once such diastereocontrol is reached, will be one that induces, in addition, large enantioselection for each diastereoisomer.

Acknowledgments

The authors wish to acknowledge funding from the Ministerio de Educación (CTQ2008-00042BQU) and Junta de Andalucía (Grants P05-FQM-0914 and P07-FQM-02870).

---

[1] See for example: a) H.-U. Reissig, R. Zimmer, *Chem. Rev.* **2003**, *103*, 1151–1196; b) F. Gnad, O. Reiser, *Chem. Rev.* **2003**, *103*, 1603–1624.

[2] a) M. P. Doyle, *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, U. K., **1995**, vol. 12, p. 421; b) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, John Wiley & Sons, New York, **1998**.

[3] H. Lebel, J.-F. Marcoux, C. Molinaro, A. B. Charette, *Chem. Rev.* **2003**, *103*, 977–1050.

[4] a) W. Kirmse, *Angew. Chem. Int. Ed.* **2003**, *42*, 1088–1093; b) H. Nishiyama, K. Aoki, H. Itoh, T. Iwamura, N. Sakata, O. Kurihara, Y. Motoyama, *Chem. Lett.* **1996**, *25*, 1071.

[5] H. Nozaki, S. Moriuti, T. Nagase, *Tetrahedron Lett.* **1966**, *7*, 5239.

[6] a) H. Nishiyama, Y. Itoh, H. Matsumoto, S.-B. Park, K. Itoh, *J. Am. Chem. Soc.* **1994**, *116*, 2223–2224; b) H. Nishiyama, *Enantiomer* **1999**, *4*, 569–574; c) H. Nishiyama, *Top. Organomet. Chem.* **2004**, *11*, 81–92.

[7] a) M. Frauenkron, A. Berkessel, *Tetrahedron Lett.* **1997**, *38*, 7175–7176; b) A. Berkessel, P. Kaiser, J. Lex, *Chem. Eur. J.* **2003**, *9*, 4746–4756.

[8] E. Galardon, P. Le Maux, G. Simmoneaux, *Chem. Commun.* **1997**, 927–928.

[9] a) W.-C. Lo, C.-M. Che, K.-F. Cheng, T. C. W. Mak, *Chem. Commun.* **1997**, 1205–1206; b) C.-M. Che, J.-S. Huang, F.-W. Lee, Y. Li, T.-S. Lai, H.-L. Kwong, P.-F. Teng, W.-S. Lee, W.-C. Lo, S.-M. Peng, Z.-Y. Zhou, *J. Am. Chem. Soc.* **2001**, *123*, 4119–4129; c) J.-L. Zhang, H.-B. Zhou, J.-S. Huang, C.-M. Che, *Chem. Eur. J.* **2002**, *8*, 1554–1562.

[10] I. J. Munslow, K. M. Gillespie, R. J. Deeth, P. Scott, *Chem. Commun.* **2001**, 1638–1639.

[11] W. Tang, X. Hu, X. Zhang, *Tetrahedron Lett.* **2002**, *43*, 3075–3078.

[12] J. A. Miller, W. Jin, S. T. Nguyen, *Angew. Chem. Int. Ed.* **2002**, *41*, 2953–2956.

[13] H. Dai, X. Hu, H. Chen, C. Bai, Z. Zheng, *J. Mol. Catal. A* **2004**, *211*, 17–21.

[14] J.-L. Zhang, C.-M. Che, *Org. Lett.* **2002**, *4*, 1911–1914.

[15] a) A. Cornejo, J. M. Fraile, J. I. García, E. García-Verdugo, M. J. Gil, G. Legarreta, S. V. Luis, V. Martínez-Merino, J. A. Mayoral, *Org. Lett.* **2002**, *4*, 3927–3930; b) A. Cornejo, J. M. Fraile, J. I. García, M. J. Gil, V. Martínez-Merino, J. A. Mayoral, *Tetrahedron* **2005**, *61*, 12107–12110; c) A. Cornejo, J. M. Fraile, J. I. García, M. J. Gil, S. V. Luis, V. Martínez-Merino, J. A. Mayoral, *J. Org. Chem.* **2005**, *70*, 5536–5544.

[16] A. Sakthivel, F. E. Pedro, A. S. T. Chiang, F. E. Kuhn, *Synthesis* **2006**, 1682–1688.

[17] a) T. Uchida, R. Irie, T. Katsuki, *Synlett* **1999**, 1163–1165; b) T. Uchida, R. Irie, T. Katsuki, *Tetrahedron* **2000**, *56*, 3501.

[18] a) S. Bachmann, M. Furler, A. Mezzetti, *Organometallics* **2001**, *20*, 2102–2108; b) C. Bonaccorsi, S. Bachmann, A. Mezzetti, *Tetrahedron: Asymmetry* **2003**, *14*, 845–854; c) C. Bonaccorsi, A. Mezzetti, *Organometallics* **2005**, *24*, 4953–4960.

[19] V. D. M. Hoang, P. A. N. Eddy, T.-J. Kim, *Tetrahedron Lett.* **2007**, *48*, 8014–8017.

[20] a) T. Portada, M. Roje, Z. Raza, V. Caplar, M. Zinic, V. Sunjic, *Chem. Commun.* **2000**, 1993–1994; b) T. Portada, M. Roje, Z. Raza, V. Caplar, M. Zinic, V. Sunjic, *Eur. J. Org. Chem.* **2007**, 838–856.

[21] J. M. Brunel, O. Legrand, S. Reymond, G. Buono, *J. Am. Chem. Soc.* **1999**, *121*, 5807–5808.

[22] H. Brunner, U. P. Singh, T. Boeck, S. Altmann, T. Scheck, B. Wrackmeyer, *J. Organomet. Chem.* **1993**, *443*, C16-C18.

[23] a) M. M. Díaz-Requejo, T. R. Belderraín, S. Trofimenko, P. J. Pérez, *J. Am. Chem. Soc.* **2001**, *123*, 3167–3168; b) M. M. Díaz-Requejo, A. Caballero, T. R. Belderraín, M. C. Nicasio, S. Trofimenko, P. J. Pérez, *J. Am. Chem. Soc.* **2002**, *124*, 978–983.

[24] A. Puglisi, M. Benaglia, R. Annunziata, A. Bologna, *Tetrahedron Lett.* **2003**, *44*, 2497–2951.

[25] M. P. Doyle, V. Bagheri, T. J. Wandless, N. K. Harn, D. A. Brinker, C. T. Eagle, K.-L. Loh, *J. Am. Chem. Soc.* **1990**, *112*, 1906–1912.

[26] J. S. Yadav, B. V. S. Reddy, P. N. Reddy, *Adv. Synth. Catal.* **2004**, *346*, 53–56.

[27] T. Niino, M. Toganoh, B. Andrioletti, H. Furuta, *Chem. Commun.* **2006**, 4335–4337.

[28] a) F. Estevan, P. Lahuerta, J. Lloret, M. Sanaú, M. A. Úbeda, J. Vila, *Chem. Commun.* **2004**, 2408–2409; b) F. Estevan, J. Lloret, M. Sanaú, M. A. Úbeda, *Organometallics* **2006**, *25*, 4977–4984.

[29] J. R. Wolf, C. G. Hamaker, J.-P. Djukic, T. Kodadej, L. K. Woo, *J. Am. Chem. Soc.* **1995**, *117*, 9194–9199.

[30] C. G. Hamaker, G. A. Mirafzal, L. K. Woo, *Organometallics* **2001**, *20*, 5171–5176.

[31] T.-S. Lai, F.-Y. Chan, P.-K. So, D.-L. Ma, K.-Y. Wong, C.-M. Che, *Dalton Trans.* **2006**, 4845–4851.

[32] W. J. Seitz, A. K. Saha, M. M. Hossain, *Organometallics* **1993**, *12*, 2604–2608.

[33] a) L. K. Woo, D. A. Sith, *Organometallics* **1992**, *11*, 2344–2346; b) D. A. Smith, D. N. Reynolds, L. K. Woo, *J. Am. Chem. Soc.* **1993**, *115*, 2511–2513.

[34] a) T. Niimi, T. Uchida, R. Irie, T. Katsuki, *Adv. Synth. Catal.* **2001**, *343*, 79–88; b) T. Uchida, T. Katsuki, *Synthesis* **2006**, 1715–1723.

[35] a) Y. Chen, K. B. Fields, X. P. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 14718–14719; b) Y. Chen, X. P. Zhang, *J. Org. Chem.* **2007**, *72*, 5931–5934.

[36] X. H. Cheng, Z. N. Li, H. L. Che, *Chin. Chem. Lett.* **1996**, *7*, 703–705.

Received: September 23, 2008