Tetrahedron Vol. 46, No 11, pp. 3889–3896, 1990
Printed in Great Britain

0040–4020/90 $3.00+.00

EFFECTS OF SECONDARY INTERACTIONS ON THE STEREOCHEMICAL OUTCOME OF RHODIUM(II) CARBOXYLATE-CATALYSED CYCLOPROPANATION OF OLEFINS

A. Demonceau,[+] A.F. Noels[+*] and A.J. Hubert[++]

[+]*Laboratory of Macromolecular Chemistry and Organic Catalysis,*

[++]*Laboratory of Organic Synthesis and Catalysis,*

University of Liège, Sart Tilman (B.6), B-4000 Liège (Belgium)

(*Received in Belgium* 12 *March* 1990)

Summary

In cyclopropanation reactions of olefins catalysed by various dirhodium(II) tetracarboxylates, it is shown that besides the well-recognized electronic and steric effets, secondary interactions between the carbenoid complex and the substrate largely determine the stereoselectivity of the cyclopropanes.

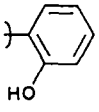
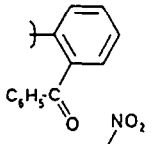
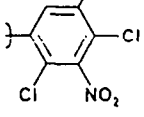
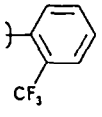
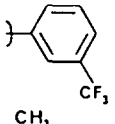
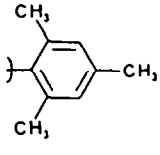
Rhodium(II) carboxylates are among the most efficient catalysts for the cyclopropanation of alkenes by diazo compounds.[1,2] Recently, the utility of these catalysts was further expanded by the recognition of their exceptional ability to promote insertion reaction into X-H bonds (X = O,[3] N,[4] and C[5]) and by their application in ylide chemistry.[6]

However, despite a large amount of work, controlling the *cis/trans* (*endo/exo*) selectivity in cyclopropanation reactions remains a largely unmet challenge, whatever the metal used as catalyst. Some rare exceptions were observed with a rhodium(II) acetamide complex that, in combination with diazoacetamides or diazoesters bearing bulky substituents gave exceptionally high *trans* (*anti*) selectivities.[7] On the contrary, complimentary enhancement of *cis* (*syn*) stereoselectivity has been achieved with rhodium(II) triarylbenzoates.[8] Moreover, just like in the above examples, it appears from many data scattered in the literature (see *inter alia* ref. 9), that increasing the steric demand at the catalyst level does not always significantly increase the stereoselectivity of the reaction products. Actually, when it does, it is not necessarily an increase in the *trans* (*exo*) selectivity (as expected on steric ground) that is observed, a clear indication that some other effects take over in the transition state.

With the exception of the cyclopropanation of 1,1-dihalogeno-4-methylpenta-1,3-dienes,[9] no systematic study on the influence of some modifications in the carboxylate ligands of Rh(II) complexes on

Table I

Catalytic cyclopropanation of styrene, cyclohexene and 1-hexene by ethyl diazoacetate [a, b, c]

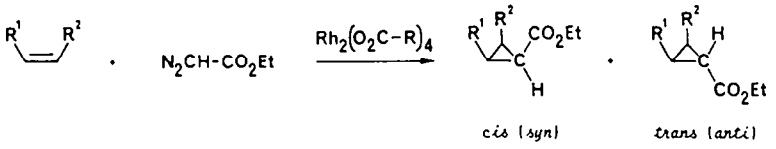
Catalyst $Rh_2(O_2C\text{-}R)_4$	Yield,[d] % (*cis/trans* or *endo/exo* ratio) Styrene	Cyclohexene[e]	1-Hexene
1. R = H	98(0.95)[b]	95(0.46)[b]	95(0.85)[c]
2. CH_3 [f]	91(0.66)	83(0.26)	86(0.68)
3. *n*-C_3H_7	99(0.62)	93(0.15)	96(0.75)
4. *n*-$C_{17}H_{35}$	98(0.66)	97(0.30)	96(0.68)
5. C_6H_5	97(0.82)[b]	96(0.39)[b]	95(0.75)[c]
6. $CH_2C_6H_5$	100(0.95)[b]	95(0.43)[b]	98(0.77)[c]
7. $CH_2CH_2C_6H_5$	100(0.86)	97(0.33)	95(0.78)
8. $CH_2C(C_6H_5)_3$	100(1.22)	96(0.61)	98(1.02)
9. 	91(1.16)[b]	91(0.54)[b]	93(0.92)[c]
10. 	98(1.17)	96(0.84)	97(1.22)
11. 	65(1.10)	30(0.77)	55(1.00)[c]
12. 	86(0.96)	98(0.56)	100(0.92)
13. 	87(0.81)	98(0.21)	100(0.76)
14. 	98(1.01)[b]	91(0.50)[b]	95(0.83)[c]

(*continued*)

15.	$CH_2CH_2C(O)CH_3$	98(0.68)	98(0.31)	93(0.81)
16.	$C(O)C_6H_5$	89(0.95)[b]	92(0.43)[b]	87(0.74)[c]
17.	CF_3	99(0.90)	91(0.44)	69(0.72)

[a, b, c] Respectively at room temperature, 60°C and 40°C.
[d] Yield based on ethyl diazoacetate added.
[e] When cyclohexene is used as substrate, the allylic insertion product (ethyl (cyclohex-2-ene)-1-yl-acetate) is formed in varying amount depending on the catalyst, *e.g.*, catalyst (yield, %) : **1** (3.5) ; **2** (2) ; **5** (2.5) ; **6** (3) ; **9** (6.5) ; **10** (3) ; **14** (3) ; **16** (6.5) ; **17** (9).
[f] Respectively 95 (0.625), - (0.26) and - (0.715), according to M.P. Doyle.[7a]

the stereoselectivity of the cyclopropanation is reported in the literature. In an effort to better understand the factors that govern the selectivity, we herein report the results of the catalytic cyclopropanation of three model olefins by ethyl diazoacetate (eq).



The various rhodium(II) carboxylates successfully synthesized and tested are described in Table I, together with the relative yields and stereoselectivities (in brackets) obtained with the three representative olefins. The overall yields in cyclopropanes are extremely good most of the time. However the choice of the catalyst is crucial as far as the stereoselectivities are concerned. Indeed, for the cyclopropanation of styrene by ethyl diazoacetate, the *cis/trans* ratio varies from 0.6 to 1.2 according to the metal counter-ion (0.15-0.84 for cyclohexene, and 0.68-1.2 for 1-hexene). *E.g.*, rhodium triphenylpropionate (**8**), salicylate (**9**) and 2-benzoylbenzoate (**10**) give the *cis* isomer as the major product while rhodium acetate (**2**), butyrate (**3**) and stearate (**4**) give the *trans* isomer predominantly. Even a more remarkable difference is observed in the catalytic cyclopropanation of cyclohexene since rhodium 2-benzoylbenzoate (**10**) gives much higher *endo/exo* stereoselectivity than rhodium butyrate (**3**) by a factor of between 5 and 6. As already pointed out in previous work, bulky rhodium catalysts (such as **10**) usually gave higher stereoselectivities than rhodium salts of *n*-carboxylic acids (**2-4**). However, a similar enhancement of the stereoselectivity was also observed with non or less bulky catalysts bearing functional side groups.

For instance, for cyclopropanation of styrene, rhodium salicylate (**9**) gave, surprisingly enough, a *cis/trans* ratio as high as 1.16, identical to that achieved with rhodium 2-benzoylbenzoate (**10**), a sterically hindered catalyst. Moreover, complex (**8**), whose triphenylmethyl group is remote from the carboxylate bridge provided particularly high stereoselectivities while rhodium(II) 2- and 3-(trifluoromethyl)benzoates (**12** and **13**, respectively) exhibited quite different reactivities especially for cyclohexene cyclopropanation (Table I).

These results show therefore the crucial influence of the rhodium(II) counter-ion on the stereochemical outcome of the cyclopropanation reaction, an aspect which has been neglected in a recent rationalisation.[1a] We suggest that cyclopropane stereochemistry is determined by at least three requirements : (i) electronic and (ii) steric effects, but also (iii) "solvation" effects ; in other words, the formation of a large number of enthalpically favourable (or unfavourable, according to the case), weakly polar or non-polar interactions in the coordination sphere. Although each interaction is only capable of making a small enthalpic contribution to the energetics of the transition state, the sum of many such interactions in the vicinity of the reactive centre is making the total enthalpic contribution significant. The involvement of such weak interactions in transition-metal-mediated reactions is more and more documented in the recent literature,[10] and in particular has been evidenced in rhodium-catalysed functionalisation of alkanes by diazoesters.[5a,11] An apparent contradiction is observed with rhodium(II) formate which, surprisingly enough, gives rise to enhanced *cis/trans* ratios compared to those obtained with rhodium acetate and its higher homologues (Table II). The reason for this could rest on the fact that with rhodium formate, strong self-association of the complex might be determinant in poorly coordinating solvents.[5a,12] That is to say, the existence of the catalyst as an oligomer in solution would result in restricted access to the active centre with, as consequence, an increase of the stereoselectivity.

Finally, the lack of efficient stereocontrol could also be due in part to an easy rotation of the carbene around the $C_{carbene}$-metal axis on the way to the activated complex or (and) to an equilibrium carbenoid $\neq$ free carbene. Although little physicochemical data are available on the rhodium-carbene bond, the above hypothesis are supported by the lability of the species and by the fact that the π back-bonding between the metal and an axially coordinated ligand is assumed to be weak in rhodium carboxylates, especially when the dirhodium core is ligated to acidic residues of low pK_a such as perfluorocarboxylates.

Table II

Catalytic cyclopropanation of representative olefins by ethyl diazoacetate [a,b,c]

Alkene	*cis/trans* (or *endo/exo*) ratio $Rh_2(O_2C\text{-}H)_4$	$Rh_2(O_2C\text{-}CH_3)_4$	$Rh_2(O_2C\text{-}n\text{-}C_3H_7)_4$
Styrene	0.95[b]	0.66[a]	0.62[a]
α-Methylstyrene	1.05[b]	1.02[b]	0.99[b]
4-Methylstyrene	0.83[b]	0.68[b]	0.67[b]
4-*t*-Butylstyrene	0.89[b]	0.76[b]	0.73[b]
4-Chlorostyrene	0.80[b]	0.64[b]	0.62[b]
Cyclopentene	0.61[c]	0.41[c]	0.41[c]
Cyclohexene	0.46[b]	0.26[a]	0.15[a]
Cycloheptene	0.51[b]	0.45[b]	0.46[b]
Cyclooctene	0.73[b]	0.77[b]	0.75[b]
Norbornene [d]	0.71[b]	0.50[a]	0.48[b]

[a,b,c] Reaction conditions same as in Table I.
[d] In equimolecular competition with styrene.

Actually, an equilibrium between free and complexed carbenes has been evidenced when alkanes are reacted with diazomalonates in the presence of perfluorinated rhodium(II) carboxylates.[13]

In conclusion, this work examplifies the facile access to cyclopropanes via Rh(II)-catalysed decomposition of diazoesters. Proper choice of the catalyst counter-ions helps determining the stereochemical outcome of the reaction. The extension of this method, however, to dienes such as 1,1-disubstituted-4-methylpenta-1,3-dienes which are precursors of pyrethroid insecticides is significantly more challenging.[2a,9] Further studies on this topics are currently in progress.

Experimental

All reactions were carried out by slow addition (3-4 h, via syringe pump) at room temperature, 40°C or 60°C, as indicated, of 1.5 mmol of ethyl diazoacetate diluted in 1 mL of olefinic substrate to 3 mL of the olefin containing 3-5 mg of catalyst. The olefins were distilled before used and kept under an inert atmosphere. All the compounds synthesized were identified by v.p.c. by comparison with authentic samples. Yields and isomer ratios were determined by v.p.c. on two columns : a 50 m capillary CP Sil 8 CB and a 1.5 m packed column, 10% FFAP on Chromosorb WAW 80-100 mesh.

The rhodium(II) carboxylates were prepared from the corresponding carboxylic acids as described in earlier papers and in the general literature. The procedure is illustrated hereafter for three new complexes, namely the trifluoromethyl derivative of benzoic acid (**12**), of 2-benzoylbenzoic acid (**10**) and of levulinic acid (**15**).

Tetrakis(o-trifluoromethylbenzoato)dirhodium(II) (12)

One gram of hydrated $RhCl_3$ ($3.8\ 10^{-3}$ mol) and 4.5 g ($2.3\ 10^{-3}$ mol) of o-trifluoromethylbenzoic acid were dissolved in 60 mL of 95% ethanol under a N_2 blanket. After addition of 0.960 g of $NaHCO_3$ (3.10^{-3} mol), the solution was refluxed for 2 h and stirred overnight at room temperature. The green solution was filtered and the solid residue washed with 3 x 10 mL of ethanol before being discarded. The alcohol solution was evaporated to dryness under vacuum and the resulting solid extracted with benzene until no further coloration of the liquid phase was observed. The benzene solution was dried (drierite), concentrated under vacuum and chromatographed on silica (70 x 2.5 cm column, Merck kieselgel 60, 35-70 mesh ASTM), with benzene-diethylether (85-15) as eluent. The green fraction was collected and air-dried. Yield 64%. The two axially ligated ether molecules can be removed by heating under vacuum. Crystallization from benzene-hexane.

$Rh_2(O_2C\text{-}C_6H_4\text{-}CF_3)_4.2Et_2O$	:	calculated	;	found (%)	
C	:	43.25	;	43.2	43.6
H	:	3.34	;	3.2	3.1

IR (KBr, ν cm^{-1}) : 1603 (m), 1592 (m), 1572 (s), 1398 (s), 1307 (s); 1268 (m), 1030 (m), 1050 (w), 850 (w).

Tetrakis(2-benzoylbenzoato)dirhodium(II) (10)

To a solution of 0.35 g ($1.33\ 10^{-3}$ mol) of hydrated rhodium trichloride in 50 mL of 95% ethanol were successively added 1.50 g of o-benzoylbenzoic acid ($6.66\ 10^{-3}$ mol) and 0.44 g $NaHCO_3$ ($5.25\ 10^{-3}$ mol). The solution was refluxed for 2 h under nitrogen and then kept overnight at room temperature. The solution was filtered and the solvent evaporated under vacuum. The solid residue was then extracted with diethylether and the resulting green solution was dried (drierite), concentrated and chromatographed on silica as described above (eluent : pure dichloromethane followed by dichloromethane - ether 9:1).
The main fraction was constituted by pure **10** (43%). Another fraction contained a mixture of **10** and of 2-benzoylbenzoic acid that could be submitted to a further purification. IR (KBr, ν cm^{-1}) 1668-59 (s, ketone), 1602 (s), 1585 (s), 1392 (s).

Tetrakis(levulinato)dirhodium(II) (15)

Same procedure and amount of reactants as above (levulinic acid 0.78 g, 6.66 10^{-3} mol). After evaporation of the ethanol solution under vacuum, the solid was extracted with hot benzene (0.5 h reflux) several times. The extracted solid was chromatographed on silica (eluent : pure toluene followed by toluene-ethyl acetate 1:1). Yield 54%. IR (KBr, ν cm^{-1}) : 1708 (s, ketone), 1581 (s), 1432 (s), 1405 (m).

Some of the other rhodium(II) carboxylates were prepared according to the following references : **3** to **7** and **17** : ref. 14, 15 and 16 ; **9** according to ref. 17 ; **14** according to ref. 8 and **11** according to ref. 18.

Acknowledgements

We thank Professor P. Teyssié for his interest in this work, and Miss N. Roppe for her skilful technical assistance. We also acknowledge I.R.S.I.A., Belgium, for a fellowship to A.D. and the Service de la Programmation de la Politique Scientifique, Brussels, for partial financial support of this research.

References and notes

(1) For recent general references on catalytic reactions of diazo compounds, see : (a) Doyle, M.P. *Chem. Rev.* **1986**, *86*, 919-939 ; *Acc. Chem. Res.* **1986**, *19*, 348-356. (b) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75-253. (c) Demonceau, A. ; Noels, A.F. ; Hubert, A.J. In "Aspects of Homogeneous Catalysis", Vol. 6 ; Ugo, R., Ed. ; D. Reidel Publishing Company : Dordrecht/Boston/Lancaster, **1988** ; p 199-232.

(2) (a) Cottens, S. ; Schlosser, M. *Tetrahedron* **1988**, *44*, 7127-7144. (b) Sundberg, R.J. ; Baxter, E.W. ; Pitts, W.J. ; Ahmed-Schofield, R. ; Nishiguchi, T. *J. Org. Chem.* **1988**, *53*, 5097-5107. (c) Reingold, I. D. ; Drake, J. *Tetrahedron Lett.* **1989**, *30*, 1921-1922.

(3) (a) Heslin, J.C. ; Moody, C.J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1417-1423. (b) Lesuisse, D. ; Berchtold, G.A. *J. Org. Chem.* **1988**, *53*, 4992-4997.

(4) (a) Barrett, A.G.M. ; Sturgess, M.A. *Tetrahedron* **1988**, *44*, 5615-5652. (b) Chorvat, R.J. ; Rorig, K.J. *J. Org. Chem.* **1988**, *53*, 5779-5781.

(5) (a) Demonceau, A. ; Noels, A.F. ; Teyssié, P. ; Hubert, A.J. *J. Mol. Catal.* **1988**, *49*, L13-L17. (b) Adams, J. ; Poupart, M.-A. ; Grenier, L. *Tetrahedron Lett.* **1989**, *30*, 1753-1756.

(6) (a) Doyle, M.P. ; Bagheri, V. ; Harn, N.K. *Tetrahedron Lett.* **1988**, *29*, 5119-5122. (b) Moody, C.J. ; Slawin, A.M.Z. ; Taylor, R.J. ; Williams, D.J. *Tetrahedron Lett.* **1988**, *29*, 6009-6012. (c) Padwa, A. ; Hornbuckle, S.F. ; Fryxell, G.E. ; Stull, P.D. *J. Org. Chem.* **1989**, *54*, 817-824, and references cited therein.

(7) (a) Doyle, M.P. ; Loh, K.-L. ; DeVries, K.M. ; Chinn, M.S. *Tetrahedron Lett.* **1987**, *28*, 833-836. (b) Doyle, M.P. ; Wandless, T.J. Third Chemical Congress of North America, Toronto, Canada, June 5-10, 1988, Abstract 332.

(8) Callot, H.J. ; Metz, F. *Tetrahedron* **1985**, *41*, 4495-4501.

(9) (a) Holland, D. ; Milner, D.J. *J. Chem. Res. (S)* **1979**, 317 ; *J. Chem. Res. (M)* **1979**, 3734-3746. (b) Demonceau, A. ; Noels, A.F. ; Anciaux, A.J. ; Hubert, A.J. ; Teyssié, P. *Bull. Soc. Chim. Belg.* **1984**, *93*, 949-952.

(10) See for instance *Remarkable Effects of a Pentafluorophenyl Group on the Stereoselective Reactions of a Chiral Iron Acyl Complex* : Ojima, I. ; Kwon, H.B. *J. Am. Chem. Soc.* **1988**, *110*, 5617-5621.

(11) Demonceau, A. ; Noels, A.F. ; Hubert, A.J. *J. Mol. Catal.* **1989**, *57*, 149-152.

(12) Doyle, M.P. ; Mahapatro, S.N. ; Caughey, A.C. ; Chinn, M.S. ; Colsman, M.R. ; Harn, N.K. ; Redwine, A.E. *Inorg. Chem.* **1987**, *26*, 3070-3072.

(13) Demonceau, A. ; Noels, A.F. ; Hubert, A.J. *J. Mol. Catal.* **1989**, *58*, 21-26.

(14) Anciaux, A.J. ; Hubert, A.J. ; Noels, A.F. ; Petiniot, N. ; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695-702.

(15) Kitchens, J. ; Bear, J.L. *Thermochim. Acta* **1970**, *1*, 537-544.

(16) Drago, R.S. ; Long. J.R. ; Cosmano, R. *Inorg. Chem.* **1981**, *20*, 2920-2927.

(17) Bancroft, D.P. ; Cotton, F.A. ; Han, S. *Inorg. Chem.* **1984**, *23*, 2408-2411.

(18) Anciaux, A.J. ; Demonceau, A. ; Noels, A.F. ; Hubert, A.J. ; Warin, R. ; Teyssié, P. *J. Org. Chem.* **1981**, *46*, 873-876.