OLEFIN CYCLOPROPANATION REACTIONS CATALYSED BY NOVEL RUTHENACARBORANE CLUSTERS

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Key Words : Olefins; Diazo Compounds; Cyclopropanation; Ruthenium; Carboranes

Abstract. Novel ruthenacarborane clusters exhibit high activity as cyclopropanation catalysts in reactions between ethyl diazoacetate and alkenes.

Rhodium(II) carboxylates and various palladium and copper complexes including copper(I) or copper(II) trifluoromethanesulfonate, are at the present time among the best catalysts for the cyclopropanation of mono- and polyolefins with diazoesters.² Little is known however on the use of ruthenium-based catalysts in those reactions^{3,4} and, more generally, in carbene chemistry.² Recently, we reported on the unique activity of various ruthenium complexes, including some diruthenium(II,II) tetracarboxylates in both the cyclopropanation and metathesis reactions.^{5,6} In this communication, we will report the first use of ruthenacarborane clusters as catalysts for the cyclopropanation of olefins with ethyl diazoacetate (eq. 1).



Ruthenium carborane complexes 1⁷ and 3^{8,9} were shown to be exceptionally effective catalysts for the cyclopropanation reaction of olefins (Tables 1 and 2). Oppositely, under the same reaction conditions, complex 2 whose carborane ligand is substituted by two methyl groups,⁷ is a poor cyclopropanation catalyst, except for activated olefins (styrenes and 2,5-dimethyl-2,4-hexadiene, Table 1). The exact reason for this surprising result is not clear at this time. Purely steric effects can be ruled out in view of the distance between the two methyl groups and the metal centre (*vide infra*).

The stereoselectivities observed for ruthenacarborane clusters 1-3 are generally comparable to or (with cyclopentene and 1,4-cyclohexadiene) higher than those for classical rhodium carboxylates,¹⁰ *i.e.* the synthesis of the thermodynamically less stable (*cis* or endo) cyclopropane isomer is favoured.

CI(Ph3P)2Ru(R2C2B9H10)



 Table 1.
 Cyclopropanation Yields and Stereoselectivities from Reactions of Ethyl Diazoacetate with

 Representative Olefins in the Presence of Ruthenacarboranes^a

Cyclopropane yield, $\%^{b}$ (stereoselectivity ^c)				
Ru-1	Ru-2	Ru-3		
93 (0.56)	46 (0.53)	91 (0.61)		
81 (0.76)	34 (0.61)	88 (0.77)		
86 (0.69)	81 (0.82)	93 (0.72)		
91 (0.82)	73 (0.79)	96 (0.78)		
89 (0.66)	77 (0.66)	93 (0.59)		
81 (1.02)	73 (1.37)	87 (1.03)		
88 (0.73)	77 (0.67)	89 (0.75)		
87 (0.73)	23 (0.56)	92 (0.73)		
96 (0.72)	61 (0.68)	97 (0.75)		
49 (0.95)	26 (0.95)	53 (0.97)		
75 (0.30)	32 (0.45)	79 (0.28)		
89 (0.50)	26 (0.59)	88 (0.49)		
91 (0.59)	16 (1.15)	87 (0.96)		
69 (0.53)	37 (0.68)	75 (0.52)		
61 (2.50)	34 (2.20)	63 (2.45)		
	Cyclopropa Ru-1 93 (0.56) 81 (0.76) 86 (0.69) 91 (0.82) 89 (0.66) 81 (1.02) 88 (0.73) 87 (0.73) 96 (0.72) 49 (0.95) 75 (0.30) 89 (0.50) 91 (0.59) 69 (0.53) 61 (2.50)	Cyclopropane yield, % ^b (stereos) Ru-1 Ru-2 93 (0.56) 46 (0.53) 81 (0.76) 34 (0.61) 86 (0.69) 81 (0.82) 91 (0.82) 73 (0.79) 89 (0.68) 77 (0.66) 81 (1.02) 73 (1.37) 88 (0.73) 77 (0.67) 87 (0.73) 23 (0.56) 96 (0.72) 61 (0.68) 49 (0.95) 26 (0.95) 75 (0.30) 32 (0.45) 89 (0.50) 26 (0.59) 91 (0.59) 16 (1.15) 69 (0.53) 37 (0.68) 61 (2.50) 34 (2.20)		

a Reaction conditions: olefin, 20 mmol; catalyst, 0.005 mmol; ethyl diazoacetate, 1mmol, diluted in 1 ml of the olefin; perfusion time, 4h; 60°C or at reflux for olefins having a boiling point lower than 60°C.

b Yield based on ethyl diazoacetate and determined by g.l.c., by comparison with authentic samples. Diethyl maleate and fumarate as well as traces of metathesis products^{5,6} represent by-products of these reactions and, with styrene and its derivatives (α-methylstyrene excepted), low amounts of polymers are also formed.

^C Cis/trans or endo/exo cyclopropane ratios.

It is moreover worth noting that, with any olefins tested, catalysts 1 and 3 gave comparable yields and stereoselectivities. This observation may be attributed to the possibility of the $1 \rightarrow 3$ rearrangement which, according to previous results,⁹ occurs in mild conditions (in benzene at 60°C) and most probably should take place in the course of the cyclopropanation reactions. No indications of such rearrangement of complex 2 (**4) have been observed even in more severe conditions. As a consequence, the high catalytic activity of ruthenacarborane 1 could be attributed to the *closo*-cluster 3 formed *in situ* whereas the poor catalytic activity of 2 could be due to its *exo-nido* structure.

In light of those observations, the regio- and stereochemical course of the cyclopropanation of isoprene¹¹ was then investigated in the presence of the three ruthenacarborane clusters. Again, the cycloaddition was practically quantitative with complexes 1 and 3 (Table 2) and occurred preferentially (> 85%) at the more electronrich double bond, illustrating therefore the electrophilic nature of the ruthenium-carbene complexes. Moreover, the yields, regio- and stereoselectivities of the reactions promoted by clusters 1 and 3 were very close and substantially higher than those observed with 2 as catalyst (see I/II molar ratio, Table 2 and equation 2). That feature was also evidenced in the Ru-carborane-catalysed competitive cyclopropanation between styrene and 1-hexene. In the presence of catalysts 1 and 3, styrene was 8 times¹² more reactive than 1-hexene while, with catalyst 2, the styrene/1-hexene selectivity dropped to 4.8.



 Table 2.
 Cyclopropanation Yields, Regio- and Stereoselectivities from Reactions of Ethyl Diazoacetate with

 Isoprene in the Presence of Ruthenacarboranes^a

	Cyclopropane yield, % ^b	Isomeric distribution, %				I/II Molar
Catalyst		I-Z	ŀE	il-Z	II-E	ratio
Ru-1	87	46.5	39	3.5	11	5.75
Ru-2	26	41.5	32.5	9	17	2.85
Ru-3	93	45.5	40.5	3.5	10.5	6.2

a,b Reaction conditions same as in Table 1.

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In conclusion, ruthenacarborane clusters 1 and 3 have been shown to be highly active and promising catalysts for the cyclopropanation reaction of olefins. Taking into account both the yields and selectivities obtained with representative alkenes, a high catalytic activity could be tentatively attributed to *closo*-ruthenacarborane clusters, whereas a poor catalytic activity could be associated to its *exo-nido* congeners. Further work along those lines is now being carried out to extend the scope of their applications and get a better understanding of the reaction mechanism.

Acknowledgements. We thank Professor P. Teyssié for his interest in this work. We also gratefully acknowledge the 'Belgian Office for the Scientific Research in the Industry and Agriculture' (I.R.S.I.A.) for a fellowship to E.S., the 'National Fund for Scientific Research' (F.N.R.S.), Belgium, for the purchase of major instrumentation and the European Communities for generous financial support (contract EC n° SCI-CT 90-0530).

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(Received in France 13 January 1992)