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OLEFIN CYCLOPROPANATION REACTIONS CATALYSED BY NOVEL RUTHENACARBORANE CLUSTERS

A. Demonceau,*[1] E. Saive,+ Y. de Froidmont, A.F. Noels, and A.J. Hubert+

Laboratory of Macromolecular Chemistry and Organic Catalysis, and +Laboratory of Organic Synthesis and Catalysis University of Liège, Sart-Tilman (B6), B-4000 Liège, Belgium

I.T. Chizhevsky, I.A. Lobanova, and V.I. Bregadze

A.N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences, ul. Vavilova 28, 117813 Moscow, Russia

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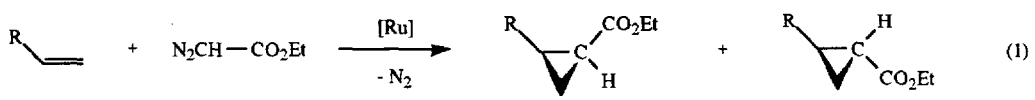
Abstract. Novel ruthenacarborane clusters exhibit high activity as cyclopropanation catalysts in reactions between ethyl diazoacetate and alkenes.

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).



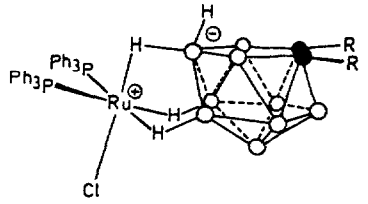
(1)

cis (endo) *trans (exo)*

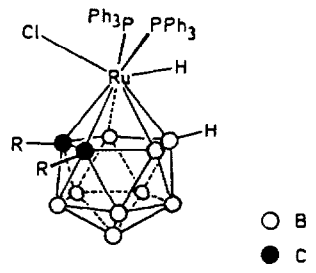
Ruthenium carborane complexes **1**[7] and **3**[8,9] were shown to be exceptionally effective catalysts for the cyclopropanation reaction of olefins (Tables 1 and 2). Oppositely, under the same reaction conditions, complex **2** whose carborane ligand is substituted by two methyl groups,[7] is a poor 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.

$Cl(Ph_3P)_2Ru(R_2C_2B_9H_{10})$



(Ru-1) R = H
(Ru-2) R = Me



(Ru-3) R = H
(Ru-4) R = Me

Table 1. Cyclopropanation Yields and Stereoselectivities from Reactions of Ethyl Diazoacetate with Representative Olefins in the Presence of Ruthenacarboranes[a]

Olefin	Cyclopropane yield, % [b] (stereoselectivity [c]) Ru-1	Ru-2	Ru-3
n-Butyl vinyl ether	93 (0.56)	46 (0.53)	91 (0.61)
Vinyl acetate	81 (0.76)	34 (0.61)	88 (0.77)
Styrene	86 (0.69)	81 (0.82)	93 (0.72)
4-Chlorostyrene	91 (0.82)	73 (0.79)	96 (0.78)
4-Methylstyrene	89 (0.66)	77 (0.66)	93 (0.59)
α-Methylstyrene	81 (1.02)	73 (1.37)	87 (1.03)
4-*t*-Butylstyrene	88 (0.73)	77 (0.67)	89 (0.75)
1-Hexene	87 (0.73)	23 (0.56)	92 (0.73)
2,5-Dimethyl-2,4-hexadiene	96 (0.72)	61 (0.68)	97 (0.75)
Cyclopentene	49 (0.95)	26 (0.95)	53 (0.97)
Cyclohexene	75 (0.30)	32 (0.45)	79 (0.28)
Cycloheptene	89 (0.50)	26 (0.59)	88 (0.49)
Cyclooctene	91 (0.59)	16 (1.15)	87 (0.96)
1,3-Cyclohexadiene	69 (0.53)	37 (0.68)	75 (0.52)
1,4-Cyclohexadiene	61 (2.50)	34 (2.20)	63 (2.45)

[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.