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Cyclopropanation Reactions Catalysed by Rhodium(I) Complexes with New Anionic Carborane Phosphine Ligands

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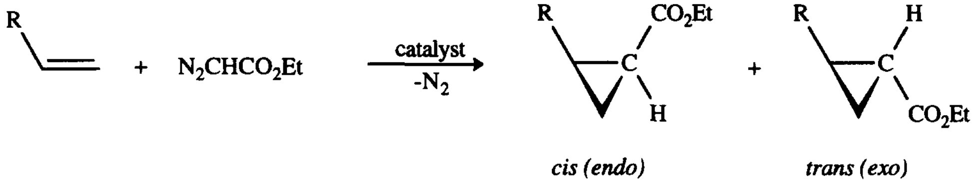
Abstract : The first set of rhodium(I) complexes **1-3** has been shown to be active for the cyclopropanation of olefins with diazoacetates. © 1997 Published by Elsevier Science Ltd.

Cyclopropanation is currently an area of significant research activity.[1] To date, direct transition-metal-catalysed carbene transfer from a diazo compound to an olefin remains the most straightforward route to cyclopropanes (Eq. 1).[2] Dirhodium(II) carboxylates and carboxamidates have been proved to be outstanding catalysts for this reaction.[3] Other rhodium complexes (*e.g.*, $Rh_6(CO)_{16}$,[4] $Rh_2(BF_4)_4$,[5] and rhodium(III) porphyrins[6]) have also been introduced as cyclopropanation catalysts but none of them has been demonstrated to be superior to rhodium carboxylates and carboxamidates. To the best of our knowledge, attempts with rhodium(I) complexes have never been successful. For instance, $Rh_2(CO)_4Cl_2$ and $Rh_2(C_2H_4)_4Cl_2$ were inefficient for the cyclopropanation of 1,1-dichloro-4-methylpenta-1,3-diene with ethyl diazoacetate at 83°C,[4] while the former catalysed the cyclopropanation of *n*-butyl vinyl ether with ethyl diazoacetate in 58% yield at room temperature.[7] In the same vein, $RhCl(PPh_3)_3$ cyclopropanated styrene in only 12% yield.[8]



(1)

We have recently reported on the use of novel ruthenium complexes with anionic phosphine ligands as efficient catalysts for olefin cyclopropanation with ethyl diazoacetate.[9] In continuation of these studies, we envisaged rhodium(I) analogues as potential candidates for the desired cyclopropanation, on the basis of the exceptional activity of related complexes in hydrogenation reactions.[10] We now wish to report the first set of rhodium(I) catalysts (**1-3**)[11] whose effectiveness for olefin cyclopropanation is noteworthy. Preliminary results are summarised in Table 1.

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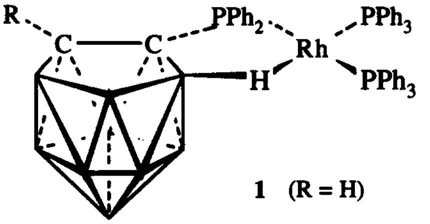

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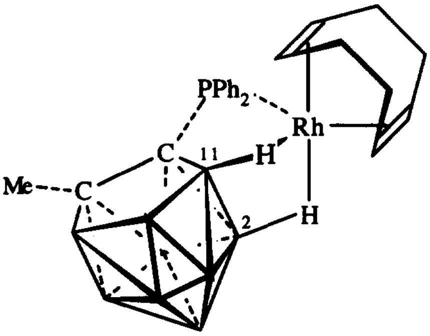

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Table 1. Cyclopropanation of Representative Olefins with Ethyl Diazoacetate[a]

Complex	Cyclopropanation yield, %[b] (*cis*/*trans* or *endo*/*exo* ratio)			
	Styrene[c]	4-Methylstyrene[c]	4-Chlorostyrene[c]	Cyclooctene
1	91 (0.88)	90 (0.68)	89 (0.51)	86 (0.69)
2	92 (0.91)	93 (0.71)	92 (0.60)	85 (0.67)
3	91 (0.86)	94 (0.70)	87 (0.52)	88 (0.72)

[a] Reaction conditions : catalyst, 0.0075 mmol; olefin, 20 mmol; ethyl diazoacetate, 1 mmol diluted by the olefin up to 1 mL; addition time, 4 h; temperature, 100°C. [b] Based on ethyl diazoacetate, and determined by GLC analysis. [c] Polymerisation of the substrate was a side reaction of the cyclopropanation; with styrene, polymer yield = 12-18% (based on styrene), M_n = 110,000-120,000 and M_w/M_n = 1.7-1.95.

In the presence of styrene, which is generally the model alkene for comparative evaluations of catalyst activity, complexes **1**-**3** proved to be very efficient (90% yield). This new set of complexes has also been investigated for cyclopropanation of other olefins. The yields usually ranged between 80 and 95%. As seen from Table 1, complexes **1**-**3** gave virtually identical yields and stereoselectivities for the cyclopropanation of four representative olefins, regardless of the ligand pattern of the complex. Activated olefins were more reactive than non-activated ones and, in competitive cyclopropanation reactions between olefins performed in the presence of complex **1**, styrene has been shown to be 10 times more reactive than cyclooctene and 1-octene (Table 3). *n*-Butyl vinyl ether is also an activated olefin; it was cyclopropanated by ethyl diazoacetate with yields ranging from 80 to 90%, but in a competitive experiment in the presence of complex **1**, *n*-butyl vinyl ether was 6 times less reactive than styrene. This selectivity is quite the reverse of that observed with $Rh_2(OAc)_4$.[12] Also noteworthy was the very low cyclopropane yield obtained with norbornene. With this substrate, 1,3-dipolar addition of ethyl diazoacetate was the preferred pathway.

Carbene addition occurred with *trans* (*exo*) diastereoselectivity, consistently favouring the most thermodynamically stable isomer. The effects of the size of the alkene substituents were studied using various 4-X-styrene derivatives. Increasing the steric bulk of X led to a significant decrease in the *cis*/*trans* ratio, as is evident from Table 2 [*cis*/*trans* ratio = 0.88 (styrene), 0.68 (4-methylstyrene), and 0.54 (4-*t*-butylstyrene)]. This could be improved further by using bulkier diazo compounds, such as *t*-butyl diazoacetate which decreased *cis*/*trans* stereoselectivity to 0.57 and 0.52, with styrene and 4-*t*-butylstyrene, respectively.[13]

In conclusion, complexes **1**-**3** constitute the first set of rhodium(I)-based catalysts effective for cyclopropanation of olefins with diazoacetates. Their potential interest, however, greatly suffers from -at least- two major drawbacks. First, these complexes are active at temperatures higher than 60°C. Second, they offer no improved selectivity compared with rhodium(II) carboxylates or copper-based catalysts. Both these results and

Table 2. Cyclopropanation of Representative Olefins with Ethyl Diazoacetate, in the Presence of Complex **1**[a]

Olefin	Cyclopropanation yield, %[b] (*cis*/*trans* or *endo*/*exo* ratio)
Styrene	91 (0.88)
4-Methylstyrene	90 (0.68)
4-*t*-Butylstyrene	93 (0.54)
4-Methoxystyrene	87 (0.60)
4-Fluorostyrene	93 (0.62)
4-Chlorostyrene	89 (0.51)
4-Bromostyrene	90 (0.47)
1,2-Dihydronaphthalene	91 (0.69)[b]
α-Methylstyrene	94 (0.89)[c]
n-Butyl vinyl ether (90°C)	88 (0.69)
Cyclooctene	86 (0.69)
1-Octene	71 (0.56)
1-Dodecene	73 (0.66)
Norbornene (80°C)	9 (0.69)[d]

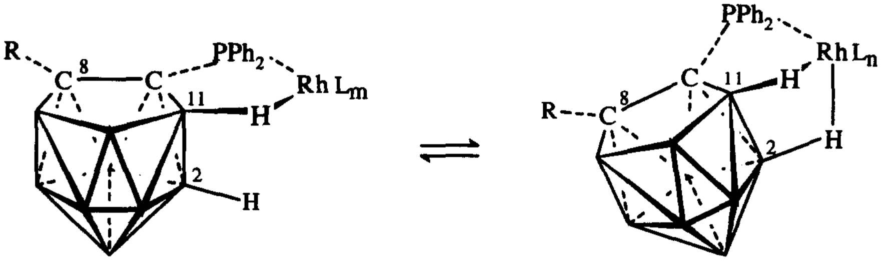
[a] Reaction conditions same as in Table 1. [b] $Rh_2(OAc)_4$ (r.t.) : yield, 93%; *endo*/*exo* ratio, 0.60. [c] *Z*/*E* ratio. [d] **3** (80°C) : yield, 6%; *endo*/*exo* ratio, 0.71.

those reported previously[9-11] suggest that the anionic phosphine ligand $[7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]^-$ has a striking positive influence on the metal centre since conventional ligands used so far gave rise to poorly active rhodium(I) catalytic systems. The specific influence of the anionic ligand could be caused by its multi-coordinating ability. The coordination takes place by means of the *exo*-cluster PPh_2 group and, depending on the ancillary ligands (triphenylphosphine, the carbene moiety and -eventually- the olefin involved in the catalytic process), by one [B(11)] or two [B(11) and B(2)] boron atom(s) through B-H-Rh agostic bonds.[10, 11, 14] This would form the basis for stereo-electronic modulation of the catalytic species. Within the catalytic cycle, an equilibrium between the dicoordinating and the tricoordinating species could be operative. The exact nature of the catalytic species is unknown, and the change of relative reactivity between styrene and *n*-butyl vinyl ether or 1-octene, upon addition of larger amounts of ethyl diazoacetate (Table 3) could be indicative of gradual modification of the catalytic centre, or by the participation of the cyclopropanes or of

Table 3. Relative Reactivities for Rh-**1** Catalysed Reactions of Ethyl Diazoacetate with Representative Olefins[a]

Olefin	Relative reactivity[b]	
4-Methylstyrene	1.06	(0.77 ; 0.66)[c]
Styrene	1.00	
4-Chlorostyrene	0.92	(0.64 ; 0.47)
α-Methylstyrene	0.33	(0.65 ; 0.69)
n-Butyl vinyl ether	0.17	(0.66 ; 0.74)[d,e]
Cyclooctene	0.10	(0.65 ; 0.64)
1-Octene	0.09	(0.66 ; 0.57)[e]
Norbornene (80°C)	0.07_5	(0.65 ; 0.73)

[a] Reaction conditions same as in Table 1, except the temperature (90°C). [b] Into brackets, the *cis*/*trans* ratio for styrene, and the *cis*/*trans* or *endo*/*exo* ratio for the co-olefin. [c] In the presence of complex **2** : 1.08 (0.78 ; 0.66). [d] $Rh_2(OAc)_4$ (r.t.) : 1.5 (0.65 ; 0.58). [e] Perfusion of an additional amount of ethyl diazoacetate (1 mmol, diluted by the olefin mixture up to 1 mL) resulted in a higher discrimination : *n*-butyl vinyl ether, 0.17 (0.66 ; 0.74) → 0.09 (0.65 ; 0.75) → 0.06 (0.64 ; 0.74); 1-octene, 0.09 (0.66 ; 0.57) → 0.05 (0.66 ; 0.58).



L (m = n, or m ≠ n) : PPh_3, $CHCO_2Et$, olefin, ...

by-products (*e.g.*, the carbene dimers (diethyl maleate and diethyl fumarate)) in the above-suggested equilibrium. Further investigations are underway to get mechanistic insights into this process, and to develop new rhodium(I) complexes with higher efficiency and enhanced stereocontrol.

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