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Cyclopropanation of Activated Olefins Catalysed by Ru-Phosphine Complexes

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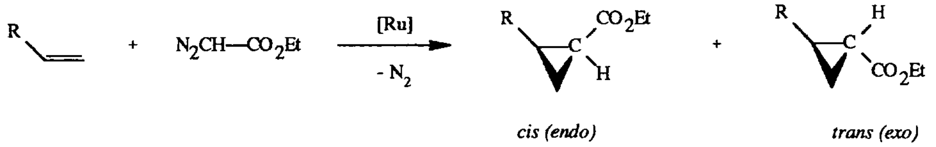
Abstract : Two novel ruthenium complexes, $RuH_3[Si(OEt)_3](PPh_3)_2$ and $Ru[Si(OEt)_3]_2(PPh_3)_2$, have been shown to catalyse the cyclopropanation of activated olefins in high yields.

Efficient and selective syntheses of cyclopropanes are of great interest in organic chemistry due to their frequent occurrence in biologically active compounds and as valuable synthetic intermediates.[2] To date, direct transition-metal catalysed carbene transfer from a diazo compound to an olefin remains the most straightforward route to cyclopropanes.[3] Rhodium(II) carboxylates have proved to be very often the catalysts of choice for promoting cyclopropanation reactions, having largely replaced traditional copper catalysts which often required higher temperatures.[3,4] Rhodium(II) carboxylates suffer however from the high cost of the metal and also from a lack of stereoselectivity. That justifies the search for cheaper and more selective catalysts. In this context, much less is known on the use of ruthenium-based catalysts.[5] We recently reported on the unique activity of various ruthenium complexes, including some diruthenium(II,II) tetracarboxylates[6,7] and ruthenacarborane clusters,[8] in both the cyclopropanation[8] and metathesis reactions.[6,7,9] On the other hand, $RuCl_2(p\text{-cymene})(PCy_3)$ and $RuCl_2(PPh_3)_3$ have also been shown to be outstanding catalysts for the metathesis of olefins[9] and especially of silicon-containing olefins.[10-13] Ruthenium species with Ru-H and Ru-Si bonds seem to be the key intermediates in the catalytic metathesis of vinylsilanes, according to the insertion-elimination mechanism proposed[12,13] although the carbene-based mechanism cannot be totally excluded. Continuing work in these laboratories directed toward the discovery of novel catalysts active in olefin cyclopropanation and/or metathesis and toward a better understanding of the parameters that direct the reaction toward olefin cyclopropanation or metathesis has led us to consider different ruthenium-based complexes as promising catalyst precursors, namely two novel hydride and silyl complexes, $RuH_3[Si(OEt)_3](PPh_3)_2$ and $Ru[Si(OEt)_3]_2(PPh_3)_2$,[14] as well as $RuCl_2(PPh_3)_3$ activated in refluxing benzene under air ($RuCl_2(PPh_3)_3/C_6H_6$).[13] The purpose of this communication is to describe preliminary results on the



(1)

cyclopropanation of various olefins by ethyl diazoacetate, catalysed by these two novel hydride and silyl ruthenium complexes as well as by $RuCl_2(PPh_3)_3$ as a commercially available model.

As shown in Table 1, the yields of cyclopropanation were often in the range 80-95% with styrene and substituted styrenes, side reactions (mostly formation of carbene dimers or azines) were almost completely suppressed, and only a small amount (0.5 mol % relative to diazo compound) of catalyst was required.

Complexes : $RuCl_2(PPh_3)_3$ (1)
$RuCl_2(PPh_3)_3/C_6H_6$ (2)
$RuH_3[Si(OEt)_3](PPh_3)_2$ (3)
$Ru[Si(OEt)_3]_2(PPh_3)_2$ (4)

Table 1. Cyclopropanation Yields and Stereoselectivities from Reactions of Ethyl Diazoacetate with Representative Olefins in the Presence of Ruthenium Complexes 1-4 [a]

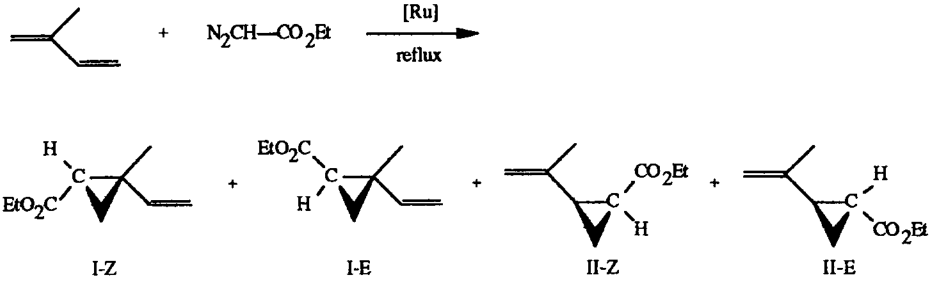
	Yield, % [b] (*cis/trans* or *endo/exo* ratio)			
Olefin	Complex: 1	2	3	4
Styrene, 20°C	37 (0.50)	38 (0.48)	33 (0.40)	41 (0.53)
Styrene, 40°C	55 (0.63)	53 (0.61)	48 (0.41)	54 (0.62)
Styrene, 60°C	93 (0.80) [c]	89 (0.79)	85 (0.42)	91 (0.68)
4-Methylstyrene	91 (0.54)	91 (0.58)	83 (0.50)	90 (0.55)
4-*t*-Butylstyrene	90 (0.71)	87 (0.56)	83 (0.57)	85 (0.59)
4-Methoxystyrene	92 (0.63)	87 (0.70)	87 (0.60)	90 (0.64)
4-Chlorostyrene	89 (0.57)	87 (0.40)	81 (0.40)	83 (0.41)
4-Bromostyrene	85 (0.47)	84 (0.65)	80 (0.47)	80 (0.62)
α-Methylstyrene	94 (0.87)	90 (0.88)	86 (0.87)	92 (0.97)
1-Hexene	6 (0.67)	9 (0.62)	6 (0.47)	6 (0.53)
1-Octene	7 (0.68)	8 (0.65)	6 (0.51)	5 (0.55)
Cyclohexene	4 (0.38)	5 (0.30)	3 (0.34)	4 (0.38)
Cyclooctene	5 (0.65)	6 (0.72)	4 (0.55)	4 (0.56)

[a] Reaction conditions : olefin, 20 mmol; complex, 0.005 mmol; ethyl diazoacetate, 1 mmol, diluted in 1 mL of the olefin; perfusion time, 4 h; temperature, 60°C , except for 1-hexene, 50°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 (1-3 turnovers) represented by-products of these reactions. With cyclohexene, the allylic C-H insertion product was also formed in 5-10% yield whereas, with styrene and its derivatives, polymers were precipitated in methanol (conversion, 6-25%; M_n, 35,000-220,000 ; PDI, 1.8-3.3).

[c] $RuCl_2(AsPh_3)_3$, 92 (0.73); $RuCl_2(SbPh_3)_3$, 94 (0.42).

The application to non activated olefins is, however, very limited. Terminal and internal linear olefins, cycloolefins or -dienes could not be cyclopropanated with ethyl diazoacetate using complexes **1-4** as catalysts (yields lower than 10%), while norbornene was selectively metathesized.[15] At 28°C, isoprene (Table 2) was cyclopropanated only in modest yields (20-30%) although ethyl diazoacetate was fully decomposed at even 20°C. In addition, temperature played a crucial role on the cyclopropanation process. For instance, with styrene (Table 1), cyclopropanation yields increase with temperature. Therefore, we conclude that this



(2)

Table 2. Cyclopropanation Yields, Regio- and Stereoselectivities from Reactions of Ethyl Diazoacetate with Isoprene in the Presence of Ruthenium Complexes 1-4 [a]

Complex	Cyclopropane yield, % [b]	Isomeric distribution, % I-Z	I-E	II-Z	II-E
1	26	14.5	73.5	4	8
2	25	14	74	4	8
3	19	11.5	78	3.5	7
4	23	10	81	3	6

[a,b] Reaction conditions same as in Table 1 (reaction temperature, 28°C).

cyclopropanation is fairly regioselective to a terminal double bond which is in conjugation with an arene group, provided the reaction is carried out at moderately high temperature (60°C, Table 1). These results are reminiscent of the catalytic activity of cobalt(II) carbenoids studied by Nakamura.[16]

The observed stereoselectivities (*cis/trans* or *endo/exo* ratio) depended -as expected- on the olefinic substrate and were much less sensitive to the catalyst precursor. In most cases, however, $RuH_3[Si(OEt)_3](PPh_3)_2$ (3) was the most selective for the *trans (exo)* isomer. Most noteworthy was the increase in the ratio of *cis* to *trans* product observed with complexes 1, 2, and 4 (but not with complex 3) upon raising the temperature (Table 1).

Styrene and a selection of *p*-substituted styrene derivatives were chosen so as to permit a study of the electronic effects of the substituents on the cyclopropanation reaction. The results (Table 1) indicate that lower yields of cyclopropanes were obtained in the presence of electron-withdrawing substituents and confirm the results observed with isoprene (Table 2), where the cycloaddition also preferentially occurred (>85%) at the electron-rich double bond. In intermolecular competitive experiments (Table 3), 4-methylstyrene was 1.6 time more reactive than styrene. All these results are consistent with the electrophilic nature of the ruthenium-carbene intermediate formed by decomposition of the diazo compound by the metal complex.

In conclusion, $RuCl_2(PPh_3)_3$ (1) and other ruthenium phosphine complexes (2-4) were found to be regioselective catalysts for the cyclopropanation of activated olefins at 60°C. Much remains to be elucidated in this reaction and especially its competition with olefin metathesis, another carbene reaction catalysed by ruthenium complexes.

Table 3 . Relative Reactivities of 4-Methylstyrene, Styrene and 4-Chlorostyrene in their Reactions with Ethyl Diazoacetate in the Presence of Ruthenium Complexes **1-4** [a]

Complex	Relative Reactivities 4-Methylstyrene	Styrene	4-Chlorostyrene
1	1.57	1	1.08
2	1.70	1	0.96
3	1.42	1	1.10
4	1.67	1	0.97

[a] Reaction conditions same as in Table 1.

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