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Olefin cyclopropanation catalysed by bis(imido) chromium(VI) complexes

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Abstract

Bis(imido) chromium(VI) complexes are efficient catalysts for promoting the cyclopropanation of activated monosubstituted olefins with ethyl diazoacetate. 2,2′-Disubstituted activated olefins and non-activated α- and cyclo-olefins, however, are much less reactive. © 1999 Elsevier Science Ltd. All rights reserved.

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Various types of cyclopropane-containing compounds occur in nature and many exhibit interesting physiological properties. Cyclopropanes are also extensively used as versatile intermediates in organic synthesis,[1] so that the stereoselective preparation of cyclopropanes is today an ever-increasing topic in organic chemistry.[2] The direct transfer of carbenes to alkenes is the most straightforward route to cyclopropanes. When diazocarbonyl compounds are used as carbene precursors, various transition–metal complexes are known to catalyse the reaction. The most efficient and most general catalysts are based on rhodium and copper.[3] Ruthenium complexes have also been recently introduced as catalysts for olefin cyclopropanation but without providing any real breakthrough.[4]

The ability of chromium complexes to catalyse olefin cyclopropanation was hitherto studied in less detail.[3a,b] In the presence of $Cr(CO)_6$[5] and $(C_6H_6)Cr(CO)_3$,[6] ethyl diazoacetate and α-diazoacetophenone reacted with electron-deficient alkenes (α,β-unsaturated carbonyl compounds and nitriles) to form derivative cyclopropane and vinyl C–H insertion products. On the other hand, in the presence of (η^2-*cis*-cyclooctene)$Cr(CO)_5$, ethyl diazoacetate and diazofluorene reacted with electron-rich alkenes such as enol ethers to give the corresponding cyclopropanes in high yields.[7]

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Table 1
Addition of ethyl diazoacetate to styrene, α-methylstyrene, and cyclooctene catalysed by complexes **1**–**3**[a]

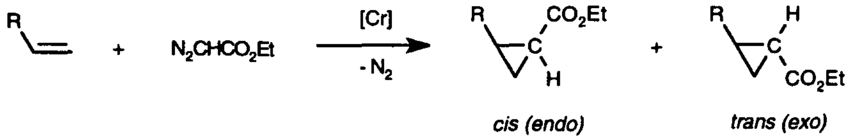
	Cyclopropanation yield, %[b] (*cis*/*trans* or *endo*/*exo* ratio)			
	Styrene		α-Methylstyrene[c]	Cyclooctene
Complex	Temperature : 60 °C	80 °C	80 °C	80°C
1	80 (0.62)[d]	90 (0.65)	64 (0.32)	3 (0.16)
2	76 (0.60)	92 (0.64)	50 (0.29)	5 (0.21)
3	81 (0.60)	89 (0.66)	54 (0.30)	3 (0.27)

[a] Reaction conditions : catalyst, 0.00375 mmol (**1**), 0.0075 mmol (**2** and **3**); olefin, 20 mmol; ethyl diazoacetate, 1 mmol diluted by the substrate up to 1 mL; addition time, 4 h. The reactions were conducted under nitrogen, using olefins distilled and kept under N_2.

[b] Based on added ethyl diazoacetate, and determined by GC using dibutyl fumarate as an internal standard.

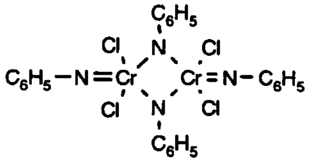
[c] At 60 °C : **1**, 27 % (*cis*/*trans* = 0.30); **2**, 26 % (*cis*/*trans* = 0.30); **3**, 39 % (*cis*/*trans* = 0.28).

[d] At 40 °C : **1**, 51 % (*cis*/*trans* = 0.60).

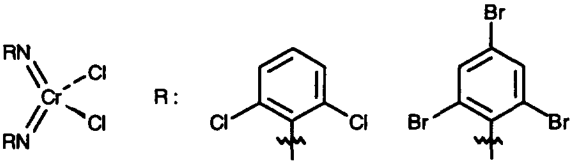


As part of our continuing effort in the search of new catalytic systems, we have synthesised[8] and tested novel imido chromium complexes as catalysts for olefin cyclopropanation. Bis(imido) chromium(VI) complexes **1**–**3** are 16 electron species with one vacant site which should — in principle — be available to the diazo compound and hence to the carbene moiety, despite the sterically protective imido ligands. Furthermore, organoimido species are ideally suited for a study of the reactivity of metal–carbene bonds because of their ability for variable electron donation and their strength of π-bonding.[9]

Chromium complexes **1**–**3** proved to promote the cyclopropanation of styrene in high yield, provided the reaction occurred at a temperature higher than 50°C (Table 1 and Fig. 1). Furthermore, these complexes displayed the same level of activity despite the striking difference in solubility between **1** and its halogenated analogues, **2** and **3**; the former is poorly soluble in olefins whereas the latter are highly soluble in these substrates.



1



2 **3**

4-Substituted styrenes were also cyclopropanated in high yield (Table 2), and neither electron-donating nor electron-withdrawing groups seemed to have any marked effect on the yield. In addition to cyclopropanes, compounds **4** were also formed in 3–10% yields. These products formally result from an insertion of the carbene into the different sp^2 C–H olefinic bonds of styrenes. Carbene dimers, diethyl fumarate and diethyl maleate, were also formed in these reactions. In the presence of α-methylstyrene, α- and cyclo-olefins, these products predominated.

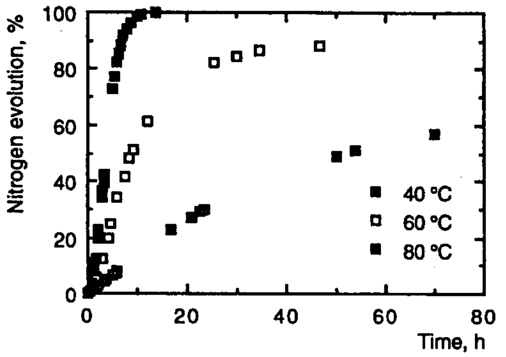
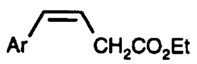


Figure 1. Influence of the temperature on the decomposition rate of ethyl diazoacetate in styrene, in the presence of complex **1**. Reaction conditions: the same as in Table 1

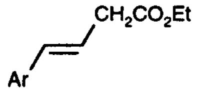
Table 2
Addition of ethyl diazoacetate to representative olefins catalysed by complex **1**[a]

Olefin	Cyclopropanation yield, %[b] (*cis/trans* or *endo/exo* ratio)	Olefin	Cyclopropanation yield, %[b] (*cis/trans* or *endo/exo* ratio)
Styrene	90 (0.65)	α-Methylstyrene	64 (0.32)
4-Methylstyrene	86 (0.46)	1-Decene[c]	6 (0.49)
4-*t*-Butylstyrene	85 (0.43)	Cyclohexene	5 (0.45)
4-Methoxystyrene	83 (0.46)	Cyclooctene	3 (0.16)
4-Chlorostyrene	91 (0.51)	Norbornene	1 -

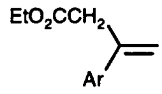
[a,b] Reaction conditions same as in Table 1 (80 °C).
[c] **2**, 7 % (*cis/trans* = 0.40); **3**, 7 % (*cis/trans* = 0.46).



4.a



4.b



4.c

The yield of formation of cyclopropanes was extremely low with non-activated terminal linear olefins and with cycloolefins (Table 2). Furthermore, it is worth pointing out that steric effects strongly affected olefin cyclopropanation. The decomposition of ethyl diazoacetate was found to be much slower in the presence of a 1,1- or a 1,2-disubstituted olefin than in the presence of the related monosubstituted one (compare α-methylstyrene versus styrene, and cyclooctene versus 1-decene in Fig. 2). Accordingly, in an equimolar competition, styrene proved to be eight times more reactive than α-methylstyrene. With norbornene, no cyclopropanation, or ring-opening metathesis polymerisation (ROMP)[10] occurred under these conditions, but 1,3-dipolar addition took place in nearly quantitative yields.

According to the literature, the generally accepted mechanism involves the formation of a reactive carbene complex intermediate, resulting from electrophilic attack of the metal centre at the carbon atom of the diazo group and subsequent elimination of N_2. Then, transfer of the carbene fragment to the alkene, regenerates the catalytically active species and the catalytic cycle starts again. The two imido ligands in the five-coordinate chromium–carbene complex are assumed to adopt a mutually cisoid orientation, by analogy to that suggested for related pentacoordinated complexes, $Cr(N\text{-}t\text{-}Bu)_2X_2$(pyridine) and $[Cr(N\text{-}t\text{-}Bu)_2X(Me_2PCH_2CH_2PMe_2)]X$ (X=Cl, Br).[8a]

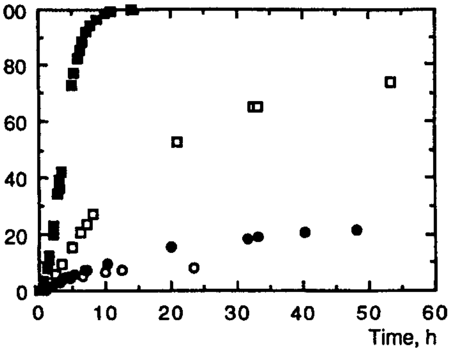
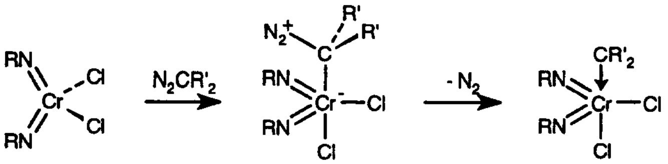


Figure 2. Influence of the substrate on the decomposition rate of ethyl diazoacetate in the presence of complex 1, at 80°C. (■) Styrene; (□) α-methylstyrene; (•) 1-decene, and (○) cyclooctene. Reaction conditions: the same as in Table 1



Depending on the nature of the ancillary ligands, chromium–carbenes have been shown to react with electron-deficient[5,6,11] or electron-rich alkenes.[7] At this stage of our research, the question of the nucleo- or electrophilicity of the chromium–carbene intermediate remains unanswered.[12] To this end, ethyl diazoacetate was reacted with ethyl acrylate in the presence of complexes 1–3 to produce cyclopropane and vinyl C–H insertion products. Pyrazoline and dimeric carbenoid products were also formed competitively, but in very low yields. An equimolar competition between ethyl acrylate and styrene revealed that the former reacted preferentially to the latter which was cyclopropanated in only minute amounts (relative reactivities: 97:3). These results clearly suggest that the reactive intermediate in these reactions catalysed by bis(imido) chromium(VI) complexes 1–3 possesses appreciable nucleophilic character. Further definitions of these reactions are under investigation.

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