Competitive Cyclopropanation and Cross-metathesis Reactions of Alkenes Catalysed by Diruthenium Tetrakis Carboxylates

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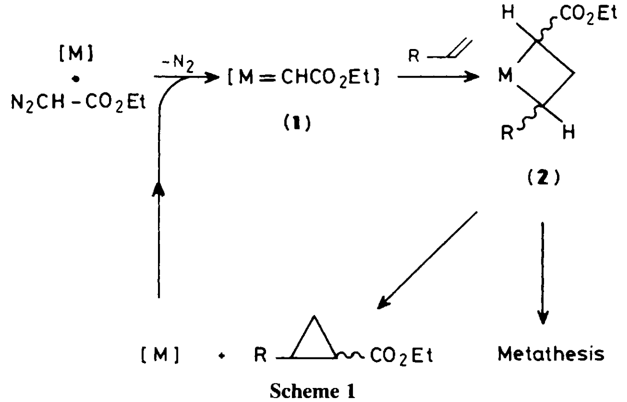
Addition of ethyl diazoacetate to a mixture of styrene and norbornene containing a catalytic amount of $Ru_2(OAc)_4$ promoted both the cyclopropanation and a selective cross-metathesis of the alkenes.

The tetrakis(acetato)diruthenium(II) complex $[Ru_2(OAc)_4]$ has recently become synthetically available.[1] Its calculated electronic configuration, $\sigma^2\pi^4\pi^{*3}\delta^{*1}$ indicates a metal–metal bond order of two, and two unpaired electrons.[2] Such complexes may exhibit different reactivity from their saturated analogues [of which the dirhodium(II)tetrakiscarboxylates, $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$ are typical representatives], especially in the field of catalysed carbene chemistry. It is well established that Rh^{II} carboxylates are outstanding carbene-transfer catalysts.[3] On the other hand, stoicheiometric reactions of diazoalkanes or diazirines with multiple metal–metal bonds have been useful in the synthesis of μ-alkylidene complexes.[4]

It is apparent that the rhodium- and ruthenium-based systems promote different reaction pathways. We now report the first observation of an efficient, competitive reaction pathway between carbene-transfer and alkene metathesis.

The interconversion of metal–carbene–alkene complexes with metallacyclobutanes has been reported,[5] and both species are known to exist in solution.[6] The involvement of such species, both in the cyclopropanation and the metathesis of alkenes, has been well documented.[7] If a common species is responsible for both reactions, the formation of cyclopropanes is a chain-termination step in the metathesis reaction and the catalyst should be short lived[8] unless re-activated in another reaction pathway. In the system described here, the active species [assumed to be metal–carbene(–alkene) complexes] were readily generated *in situ* by ruthenium acetate catalysed decomposition of ethyldiazoacetate (Scheme 1).

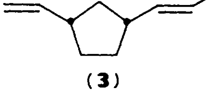


Scheme 1

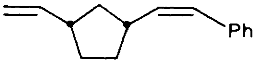
In a typical procedure, ethyldiazoacetate (2.5 mmol.) was slowly added over 3 h *via* an automatic syringe to a neat mixture of bicyclo[2,2,1]hept-2-ene (norbornene, 22 mmol) and styrene (22 mmol) containing $Ru_2(OAc)_4$ (2.5×10^{-2} mmol) at 60 °C. The reaction was performed under an inert atmosphere with purified and degassed reactants.

After quenching, the reaction mixture was found to contain more products than were expected from a straightforward carbene-transfer reaction, namely the cyclopropanes together with diethyl maleate and fumarate. The extra products were shown to result from a metathesis reaction. The yields of cyclopropanated styrene and norbornene were 35—40 and 2% respectively (based on ethyldiazoacetate, average of at least 5 experiments), compared to 65 and 26% with Rh^{II} acetate as catalyst.[3b]

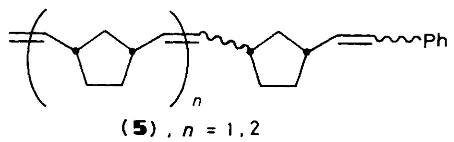
The major two new products were isolated and purified for analysis. They were unambiguously assigned structures (**3**) and (**4**) [ratio (**3**):(**4**) = 5.4] on the basis of spectral data (g.c.-m.s., i.r., ^{13}C and ^1H 2D n.m.r.). This corresponded to a turnover number (t.o.n.) of 35—50, based on ruthenium acetate.



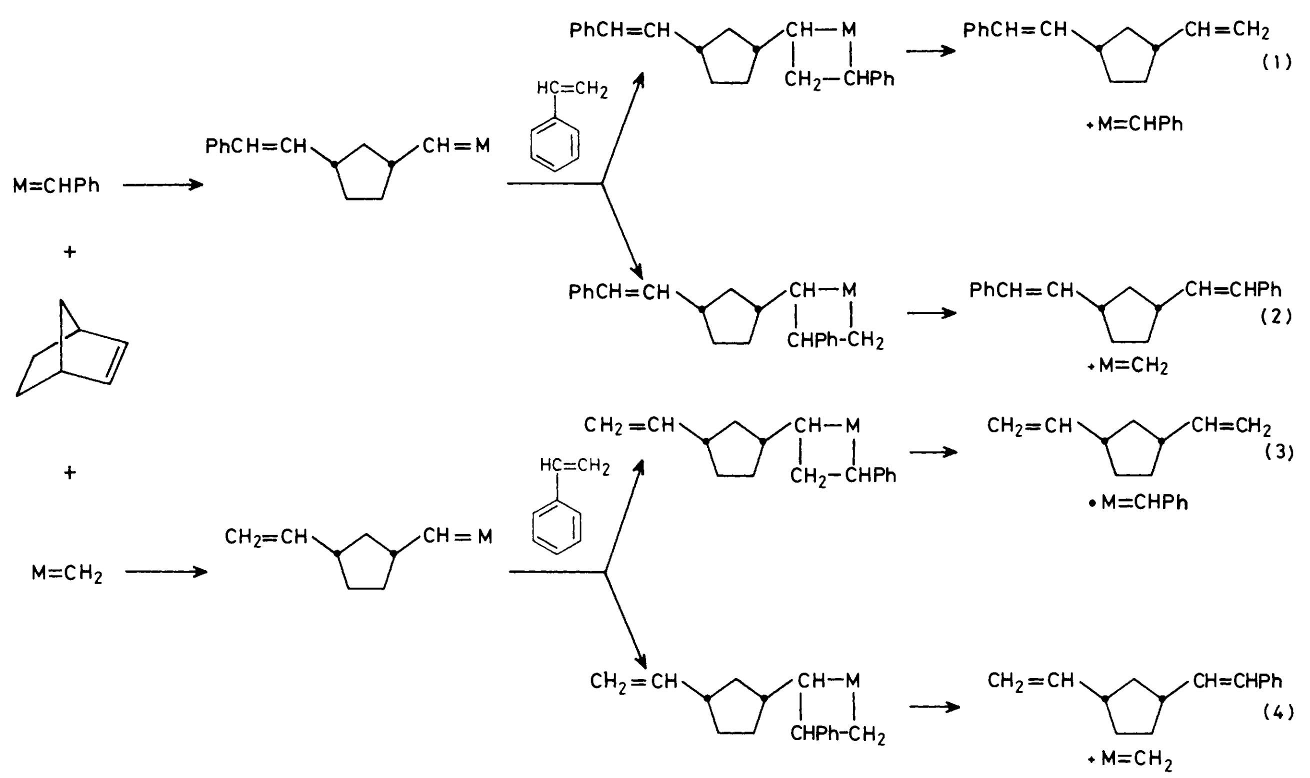
(**3**)



(**4**)



(**5**), *n* = 1, 2



Scheme 2

Although present in close to stoicheiometric amounts (t.o.n., 1 to 5), most of the other unknowns were identified by vapour phase chromatography (v.p.c.) by comparison with authentic samples on two different g.c. columns as ethene (gas phase), ethyl acrylate, and cinnamate (liquid phase). Phenylcyclopropane was also present in minute amounts. Oligomers of MW 292 (3 isomers, globally 1 styrene + 2 norbornene) and 386 (1 styrene + 3 norbornene) were detected by g.c.-m.s. Higher molecular weight oligomers were too heavy to be separated by g.c. but a polymer was reprecipitated from methanol. This was not fully characterised but showed i.r. absorption bands characteristic of aromatic ring protons and of a conjugated ester at 1719 cm^{-1}.

The presence of both ethyldiazoacetate and $Ru_2(OAc)_4$ was necessary to promote the reaction. Varying the ratio of styrene : norbornene (0.5—2) induced only marginal differences. The amount of (**3**) and (**4**) formed was directly related to the amount of added diazoester. Indeed, if we assume that species like (**1**) initiate the reaction, further addition of the diazoester reactivates the system (Scheme 1). The process is catalytic in ruthenium. It is important to note that this reaction proceeds in neat alkenes, in the presence of ester functionalities and without addition of a cocatalyst.

The observed products of cross-metathesis may be produced by reactions (**1**) or (**4**), Scheme 2. The former reaction is assumed to be more likely since it involves the intermediacy of the less crowded 1,3-disubstituted metallacycle.[5] This implies that the substituted metallacarbene is the major chain-carrier and supports the trend already reported for other systems.[9,10]

It is interesting to note that practically the same selectivities for the products of cross-metathesis were obtained with two quite different catalysts and alkenes, *i.e.* the ruthenium-based systems of this work (styrene and norbornene) and the tungsten-based system, described by Bencze *et al.*,[10] for the cross-metathesis of hex-1-ene and bicyclo[2,2,1]hepta-1,4-diene. This implies that the mechanism for these two reactions are closely related and that the conclusions drawn for the tungsten-based catalyst should also be valid for the system reported here. A major difference is that the ruthenium-based system (a group 8 metal) was also capable of simultaneously promoting cyclopropanation reactions.

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