Mechanism of the *cis–trans* Isomerization in Metathesis of Olefins

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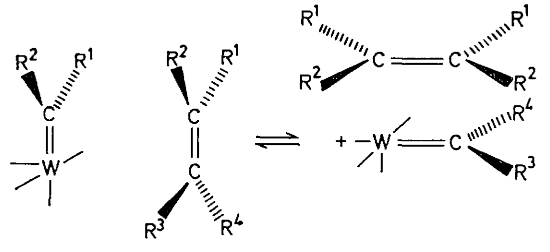
Summary A model is proposed which accounts for both the observed metathesis and the *cis–trans* isomerisation, as measured by the relative amounts of the various olefins produced at low conversion from the reaction of *cis*-pent-2-ene on a tungsten catalyst.

METATHESIS of acyclic olefins has been investigated intensively in the last decade,[1] but only a few studies have been devoted to the stereochemical aspect of the reaction.[2–5] We have shown previously[4] that the *cis–trans* isomerisation which occurs to a great extent during metathesis is a result of the metathesis itself and not a cationic side reaction. This was mentioned in the initial studies of Calderon *et al.*[2] although no evidence was given concerning the metathetic mechanism of this *cis–trans* isomerisation. If *cis–trans* isomerisation of the starting olefin is an equally probable alternative to metathesis, there must be a simple kinetic relationship between the respective rates of both reactions, related to the probability of co-ordination of the olefin to the active catalyst in such a way that it will result in metathesis or geometric isomerisation.



SCHEME 1

We now propose a model for the co-ordination of the olefin that explains respective occurrence of *cis–trans* isomerisation and metathesis and which is based on kinetic data. It has been shown that olefin metathesis obeys a one-carbene exchange mechanism,[6] initially proposed by Chauvin on kinetics grounds[7] as well as from studies on model reactions.[8] According to this mechanism an olefin, co-ordinated to a metallo-carbene unit, passes through a four-centre transition state to form a new olefin and a new metallo-carbene (Scheme 1).

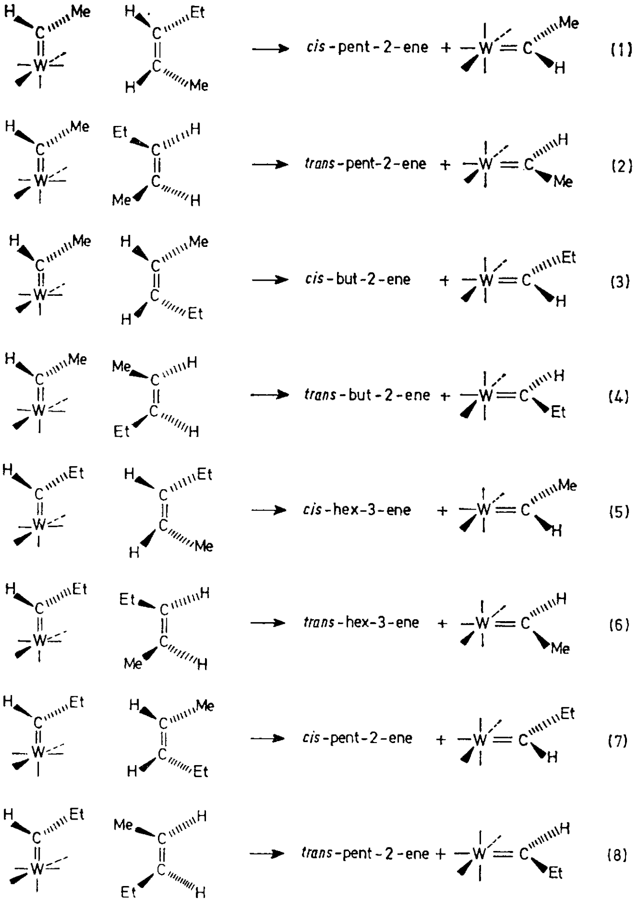
The stereochemical model proposed is based on this mechanism; we shall consider the metathesis of *cis*-pent-2-ene and assume the equally probable formation of two metallo-carbene units: W=CH–Me and W=CH–Et. There are four possibilities of co-ordination of this olefin for each carbene–tungsten unit (Scheme 2).

TABLE. Relative rates of *cis–trans* isomerisation and of metathesis at low conversion during metathesis of *cis*-pent-2-ene[a]

Catalysts	Co-catalyst	Ratio *trans/cis* C_4	Ratio *trans* C_5/*trans* C_4
$[W(CO)_5 PPh_3]$	$EtAlCl_2 + O_2$	$0{\cdot}83 \pm 0{\cdot}07$[b,c]	$2{\cdot}65 \pm 0{\cdot}3$[b]
$[W(CO)_5P(OPh_3)]$	$EtAlCl_2 + O_2$	0·83	2·80
$[WCl_6]$[d]	Me_4Sn	0·76	3

[a] Experimental conditions: chlorobenzene solvent, temp. 25 °C, $W/Al = 4$, $O_2/Al = 1{\cdot}5$, olefin/W = 100. [b] Average value deduced from 12 experiments. [c] A ratio *trans/cis* C_4 of 0·73 corresponds to 0% conversion (ref. 9). [d] $W/Sn = 1$, olefin/W = 100.

Depending on the type of co-ordination, the reaction products will be either identical to the starting olefin [reactions (1) and (7)], the *trans* isomer of the starting olefin [reactions (2) and (8)], the *cis* isomer of but-2-ene [reaction (3)], the *trans* isomer of but-2-ene [reaction (4)], the *cis* isomer of hex-3-ene [reaction (5)], or the *trans* isomer of hex-3-ene [reaction (6)].



SCHEME 2

These eight reactions are the only ones which occur at 0% conversion. Support for this model would come from a study of the product distribution at low conversion. In effect if the various types of co-ordination of the olefin to the tungsten are not drastically dependent on steric hindrance between the alkyl groups of the olefin and the alkyl group of the carbene, one can assume that all these reactions proceed at about the same rate; then, since *trans*-pent-2-ene is produced by two different reactions [(2) and (8)] whereas *trans*-but-2-ene is the product of only one reaction (4), the rate of formation of *trans*-pent-2-ene should be about twice that of *trans*-but-2-ene.

In order to determine whether the olefin is co-ordinated and/or reacts in such a way that the R group of the carbene and of the olefin are in a *cis* or *trans* position, one has to consider the respective rates of reactions (4) and (3) or (6) and (5) at 0% conversion. Previous results[9] have shown that the *trans*/*cis* ratios of but-2-enes and hex-3-enes at 0% conversion were 0·73 and 0·88, respectively, regardless of the nature of the catalyst in the homogeneous phase. Therefore steric factors are not very important in relation to the *cis* or *trans* approach of the olefin with respect to the metallocarbene, or its reaction once it is co-ordinated.

It was also possible to compare the rate of formation of *trans*-pent-2-ene with that of *trans*-but-2-ene at very low conversion. Many experiments were performed with *cis*-pent-2-ene and various catalytic systems derived from tungsten (Table). At low conversion the ratios *trans* C_5/*trans* C_4 were 2·65 ± 0·3 whereas a value of 2 would be expected from the occurrence of eight equally probable reactions at 0% conversion. The fact that we observe a *trans*/*cis* ratio close to unity is in good agreement with the fact that the ratio of isomerisation rate to metathesis rate is close to two, in the framework of a carbene-type mechanism. For a concerted mechanism,[3] the *trans*/*cis* ratios at 0% conversion are determined by the respective probabilities of a conrotatory or a disrotatory process,[3] whereas the ratio of isomerisation rate to metathesis rate is determined by the geometry of approach of the second olefin with respect to the first. Therefore these two ratios should vary in a completely independent way.

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