The Origins of Stereoselectivities in Olefin Metathesis

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A detailed study of the microstructures of ring-opened polymers of norbornene and several methyl derivatives, using salts of Ru and Os as catalysts, shows that the widely noted stereoselective feature of *cis* giving *cis* and *trans* giving *trans* in olefin metathesis is attributable to different forms of metallacarbene propagating species rather than to different configurations of putative metallacyclobutanes derivable from the same metallacarbene.

Ring-opened polymers of norbornene made using olefin metathesis catalysts[1,2] are almost invariably 'blocky' with respect to *cis* and *trans* junctions when the fraction of *cis* double bonds, σ_c is $\geqslant 0.35$. There is then a tendency to form *cis* after *cis* and *trans* after *trans* junctions, which shows that at least two kinetically distinct metallacarbenes propagate the reaction as shown in Scheme 1 (P_c and P_t are the propagating species, M is the monomer, and k_{cc}, k_{ct}, k_{tt}, and k_{tc} are rate constants[2] such that $r_cr_t > 1.0$).

We have previously argued[1] that the major distinction between P_c and P_t (Scheme 2) is that addition of the next monomer unit can occur with the newly formed *cis* double bond still in the co-ordination sphere of the metal, so with P_c steric compression forces the next monomer molecule to enter preferentially in the *cis* orientation, *i.e.* r_c has values $>1.0 \rightarrow \infty$. However before P_t reacts it must convert into a species, P, by the departure of the newly formed *trans* unit leaving a vacancy; the major steric factor is then the avoidance

$$\mathrm{P}_c + \mathrm{M} \longrightarrow \xrightarrow{k_{cc}} \longrightarrow \mathrm{P}_c$$

$$r_c = \frac{k_{cc}}{k_{ct}}$$

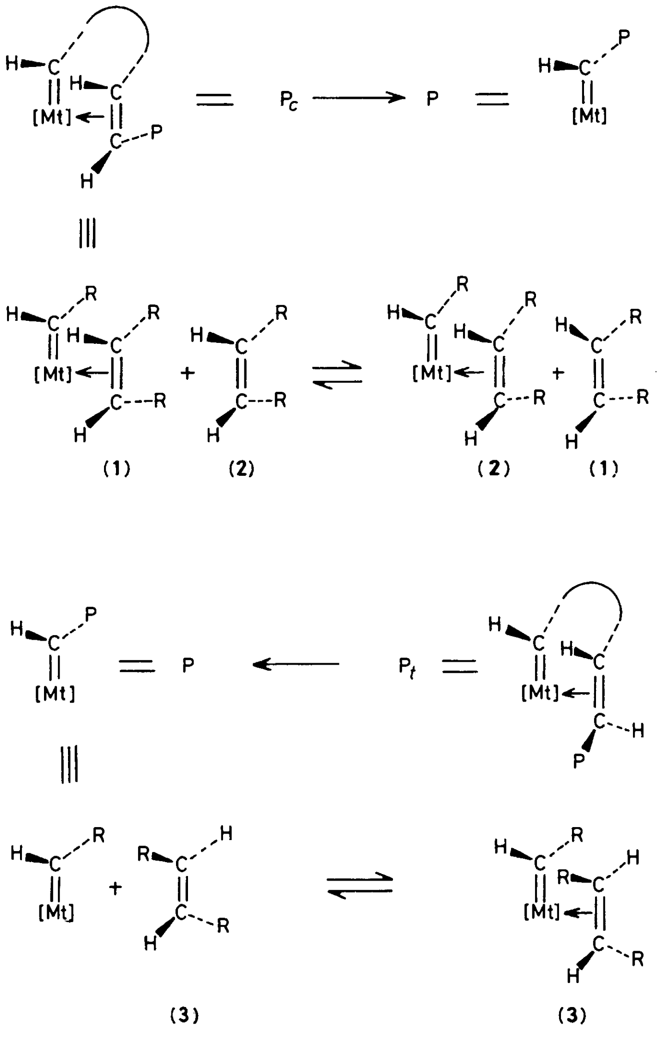
$$\mathrm{P}_c + \mathrm{M} \longrightarrow \xrightarrow{k_{ct}} \longrightarrow \mathrm{P}_t$$

$$\mathrm{P}_t + \mathrm{M} \longrightarrow \xrightarrow{k_{tt}} \longrightarrow \mathrm{P}_t$$

$$r_t = \frac{k_{tt}}{k_{tc}}$$

$$\mathrm{P}_t + \mathrm{M} \longrightarrow \xrightarrow{k_{tc}} \longrightarrow \mathrm{P}_c$$

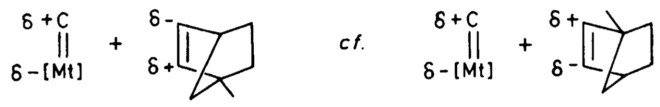
Scheme 1



Scheme 2

of repulsion between vicinal substituents in a *cis* orientation on the putative metallacyclobutane. Values of r_t are therefore $\geqslant 1.0 \rightarrow \infty$. These descriptions of P_c, P_t, and P are realistic because *cis*-alk-2-enes are dipolar and are thus better donor ligands than their *trans* isomers, so *cis* units should not only remain more strongly complexed to the metal[3] but in that position be sterically much less prohibitive than the corresponding *trans* to monomer entry.

In metathesis of n-alk-2-enes, *e.g.* n-pent-2-enes,[4] there is often a strong tendency to form *cis* from *cis* and *trans* from *trans* olefins and it is widely believed[5—7] that this stereoselective feature, and those of ring-opened polymers as well,[5] can be explained in terms of the energetics of various puckered forms of the relevant metallacyclobutanes. However, the polymer studies suggest that an explanation[8] based on different metallacarbenes, analogous to P_c and P, rather than one based solely on the formation of different metallacyclobutanes from the same metallacarbene, analogous to P, is much more likely. The idea that the characteristics of the events in a given catalytic cycle are governed to some extent by the nature of the events in the preceding cycle is, after all, in accordance with the fact that olefin metathesis is a chain reaction. This novel explanation is illustrated in Scheme 2 where propagation of the metathesis of *cis*-pent-2-ene is shown as occurring *via* displacement of a *cis* product by *cis* reactant in a *cis* orientation with respect to the alkyl group of the alkylidene ligand. By way of contrast in the metathesis of *trans*-pent-2-ene the newly formed *trans* unit has to depart before *trans* reactant may enter into complexation, which it does with a preferential *trans* orientation. In order to allow for all possibilities including degenerate steps, R in Scheme 2 is either a methyl or an ethyl group, (**1**) is either *cis*-hex-3-ene or *cis*-but-2-ene, and (**2**) and (**3**) are respectively *cis*- and *trans*-pent-2-ene, both of which may have either a head–tail or tail–head orientation.



(A)

Here we present new evidence which strongly supports the mechanistic ideas contained in Schemes 1 and 2. The ring-opened polymers of norbornene (NBE) and of several derivatives including 5,5-dimethyl, *transoid*-7-methyl (7-MNBE), and 1-methyl (1-MNBE) made using $\mathrm{RuCl_3 \cdot 3H_2O}$ as catalyst in alcoholic chlorobenzene solution at 60 °C are essentially all-*trans* (σ_c *ca.* 0.0), atactic,[1] and in the case of 1-MNBE without the head–tail bias which is widely observed with this monomer and other metathesis catalysts.[9] It therefore seemed useful to study the effect on polymer structures of substituting the $\mathrm{Cl^-}$ ligand by the much harder $\mathrm{CF_3CO_2^-}$ ligand in the Ru complex. This was thought to provide a test of the idea that a key step in the mechanism of metathesis is the direct [2 + 2] cycloaddition[8,9] of C=[Mt] and C=C, a step believed to govern stereoselectivities because of the importance of steric and polar factors associated with these reactive moieties and their approach to each other. This is depicted in (A) for P and 1-MNBE, but the ideas also apply to P_c.

A Ru trifluoroacetate complex,† prepared by prior reaction of $\mathrm{RuCl_3 \cdot 3H_2O}$ with an excess of $\mathrm{CF_3CO_2Ag}$ was therefore used as catalyst and the σ_c values for the polymers were found to have markedly increased, $\sigma_c \geqslant 0.5$, with the blockiness parameter, $r_t r_c$, >1.0, and in the case of 1-MNBE with a significant head–tail bias in the *trans* junctions as well as in the *cis* junctions.[9] All of this was expected on the basis that the $\mathrm{CF_3CO_2^-}$ ligands would render the C=[Ru] propagating species more polar and more reactive. Both of these factors will encourage participation by P_c in contrast to the case of $\mathrm{RuCl_3 \cdot 3H_2O}$ where P seems to be the only propagating

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† Although elemental analyses of the trifluoroacetate and acetate complexes (*vide infra*) agreed respectively with the formulae $\mathrm{Ru_2(CF_3CO_2)_4 \cdot 2H_2O}$ and $\mathrm{Ru_2(MeCO_2)_4Cl}$, the exact compositions of these ruthenium salts is not of primary significance since in each case only a small fraction of the metal ions seems to initiate polymerization.

species.[1] A more reactive species also means that P is sterically less discriminating with r_t values approaching unity rather than infinity. In this way both P_c and P are involved in raising the σ_c value in such a dramatic fashion from 0.0 to $\geqslant 0.5$.

The most remarkable result was obtained using 7-MNBE at 70 °C when the *cis* junctions were found to be syndiotactic but the *trans* junctions atactic, with $\sigma_c = 0.56$, $r_c = 3.2$, and $r_t = 2.1$.‡ These features confirm the descriptions of P_c and P and the validity of Schemes 1 and 2 because the structure of P_c, with the newly formed *cis* double bond as a ligand, preserves its chiral integrity as P_{1c} or P_{rc}[1] leading to the formation of syndiotactic polymer whereas, when the last formed double bond is *trans,* fast relaxation of P to a symmetrical form, leading to atactic polymer, is clearly feasible. The blockiness and the tacticities taken together therefore strongly confirm the claim that distinctive metallacarbenes are responsible for formation of *cis* and *trans* units.

When a Ru acetate complex, made in the same way using $MeCO_2Ag$, was the catalyst the polymers were the same as those obtained with $RuCl_3 \cdot 3H_2O$ thereby confirming that the hardness of the $CF_3CO_2^-$ ligand is the genuine cause of the effects observed. The C=[Ru] propagating species with $CF_3CO_2^-$ ligands was also shown to be more reactive by the following simple test. A 4:1 mixture of cyclopentene:NBE was polymerized using the trifluoroacetate catalyst and the polymer was found to contain significantly more units from the less reactive cyclopentene[10] than when the corresponding chloride or acetate complexes were used.

In contrast to $RuCl_3 \cdot 3H_2O$, the behaviour of $OsCl_3$ as a catalyst closely resembles that of the Ru trifluoroacetate complex. This is attributed to a substantial increase in ligand field effects and to the importance of the polar factor brought about now, where the ligands are the same, by changing the metal in the groups from the 4d to the 5d row. The importance of the polar factor for $OsCl_3$ is especially evidenced by the poly(1-MNBE) formed where there is a strong head–tail bias.[2,9] The marked increase in the ratios of degenerate to productive metathesis of n-alk-1-enes from comparable Mo to W based systems[11] is another example of the importance of head–tail bias and the significance of the polar factor in the [2 + 2] cycloaddition mechanism as the ligand field increases down the periodic groups.

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‡ The corresponding poly(NBE) had $\sigma_c = 0.5$, $r_c = 1.3$, and $r_t = 1.3$.

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