Stereochemical Behaviour of *cis*- and *trans*-Cyclo-octene in Metathesis

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With the catalyst $Mo(NO)_2Cl_2(PPh_3)_2$ + $EtAlCl_2$, *cis*- and *trans*-cyclo-octenes give respectively *cis*- and *trans*-polyoctenes; cyclic and acyclic olefins have a similar stereochemical behaviour in metathesis but, depending on the strain of the ring, the expected retention of configuration of the starting olefin may be attenuated.

We have recently proposed a simple theory which accounts for the stereochemistry of metathesis of both cyclic and acyclic olefins.[1] This theory is based on the relative energy levels of two consecutive intermediates of the catalytic reaction, namely the metallo–carbene–olefin complex and the metallacyclobutane. If the co-ordinated olefin has an energy which is smaller than that of the two possible metallacyclobutanes leading to the *cis*- and *trans*-isomers, the resulting stereoselectivity will be governed by the energy levels of these two metallacycles. If the co-ordinated olefin has an energy which is higher than that of the *cis*- and *trans*-directing metallacyclobutanes, the system will lose its stereoselectivity and have a *trans/cis*-ratio of unity. In general, most acyclic olefins belong to the first category and most cyclic olefins belong to the second category owing to the exothermic release of strain energy which has already partially occurred in the metallacyclobutane intermediate. In fact, from a stereochemical point of view, the distinction between cyclic and acyclic olefins is arbitrary. The important parameter appears to be the strain enthalpy of the ring; an unstrained cyclic olefin should have a stereochemical behaviour comparable with that of an acyclic olefin. We give here experimental support in favour of this hypothesis; with the catalyst $Mo(NO)_2Cl_2(PPh_3)_2$ in conjunction with $EtAlCl_2$, *cis*-cyclo-octene gives at low conversion predominantly a *cis*-polyoctene whereas *trans*-cyclo-octene gives predominantly a *trans*-polyoctene. With norbornene (a highly strained olefin), the same catalyst was previously found to be non-stereoselective.[1]

The catalyst $Mo(NO)_2Cl_2(PPh_3)_2$ + $EtAlCl_2$ was chosen because of its high stereoselectivity with acyclic olefins[2] and its lack of stereoselectivity with norbornene.[1] The experimental procedure for the metathesis of *cis*- and *trans*-cyclo-octene has already been described.[1,3] In order to obtain reliable stereochemical information, the reaction was quenched after 1 min. Polymer analysis[1] at various times (from 0.5 to 5 min) indicated no significant change in the structure of the oligomers and the polymer. It was also found that changes in the Al/Mo ratio (from 4 to 10) had no effect on the microstructure of the polymer.

In contrast with norbornene, *cis*-cyclo-octene gave a *cis*-polymer and its stereochemical behaviour was similar to that of *cis*-pent-2-ene, in agreement with the small strain enthalpy of this olefin (ΔH = 25.1 kJ/mol, ref. 4). *trans*-Cyclo-octene gave a *trans*-polymer but the retention of configuration was much smaller than that obtained with *trans*-pent-2-ene. This difference arises from the high strain enthalpy of this *trans*-cyclic olefin (ΔH = 64.0 kJ/mol, ref. 4) (Table 1).

Table 1. Stereoselectivity of the metathesis of various acyclic and cyclic olefins with $Mo(NO)_2Cl_2(PPh_3)_2$ + $EtAlCl_2$.

Olefin	*trans/cis*-ratio of double bonds in the product
cis-Pent-2-ene[a]	0.20[d]
cis-Cyclo-octene[b]	0.50[e]
Norbornene[c]	1.0[e]
trans-Pent-2-ene[a]	12.5[d]
trans-Cyclo-octene[b]	1.2[e]

[a] *t* 25 °C; solvent: PhCl; [olefin] = 0.17 mol l^{-1}; olefin : Mo : Al = 100 : 1 : 6. [b] *t* 25 °C; solvent: PhCl; [olefin] = 0.4 mol l^{-1}; olefin : Mo : Al = 100 : 1 : 10. [c] *t* 25 °C; solvent: PhCl; [olefin] = 0.4 mol l^{-1}; olefin : Mo : Al = 100 : 1 : 4. [d] *trans/cis*-ratio of but-2-enes at 0% conversion. [e] *trans/cis*-ratio of double bonds in the polymer; reaction time: 1 min.

Until now, it was commonly believed that the unusual stereochemical behaviour of cyclic olefins compared with acyclic olefins was due to a possible retro-co-ordination of the last double bond of the polymeric chain to the propagation centre.[5,6] In fact, our results indicate that this hypothesis is not necessary to explain the stereochemical behaviour of cyclic olefins. Cyclic olefins behave as acyclic olefins; the important parameter is the strain of the ring which, for a given catalyst, will moderate or cancel in the polymer the expected retention of configuration of the starting olefin.

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References

1. C. Larroche, J. P. Laval, A. Lattes, M. Leconte, F. Quignard, and J. M. Basset, *J. Org. Chem.*, 1982, **47**, 2019.
2. M. Leconte and J. M. Basset, *J. Am. Chem. Soc.*, 1979, **101**, 7296.
3. N. Taghizadeh, F. Quignard, M. Leconte, J. M. Basset, C. Larroche, J. P. Laval, and A. Lattes, *J. Mol. Catal.*, 1982, **15**, 219.
4. S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968, p. 179.
5. E. A. Ofstead, J. P. Lawrence, M. L. Senyek, and N. Calderon, *J. Mol. Catal.*, 1980, **8**, 227.
6. H. H. Thoi, K. J. Ivin, and J. J. Rooney, *J. Mol. Catal.*, 1982, **15**, 245.