

# Methylaluminumoxane as a novel catalyst and cocatalyst for ring-opening metathesis polymerisation of norbornene

Valia Amir-Ebrahimi, John J. Rooney\*

School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, Northern Ireland, UK

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## Abstract

Methylaluminumoxane (MAO) alone acts as a weak catalyst for the ring-opening metathesis polymerisation of norbornene, thereby providing good evidence that some transient  $[Al]=C<$  metallacarbenes are formed and propagate the reaction. A novel general mechanism of initiation involving generation of metallacyclopentanes, followed by ring contraction to metallacyclobutanes, is proposed.

Methylaluminumoxane is also a very effective cocatalyst for Mo and W chlorides, and especially for non-ionic carbonyl compounds of these two metals. Remarkably *cis/trans* highly stereo-blocky polymers are obtained which for the first time show clear resolution (*m/r*) on some of the  $^{13}C$  NMR lines.

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## 1. Introduction

Although all the highly active olefin metathesis catalysts are based on transition metal compounds especially those of Mo, W and Ru, there have been reports ever since 1978 that some compounds of main groups metals alone have low metathetic activity. Thus it was claimed [1] that  $EtAlCl_2$  causes the ring-opening polymerisation of norbornene (NBE) to give a largely *trans*-material together with addition oligomers. Silica–alumina is also activated by  $SnMe_4$  for metathesis [2–4], and most interesting is the report [5] that  $MgCl_2$ , especially that prepared by Grignard–Wurtz coupling reactions, catalyses metathesis of a variety of substrates, both alkenes and cycloalkenes. These reports suggest that under reaction conditions tiny amounts of aluminium and magnesium carbenes are formed and propagate the reaction by the normal [2 + 2] cycloaddition and cycloreversion steps between  $>C=C<$  and  $[metal]=C<$  entities. However, although the formation of  $RCH-MgCl$  metalla-radicals by matrix isolation has been claimed recently and theoretically discussed [6],  $[Al]=C<$  and  $[Mg]=C<$  compounds have never been synthesised, so the question always arises that some contamination by transition metals is responsible. We were therefore interested

to check the activity of methylaluminumoxane (MAO) that is now commercially available, since its degree of purity is much higher than that of  $EtAlCl_2$  or alumino-silicates.

## 2. Experimental and results

Aldrich MAO, provided as a 10% solution in toluene, was transferred in 0.5–1.0 ml aliquots in a syringe via a rubber serum cap into a small flask containing 0.2 g NBE in 1.0 ml dry chlorobenzene as solvent. Polymer slowly settled out as a colourless gel over about 2.0 h. This was dissolved in chloroform and methanol then added, which precipitated out the polymer as a fine white powder that was isolated by centrifugation.  $^1H$  and  $^{13}C$  NMR spectra in  $CDCl_3$  were recorded on a Bruker Avance DRX 300 and DPX 500 spectrometer at 75 and 125 MHz, respectively. Chlorobenzene and dioxan were dried by distillation and MAO used as purchased.

The  $^{13}C$  NMR shown in Fig. 1 revealed that the product had a *cis* content ( $\sigma_c$ ) of 68% and was quite blocky ( $r_c \cdot r_t = 11$ ), in contrast to the largely *trans*-polymer obtained using  $EtAlCl_2$  as catalyst [1]; the polymer is random when blockiness expressed as  $r_c \cdot r_t = tt \cdot cc / tc \cdot ct = 1.0$  [7].

Various attempts were made to increase the activity of the initiator by using several additives which might induce the

\* Corresponding author.

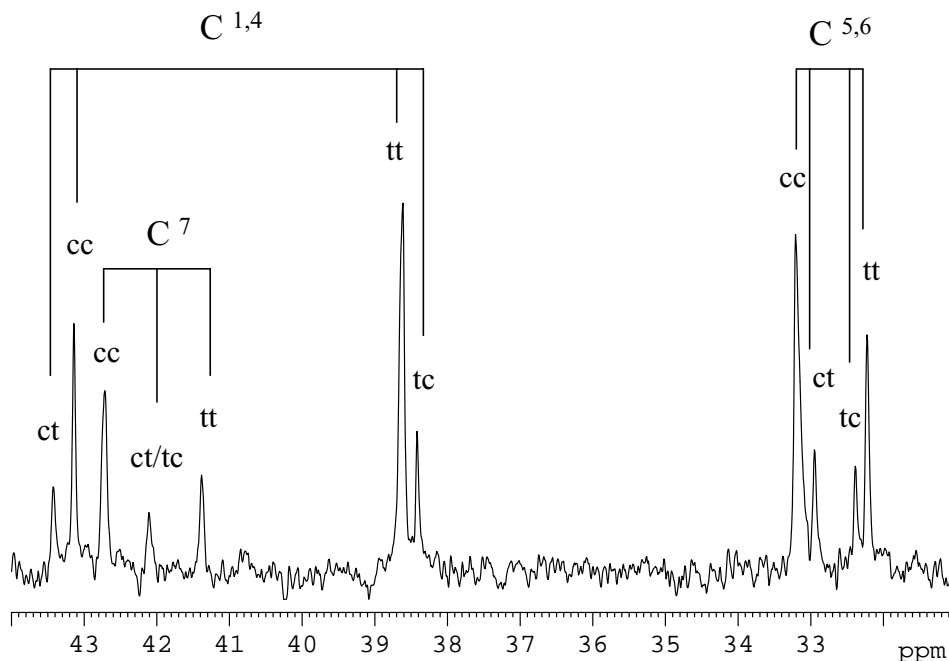


Fig. 1.  $^{13}\text{C}$  NMR spectrum of Poly-NBE made using MAO alone.

removal of a hydride ion or of a proton from the  $\text{CH}_3\text{-[Al]}$  functionality, thereby generating  $\text{CH}_2\text{=[Al]}$  carbenes, but with little success. However two interesting features were noted. The addition of triphenylphosphine caused an increase in the *cis* content to 77% with extreme blockiness ( $r_c \cdot r_t = 24$ ) whereas, the addition of the dehydrogenation reagent 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) caused preferential partial dehydrogenation of the *cis* units in the polymer, and especially those flanked by *trans* units. This was evident from the  $^{13}\text{C}$  NMR spectrum where only *ccc* and *ttt* peaks were present in the usual olefinic region, and the *ct/tc* peak for  $\text{C}^7$ , between the *cc* and *tt* lines, was eliminated. New peaks for unsaturated carbon were also noted and a new olefinic proton peak was observed in the corresponding  $^1\text{H}$  NMR spectrum, thereby confirming dehydrogenation. No significant metathesis activity was observed when MAO was used with other cyclic olefins, including cyclopentene and norbornadiene.

MAO was then investigated as a cocatalyst for several transition metal compounds. In these experiments MAO solution (0.2–1.0 ml) was added to a solution of the transition metal salt or compound in dry chlorobenzene (1.0 ml) and NBE (0.2 g) in 1.0 ml chlorobenzene then added via a serum cap. In the case of  $\text{MoCl}_5$  (10–30 mg) the solution maintained its brown colour in the presence of MAO and vigorous instantaneous polymerisation took place with a reactivity at least as high as that observed for a  $\text{MoCl}_5/\text{SnMe}_4$  catalyst. The polymer was dissolved in  $\text{CHCl}_3$ , isolated in the usual way and its  $^{13}\text{C}$  NMR spectrum was recorded. Using lower amounts of MAO (0.2–0.5 ml), the behaviour of the catalyst was very similar to that of  $\text{MoCl}_5/\text{SnMe}_4$  [7]; the *cis* content was 58% and the *c/t* distribution random ( $r_c \cdot r_t = 1.2$ )

(Fig. 2). Similar results were also observed using  $\text{NbCl}_5$  ( $\sigma_c = 48\%$ ) and  $\text{WCl}_6$  ( $\sigma_c = 36\%$ ) with fairly random *c/t* distribution. This behaviour did not change for these Nb and W salts even when 1.0 ml of MAO solution was used in the reaction. Interestingly  $\text{W}(\text{CO})_6$  was rendered highly active using 1.0 ml solution of MAO, giving a blocky polymer ( $r_c \cdot r_t = 9.4$ ) with 56% *cis* units.

The most remarkable results were obtained where a larger amount of MAO solution, 1.0 ml, was used with various Mo compounds. In the case of  $\text{MoCl}_5$ , the *cis* content of the polymer was 58% and  $r_c \cdot r_t = 7$ . This blocky polymer, whose  $^{13}\text{C}$  NMR spectrum is shown in Fig. 3, was quite unique since for the first time ever in a great number of samples studied over three decades, the *cc* [ $\text{C}^7$ ] peak was clearly resolved by tacticity splitting into two distinct lines, and the same was true for the *cc* peak of the  $\text{C}^{5,6}$  carbon. We were able to assign the peaks as due to meso (*m*) and racemic (*r*) units, respectively, in the following way. Using an  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$  catalyst [7], a sample of all *cis*, all syndiotactic (*r*) poly-NBE was made whose  $^{13}\text{C}$  consists of four sharp lines only [7]. These are *ccc* [ $\text{C}^{2,3}$ ] *cc* [ $\text{C}^7$ ], *cc* [ $\text{C}^4$ ] and *cc* [ $\text{C}^{5,6}$ ] (see Fig. 3b in [7]). When a 1/1 mixture of this polymer and that of the sample whose  $^{13}\text{C}$  NMR spectrum is shown in Fig. 2 was prepared, the resulting spectrum is that of Fig. 4. The *cc* [ $\text{C}^7$ ] and the *cc* [ $\text{C}^{5,6}$ ] peaks are still clearly resolved into doublets and all the peaks easily distinguished and assigned. Obviously  $\text{MoCl}_5/\text{MAO}$  makes *cis* junctions which are largely isotactic [8], and the polymer is so sterically blocky that it looks as if it is a mixture of two separate polymers (very few *cis* (*r*) *cis* (*m*) junctions). The only other example of this kind of behaviour is the incipient *m/r* splitting of the *cc* lines in the  $^{13}\text{C}$  NMR of a high *cis*

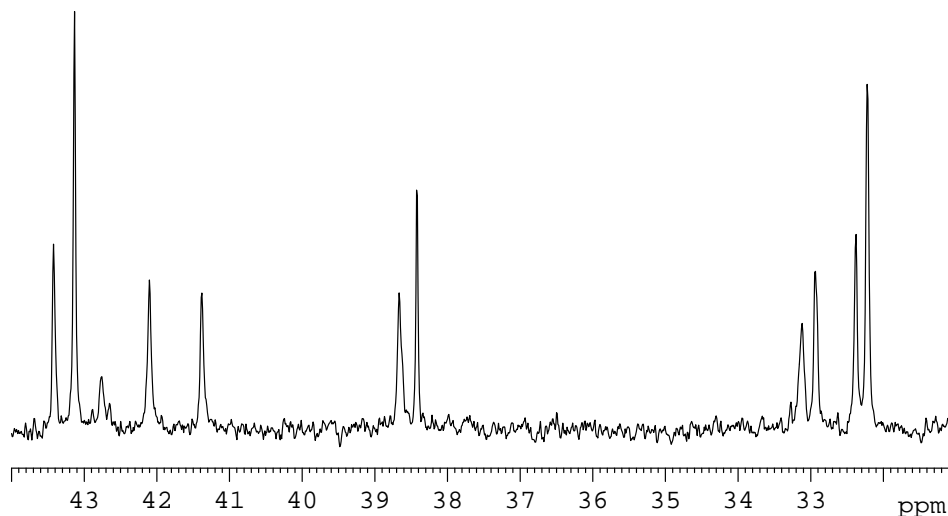


Fig. 2. Poly-NBE made using  $\text{MoCl}_5$  with MAO. Line assignment as in Fig. 1.

blocky polymer of NBE made using the well-defined Basset W-based catalyst [9].

An even more striking polymer was obtained using 1.0 ml solution from a new fresh batch of MAO whose  $^{13}\text{C}$  spectrum is shown in Fig. 5, with the *cis* content = 71%, and blockiness  $r_c \cdot r_t = 17$ .

Among other remarkable results is the reaction of NBE using dry dioxan as the solvent for  $\text{MoCl}_5$  catalyst with MAO (0.5 ml solution) in which the *cis* content rose to 85% with

$r_c \cdot r_t = 12$ . This effect of the ether confirmed that the Mo carbenes are propagating the reactions since the same effect on the *cis* content is observed when various ethers were used as solvent with  $\text{MoCl}_5/\text{Sn}(\text{CH}_3)_4$  catalyst system [7]. MAO was also used as a cocatalyst for  $\text{Mo}(\text{CO})_6$  rendering it highly active, resulting in a polymer with a *cis* content of 92% and  $r_c \cdot r_t = 16$ , where the *cis* junctions are also mainly isotactic. As a cocatalyst it also activated  $[\text{CpMo}]_2(\text{CO})_3$  for metathesis, here the *cis* content was 55% with  $r_c \cdot r_t = 6.0$ .

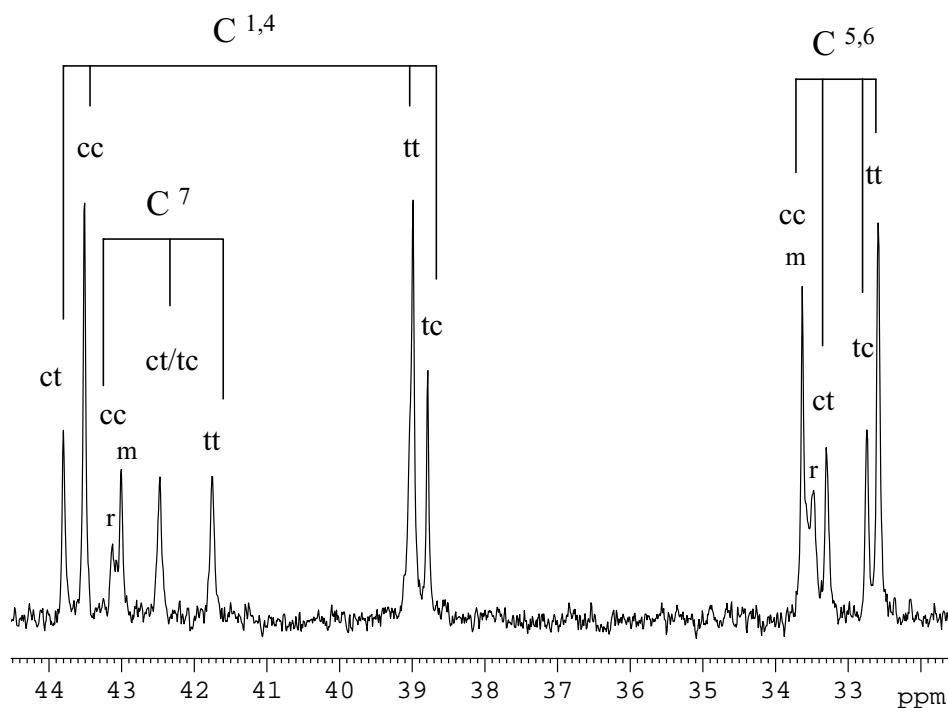


Fig. 3. Poly-NBE made using  $\text{MoCl}_5$  with excess MAO.

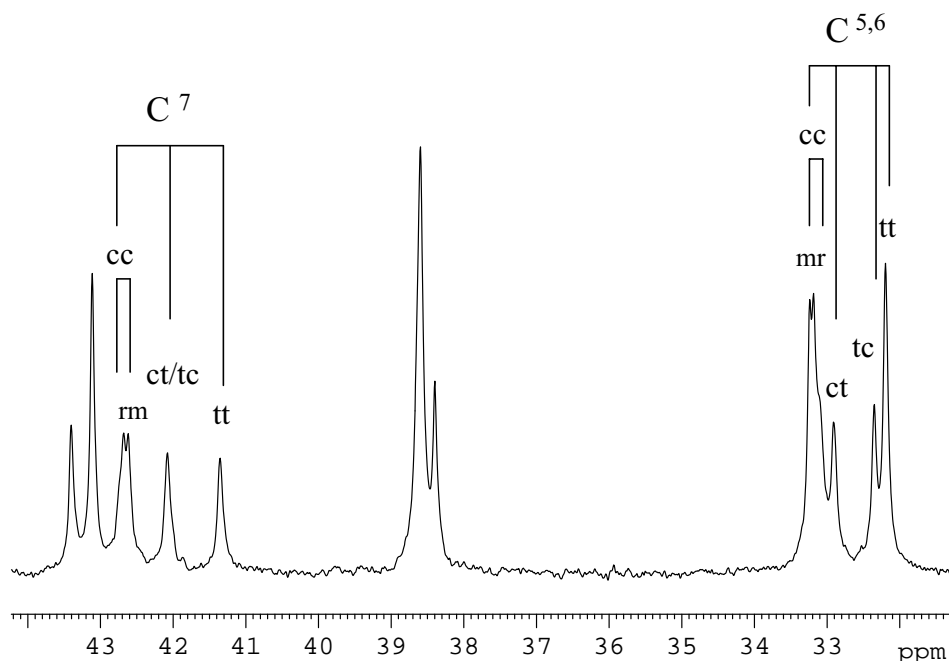


Fig. 4.  $^{13}\text{C}$  NMR spectrum of the 1/1 mixture of poly-NBE made using (1)  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$  catalyst system and (2)  $\text{MoCl}_5$  with excess MAO.

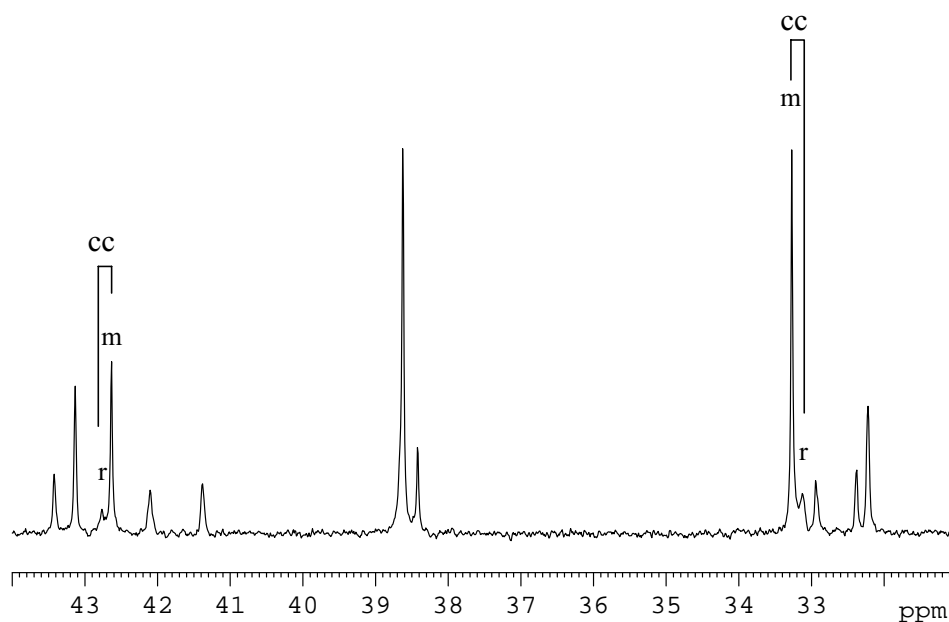
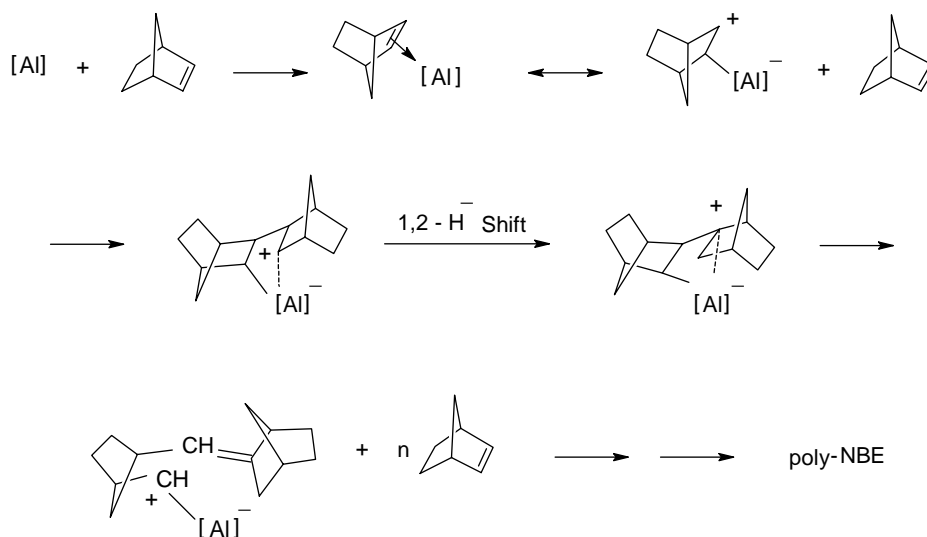


Fig. 5. Highly blocky Poly-NBE made using  $\text{MoCl}_5$  with excess fresh MAO. Line assignment as in Fig. 3.

### 3. Discussion and conclusion

The fact that MAO alone causes the metathesis of NBE confirms that main group, electron-deficient metal ions such as  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ , can form carbenes and propagate [2+2] cycloaddition and cycloreversion reactions. There is no evidence that the methyl group in MAO is the source of the first carbene, and we are now inclined to consider the view

that there is a general mechanism involved which also applies to unicomponent transition metal catalysts where there is no obvious route to initiation [10]. This new mechanism requires metallacyclopentane formation from two olefinic molecules and an electron-deficient metal ion, followed by contraction to a metallacyclobutane via 1,2-hydride shift in a transient metallacarbenium ion. This mechanism is illustrated here for MAO in Scheme 1, but it also applies to W,

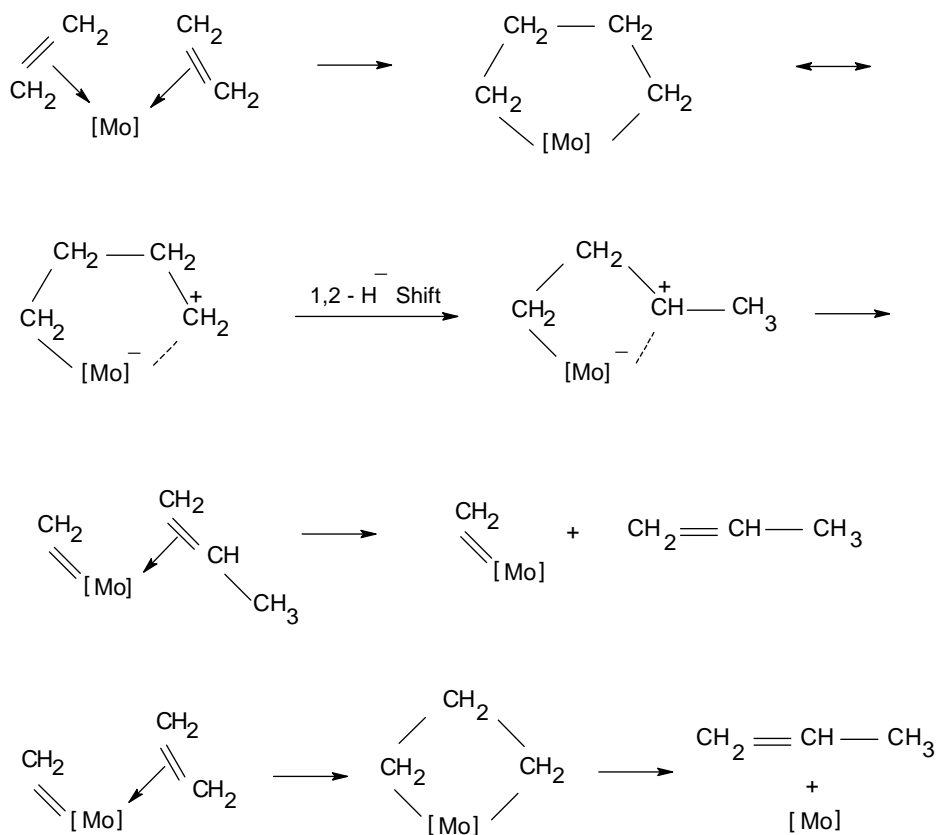


Scheme 1.

Mo, Re, Ru ions, etc. in unicomponent catalysts without a carbene ligand, or obvious precursor of such a ligand.

The  $[Al]$  in Scheme 1 is intended to represent  $AlX_3$  in which at least two ligands are oxide ions. The propagating species is then,  $RCH^+ [AlX_3]^-$ , which is carbenoid. However, the active site density is probably so low that any mech-

anism is speculative. A further correspondence with acidic unicomponent catalysts such as  $WCl_6$  and  $ReCl_5$  [10] is that using NBE with MAO or  $EtAlCl_2$  [1], a significant amount of addition oligomerization also occurs simultaneously with ROMP. We had previously suggested that hydride intermediates are responsible for initiation of both these reactions

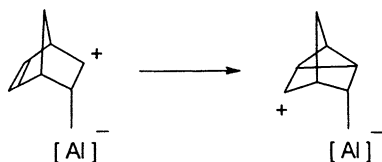


Scheme 2.

using the acidic transition metal salts, as well as  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  catalysts, but current work on Ru-based initiators indicates that this is not correct.

The above mechanism can also be applied, as in Scheme 2, to explain several examples of metathesis of alkenes on classical heterogeneous catalysts, especially the homologation reaction of ethene to propene on  $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$  catalyst [11].

Metallacyclopentanes and corresponding metallacarbenium ions are the most likely intermediates in the catalysed dimerization of norbornadiene, e.g. by Co [12] and Rh [13] ions. Since both [3 + 3] and [3 + 2] cycloadditions occur, respectively, in these dimerizations, intermediate homoallylic rearrangement of one or both metal-complexed dienes must be occurring, and this is strongly indicative of a carbonium ion mechanism. The strong propensity for the norbornenyl carbonium ions to form the isomeric nortricyclic ions by the homoallylic route, shown below, would also mitigate against norbornadiene undergoing ROMP using MAO as catalyst.



The preferential dehydrogenation by DDQ of *cis* units adjacent to *trans* units is due to the torsional strain imposed on the former by the *trans* unit, considered as a stereo-irregularity in the high *cis*-polymer chain. Some evidence for this idea is the observation that the *ctt* [ $\text{C}^{2,3}$ ] line in the  $^{13}\text{C}$  NMR spectra of high *cis*-blocky polymers is invariably displaced from the position expected and observed for low *cis* content polymer with respect to the remaining three lines *ctc*, *ttc*, and *ttc* of this quartet [14].

While methylation of the transition metal ions using both MAO and  $\text{SnMe}_4$  may well occur and be the source of the first metallacarbenes, the fact that  $\text{SnPh}_4$  is comparable in its activity to  $\text{SnMe}_4$  as a cocatalyst remains a mystery since there is no easy way for a phenyl group as a ligand to convert into a carbene ligand.

In conclusion, MAO is not only very interesting in its own right as a source of carbenes, but it is also a highly effective cocatalyst, comparable to  $\text{SnR}_4$ . However, it is more active for transition metal halides and, unlike  $\text{SnR}_4$ , is also very efficient in activating non-ionic carbonyl compounds of Mo and W; in this context, it should be explored further.

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## References

- [1] K.J. Ivin, J.J. Rooney, C.D. Stewart, J. Chem. Soc. Chem. Commun. (1978) 603.
- [2] M.J.D.M. Jannini, R. Buffon, A.M. deWit, J.C. Mol, J. Mol. Catal. A: Chem. 133 (1998) 201.
- [3] R. Buffon, M.J.D.M. Jannini, A. Abras, J.C. Mol, A.M. deWit, F.J.A. Kellendonk, J. Mol. Catal. A: Chem. 149 (1999) 275.
- [4] H.-G. Ahn, K. Yamamoto, R. Nakamura, H. Niiyama, Chem. Lett. (1992) 503.
- [5] P. Buchacher, W. Fischer, K.D. Aichholzer, F. Stelzer, J. Mol. Catal. A: Chem. 115 (1997) 163.
- [6] W.D. Bare, A. Citra, C. Trindle, L. Andrews, Inorg. Chem. 39 (2000) 1204.
- [7] V. Amir-Ebrahimi, J.G. Hamilton, J.J. Rooney, Ring Opening Metathesis Polymerization and Related Chemistry, Kluwer Academic Publishers, Dordrecht, 2002, p. 45.
- [8] T. Sunaga, K.J. Ivin, G.E. Hofmeister, J.H. Oskam, R.R. Schrock, Macromolecules 27 (1994) 4043.
- [9] J.-M. Basset, M. Leconte, F. Lefebvre, J.G. Hamilton, J.J. Rooney, Macromol. Chem. Phys. 198 (1997) 3499.
- [10] D.T. Lavery, J.J. Rooney, J. Chem. Soc., Faraday Trans. I 79 (1983) 869.
- [11] P.P. O'Neill, J.J. Rooney, J. Am. Chem. Soc. 99 (1972) 4383.
- [12] G.N. Schrauser, B.N. Bastian, G.A. Fosselius, J. Am. Chem. Soc. 88 (1966) 4890.
- [13] N. Acton, R.J. Roth, T.J. Katz, J.K. Frank, C.A. Maier, I.C. Paul, J. Am. Chem. Soc. 94 (1972) 5446.
- [14] B. Al Samak, V. Amir-Ebrahimi, D.G. Corry, J.G. Hamilton, S. Rigby, J.J. Rooney, J.M. Thompson, J. Mol. Catal. A: Chem. 160 (2000) 13.