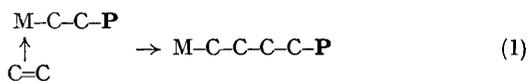


Mechanism for the Stereospecific Polymerization of Olefins by Ziegler–Natta Catalysts

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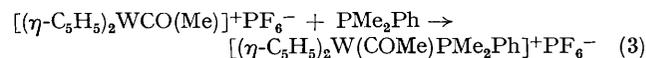
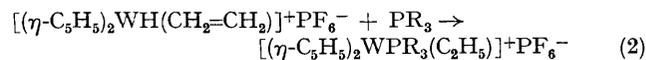
Summary A mechanism for the stereospecific polymerization of olefins by Ziegler–Natta catalysts is developed which differs significantly from previous mechanisms in the proposal that it proceeds *via* a 1,2-hydrogen shift from the α -carbon of the polymer chain and formation of metallocycle and carbene intermediates.

THE dimerisation, oligomerisation, and Ziegler–Natta polymerization of olefins may be catalysed by pure alkyl–aluminium compounds, by transition metal compounds alone, and by mixtures of transition metal– and alkyl–aluminium compounds.^{1–3} There is little direct evidence for the detailed nature of the catalytic sites but it has been generally proposed that a key step in the mechanism is insertion of a co-ordinated olefin into a metal–carbon chain, *viz.* reaction (1), where **P** = polymer chain. How-



ever, as far as we are aware there are no unambiguous examples where a characterised metal–alkyl–olefin compound may be induced to react giving the expected insertion product. For example, we have studied the reaction of the

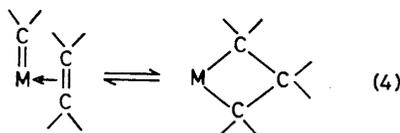
new compounds $[\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{ethylene})(\text{alkyl})]^+\text{PF}_6^-$ where $\text{M} = \text{Mo}$, alkyl = Me; and $\text{M} = \text{W}$, alkyl = Me, $\text{CH}_2\text{CO}_2\text{Me}$, CH_2CN , $\text{CH}_2\text{-CH=CH}_2$, and have found no evidence for insertion of the ethylene into the metal–alkyl bond.^{4,5} In contrast, insertion of olefins into metal–hydrogen or insertion of carbon monoxide into metal–alkyl bonds is well established. Examples of these reactions, which are of compounds closely related to those described above, are given in reactions (2) and (3).



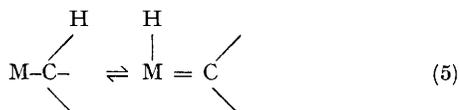
We also note that there is a close identity between catalysts which cause Ziegler–Natta polymerization and those which give rise to olefin metathesis. There are many systems where metathesis is accompanied by oligomerization of the olefin,⁶ and often the same catalyst, or virtually identical catalysts, effects both ring-opening polymerization of cycloalkenes and Ziegler–Natta polymerization of the same cycloalkenes and ethylene as well.^{7–10} Now there is

convincing evidence that pure EtAlCl_2 can cause ring-opening polymerization of norbornene.¹¹ Thus even alkyl-aluminium compounds alone can give rise to both ethylene polymerization¹ and olefin metathesis reactions.

Observations such as these prompted our attention to the possibility that the carbon-carbon bond-forming step in the Ziegler-Natta polymerization of olefins might be identical to that in metathesis (including ring-opening polymerization). On the basis of considerable evidence⁶ it is now generally accepted that metathesis involves metallocyclobutane and metal-olefin-carbene interconversions as the key steps in breaking and formation of carbon-carbon bonds, *e.g.*, reaction (4). There is also evidence that



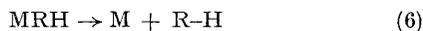
transition metal-alkyls can give rise to the reversible elimination of α -hydrogen, *e.g.*, reaction (5).⁵ This inter-



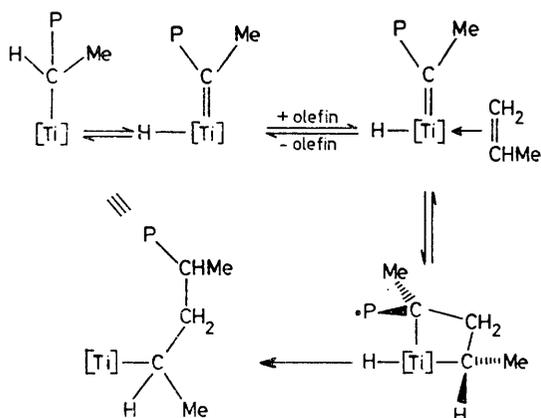
conversion may be more simply described as a 1,2-hydrogen shift such as is well established to occur in carbonium ion chemistry,¹² *viz.* $\text{R}_2\text{CH}-\text{C}^+\text{HR} \rightarrow \text{R}_2\text{C}^+-\text{CH}_2\text{R}$.

The most active Ziegler-Natta catalysts^{1,3} employ metal compounds with none or few non-bonding *d*-electrons so that analogous 1,2-hydrogen shifts utilising the electron-deficient π -orbitals of the metal might be expected to occur rapidly.

The reversible elimination reaction whereby transition metal-alkyl-hydride derivatives give alkanes is also well established, *e.g.*, in catalytic hydrogenation, reaction (6).



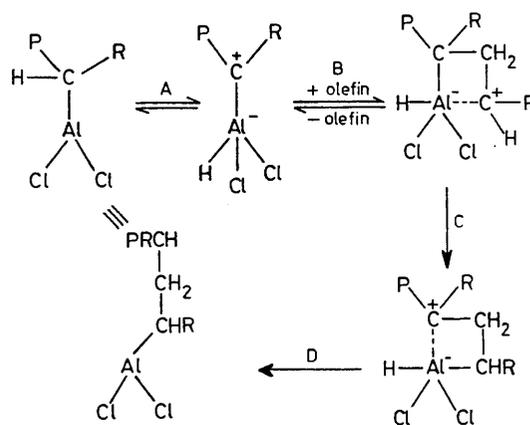
The three reactions (4)–(6) may be combined to give rise to a mechanism for homogeneous and heterogeneous



SCHEME 1. P = polymer

transition metal catalysed polymerization of olefins which may be written as shown in Scheme 1.¹³

In the light of the preceding communication we may write an essentially similar mechanism for oligomerization of olefins by an aluminium centre, Scheme 2.



SCHEME 2

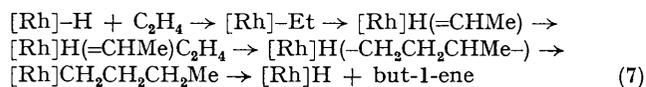
As far as we are aware, these mechanisms are entirely compatible with known data. For example, the stereospecific polymerization of propene may be discussed in terms of the relative orientation of substituents on the metallocyclobutane ring. Thus, when the two methyl groups are on the same side of the ring (Scheme 1) polymerization will give the syndiotactic polymer. If the addition of the propene occurs so that the methyl groups are placed on opposite sides of the ring then the polymer will be isotactic.

In view of the unlikelihood that '*d*-orbitals' may make a substantial contribution to the bonding of organo-aluminium compounds we have represented the species in Scheme 2 in terms of idealised canonical transition states. Since titanium *d*-orbitals are available for bonding we may choose to represent the steps in Scheme 1 as intermediates, although the polarisation of the covalent bonds would be expected to be the same as is suggested in Scheme 2.

The representation given in Scheme 2 provides insight into the more intimate features of the mechanism. For example, the olefin addition (step B) is indicated to proceed *via* 'carbonium ion' attack on the most nucleophilic olefin carbon, followed by relocation of the positive charge on the tertiary carbon (step C). The reductive elimination (Scheme 1) may also be viewed as H^- transfer to the tertiary carbonium ion (Step D). This representation also relates to the metal catalysed rearrangements of small ring organic compounds where $\text{M}-\text{C}^{\ominus}\text{C}^{\oplus}$ carbenoid species are postulated.¹⁴ A similar representation has been used to explain the strongly stereospecific nature of metathesis of α -olefins.¹⁵

If the proposed hydrogen transfer (step D) is slow, or if there is a means of removing the hydrogen ligand from the metal centre, then the catalyst will become a metathesis catalyst. Thus the same, or similar, catalysts may give rise to oligomerization, Ziegler-Natta polymerization, or metathesis, or all three, as is observed.

It is a corollary of the above that the dimerisation of ethylene to but-1-ene by rhodium¹⁶ (or tungsten¹⁷) may proceed *via* the steps in reaction (7).



In conclusion, we assert that reactions which proceed by insertion of an olefin into a metal-carbon single bond may be the exception rather than the rule.

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