Ziegler–Natta Catalysis: an Alternative Mechanism involving Metallacycles

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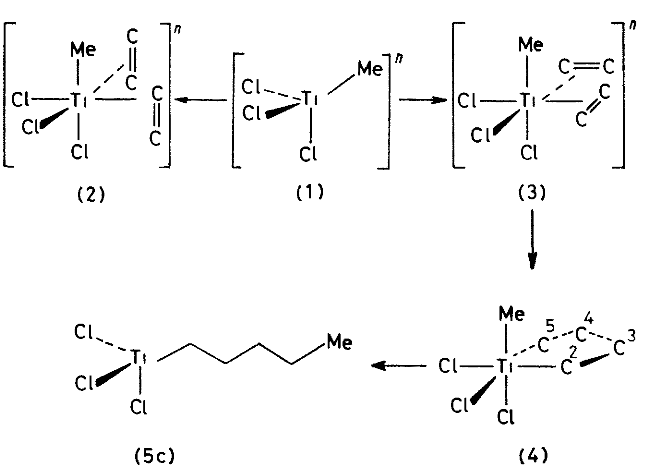
Summary Semi-empirical molecular orbital calculations suggest a new catalytic sequence for Ziegler–Natta polymerization involving a metallacyclopentane intermediate.

ZIEGLER–NATTA polymerization of olefins, an important industrial process, is still poorly understood. A key step in the widely accepted Cossee–Arlman mechanism[1] is the insertion of a co-ordinated olefin into a metal–carbon bond. Green and co-workers,[2] having noted the lack of unambiguous examples of well characterized metal–alkylolefin compounds in which the olefin could be induced to insert, recently proposed an alternative mechanism which does not include such a step. The proposal that catalytic olefin dimerization may occur through metallacyclopentanes[3] led us to undertake semiempirical molecular orbital calculations[4] to explore the possible involvement of such species in olefin polymerization.



a; $n = 0$
b; $n = -1$
c; $n = -2$

SCHEME.

The complexes $[TiCl_3Me]^n$ (**1**) were used as models for hypothetical catalyst sites in three oxidation states of titanium (IV, III, and II; d^0, d^1, and d^2, respectively), with the methyl group representing the growing polymer chain. The positions of alkyl and/or olefin fragments were optimized with respect to the $TiCl_3$ fragment.[4]

The co-ordination of two ethylene molecules to (**1**) may result in complexes (**2**) and (**3**) (Scheme). The preferred orientation of the ethylene ligands is highly dependent on the formal oxidation state. For Ti^{IV}, (**2a**) in which the ethylene ligands are parallel is preferred to (**3a**) (0·5 eV) whereas (**3c**) with the titanium and four olefin carbon atoms coplanar is preferred (0·6 eV) by Ti^{II}. The structures (**2b**) and (**3b**) are of similar energy.

The preference of Ti^{II} for structure (**3c**) is explained by the highest occupied molecular orbital (HOMO (A) (Figure). The HOMO (A) is a titanium d-orbital which is strongly stabilized through retrodative bonding to both ethylene ligands. Moreover the two ethylene ligands are symmetrically disposed toward coupling to give the titanacyclopentane complex (**4c**). Significantly this orbital is not occupied in the Ti^{IV} case. The conversion of (**3c**) into (**4c**) includes a change in formal oxidation state ($Ti^{II} \rightarrow Ti^{IV}$) which for (**3a**) to (**4a**) ($Ti^{IV} \rightarrow Ti^{VI}$) and (**3b**) to (**4b**) ($Ti^{III} \rightarrow Ti^{V}$) would be highly unfavourable. Consistently, whereas (**4c**) is of lower energy than (**3c**), the converse is true for (**3a, b**) with respect to (**4a, b**). Equilibria involving bis-olefin–metal and metallacyclopentane derivatives are known.[5–8]

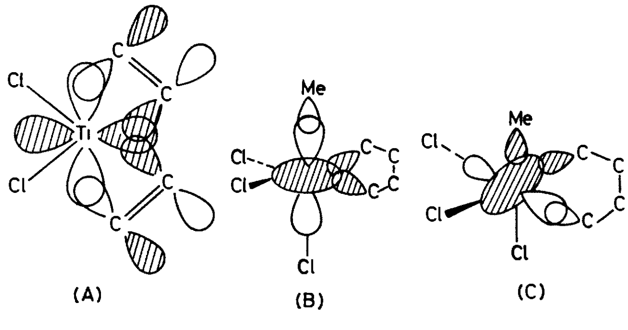


FIGURE. Schematic representation of the HOMO of (A), the bisolefin complex (**3**), with the axial methyl and chloride groups omitted, (B), the metallacyclopentane complex (**4**), (C), complex (**4**) with distortion in metallacycle.

The HOMO of (**4c**) is schematically represented by (B) in the Figure. We find constructive overlap between two of the titanium-bound carbon atoms through a titanium d_{z^2} type orbital. A pathway is therefore provided for reductive elimination of these two carbon atoms. Metallacyclopentanes can reductively eliminate cyclobutane in high yield.[5,8,9] Small distortions in the metallacycle can alter the shape of the HOMO [(C) in the Figure] so that the constructive overlap occurs between the methyl carbon atom and an α-carbon atom of the metallacycle. Reductive elimination at this point would give (**5c**), with some gain in energy from the release of ring strain. The conversion of (**4**) into (**5**) resembles the thermal decomposition of a platinacyclopentane in the presence of methyl iodide to give pentenes.[9,10]

While not wishing to dismiss the probable importance of an olefin insertion mechanism, we propose that under certain circumstances, polymerization may also occur at Ti^{II} centres according to the sequence (**1c**) → (**3c**) → (**4c**) → (**5c**).

Calculations in which propylene replaces ethylene in the above sequence indicate that 2,4-dimethyltitanacyclopentane is more stable than other possible isomers arising from two propylenes. Puckering in the optimized metallacycle differentiates pseudo axial and equatorial positions on the ring carbon atoms. Equatorial rather than axial methyl substitution is favoured because of unfavorable 1,3-interactions involving axial ligands on the titanium centre. Electronic factors favour disubstitution of the equatorial positions in the order 3,4 > 2,4 > 2,5.[11] However, steric interference in the 3,4-isomer causes the calculated order of stability to be 2,4 > 3,4 > 2,5. The equatorial positions of the 2,4-dimethyltitanacyclopentane are on the same side of the ring. Furthermore, both substituted carbon atoms of the metallacycle are chiral. Reductive coupling of one side of the metallacycle with the polymer chain would place a chiral centre either α or β to the titanium centre Stereoselectivity in co-ordinating propylene molecules and subsequent reductive eliminations might thereby be directed, resulting in isotactic polymers.

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