STRUCTURE-ACTIVITY AND STRUCTURE-SELECTIVITY CORRELATIONS
IN METALLOCENE-BASED CATALYSTS FOR α -OLEFIN POLYMERIZATION

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Abstract: Zirconocene complexes carrying substituents at various positions of their ring-bridged ligand frameworks were studied as catalysts for methylalumoxane-activated propene polymerization. Effects of different substitution patterns on catalyst activities and on chain lengths and stereo- and regio-regularities of the polymers produced are correlated with geometrical features of the complexes, e.g. with parameters describing their structural rigidity or the aperture and obliquity of their coordination gaps.

INTRODUCTION

Information about the catalytic properties of different ansa-metallocene complexes in α -olefin polymerization systems is rapidly accumulating at present (Ref. 1). This pile-up of data regarding e.g. the effects of different shapes and geometries of these complexes on their catalytic activities and selectivities vis-a-vis different olefins, and on the microstructures and molecular weight distributions of the polymers produced, appears to call for a working model which would allow to deduce or even to predict the effects of different complex structures on the behavior of these metallocenes as polymerization catalysts.

Foundations for such a modeling have indeed been laid already: Molecular-mechanics studies on alternative chain-growth transition states have been developed to a considerable degree of refinement for ethylene-bis(tetrahydro-indenyl) zirconium catalysts by Corradini and his group (Ref. 2). Future extensions of related models to comparative studies of ansa-metallocene catalysts with different ligand frameworks will have to take into consideration a serious complication, however: A high degree of structural deformability has recently become apparent for many of these ansa-metallocene complexes, which had so far been thought to adhere quite rigidly to a C_2 -symmetric geometry.

STRUCTURAL DEFORMABILITY OF ansa-METALLOCENE COMPLEXES

Deviations from C_2 -symmetry have been observed since some time for ansa-metallocene complexes with sterically demanding ring-substituents (Refs. 3,4); more recently we have seen similar distortions in crystal structures of ansa-metallocenes even in the absence of serious packing effects (Ref. 5).

Fig.1 Distorted titanocene complexes with C_2 -bridges (Ref. 5).

An analysis of intramolecular non-bonding distances in these complexes reveals the presence of repulsive contacts of the β -H and C atoms of each C_5 -ring ligand with the closely adjacent halide ligands at the metal center. This repulsion is partially relieved when the whole ligand framework is rotated so as to place the interannular bridge away from the C_2 -axis of the MX_2 moiety by an angle of $\theta \approx 20^\circ$. Potential-energy curves with double minima at $\theta \approx 20^\circ$ or with very flat energy profiles, which indicate rotational deformations around the C_2 -symmetric minimum at $\theta \approx 0^\circ$ with unusually small or even negative force constants (Fig. 2), are indeed obtained by a molecular-mechanics study of intramolecular van-der-Waals repulsions in these ansa-metallocenes.

Equal numbers of C_2 -symmetric ($\theta=0^\circ$) and distorted ($\theta\approx 20^\circ$) complex molecules recently observed in the crystal structure of $(CH_3)_2Si(C_5H_4)_2Zr(\mu-CH_2)_2Si(CH_3)_2$ by Petersen and coworkers (Ref. 6) underscore the indifference of these complexes to the mutual alignment of their ring-ligand and ZrX_2 fragments.

Fig. 2. Energy profiles for rotation of the ligand framework of ansa-metalloenes out of axial alignment with the MCl_2 group.

Alkyl substituents at the C_5 -rings affect the energy profiles for these rotational distortions: An alkyl substituent in one of the β -positions of each C_5 -ring causes a shift of the double minima to even larger values of $\theta\approx 32^\circ$ and even lower energies. β -Substituted ansa-metalloenes, which are used as chiral catalysts for iso-tactic olefin polymerization, are thus unlikely to maintain a C_2 -symmetric geometry in solution, as is usually assumed for these species. Alkyl substituents in an α -position at each C_5 -ring, on the other hand, generate a rather narrow potential well at $\theta=0^\circ$. These α -substituents thus tend to stiffen the C_2 -symmetric geometry of a chiral ansa-metalloene. For ansa-metalloenes carrying both α - and β -substituents at each C_5 -ring, one might assume that both effects will tend to cancel, thus resulting in an overall deformability similar to that of their unsubstituted parent compounds.

As a semi-quantitative estimate of relative deformabilities for differently structured ansa-metallocenes, we propose to use the '10%-deformability angle', θ_{10} , i.e. that value of θ which is exceeded by no more than 10% of all molecules at room temperature. This angle is obtained, e.g. from Fig. 2, as that value of θ at which the relative potential energy reaches a value of $2.3 \cdot RT = 5.7$ kJ/mol. In this manner we obtain a value of $\theta_{10} \approx 35^\circ$ for most unsubstituted ansa-titanocenes and ansa-zirconocenes; β -substituents appear to increase this value to $\theta_{10} \approx 50^\circ$, while α -substituents would reduce the deformability angle to $\theta_{10} \approx 15^\circ$.

More thorough studies, by theoretical as well as experimental techniques, of the relative deformabilities in differently structured ansa-metallocenes are now required, as this parameter will undoubtedly affect properties of ansa-metallocene complexes as olefin polymerisation catalysts, especially those for which a strong temperature sensitivity is observed.

STERIC EFFECTS OF RING-LIGAND SUBSTITUENTS

Since a more refined molecular-modeling approach appears to be precluded at present by the prevailing uncertainty with regard to the rotational deformability of ansa-metallocene complexes, we have tried to find a simple, yet robust measure for the steric accessibility of the metallocene coordination sites which govern the ligand-exchange and -transformation reactions of these catalysts. Instead of the frequently quoted 'wedge angle', which measures the deviation of the two C_5 -ring mean planes from each other (and will thus not be sensitive to ring substituents of different size), we propose to use in this regard the respective 'coordination gap aperture' angle: We define this parameter as the largest possible angle spanned by those two planes through the metal center, which touch the inner van-der-Waals outline of each of the C_5 -ring ligands (Fig. 3). It provides a very simple measure of how much space a metal-bound substrate molecule or reaction complex can maximally occupy (Ref. 7).

Fig. 3. Van-der-Waals outlines with coordination gap apertures for $(C_5H_5)_2ZrCl_2$ (left) and $(C_5(CH_3)_5)_2ZrCl_2$ (right, Refs. 8,9).

Gap aperture values obtained from crystal structures of a number of zirconocene complexes range from about 55° for the permethylated zirconocene species $[(C_5(CH_3)_5)_2ZrN_2]_2N_2$ up to 110° for the very open framework of the dimethylsilyl-bridged complex $(CH_3)_2Si(C_5H_5)_2ZrCl_2$, with intermediate values of 75° and 95° for the ethano-bridged permethyl complex $C_2H_4(C_5(CH_3)_4)_2ZrCl_2$ and the normal zirconocene dichloride $(C_5H_5)_2ZrCl_2$, respectively (Refs. 8-11). In bridged metallocene species, coordination gap apertures vary somewhat with the length of the interannular bridge; they depend most critically, however, on the size of the respective β -substituents.

When this concept is applied to chiral ansa-metallocenes with substituents of different size (e.g. an H atom and a methyl group) at the two β -positions of each C_5 -ring, we arrive at gap aperture values of 90° for the β -phenyl-substituted complex $(CH_3)_2Si(C_5H_2-2-CH_3-4-C_6H_5)_2ZrCl_2$ and of 80° for its β -*t*-butyl substituted analog $(CH_3)_2Si(C_5H_2-2-CH_3-4-C(CH_3)_3)_2ZrCl_2$ (Fig. 4).

Fig. 4. Van-der-Waals outlines and coordination gap aperture and obliquity angles for dimethylsilyl-bridged zirconocene complexes with β -phenyl (top) and β -*t*-butyl substituents (bottom).

For these chiral ansa-metallocenes it is apparent from Fig. 4 that the line of view along the two tangential planes, which span the maximal gap aperture, does not coincide with the mid-plane of the complex molecule any more: The latter is now slanted against the plane which bisects the gap aperture angle. The '**coordination gap obliquity**' angle, by which gap aperture intersection and metallocene mid-plane deviate from each other, amounts to ca. 20° for the β -phenyl-substituted complex and to ca. 30° for its β -t-butyl-substituted counterpart. As enantiomer pairs yield obliquity angles of opposite sign, the latter can serve for these complexes as a new descriptor for their sense of chirality; it is obviously most closely linked to the enantiofacial preference experienced by a prochiral α -olefin molecule.

Chiral ansa-metallocenes which carry in their β ring positions methyl, i-propyl or cyclohexyl groups yield, from crystal structure and model considerations, rather similar gap aperture and obliquity angle data as their β -phenyl-substituted congeners if one considers these substituents in their least obtrusive conformation (Fig. 4). Likewise, β -substituents with a tertiary C atom, such as 1-methyl-cyclohexyl groups, are practically indistinguishable from t-butyl substituents in this regard.

In a similar manner, one can characterise steric effects of any α -substituents present in an ansa-metallocene complex by the degree to which they narrow the lateral 'vision' in the coordination gap. We define the '**lateral extension**' angle in these ansa-metallocenes as that spanned by those two planes through the metal center which hinge on a line perpendicular to the coordination gap bisector plane and touch the van-der-Waals outline of the α -substituents on either side of the complex. A lateral extension angle of 190° is obtained in this way for ansa-metallocenes with unsubstituted α -positions; this value would be reduced to ca. 170° when two α -methyl groups are present at each C_5 -ring (Fig. 5). For chiral ansa-metallocenes with two different α -substituents (e.g. an H atom and an alkyl group) at each ring, the lateral coordination gap extension will primarily

be governed by the size of the α -substituent located opposite to the larger β -substituent, since this α -substituent protudes farther into the oblique coordination gap (c.f. Fig. 4).

Fig. 5. Lateral coordination gap extension for unsubstituted and for α, α -dimethyl-substituted ansa-zirconocene complexes.

STERIC REQUIREMENTS FOR ALTERNATIVE CHAIN GROWTH REACTIONS

Following a similar line of reasoning, the steric requirements for a given metal-centered reaction transition state can be estimated by finding those two planes through the metal center which touch the outline of van-der-Waals envelop of the reaction complex under consideration. As these reaction complexes are less well defined than the ansa-metallocene frameworks discussed above, several assumptions have to be made for such an analysis.

Fig. 6. Transition state with α -agostic interaction, assumed for stereo-regular insertion of propene into the Zr-polymer bond.

For regio- and stereo-regular α -olefin insertions into a metal-bound alkyl chain we assume the transition state shown in Fig. 6, since an agostic interaction of one of the α -C-H bonds with the cationic metal center is now supported by experimental data (Ref. 12,13). We further assume that the steric demand of such a reaction complex is governed by the size of the four substituents which flank the incipient C $\cdots$ C bond. Those two planes through the metal center which touch the van-der-Waals outlines of each pair of substituents on the top and bottom sides of this complex then define the associated 'reaction complex aperture'. As shown in Fig. 7, this aperture angle amounts to 96° . Such a reaction complex will have its maximal vertical extension of ca. 5 Å at a distance of ca. 3 Å from the metal center.

Fig. 7. Spatial extension and aperture and obliquity angles for the olefin-insertion reaction complex represented in Fig. 6.

The anti arrangement of the two alkyl groups adjacent to the incipient C $\cdots$ C bond will necessarily cause the plane bisecting the reaction complex wedge to deviate from the plane containing the Zr-bound ligand atoms, i.e. from the plane bisecting the ring centroid-metal-centroid angle. The 'reaction complex obliquity' angle thus defined amounts to ca. 30° . Its sign designates the stereochemical course of the insertion reaction; the re-facial orientation of the propene insertion shown in Fig. 7 is associated with a negative deviation of the metal-ligand plane from the plane bisecting the reaction complex outline.

This analysis would indicate that reaction complexes of this type will perfectly fit into the coordination gap of chiral ansa-metallocenes with respect to both their aperture and their obliquity angles. If vertical gap extension rather than aperture angles are considered, the less hindered, phenyl- or sec-alkyl-substituted complexes would even appear to leave some vertical play for the olefin insertion complex considered above. In accord with this notion, we observe extremely high activities together with reasonable, but somewhat temperature-sensitive stereoregularities for these complexes (Ref. 14); for β -tertiary-alkyl substituted complex catalysts, on the other hand, the very tight fit between reaction-complex wedge and coordination gap is associated with a distinctly reduced activity and with a very high and hardly temperature-sensitive stereoregularity: It appears quite impossible to accommodate a reaction complex with opposite obliquity (i.e. with opposite enantiofacial olefin orientation) in the narrow coordination gap of these complexes without a serious mismatch of coordination geometries at the metal center.

For complexes with still narrower coordination gap, e.g. for the permethylated zirconocene species depicted in Fig. 1, such a reaction complex appears to be altogether inconceivable. Here, the growing alkyl chain is unlikely to be oriented as in Fig. 6. The actual transition state geometry for olefin insertions in these narrow-gap complexes obviously needs further clarification, as do those which lead to stereo-error formation in *t*-alkyl-substituted ansa-metallocene polymerisation catalysts.

In distinction to classic solid-state catalysts, most of the homogeneous metallocene-based polymerisation catalysts yield regio-errors (i.e. 2-1 and 1-3 insertions) with relatively high frequencies of 1-2% (Ref. 14-16). These misinsertions contribute to reduced melting points, and possibly also to premature chain growth termination in homogeneously produced polyolefins.

In terms of steric requirements, the transition state leading to these misinsertions differs from that for regular insertions mainly by its increased lateral extension. Based on the model shown in Fig. 8, we estimate a lateral extension of ca. 155° for the reaction complex leading to regular olefin insertion. As this value is smaller by ca. 35° than the lateral gap extension in ansa-metallocenes with unsubstituted α -positions, it is apparent that a reaction complex of this kind is free to undergo sizeable rotational fluctuations relative to the ligand framework, as discussed in the initial part of this communication.

Fig. 8. Lateral extensions for transition states leading to regular olefin insertion (left) and 2-1-misinsertions (right).

For the reaction complex presumably required for 2-1 misinsertions, on the other hand, one can estimate an increased lateral extension of 170° (Fig. 8). In accord with this analysis, we observe distinctly reduced rates of regio-errors in those complexes (Ref. 14) where α -substituents narrow the lateral coordination gap extension to values below 180° (c.f. Fig. 5). Substantial further progress in the performance of metallocene-based olefin polymerisation catalyst might thus be expected from a better control of these misinsertions by complex geometries with still smaller lateral coordination gap extension.

Finally, one might note that the transition state for β -hydrogen transfer from the growing polymer chain to the metal center, the most frequently observed chain-growth termination process, is likely to have a very large reaction complex aperture of ca. 105° (Fig. 9). This process would thus appear to be even more strongly suppressed than regular chain-growth insertion in ansa-metallocenes with narrow gap apertures. Indeed we generally find relatively high molecular weights for polypropylenes produced by narrow-gap complexes with bulky β -substituents.

Fig. 9. Assumed transition state geometry (left) and reaction complex aperture (right) for chain termination by β -H transfer.

So far, we have restricted our considerations to chain-growth models with simple CH_3 substituents both at the inner olefin terminus and at the growing alkyl chain; inspection of related models with longer alkyl chains will usually yield conformers which adhere to the aperture angles indicated. Complications will arise, however, for reaction complexes containing branched alkyl groups; these effects as well as steric effects on equilibria involving ion pairs and other intermolecular aggregates must be considered during further stages of refinement.

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