Synthesis and Characterisation of Chiral Metallocene Cocatalysts for Stereospecific α -Olefin Polymerisations

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INTRODUCTION

Homogeneous ethylene polymerisation catalysts containing $(C_5H_5)_2TiCl_2$ and various aluminum alkyls - first described by Natta, Pino and co-workers (1) - were being actively studied about fifteen to twenty years ago by a number of research groups (2-8). Similar reaction systems can also lead to nitrogen-fixing $(C_5H_5)_2Ti$ -alkyl complexes, the identification of which was, at that time, the aim of much of my research, then at the University of Michigan. Questions related to polymerisation catalysis by these titanocene derivatives became a topic of increased personal interest to me, when Professor Overberger joined the Department there in 1968, who had then just completed a series of studies on the $(C_5H_5)_2TiCl_2/AlEt_2Cl$ -induced polymerisation of styrene (9). These reactions - whatever their detailed mechanism - raised the question whether an isotactic polymer of styrene or another vinyl derivative might not be produced if some chiral organometallic molecule acts as a stereospecific polymerisation catalyst. These ideas gradually developed into our first attempts to prepare complexes of this kind and then into a formal DFG project to synthesize chiral "ansa-metallocenes": These sandwich molecules were to contain two suitably substituted ring ligands connected by a chelate bridge, so as to retain them in a well-defined "stereorigid" chiral molecular shape. The fixation of ligand geometry by a chelate bridge had been found to be beneficial for other types of stereoselective homogeneous catalysts (10); it was our hope that it would also facilitate the interpretation of any stereoselectivity that might be observed with these compounds.

Our project "Chirale ansa-Metallocene" emerged from a special program on "Homogenkatalyse", sponsored by DFG from 1973 to 1978. The work of Professor Kaminsky on alumoxane-activated zirconocene catalysts (11), which he reported during this DFG program, substantially encouraged us in our efforts to synthesize ansa-metallocenes of potential use in α -olefin polymerisation catalysis.

SYNTHESIS OF RACEMIC ansa-METALLOCENES

From our initial attempts to synthesize chiral ansa-metallocenes (12) it soon became clear that the formation of substitutional isomers and of metal-ring linkage diastereomers caused more serious problems than anticipated. The synthesis of substitutionally uniform bis-cyclopentadienyl ligand molecules proved to be achievable, rather straightforwardly, by a number of approaches - by use of electronic (13) or of steric (14,15) effects to induce regioselective substitution or by the reductive coupling of appropriately substituted fulvenes (14,16).

Fig. 1. Regioselective formation of a bisubstituted ansa-titanocene by use of steric effects (14)

Fig. 2. Formation of a chiral ansa-titanocene with configurationally stable ligand framework by reductive coupling of a dihydropentalene derivative (16)

The concurrent formation of meso diastereomers along with the desired racemic product, however, still is a major obstacle for an efficient synthesis of metallocenes containing various bridging and terminal substituents. Despite considerable variations in type and conditions of the metal-ligand linkage reaction, comparable amounts of meso and racemic products were invariably obtained even with bulky trimethylsilyl or t-butyl ring substituents (14,15), which might be assumed to avoid each other in an axially symmetric, racemic product geometry.

Apparently, the configuration of the chiral intermediate formed by attachment of the metal to one of the two interconnected, substituted cyclopentadienyl rings induces only negligible enantiofacial selectivity for the consecutive reaction step in which the chelate ring is closed by attachment of the metal to the second ring ligand. Which factors might be put to work to increase the enantiofacial selectivity of this ligand exchange reaction is not clear at present.

Fig. 3. Model for the chelate-ring closure step in the formation of a bisubstituted ansa-metallocene: Attachment of the metal to the re or si face of the second ring is kinetically controlled by the arbitrary enantiofacial position of the cationic leaving group (Li, MgCl, R₃Sn)

In one particular case, this problem was completely and efficiently solved by utilizing bis-indenyl ethane as a ligand molecule (13). Reaction of its dilithium salt with ZrCl₄ and subsequent hydrogenation yielded exclusively the desired racemic diastereomer of C₂H₄-(tetrahydroindenyl)₂ZrCl₂. A meso/racemate mixture of the titanium analogue is obtained from an analogous reaction with TiCl₄ or TiCl₃, but this product mixture is completely converted to the racemic diastereomer by a photoinduced rearrangement. Other chirally bisubstituted ansa-metallocenes also show a photoinduced meso-racemate conversion; in these cases, however, both diastereomers were present in about equal concentrations in the final, photostationary state (15). Apparently, steric or electronic interactions of yet unknown origin steer the metal-ring linkage formation reaction in the direction of the racemic isomer in the case of these ethylene-bridged bis-indenyl and bis-tetrahydroindenyl complexes. These complexes were mainly utilized, so far, to study the homogeneous catalysis of isotactic α -olefin polymerisation in the presence of methylalumoxane (17-20), since a separation of the meso/racemate mixture obtained in other cases - though feasible by chromatography or fractional crystallisation - proved cumbersome.

ENANTIOMER SEPARATION AND CHARACTERISATION

In order to provide optically pure complexes - rather than racemates - for further studies on the stereochemical origins (20) of the high degree of isotacticity observed with these α -olefin polymerisation catalysts (18), we have investigated possibilities to obtain their separate enantiomers. The stereochemical designation of these ansa-metallocene enantiomers is based on an adaption by Schllögl (21) of the Cahn-Ingold-Prelog rules (22): In a metallocene derivative, the metal is viewed as being σ -bonded to each of the ring carbon atoms.

Designation of the configuration at the bridge-head carbon atom - for which its metal neighbour has highest priority, followed in that order by its substituted and its unsubstituted ring neighbours and, finally, the C atom of the interannular bridge - is sufficient for an unambiguous description of the sense of helicity of the complex molecule.

The S-configured titanium complex was obtained via a stereoselective exchange of its chloride ligands against an S-binaphthol ligand (13). More widely applicable is a method based on conversion of the dichloro titanium and zirconium complexes into diastereomeric O-acetyl mandelic acid derivatives, which are cleanly separable by crystallisation, and from which the dichloro derivatives are easily regenerated (23).

Fig. 4. Stereoselective formation of an S-binaphthol complex from the S-configured ethylene bis(tetrahydroindenyl) titanium dichloride (13)

Fig. 5. Formation of diastereomeric O-acetyl-mandelic acid derivatives from racemic ethylene bis(tetrahydroindenyl) titanium dichloride (23)

The crystal structures of the diastereomeric O-acetyl-R-mandelic acid derivatives revealed, to our surprise, that different conformations of the interannular bridge, and hence of the substituted ansa-metallocene framework as a whole, are adopted in these diastereomer pairs: In the crystalline diastereomer containing the 1S-configured ansa-metallocene, the ethylene bridge has an M conformation (λ in the Corey-Bailar notation (24)) which places the tetramethylene substituents in their normal "forward" position. The diastereomer with 1R configuration however also contains the ethylene bridge in its M (i.e. λ) conformation. This R- λ geometry, which places the tetramethylene substituents in a "backward" position, has not been observed in any other derivative; its adoption in this instance is undoubtedly caused by the necessity to allow for reasonably close crystal packing while avoiding repulsive

interactions with the bulky mandelate groups. From a comparison of the R- δ structure (computer-generated by mirroring its S- λ counterpart) with the unusual R- λ conformer it is apparent that the ring-substituent atoms 4 and 5 are closer to the in-plane oxygen ligand atoms in the latter; these unfavourable interactions in the R- λ (and S- δ) conformer probably contribute to their reduced tendency to undergo crystallisation. To which degree the less-favourable conformer of each enantiomer is present in equilibrium in solutions of these compounds, or of intermediates involved in α -olefin polymerisation catalysis remains unknown at present. At any rate, conversion to these diastereomeric mandelic acid derivatives provides a convenient means to monitor the degree of enantiomeric purity on a microanalytical scale by $^1\text{H-NMR}$ spectroscopy, for instance in the course of a catalytic reaction (23).

Fig. 6. Different conformers of an R-configured ethylene bis(tetrahydroindenyl) metal complex, derived from the structures in Fig. 5

CONCLUSIONS

Further efforts are now to be directed at a systematic variation of substituents and bridging groups in these chiral ansa-metallocenes in order to delineate optimal spatial requirements for the stereo-selective catalysis of α -olefin polymerisation as well as of other catalytic C-C bond formation reactions. Substitution with functional groups other than hydrocarbon residues might be desirable in order to stabilize the crucial - presumably cationic (25,26) - intermediates essential for α -olefin polymerisation and to facilitate their stereo-specific transformation reactions. Prerequisite for studies of this kind is a possibility to induce selective formation of racemic rather than meso-configured ansa-metallocenes, i.e. to gain a means of control on the stereochemistry of the chelate ring formation reaction.

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