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D/A-Metallocenes: The New Dimension in Catalyst Design

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Summary: D/A metallocenes constitute a novel unique class of catalysts, in that they are able to express structural information within the elementary steps of the catalytic cycle out of bridged as well as out of unbridged states due to the coexistence of donor (D) and acceptor (A) atoms in complex sandwich structures. Highly polarized transannular bridging interactions as well as Lewis basic and Lewis acidic functionalities in unbridged states are the prerequisites which define a modular highly flexible catalyst system with outstanding options to tailor materials and processes.

Keywords: D/A metallocenes; long chain branching; monomodal/multimodal molecular weight distributions; polyethylene; polymerization catalysts; polypropylene; short chain branches; ultrahigh molecular weight polyolefins

Introduction

Classical metallocene catalysts are either unbridged or covalently bridged. The range of properties has been extended further by halfsandwich catalysts, in particular those with constrained geometry. Structural features have created domains of best applicability for each subclass. Intensive optimization efforts worldwide over two decades have resulted in high level catalyst profiles, but at the same time have defined system-inherent borderlines and limitations which can only be overcome by novel catalyst concepts.

The D/A Metallocene Principle

D/A metallocenes constitute a new dimension in catalyst design. [1-12] Characteristic feature is the incorporation of donor and acceptor atoms into sandwich structures, resulting in highly polarized bonding interactions, which specifically restrict the rotation of the π-ligands and widen the aperture angle. The reverse process, which eliminates the dipolar interaction, shrinks the aperture angle and favors ring rotation.(2) The energy hypersurface for the

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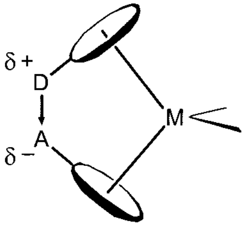
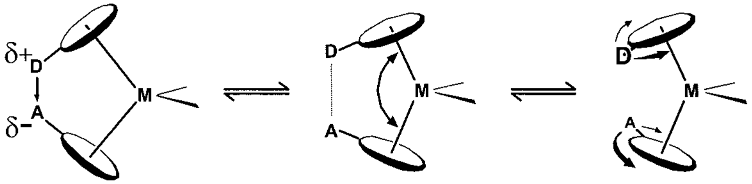


(1)

structural changes is controlled by D and A and the nature of the donor and acceptor substituents. The actual state the system is in is temperature dependent and can be selected. It controls the architecture and the ensemble of the formed macromolecules and thereby the material properties.



(2)

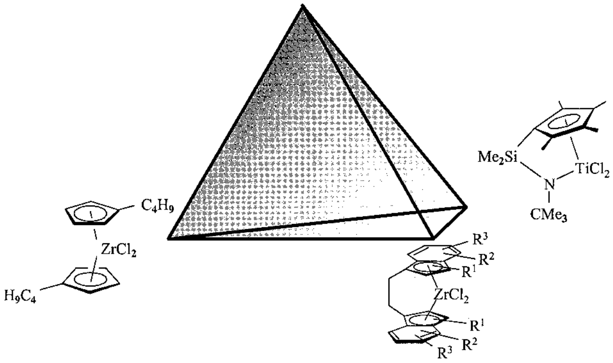
The bonding D/A interaction is best described as originating from a stabilizing in-phase combination of an occupied lone pair orbital on the donor with an empty orbital of appropriate symmetry on the acceptor. The closer the two orbitals come in energy, the stronger the energy gain, which is therefore related to donor lone pair ionization energies and acceptor electron affinities. The stabilizing 2-electron/2-orbital interaction results in an electron delocalization i.e. a transfer of electron density from D to A, which in turn generates positive and negative partial charges on D and A respectively.

Thus, a dipolar interaction of variable size and orientation is introduced into the catalyst due to D/A coupling. Vice versa, the reverse process destroys the high dipole moment via a heterolytic D/A-splitting, regenerating the uncharged donor and acceptor substituents e.g. D: NR_2, PR_2, SbR_2, OR, SR, SeR, F, Cl, Br etc and A: BR_2, AlR_2, GaR_2, etc. At the same time it shrinks the aperture angle and favors ring rotation. (Breaking a covalent bridge in *ansa*-metallocenes would involve a homolytic process, which generates highly unstable radical intermediates and destroys the catalyst.)

The unbridged state is favored by weak D/A interactions, high strain energy in the bridged state (e.g. due to bulky substituents) and of course by high temperatures. Accordingly, the bridged state is favored by strong D/A interactions, low strain energy in the bridged state and by lower temperatures.

The ease, with which this bridged-to-unbridged transition takes place, can be tailored. The choice of the heteroatoms together with the nature of the donor and the acceptor substituents offer extraordinary modules for the design of novel catalysts. Macromolecular architectures obtained via D/A metallocene catalysis are controlled by the actual state(s) the chosen D/A catalyst system is in. It offers single-site, dual-site and multi-site catalyst options. The temperature dependant existence and coexistence of two stable forms (bridged/unbridged) of the same compound establishes a new dimension in catalyst design. It not only dissolves the borderline between the classical two metallocene subclasses but also, due to D/A-specific electronic consequences even the borderline between metallocenes and constrained geometry catalysts (3).

D/A-Metallocenes



(3)

Thereby it opens the way to material properties that are at least difficult, and in some cases impossible to achieve with the traditional systems.

The novel D/A lead structures, which include reversible one-, two- and more-atom bridges, introduce in metallocene catalysis a broad range of additional and new control instruments, all of which can be used to optimize the catalytic behavior. Different donor and acceptor heteroatoms, charged and/or uncharged, together with an enormous chemical variability and selectable bulkiness of the corresponding substituents and the attached hydrocarbon or heterocyclic π-ligands provide efficient means to precisely tune stereochemical and dynamic properties and to optimize catalyst performance.

D/A Metallocene Syntheses and Structures

There are three main synthetic routes to D/A metallocenes of general applicability (1). The donor route, which is based on reacting a preformed donor halfsandwich complex with an acceptor ligand (2). The acceptor route, which is based on reacting a preformed acceptor halfsandwich complex with a donor ligand (3). The donor-acceptor route, which is based on reacting a preformed D/A ligand with a suitable metal precursor.

$$\begin{array}{llll}
\bullet\ \textbf{D ligand} & \xrightarrow{\textbf{MX}_n} & \textbf{D halfsandwich} & \xrightarrow{\textbf{A ligand}} \textbf{D/A metallocene} \\
\bullet\ \textbf{A ligand} & \xrightarrow{\textbf{MX}_n} & \textbf{A halfsandwich} & \xrightarrow{\textbf{D ligand}} \textbf{D/A metallocene} \\
\bullet\ \textbf{D ligand +} & \longrightarrow & \textbf{D/A ligand} & \xrightarrow{\textbf{MX}_n} \textbf{D/A metallocene} \\
\quad\ \textbf{A ligand} & & &
\end{array} \tag{4}$$

Route 1 provides access to numerous D/A metallocenes even in only one set of experiments i.e. with the same central metal and the same donor substituted π-ligand. Structure/activity and structure/selectivity relationships can be elucidated in a straightforward manner, just by variing the acceptor containing moiety. Likewise route 2 provides any desired number of D/A metallocenes being derived from one and the same metal always carrying the same acceptor substituted π-ligand. The observable changes in the catalytic profile, in this case result from varying the donor containing building block. Route 3, for example, takes advantage of a preformed D/A ligand, which can be reacted with various transition metal precursors. In order to optimize the yield of a selected catalyst, one may test all three routes for the same target molecule.

A large number of D/A metallocenes has been synthesized for which crystals suitable for X-ray structure analyses have been obtained. These have provided direct proof, that the above described D/A interactions are operative. Representative D/A-bridged metallocene X-ray structures have been obtained for example for titanium and zirconium complexes with

cyclopentadienyl, indenyl, fluorenyl, or phospholyl ligands, carrying dimethylamino-, dimethylphosphino-, diethylphosphino-, diisopropylphosphino-, diphenylphosphino-, dichloroboranyl-, dimethylboranyl, or bis(pentafluoropenyl)boranyl-substituents.[11,12]
For corresponding examples, see (5) and Figures 1 and 2.
In addition, multinuclear magnetic resonance methods have been used to identify the presence and the relative strength of D/A interactions of such metallocenes in solution. Especially, P-31 and B-11 NMR chemical shifts and one-bond nuclear spin-spin coupling constants are powerful means for solution studies.

Last-not-least, the polymerization results provide direct evidence if, under the activation and polymerization conditions chosen, the catalyst system under investigation is actually D/A-bridged, D/A-unbridged or both.

D/A Metallocenes, the Leading Edge in Polymerization Catalysis

The synthetic donor and acceptor „tool box“ proves to be an ideal, highly flexible modular system to easily identify and develop the best catalyst for a specific application.
This way, substantial progress has been made in prominent areas of catalyst research and development: e.g. the polymerization temperature optimum of the catalyst can be adjusted to process requirements. The polymer molecular weight can be controlled at any desired level even at elevated temperatures. Molecular weight distributions can be modelled. In propene polymerization regioerrors such as 2,1- and 1,3-misinsertions can be efficiently suppressed. High molecular weight PPs are accessible with strongly differing stereochemical compositions. Sequential type homo- and copolymers with unusual microstructures can be tailored. Last-not-least, D/A-based polymers offer, when necessary, improved rheology through bimodal molecular weight distributions and/or through long chain branching.
In the following, two prominent polyolefin material areas are addressed to outline the stated merits of D/A metallocene polymerization catalysis: polyethylene and polypropylene.

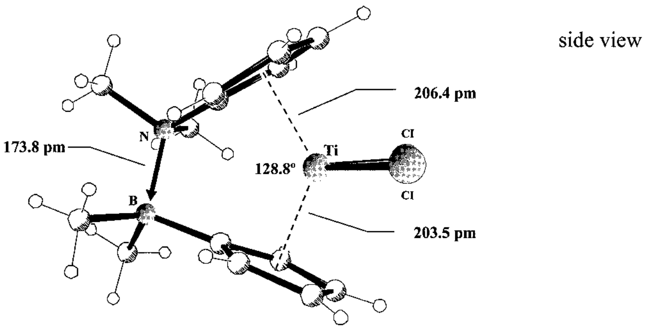


Figure 1. X-ray Structure of [(cp)Me$_2$NBMe$_2$(cp)TiCl$_2$]

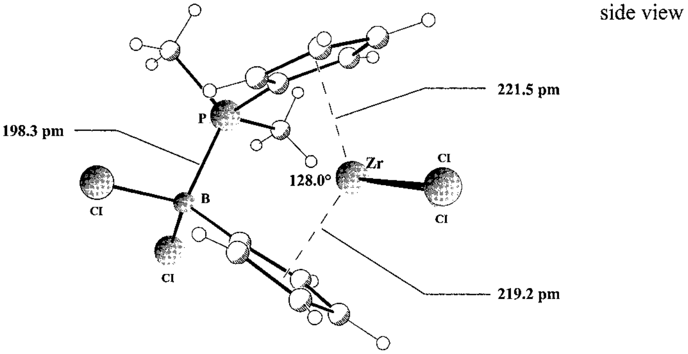


Figure 2. X-ray Structure of [(cp)Me$_2$PBCl$_2$(cp)ZrCl$_2$] [1]

(cp)Me$_2$NBMe$_2$(cp)TiCl$_2$],
[(cp)Ph$_2$PBCl$_2$(cp)TiCl$_2$],
[(cp)Me$_2$PBCl$_2$(cp)ZrCl$_2$],
[(cp)Me$_2$PB(C$_6$F$_5$)$_2$(cp)ZrCl$_2$],
[(Me$_4$phospholyl)BMe$_2$(cp)TiCl$_2$], (5)
[(ind)Et$_2$PBCl$_2$(cp)ZrCl$_2$],
***meso*-[(ind)Ph$_2$PBCl$_2$(ind)ZrCl$_2$],**
***rac*-[(ind)Ph$_2$PBCl$_2$(ind)ZrCl$_2$],**
[(flu)Et$_2$PB(C$_6$F$_5$)$_2$(cp)ZrCl$_2$].

Polyethylene

Linear high melting high density polyethylene (0.97 g/cm^3) is obtainable with the featured D/A metallocene catalysts. For example (cp)$Et_2PB(C_6F_5)_2$(cp)$ZrCl_2$/MAO produces 148 tons high molecular weight HDPE per mol Zr and hour at 60 C and 10 bar ethylene with a PE melt temperature of 139 C (DSC, 2. heating) and an intrinsic viscosity of 3.56 dl/g (measured in ODCB at 140 C), which corresponds to a viscosity average molecular weight of 323 kg/mol. All PE molecular weight ranges are accessible, including ultrahigh molecular weight polyethylenes (UHMW-PE). If one uses instead of the D/A bis(cp)metallocene the corresponding D/A (flu)(cp)metallocene in an otherwise identical ethylene polymerization experiment, the intrinsic viscosity of the PE formed reaches 13.25 dl/g (!). Whereas the former PE has a polydispersity of 2.5, for the latter PD = 7.8. Monomodal but also bimodal or multimodal molecular weight distributions can be tailored. Without the need of a two-reactor/zone technology one may simply take advantage either of (1) two matched D/A metallocenes, preselected according to PE molecular weight or of (2) the coexistence of bridged and unbridged D/A states at a specific temperature, i.e. by choosing between single site, dual site, multi site options, inherent to the D/A catalyst concept.

Due to the excellent capability of D/A-bridged metallocenes to incorporate comonomers, polyethylenes with any desired amount of short chain branches along the main chain can be produced, necessary to fill the needs for any specific application. These short chain branched polyethylenes (SCB-PE) can be synthesized by copolymerizing ethylene with 1-olefins such as propene, 1-butene, 1-hexene, 4-methyl-1-pentene, or 1-octene. The different products obtained with D/A catalysts may be classified according to their density as medium density polyethylene (MDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), ultra low density polyethylene (ULDPE). With increasing amounts of incorporated 1-olefins the density drops, as does the melt temperature and the crystallinity. Relatively high amounts of uniformly incorporated 1-olefins such as 50 weight% result in high performance elastomers, characterized by high molecular weight and a low glass transition temperature e.g. –65 C for 1-hexene. Fully amorphous low-Tg-types without any melt endotherm are accessible out of bridged D/A states, whereas unbridged metallocene structures disfavor a uniform high incorporation of 1-olefins and accordingly result in semicrystalline materials due to crystallizing polyethylene sequences.

Lower T_m/moderate T_g values usually result from higher ethylene/lower 1-olefin copolymer compositions. The especially attractive high T_m/low T_g property profile of sequential thermoplastic elastomers becomes available using the D/A steering potential.

Outstanding catalytic features come from specific D/A metallocenes, which give efficient access to long chain branched polyethylene architectures (LCB-PE).

Polypropylenes

Isotactic polypropylenes (i-PP) with melt temperatures of 160 – 168 C and high to very high molecular weights can be synthesized using the D/A approach, thus taking advantage of the high regio- and stereocontrolling power of D/A systems. PP samples with 99-100 % isotactic pentads have been prepared. Conventional isospecific ansa-metallocenes show a pronounced correlation of the PP DSC melt temperature with the NMR *mmmm* pentad concentration. In some D/A-catalyzed polymerizations, however, the high *mmmm* value can be reduced considerably by raising the polymerization temperature without loosing the high melting property. This observation is consistent with the presence of a temperature window, which is defined by the coexistence of bridged and unbridged D/A states. A high melting crystalline phase formed from long isotactic sequences is produced out of the stereoselective bridged state, whereas the unbridged state generates atactic sequences forming an amorphous phase. The ratio of isospecific and aspecific sites depends on the temperature. In this way elastified isotactic polypropylenes with improved mechanical properties can be tailored. Whereas, high propylene/low ethylene compositions resulting from stereospecific catalysts show an improved low temperature behavior due to crystallizing high T_m isotactic or syndiotactic polypropylene sequences interrupted by noncrystallizing low-T_g statistical EP copolymer sequences.

Furthermore, high molecular weight essentially atactic polypropylenes with enhanced isotactic or syndiotactic contents have been accessed, which possess the attractive features of elastomeric polypropylenes (e-PP). The manifold D/A options for precisely controlling the PP microstructures allow to tailor the material properties according to the targeted applications of high or low modulus materials.

Unexpectedly, novel long chain branched polypropylene architectures (LCB-PP) highlight the D/A metallocene success story.

In summary, we have succeeded to specifically develop novel high performance D/A metallocenes polymerization catalysts (6) for a variety of target materials such as high melting crystalline thermoplastic materials with improved processability, amorphous thermoplastic materials with high Tg, as well as semicrystalline thermoplastic elastomers with tailored green strength and amorphous polyolefin elastomers with very low Tg.

D/A Metallocenes:

catalysts with added temperature stability
option for ultra high molecular weight
mono- and bimodal molecular weight distributions (6)
excellent regio-and stereocontrol
access to sequence polymers
access to long chain branching

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