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Catalytic Dimerization Reactions of α-Olefins and α,ω-Dienes with Cp$_2$ZrCl$_2$/Poly(methylalumoxane): Formation of Dimers, Carbocycles, and Oligomers

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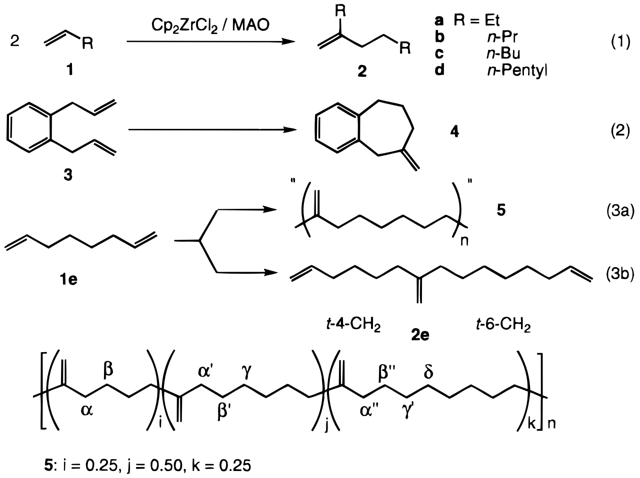
Zirconocene/alumoxane catalysts are known to polymerize α-olefins;[1] chiral zirconocene complexes are especially useful in the stereospecific synthesis of stereoregular polymers[2] or chiral oligomers.[3] Numerous investigations on this topic have shown that a large alumoxane excess (e.g. Al/Zr ratios of 500:1 up to 10000:1) is most favorable for this polymerization process.[4]

In contrast to this, the use of low Al/Zr ratios has been much less frequently discussed in the literature.[5] In at least one case this leads to the selective formation of α-olefin dimers instead of polymers.[6] We wish to report the application of low Al/Zr ratio zirconocene/poly(methylalumoxane) (MAO) catalysts to the conversion of dienes to cyclization products and oligomers with unsaturated intrachain and endgroup functionality.

In our hands, reaction of the 1-alkenes **1a**−**d** with a catalyst prepared by mixing Cp$_2$ZrCl$_2$ (0.3−1.0 mol %) and a solution of MAO[7] in toluene (ratio Al/Zr ca. 1:1) forms dimeric products **2a**−**d**[8] at modest rates (TON = ca. 6.1 min^{-1} at 25 °C after a brief induction period) without significant portions of higher oligomers (Scheme 1, eq 1). After 1 day at room temperature (RT) no starting material **1** is detectable in the reaction mixture, and the analytically pure dimers **2** can be isolated by fractional distillation directly from the reaction mixtures in 80−90% yields.

We decided to investigate whether this dimerization catalyst might cyclize α,ω-dienes,[9] e.g. to form a seven-membered carbocycle.[10] Reaction of *o*-diallylbenzene[11] **3** with Cp$_2$ZrCl$_2$/MAO (3 days, RT, 1 mol % Zr, Al/Zr = 4:1) does indeed give the benzannulated methylenecycloheptane **4**, which was separated from nonvolatile byproducts by distillation and purified by column chromatography (SiO$_2$/pentane, 70%) (Scheme 1, eq 2).

Scheme 1



However, a starting material structure that holds the cyclizing olefinic groups in proximity to one another appears to be required to achieve cyclization, because all the simple dienes we have so far investigated lead with high efficiency to linear oligomers rather than rings. For example, treatment of 1,7-octadiene (**1e**) with the same Cp$_2$ZrCl$_2$/MAO mixture gives an oligomeric material **5** (Scheme 1, eq 3a). The polycondensation product **5** can be obtained either as lower oligomeric (1 day, RT, $M_w = 1600$, $M_w/M_n = 2.0$)[12] or higher oligomeric materials (3 days, RT, $M_w = 5400$, $M_w/M_n = 2.6$). Conversion to oligomer is quite selective; to date we have not observed the formation of higher molecular weight materials, by either variation of reaction temperature or time, variation of olefin/Zr/Al ratios, or addition of an inert solvent (toluene).[13]

Under most conditions it is difficult to stop the diene reaction at the simple dimer stage. However, this can be accomplished by running the reaction in dilute toluene solution with slow addition of **1e** to the catalyst. Under these conditions 5% conversion to the dimeric species can be achieved, and the dimer **2e** can be isolated in 4% yield; no cyclic or other product is detectable by ^{1}H NMR (Scheme 1, eq 3b). This suggests that the dimer is the first-formed product and that it is converted to oligomer by catalyst-mediated reaction with monomer or other dimeric/oligomeric fragments.

Careful examination of the oligomeric products by NMR has provided information about the overall course of the oligomerization, as well as the reason for the selective conversion to material of moderate molecular weight. First, ^{1}H NMR analysis demonstrates that the oligomeric mixture contains a certain amount of internal di- or tri-substituted double bonds (ca. 10% of the integral of the =CH$_2$ protons). This indicates that the catalyst is capable of alkene isomerization as well as dimerization, presumably via a minor amount of 2,1 insertions. α-Olefinic endgroups that have been converted to internal

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(1) (a) Andresen, A.; Cordes, H.-G.; Herwig, J.; Kaminsky, W.; Merck, A.; Mottweiler, R.; Pein, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 630. (b) Sinn, H.; Kaminsky, W.; Vollmer, H.-J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 396.

(2) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Review: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(3) Kaminsky, W.; Ahlers, A.; Möller-Lindenhof, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1216.

(4) (a) Kolthammer, B. W. S.; Mangold, D. J.; Gifford, D. R. *J. Polym. Sci. A* **1992**, *30*, 1017. (b) Jüngling, S.; Mülhaupt, R. *J. Organomet. Chem.* **1995**, *497*, 27. (c) Janiak, C.; Versteeg, U.; Lange, K. C. H.; Weimann, R.; Hahn, E. *J. Organomet. Chem.* **1995**, *501*, 219.

(5) Slaugh, L. H.; Schoenthal, G. W. U.S. Patent 4,658,078, 1987; *Chem. Abstr.* **1987**, *107*, P39178s.

(6) For examples of other catalytic systems useful for dimerizing alkenes, see: (a) Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-sa'doun, A. W. *Catalysis Today* **1992**, *14*, 1. (b) A.-Sa'doun, A. W. *Appl. Catal. A*: *Gen.* **1993**, *105*, 1. (c) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610. (d) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74 and references cited in these papers. We are grateful to Prof. Bercaw for calling our attention to ref (d).

(7) MAO (solution in toluene) was either purchased from Akzo Chemicals Inc., Chicago, or prepared following a literature procedure: Resconi, L.; Boss, S.; Abi, L. *Macromolecules* **1990**, *23*, 4489.

(8) **2a**: Onopchenko, A.; Cupples, B. L.; Kresge, A. N. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 182. **2b**: Bestmann, H. J.; Rösel, P.; Vostrowsky, O. *Liebigs Ann. Chem.* **1979**, 1189. **2c**: Liu, H. Q.; Deffieux, A.; Sigwalt, P. *Makromol. Chem.* **1991**, *192*, 2111.

(9) A cyclization reaction of α,ω-dienes using Cp$_2$ZrMe$_2$-catalysis and a stoichiometric amount of Al$_2$Me$_6$ has been reported, see: Shaughnessy, K. H.; Waymouth, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 5873.

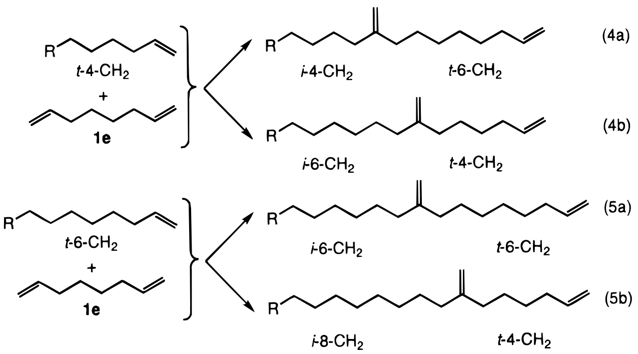
(10) There are only very few examples of a transition-metal catalyzed seven-membered ring formation. Review: Dyker, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2223.

(11) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 1557.

(12) Molecular mass analysis by GPC. Because of their low volatility, the oligomeric mixtures are difficult to analyze by gas chromatography. In the EI-MS spectra M$^+$ signals for species up to *m/z* 880 (*n* = 8) can be observed.

(13) We see no detectable amounts of cyclic products, which contrasts with observations made in the reactions of dienes with conventional Ziegler−Natta systems, cf.: (a) Ruiz de Ballesteros, O.; Venditto, V.; Auriemma, F.; Guerra, G.; Resconi, L.; Waymouth, R. M.; Mogstad, A.-L. *Macromolecules* **1995**, *28*, 2383. (b) Mitani, M.; Oouchi, K.; Hayakawa, M.; Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1995**, 905, as well as with Scandium catalysts (ref 6d).

Scheme 2



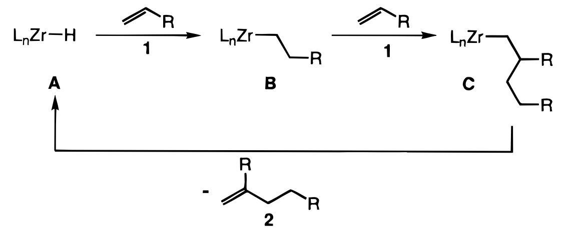
alkenes are unreactive toward further dimerization reaction, and this might be the molecular weight limiting process.

Concerning the overall structure of the oligomers, it appears that the material formed from 1,7-octadiene contains internal vinylidene units separated by either aliphatic tetramethylene, hexamethylene, or octamethylene moieties.[14] Evidence for this is provided by the presence of four different types of resonances for the olefinic carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum due to four possible different environments for the vinylidene units,[15] which is consistent with the constitution of **5** illustrated in Scheme 1. There are three sets of resonances for the aliphatic carbon atoms, each consisting of three lines: set 1: α-CH_2, α'-CH_2, α''-CH_2; set 2, β-CH_2, β'-CH_2, β''-CH_2; and set 3, γ-CH_2, γ'-CH_2, and δ-CH_2. For stoichiometric reasons, j equals $i + k$.

The formation of this distribution of oligomer isomers can be understood by considering an overall dimerization process in which, formally, one of the two C−C double bonds is retained and the other one is converted into a C−C single bond. We assume that the initial step in the formation of oligomer **5** is the dimerization of 1,7-octadiene **1e**. The dimeric product **2e** has two α-olefinic ends, which are reactive in further dimerization steps. However, the two terminal double bonds in **2e** are not equivalent; one of the terminal bonds is attached to an aliphatic tetramethylene unit, and the other one has a hexamethylene moiety (abbreviations t-4-CH_2 and t-6-CH_2 in Scheme 1, eq 3b). The terminal α-olefinic groups in dimer **2e** can react with another equivalent of **2e** or with 1,7-octadiene **1e**. In the latter case there are four different products possible (Scheme 2). Upon reaction of a tetramethylene terminus (t-4-CH_2) with **1e** either an internal tetramethylene unit (i-4-CH_2) and a hexamethylene terminus (t-6-CH_2) can be formed (eq 4a) or an internal hexamethylene unit (i-6-CH_2) and a t-4-CH_2 terminus are generated (eq 4b). On the other hand, the reaction of a t-6-CH_2 unit with **1e** also has two possibilities. One is the formation of i-6-CH_2 and t-6-CH_2 (eq 5a), and the second is the formation of i-8-CH_2 and t-4-CH_2 (eq 5b).

Following this logic further, as the isomers shown in Scheme 2 continue to oligomerize, reactions of t-4-CH_2 and t-6-CH_2 with themselves or each other give six possible combinations. Here only internal aliphatic units are formed, either i-4-CH_2, i-6-CH_2, or i-8-CH_2; no terminal t-4-CH_2 or t-6-CH_2 units are generated (see supporting information for details). This makes it clear that there are three different internal aliphatic methylene chains possible: i-4-CH_2, i-6-CH_2, and i-8-CH_2. Terminal α-olefinic endgroups are always t-4-CH_2 or t-6-CH_2. A computer simulation of the formation and statistical distribution of tetramethylene, hexamethylene, and octamethylene units using this analysis and an iteration algorithm results in $i = 0.25$, $j = 0.50$, and $k = 0.25$. This prediction is in excellent agreement with the values obtained by careful integration of the $^{13}C\{^1H\}$ NMR spectrum, although the latter gives an experimental error of about 5% due to the signal-to-noise ratio and imperfect spectral resolution.

Scheme 3



A final question concerns the detailed mechanism by which the overall vinyl dimerization reaction illustrated in Schemes 1 and 2 actually occurs. We suggest the sequence of well-known elementary steps shown in Scheme 3. We proposed that the catalytically active species in this process is a hydridozirconium complex (**A**).[16] Insertion of the 1-alkene **1** into the Zr−H bond gives the Zr−alkyl complex **B**, which can either β-eliminate to re-form the starting materials or insert into another equivalent of **1** to form **C**. β-Elimination of **2** from **C** regenerates the hydrido complex **A**. We believe that the formation of only dimeric product might be caused by the presence of a chlorine rather than an alkyl ligand coordinated to the active Zr catalyst;[17] the presence of Cl apparently makes β-elimination occur more rapidly than further insertion. In support of this hypothesis, we observe that, when treated with 1-alkenes, the systems $Cp_2Zr(Me)Cl$[18] /MAO and Cp_2ZrMe_2/LiCl/MAO also give only dimeric product, whereas Cp_2ZrMe_2/MAO and Cp_2ZrCl_2/(large excess MAO) form higher oligomeric products. In the latter cases one expects that all the chloro ligands at the polymerizing Zr centers have been displaced by methyl groups; in the former cases substantial numbers of Cl ligands may be retained.

The oligomers formed in these reactions are unique because they contain terminal methylene units along the chain, which could provide a potential method for introducing novel functional groups at these positions. Further studies underway in our laboratory are directed at obtaining a better understanding of the mechanism of the oligomerization reaction and at extending this type of transformation to other dimerization catalysts and to a wider range of dienes and multiply unsaturated compounds.

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Supporting Information Available: Experimental details, characterization data for all products, and an outline of the structure analysis of **5** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[14] There is only one precedent for a polymeric compound of similar constitution: (a) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392. (b) Jia, L.; Yang, X.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 1547.

[15] The four possible different environments for a vinylidene unit are as follows: $(CH_2)_4(C{=}CH_2)(CH_2)_6$, $(CH_2)_6(C{=}CH_2)(CH_2)_6$, $(CH_2)_4(C{=}CH_2)(CH_2)_8$, $(CH_2)_6(C{=}CH_2)(CH_2)_8$.

[16] We assume that the reaction is initiated by an insertion reaction between a Zr−CH_3 complex and a C=C double bond, followed by β-elimination to give the catalytically active Zr−H species.

[17] The reaction between Cp_2ZrCl_2 and MAO in 1:1 ratio, without alkene present, has been reported before, see: Cam, D.; Giannini, U. *Makromol. Chem.* **1992**, *193*, 1049.

[18] Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321.