

Catalytic oligomerization of α -olefins in the presence of two-stage activated zirconocene catalyst based on 6,6-dimethylfulvene ‘dimer’

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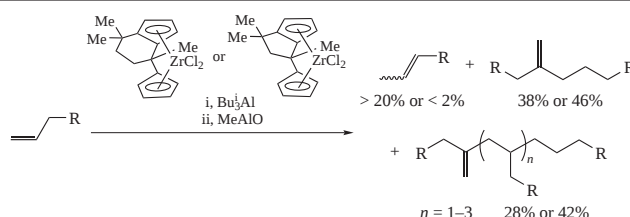
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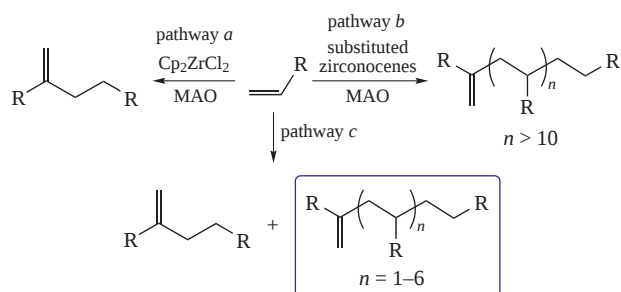
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Zirconocene obtained from 6,6-dimethylfulvene ‘dimer’, being activated subsequently with triisobutylaluminium and methylalumoxane, catalyzes transformation of α -olefins into a mixture of vinylidene oligomers with minimal losses to isomerization, which allows one to consider this catalyst perspective for the synthesis of branched hydrocarbons with uniform structure.



Branched unsaturated hydrocarbons are traditionally considered as starting compounds for the preparation of synthetic oils and lubricants.^{1–8} Such hydrocarbons can be obtained via oligomerization of α -olefins. Traditional electrophilic catalytic systems based on zeolites,^{9–11} AlCl_3 ,¹² alkyl aluminum chlorides^{13,14} or $\text{BF}_3\text{-ROH}$ ^{15,16} provide mixtures of branched products with internal C=C bonds, and cycloparaffins. Structurally uniform oligomers of α -olefins with a highly reactive $>\text{C}=\text{CH}_2$ fragment can be synthesized using zirconocene catalysts. In the presence of a minimal excess of methylalumoxane (MAO) as an activator, zirconocene dichloride (C_5H_5)₂ZrCl₂ catalyzes the formation of α -olefin ‘dimers’^{17–19} (Scheme 1, pathway a). In the presence of substituted zirconocene dichlorides activated by excess of MAO^{20,21} or dimethylzirconocene/perfluoroarylborate systems,^{22–24} α -olefin higher oligomers are the main products (pathway b). The problem of one-stage synthesis of low molecular weight oligomers with a vinylidene structure (pathway c) remains unsolved.

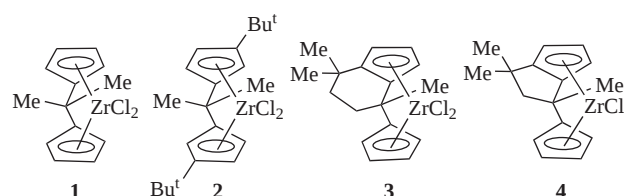


Scheme 1

The current level of research, regarding the influence of zirconocene structure on the catalytic properties in the oligomerization of α -olefins at low Al/Zr ratios, is fragmentary. We have recently²⁵ performed an effective catalytic oligomerization of hex-1-ene using a two-stage activation of zirconocene dichlorides with triisobutylaluminium (TIBA) and a minimal

(~10 equiv.) excess of MAO. In the course of these experiments, it was found that *ansa*-complexes $\text{Z}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$ (Z is one, two or three-atom bridge) demonstrate a high productivity in α -olefin dimer formation.

Based on the premise that the introduction of additional substituents into an *ansa*-zirconocene molecule should shift the reaction toward oligomer production, we investigated a number of *ansa*-zirconocenes **1–4** regarding the oligomerization of hex-1-ene.[†]



Synthesis of compound **4** was conducted in accordance with Scheme 2 using transmetalation of di-SnMe₃ derivative of 6,6-dimethylfulvene ‘dimer’, bis-cyclopentadiene **5**, by ZrCl₄.[‡]

In the molecular structure of complex **4** (Figure 1),[§] the coordination environment of Zr atom may be treated as a distorted

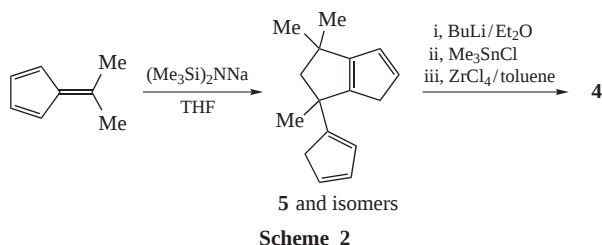
[†] Complexes **1–3** were prepared in accordance with published protocols: **1**,^{26,27} **2**²⁸ and **3**.²⁹

[‡] 3-(Cyclopenta-1,3-dien-1-yl)-1,1,3-trimethyl-1,2,3,4-tetrahydropentalene **5** (mixture of isomers). A solution of NaN(SiMe₃)₂ (3.1 g, 20 mmol) in THF (20 ml) was added to a cooled (0°C) solution of 6,6-dimethylfulvene (21.2 g, 200 mmol) in THF (180 ml). The mixture was allowed to warm to room temperature, stirred for 8 h, poured into 200 ml of 5% aq. NH₄Cl, extracted with pentane (3 × 100 ml). The combined organic fractions were dried over MgSO₄, evaporated under reduced pressure and distilled in vacuo collecting the fraction with bp 95–105°C (0.05 Torr) as a pale-yellow liquid, yield 13.2 g (62%). ¹H NMR (CDCl₃, 20°C) δ : 1.10–1.44 (group of s, 9H), 2.15 (m), 2.43 (m, 2H), 2.79 (br. s, 2H), 2.95 (br. s, 2H), 5.78–6.49 (group of m, 5H).

Table 1 α -Olefin oligomerization catalyzed by zirconocenes **1–4** (0.1 mmol of zirconocene, 200 mmol of α -olefin, 60 °C; 2 mmol of TIBA, 30 min, first activation step; 1 mmol of MAO, 4 h, second activation and oligomerization step).

Catalyst	4 h conversion (%) ^a	Dimer yield (%) ^a	Oligomers yield (%) ^a	Alk-2-enes yield (%) ^a	Dimer (wt%) in C ₁₂ –C ₃₀ fraction ^b	Trimer (wt%) in C ₁₂ –C ₃₀ fraction ^b	Tetramer (wt%) in C ₁₂ –C ₃₀ fraction ^b	Pentamer (wt%) in C ₁₂ –C ₃₀ fraction ^b
1 ^d	75	63	6	6.1	91.5	7.2	1.3	0
2 ^d	21				Polymer, $M_n = 3730$, $M_w = 14000$ ^c			
3 ^d	82	38	28	> 16	57.6	22.7	11.1	8.7
4 ^d	90	46	42	< 2	52.0	24.8	13.6	9.6
4 ^e	88	46	41	< 2	52.7	25.1	13.8	8.4
4 ^f	86	45	38	< 2	58.2	25.9	15.9	not determined

^a Estimated by the analysis of ¹H NMR spectra. ^b GC data. ^c GPC data. ^d Hex-1-ene was used. ^e Oct-1-ene was used. ^f Dec-1-ene was used.



tetrahedron (assuming that η^5 -C₅ rings occupy one coordination site). The Zr–C distances vary in wide range 2.440(1)–2.583(1) Å. The main geometric parameters for molecule **4** are very close to the respective average values for closely related complex **3**³⁰ and *ansa*-zirconocene **1** retrieved from CSD.³¹

The catalytic properties of **1–4**, activated subsequently with 20 equiv. of TIBA and 10 equiv. of MAO, were investigated in the oligomerization of hex-1-ene (Table 1). Complex **1** mainly catalyzed dimer formation with an ~6% of isomerization products,

The product thus obtained (13.2 g, 62 mmol) dissolved in diethyl ether (200 ml) was treated with BuLi (100 ml, 1.6 M solution in hexanes, 160 mmol) at –20 °C. After slow heating to room temperature and 2 h of stirring, the colourless precipitate of dilithium derivative **5a** was filtered off and dried *in vacuo*. The yield was 8.9 g (64%). ¹H NMR (THF-*d*₆, 20 °C) δ : 1.21 (s, 3H), 1.29 (s, 3H), 1.74 (s, 3H), 2.16 (d, 1H, ³J 12.5 Hz), 2.86 (d, 1H, ³J 12.5 Hz), 5.10 (m, 1H), 5.21 (m, 1H), 5.47 (m, 1H), 5.58 (m, 2H), 5.68 (m, 2H). The product contains Et₂O (1:1).

η^5 -3-(η^5 -Cyclopentadienyl)-1,1,3-trimethyl-1,2,3,4-tetrahydropentalenyl dichlorozirconium(IV) **4**. A suspension of **5a** (3.51 g, 11.8 mmol) in diethyl ether (50 ml) was cooled to –40 °C, and Me₃SnCl (5 g, 25 mmol) in diethyl ether (20 ml) was added with stirring. The mixture was allowed to warm to room temperature, and then was filtered. The filtrate was evaporated under reduced pressure, toluene (20 ml) was added and then evaporated for complete elimination of Et₂O. The residue was dissolved in toluene (40 ml), ZrCl₄ (2.8 g, 12 mmol) was added with stirring. After keeping at 60 °C for 6 h the mixture was cooled to room temperature, the solution was separated by decantation, and evaporated to *ca.* 15 ml. Hexane (10 ml) was added. After 16 h of crystallization at 0 °C, the product was filtered off, washed with pentane and dried *in vacuo*. The yield was 2.72 g (62%), yellowish crystals. ¹H NMR (CDCl₃, 20 °C) δ : 1.31 (s, 3H), 1.38 (s, 3H), 1.92 (s, 3H), 2.48 (1H), 2.87 (1H, AB, CH₂, ²J 14.4 Hz), 5.46 (d, 1H), 5.82 (m, 2H), 6.24 (m, 1H), 6.51 (q, 1H), 6.70 (t, 1H), 6.78 (q, 1H). ¹³C NMR (CDCl₃, 20 °C) δ : 24.9, 26.6, 38.5 (Me), 40.2, 46.2 (C), 55.4 (CH₂), 100.2, 106.4, 109.7, 114.5, 116.5, 125.6, 127.4 (=CH), 121.5, 125.2, 144.0 (=C). Found (%): C, 51.22; H, 4.90. Calc. for C₁₆H₁₈Cl₂Zr (%): C, 51.60; H, 4.87.

[§] Crystallographic data for **4**: C₁₆H₁₈Cl₂Zr, $M = 372.42$, monoclinic, space group $P2_1/c$, $a = 10.8881(5)$, $b = 13.2314(7)$ and $c = 10.4702(5)$ Å, $\beta = 92.697(1)^\circ$, $V = 1506.72(13)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.642$ g cm^{–3}, $F(000) = 752$, $\mu(\text{MoK}\alpha) = 1.068$ mm^{–1}, $T = 150(2)$ K, 14480 reflections measured, 3976 independent reflections ($R_{\text{int}} = 0.0208$), 244 parameters, $R_1 = 0.0199$ [3685 reflections with $I > 2\sigma(I)$], $wR_2 = 0.0528$ (all data), GOF = 1.034, $\Delta\rho_{\text{max}} = 0.523$ e Å^{–3}, $\Delta\rho_{\text{min}} = -0.279$ e Å^{–3}.

CCDC 1430370 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

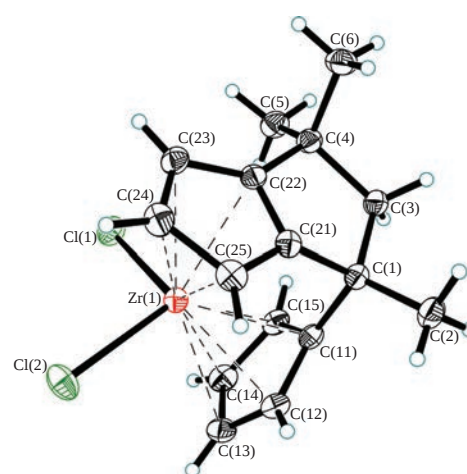


Figure 1 Molecular structure of **4**. Displacement ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): Zr(1)–Cl(1) 2.4453(4), Zr(1)–Cl(2) 2.4399(4), Zr(1)–C(25) 2.4399(13), Zr(1)–C(21) 2.4411(13), Zr(1)–C(11) 2.4491(13), Zr(1)–C(12) 2.4697(13), Zr(1)–C(15) 2.4772(13), Zr(1)–C(22) 2.5204(13), Zr(1)–C(24) 2.5348(14), Zr(1)–C(14) 2.5535(14), Zr(1)–C(13) 2.5597(14), Zr(1)–C(23) 2.5825(14), Cl(2)–Zr(1)–Cl(1) 99.354(14), C(21)–C(1)–C(2) 115.44(12), C(21)–C(1)–C(11) 100.00(10), C(2)–C(1)–C(11) 113.02(11), C(21)–C(1)–C(3) 101.23(10), C(2)–C(1)–C(3) 113.74(12), C(11)–C(1)–C(3) 112.11(11).

hex-2-enes. Complex **2** bearing two bulky *tert*-butyl substituents, β -anomeric to the bridge, even in the presence of minimal excess of MAO, changed the direction of the reaction toward polymer formation. Complex **3** turned out to be much more active, when compared with **1** and **2**, and gave a mixture of dimer and higher oligomers. However, in the course of the reaction, about 20% of initial hex-1-ene was transformed into a ballast of inert hex-2-enes. Complex **4**, despite its structural similarity to **3**, demonstrated a highest productivity, catalyzing dimer and higher oligomer formation in approximately equal ratio; the partial loss of the monomer through internal hex-2-ene formation amounted to less than 1%. Oct-1-ene and dec-1-ene in the presence of **4** also formed a mixture of dimers and lower oligomers with a high fraction of desired product and minimal alk-2-ene content (see Table 1).

In conclusion, zirconocene **4** is an effective pre-catalyst in the oligomerization of α -olefins, forming a mixture of dimers and lower oligomers which can be useful as the starting compounds for the obtaining of various functional petrochemical products.

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Online Supplementary Materials

Supplementary data associated with this article (preparation of and X-ray data for **4**, oligomerization experiment details, oligomer characteristics) can be found in the online version at doi: 10.1016/j.mencom.2017.01.010.

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