Zirconocene–alumoxane (1:1) – a catalyst for the selective dimerization of α-olefins

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Abstract

A well known catalytic system for the oligomerization of 1-alkenes is zirconocene dichloride (Cp₂ZrCl₂), when activated by a large excess of methylalumoxane (MAO). Surprisingly, when activated by only 1 equiv. of MAO, Cp₂ZrCl₂ selectively and catalytically dimerizes α-olefins without formation of any higher oligomeric species. This reaction is shown to be general for a number of α-olefins. The conversion of α-diallylbenzene gives a seven-membered cyclic product in an intramolecular dimerization reaction. A possible mechanism for the dimerization process involving a zirconium–hydrido species as the catalyst is formulated, and evidence for it is given by detection of by-products and a deuteration experiment.

Keywords: Catalysis; Dimerization of olefins; Zirconocene complexes; Alumoxane complexes

1. Introduction

There are many transition metal systems that are known to catalyze the dimerization of 1-alkenes (α-olefins) [1]. Two pathways that have been identified for this class of reactions (Scheme 1) involve (i) metallacycle formation followed by β-elimination and reductive elimination [1c], and (ii) hydrometallation of the alkene to give a metal alkyl, followed by migratory insertion of a second alkene into the M–alkyl bond and then β-elimination of the dimer [1d,e].

The second (migratory insertion) pathway is closely related to the mechanism of Ziegler-Natta polymerization [2,3]. The critical difference between Ziegler-Natta polymerization and the related dimerization is the β-elimination (chain transfer) step. In systems that give dimerization, this step is fast relative to migratory insertion of additional alkene into the first-formed metal alkyl complex. In polymerization the rate of β-elimination is slow relative to that of migratory insertion, allowing chain propagation to dominate over chain transfer.

Because of this close mechanistic relationship between dimerization and polymerization, it seems reasonable that

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1 Dedicated to Professor Jack Halpern, a valued friend and colleague, for his past and current contributions to chemistry.

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process [6]. Lower Al/Zr ratios give lower molecular weight materials, but such low Al/Zr ratio systems have been much less frequently discussed in the literature [7,8].

Recently, we reported in preliminary form [9] that a Al/Zr ratio of about 1:1 leads to the selective formation of α-olefin dimers 2 (Scheme 1). Given the ready availability of simple 1-alkenes, this catalytic C–C bond formation reaction provides access to a number of hydrocarbon building blocks, simple 1-alkenes, this catalytic C–C bond formation reaction makes it potentially important 2. We therefore decided to investigate the mechanism of the reaction. This paper reports our results, the most important of which provides information on the effect of dissolved chloride ion on the rate of chain transfer in zirconocene-catalyzed olefin oligomerization reactions.

2. Experimental

All manipulations involving MAO were performed in a glovebox using rigorously anaerobic and anhydrous conditions. The commercially available olefins, 1a–1g, were dried over CaH2 and freshly distilled in flame dried glassware from CaH2 under an Ar-atmosphere before use. A sample of 7 was prepared from phenylacetone and methyltriphenylphosphonium bromide using a standard procedure [12]; 2-bromo-l-alkene were purchased from Aldrich. MAO (solution in toluene) was either purchased from Akzo Chemicals Inc., Chicago, or prepared according to a literature procedure [17]. All solvents were freshly distilled from sodium-diphenylketyl before use. Column chromatography was accomplished with Merck silica gel (type 60, 0.063–0.200 mm). Impregnation of silica gel with silver nitrate was performed following a literature procedure [18].

Impregnation of silica gel with silver nitrate was performed following a literature procedure [18]. 

**2.1. 2-Ethyl-l-hexene (2a) [19]**

Zirconocene dichloride (300 mg, 1.03 mmol) and MAO (1.05 mmol, 1.52 g of a 4% solution in toluene) were mixed in a 20 ml Schlenk flask and 1-butene (1a) (7.67 g, 136.7 mmol) was added by condensation at −78°C. The mixture was stirred for 1 day at r.t. By means of 1H NMR no 1-buten-1e (1a) was detectable in the crude mixture, from which the product was obtained by fractional distillation through a 10 cm Vigreux-column, b.p. 116°C/760 mm, colorless liquid, yield: 5.75 g (51.3 mmol, 75%).

1H NMR (400 MHz, CDCl3): δ 0.92 (t, J = 7.2 Hz, 3H; CH3), 1.04 (t, J = 7.4 Hz, 3H; CH3), 1.28–1.37 (m, 2H; CH2), 1.38–1.46 (m, 2H; CH2), 2.00–2.06 (m, 4H; CH2), 4.70 (s, 2H; =CH2) ppm. 13C{1H} NMR (100 MHz, CDCl3): δ 12.34 (CH3), 13.96 (CH3), 22.57 (CH2), 28.77 (CH2), 30.16 (CH2), 36.04 (CH2), 107.34 (CH2), 151.61 (C) ppm. IR (neat): 3082 (m), 3026 (m), 2980 (vs), 2933 (vs), 2870 (vs), 2733 (w), 1782 (w), 1645 (s), 1464 (w), 1377 (m), 1107 (w), 887 (s), 729 (s), 694 (m), 463 (m) cm−1. MS (EL, 70 eV): m/z (%) : 112 (20) [M*], 83 (7), 70 (100), 55 (72). Anal. Calc. for C15H24 (242.36): C, 85.63; H, 14.37. Found: C, 85.81; H, 14.22%.

The alkenes 2b–2f are prepared analogously:

**2.2. 2-Propyl-l-heptene (2b) [20]**

From 1-pentene (1b) (7.53 g, 107 mmol), Cp2ZrCl2 (93 mg, 0.32 mmol), MAO (0.86 mmol, 1.25 g of a 4% solution in toluene), b.p. 110°C/130 mm, colorless liquid, yield: 6.65 g (47.4 mmol, 89%). 1H NMR (400 MHz, CDCl3): δ 0.89 (t, J = 7.0 Hz, 3H; CH3), 0.90 (t, J = 7.3 Hz, 3H; CH3), 1.27–1.37 (m, 4H; CH2), 1.38–1.50 (m, 4H; CH2), 1.97–2.01 (m, 4H; CH2), 4.69 (s, 2H; =CH2) ppm. 13C{1H} NMR (100 MHz, CDCl3): δ 13.84 (CH3), 14.04 (CH3), 20.97 (CH2), 22.69 (CH2), 27.61 (CH2), 31.79 (CH2), 36.08 (CH2), 38.30 (CH2), 108.59 (CH2), 149.87 (C) ppm. IR (neat): 3072 (m), 2958 (s), 2929 (s), 2862 (s), 1784 (w), 1645 (m), 1464 (s), 1379 (m), 889 (s), 739 (w) cm−1. MS (EL, 70 eV): m/z (%): 110 (28) [M*], 97 (18), 84 (40), 69 (33), 58 (59), 56 (100). Anal. Calc. for C16H30 (240.27): C, 85.63; H, 14.37. Found: C, 85.66; H, 14.62%.

**2.3. 2-Butyl-l-octene (2c) [21]**

From 1-hexene (1e) (10.1 g, 120 mmol), Cp2ZrCl2 (114 mg, 0.39 mmol), MAO (2.15 mmol, 3.12 g of a 4% solution in toluene), b.p. 88°C/8 mm, colorless liquid, yield: 9.1 g (54.1 mmol, 90%). 1H NMR (400 MHz, CDCl3): δ 0.90 (t, J = 7.0 Hz, 3H; CH3), 0.91 (t, J = 7.3 Hz, 3H; CH3), 1.27–1.45 (m, 12H; CH2), 1.99–2.03 (m, 4H; CH2), 4.70 (s, 2H; =CH2) ppm. 13C{1H} NMR (100 MHz, CDCl3): δ 13.99 (CH3), 14.09 (CH3), 22.60 (CH2), 22.76 (CH2), 27.91 (CH3), 28.79 (CH2), 30.26 (CH2), 36.08 (CH2), 38.29 (CH2), 108.59 (CH2), 149.87 (C) ppm. IR (neat): 3072 (m), 2958 (s), 2929 (s), 2862 (s), 1784 (w), 1645 (m), 1464 (s), 1379 (m), 889 (s), 739 (w) cm−1. MS (EL, 70 eV): m/z (%): 110 (28) [M*], 97 (18), 84 (40), 69 (33), 58 (59), 56 (100). Anal. Calc. for C16H30 (240.27): C, 85.63; H, 14.37. Found: C, 85.66; H, 14.62%.

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2.5. 5-Methyl-2-(methylthyl)-1-hexene (2e)

Zirconocene dichloride (220 mg, 0.73 mmol) and MAO (2.41 mmol, 3.50 g of a 4% solution in toluene) were mixed in a 20 ml Schlenk flask and 3-methyl-1-butene (1e) (9.55 g, 136 mmol) was added by condensation at −78°C. The mixture was stirred for 1 day at rt. By means of $^1$H NMR, the composition of the crude reaction mixture was determined to be 2-methyl-2-butene (4) (77%), 2-methyl-1-butene (5) (17%) and dimer (2e) (6%); no starting material was left. The isomeric pentenes were removed in the rotavapor under reduced pressure, and the product was obtained from the residue by fractional distillation through a 10 cm Vigreux-column at 120 mm, b.p. 85°C/120 mm, colorless liquid, yield: 250 mg (1.78 mmol, 3%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.96 (d, J = 6.6 Hz, 6H; CH$_3$), 1.09 (d, J = 6.8 Hz, 6H; CH$_3$), 1.35–1.41 (m, 2H; CH$_2$), 1.61 (nonet, J = 6.6 Hz, 1H; CH), 2.06–2.10 (m, 2H; CH$_2$), 2.30 (heptet, J = 6.8 Hz, 1H; CH), 4.73 (s, 1H; =CH)$_2$, 4.79 (s, 1H; =CH) ppm. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): $\delta$ 21.91 (CH$_3$), 22.61 (CH$_3$), 28.00 (CH), 32.32 (CH$_2$), 33.80 (CH), 37.59 (CH$_2$), 105.98 (=CH$_2$), 156.43 (=C) ppm. IR (neat): 3084 (m), 3028 (m), 2958 (s), 2929 (s), 2872 (s), 1643 (m), 1497 (w), 1466 (s), 1383 (m), 1365 (m), 1261 (m), 1095 (s), 1030 (m), 887 (s), 806 (m), 729 (s), 694 (m), 463 (w) cm$^{-1}$. MS (70 eV, EI): m/z (%): 130 (27) [$M^+$], 97 (7), 84 (67), 69 (100), 55 (35). $\text{Anal. Calc. for } C_{12}H_{24}O (140.27): C, 85.63; H, 14.37$. Found: C, 85.91; H, 14.31%.

2.6. 6-Methyl-2-(2-methylpropyl)-1-heptene (2f) [1d]

From 3-methyl-1-pentene (1f) (7.20 g, 85.6 mmol), Cp$_2$ZrCl$_2$ (100 mg, 0.34 mmol), MAO (1.74 mmol, 700 mg of a 14% solution in toluene), b.p. 78°C/12 mm, colorless liquid, yield: 6.46 g (38.4 mmol, 90%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.87 (d, J = 6.5 Hz, 6H; CH$_3$), 0.88 (d, J = 6.6 Hz, 6H; CH$_3$), 1.15–1.20 (m, 2H; CH$_2$), 1.38–1.46 (m, 2H; CH$_2$), 1.55 (nonet, J = 6.6 Hz, 1H; CH), 1.75 (nonet, J = 6.6 Hz, 1H; CH), 1.89 (d, J = 7.1 Hz, 2H; CH$_2$), 2.19 (t, J = 7.6 Hz, 2H; CH$_2$), 2.67 (m, 1H; =CH), 4.72–4.73 (m, 1H; =CH) ppm. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): $\delta$ 22.57 (CH$_3$), 22.68 (CH$_3$), 25.61 (CH), 26.10 (CH), 28.02 (CH), 36.05 (CH$_2$), 38.89 (CH$_2$), 46.09 (CH$_2$), 110.01 (=CH$_2$), 148.81 (=C) ppm. IR (neat): 3072 (m), 2954 (s), 2929 (s), 2869 (s), 2846 (s), 1786 (w), 1643 (m), 1466 (s), 1385 (m), 1367 (m), 1336 (w), 1169 (m), 891 (s) cm$^{-1}$. MS (70 eV, EI): m/z (%): 168 (33) [$M^+$], 111 (11), 98 (9), 83 (56), 70 (44), 56 (100). $\text{Anal. Calc. for } C_{12}H_{24}O (168.32): C, 85.63; H, 14.37$. Found: C, 85.48; H, 14.43%.

Zirconocene dichloride (214 mg, 0.73 mmol) was mixed with MAO (2.67 mmol, 3.88 g of a 4% solution in toluene), allylbenezene (1g) (7.80 g, 66 mmol) was added and the mixture was stirred at rt for 2 days. The major part of the toluene was removed by rotary evaporation at 50°C in vacuo. The residual oil was chromatographed on SiO$_2$ using petroleum ether (b.p. 40–60°C) as eluent. After a first band containing a small amount of toluene, a second fraction ($R_F = 0.50$) of 454 mg of a mixture of 6 and 7 (ratio by $^1$H NMR = 1:2) was eluted. Further elution gave a third fraction ($R_F = 0.35$) containing the product 2g (yield: 6.32, 26.7% mmol, 81%, colorless oil). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.95–2.03 (m, 2H; CH$_2$), 2.34 (t, J = 7.5 Hz, 2H; CH$_2$), 2.79 (t, J = 7.7 Hz, 2H; CH$_2$), 3.55 (s, 2H; CH$_2$), 5.00 (s, 1H; =CH), 5.08 (s, 1H; =CH), 7.36–7.50 (m, 10H; CH$_2$)$_2$ ppm. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): $\delta$ 29.33 (CH$_2$), 34.92 (CH$_2$), 35.42 (CH$_2$), 42.99 (CH$_2$), 111.31 (=CH$_2$), 125.62 (CH), 125.99 (CH), 128.21 (4 CH), 128.34 (2 CH), 128.94 (2 CH), 139.64 (C), 142.34 (C), 148.54 (=C) ppm. IR (neat): 3082 (m), 3062 (m), 3026 (s), 2997 (w), 2933 (s), 2858 (s), 1944 (m), 1871 (m), 1803 (m), 1645 (s), 1603 (s), 1583 (m), 1495 (s), 1452 (s), 1076 (m), 1030 (m), 893 (s), 737 (s), 698 (s), 492 (m) cm$^{-1}$. MS (70 eV, EI): m/z (%): 236 (22) [$M^+$], 145 (22), 132 (13), 117 (24), 104 (100), 91 (39), 65 (7). $\text{Anal. Calc. for } C_{18}H_{20}O (236.36): C, 91.47; H, 8.53$. Found: C, 91.62; H, 8.67%.
2.8. Purification of (E)-1-phenylpropene (6) and 2-methyl-3-phenylpropene (7)

A 200 mg mixture of 6 and 7 obtained in the preparation of 2g was chromatographed on silica gel impregnated with AgNO₃ (pentane/EtOH 50:1, column size: 2 cm diameter, 15 cm length). Several fractions (each 10 ml) were collected. Fractions 4 to 6 contained 60 mg (0.51 mmol) of 6, fractions 8 to 12 contained 120 mg (0.91 mmol) of 7. Both compounds were identified by comparing by GC and their ¹H NMR spectra with those of authentic samples.

2.9. 4-Methylene-benzocycloheptane (9)

Zirconocene dichloride (63 mg, 0.216 mmol) was mixed with MAO (0.787 mmol, 1.12 g of a 4% solution in toluene). Diene 8 (3.52 g, 22.2 mmol) was added and the mixture was stirred at r.t. After 3 days no 8 was detectable by ¹H NMR. Pentane (20 ml) and water (0.5 ml) were added to the mixture, and after stirring for 30 min the mixture was filtered over Na₂SO₄. The Na₂SO₄ was washed with portions of pentane (3 × 10 ml) and the solvent was removed from the residual oil was heated to 150°C and transferred under high vacuum into a N₂-l-cooled trap. Chromatography of this condensate (SiO₂, pentane) yielded analytically pure 9, RF = 0.50, b.p. 89°C/13 mm, colorless liquid, yield: 2.46 g (15.5 mmol, 70%). ¹H NMR (400 MHz, CDCI₃): δ 1.76-1.81 (m, 2H; 6-CH₂), 2.52 (t, J=6.2 Hz, 2H; 7-CH₂), 2.92-2.94 (m, 2H; 5-CH₂), 3.51 (s, 2H; 3-CH₂), 4.77 (s, 1 H; =CHH), 4.82 (s, 1H; =CHH) ppm. ¹³C{¹H} NMR (100 MHz, CDCI₃): δ 28.42 (6-CH₂), 35.20 (7-CH₂), 40.02 (5-CH₂), 7.25 (m, 4H; Ar-H) ppm.

2.11. Determination of turnover numbers

Cp₂ZrCl₂ (12.0 mg, 0.0411 mmol) and MAO (0.241 mmol, 350 mg of a 4% solution in toluene) were mixed, and the mixture was stirred ~15 min at r.t. 1-Hexene (1c) (6.52 g, 77.5 mmol) was added, and the mixture was stirred at r.t. At intervals, approximately 0.1 g samples were taken from the reaction mixture and quenched by adding 1 g CDCl₃ and 0.1 g D₂O. Conversion values were obtained by integration of ¹H NMR spectra versus internal toluene (from MAO solution) standard. The reaction of Cp₂Zr(H)Cl (11.0 mg, 0.0427 mmol), MAO (0.221 mmol, 320 mg of a 4% solution in toluene) and 1-hexene (1c) (5.92 g, 70.3 mmol) was run and monitored similarly.

2.12. 2-Deutero-1-hexene (lh) [23]

At −78°C, 2-bromo-1-hexene (16) (12.0 g, 73.0 mmol) was added over 15 min to a mixture of di-n-butylether (200 ml) and t-butyllithium (220 mmol, 146 ml of a 1.5 molar solution in pentane). The mixture was stirred 2.5 h at −78°C, and then the volatile materials were removed in high vacuum at −20 to −10°C for 1.5 h, and finally at 0°C for 0.5 h. The mixture was cooled again to −78°C, and D₂O (10 ml) was added dropwise. After slow warming to room temperature (1 h), the solution was decanted from the colorless solid and distilled through a 10 cm Vigreux column at 760 mm. The fraction between 60 and 64°C contained the product lh (yield: 4.35 g, 51.2 mmol, 70%). The D-incorporation was 96% by integration of the ¹H NMR spectrum and 94% by EI MS; the sample contained a small amount of pentane. ¹H NMR (400 MHz, CDCl₃): δ 0.90 (t, J = 7.2 Hz, 3H; CH₃), 1.29-1.47 (m, 4H; CH₂), 2.04 (t, broad, 2H; CH₂), 4.95 (s, broad, 1H; =CHH), 5.01 (s, broad, 1H; =CHH) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 13.72 (CH₃), 22.19 (CH₂), 31.18 (CH₂), 33.42 (CH₂), 113.8 (=CH) ppm. IR (neat): 3070 (m), 2964 (s), 2928 (m), 2359 (m), 1470 (s), 1457 (s), 1240 (m), 1138 (m), 1072 (m), 996 (s), 968 (s), 798 (s), 742 (s) cm⁻¹. MS (EI, 70 eV): m/z (%): 85 (35) [M⁺], 65 (100). HR MS (70 eV, EI): calc.: 85.1002; found: 85.1000.

2.13. 2-Butyl-4,4-dideutero-1-octene (2h)

As described for the preparation of 2e, deuterated 1-hexene (1h) (2.93 g, 24.4 mmol), Cp₂ZrCl₂ (190 mg, 0.65 mmol) and MAO (4.05 mmol, 1.63 g of a 14.4% solution in toluene) were converted to the dimer 2h, b.p. 85°C/10 mm, colorless liquid, yield: 2:10 g (12.3 mmol, 72%). By EI MS, no non-deuterated product 2e (m/z = 168) was detectable, and the ratio of mono-deuterated 2f (m/z = 169) to di-deuterated product 2h (m/z = 170) was 20:80. Higher volatile by-products and parts of the solvent were trapped in a liquid nitrogen cooled flask between distillation apparatus and vacuum pump. This material (1.22 g) was determined by ¹H NMR and GC to be a mixture of toluene (86 mol%), E- and Z-2-hexene (6 mol%) and 2-methyl-1-hexene (3) (8 mol%). ¹H
NMR (400 MHz, CDCl₃): δ 0.89 (t, J = 7.2 Hz, 3H; CH₃), 0.91 (t, J = 7.3 Hz, 3H; CH₃), 1.27-1.42 (m, 10H; CH₂), 1.98 (s, broad, 2H; α-CH₂), 2.00 (t, broad, J = 7.6 Hz, 2H; α-CH₂), 4.69 (s, 2H; =CH₂) ppm. ²H NMR (61.4 MHz, CHCl₃): δ 1.44 (s, broad, CD₂) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 13.96 (s, CH₃), 14.06 (s, CH₃), 22.60 (s, CH₂), 22.76 (s, CH₂), 27.12 (pentet, J(¹³C,²H) = 19.2 Hz, 4-CH₂), 29.07 (s, 5-CH₂), 30.15 (s, 2'-CH₂), 31.90 (s, 6-CH₂), 35.89 (s, 1'-CH₂), 36.09 (s, 3-CH₂) ppm. IR (neat): 3072 (m), 2958 (s), 2871 (m), 1500 (s), 836 (s), 798 (w), 729 (w) cm⁻¹. MS (EI, 70 eV): m/z (%): 170 (16) [M⁺], 128 (4), 113 (10), 98 (8), 85 (5), 83 (6), 70 (28), 56 (100); HR MS (70 eV, EI): calc.: 169.1941; found: 169.1937.

### 2.14. 2-Butyl-4-deutero-1-octene (2i)

As described for the synthesis of 2h, 1-hexene with 75% deuterium incorporation in the 2-position (by ¹H NMR) was converted to a mixture of the dimers 2e, 2f and 2h (ratio: 10/45/45 by EI MS, statistically expected 6/38/56), which was purified by fractional distillation at 15 mm. In the ¹³C{¹H} NMR (100 MHz, CDCl₃) spectrum, apart from resonances for 2e and 2h, the following signals are observed for the monodeuterated compound 2f: δ 13.96 (s, CH₃), 14.06 (s, CH₃), 22.60 (s, CH₂), 22.76 (s, CH₂), 27.52 (t, J(¹³C,²H) = 19.2 Hz, 4-CH₂), 29.25 (s, 5-CH₂), 30.15 (s, 2'-CH₂), 31.90 (s, 6-CH₂), 35.89 (s, 1'-CH₂), 36.09 (s, 3-CH₂), 108.44 (s, 1-CH₂), 164.54 (m), 1466 (s), 1379 (m), 1261 (m), 1101 (m), 1018 (m), 887 (s), 729 (w) cm⁻¹. MS (EI, 70 eV): m/z (%): 170 (16) [M⁺], 128 (4), 113 (10), 98 (8), 85 (5), 83 (6), 70 (28), 56 (100); HR MS (70 eV, EI): calc.: 169.1941; found: 169.1937.

### 3. Results and discussion

A catalyst prepared by mixing Cp₂ZrCl₂ and a solution of methylalumoxane in toluene (ratio Al/Zr ~ 1:1) ³ dimerizes up to 500 equiv. of the 1-alkenes 1a-d and 1f. After 1 day at r.t. no starting materials 1 are detectable in the reaction mixtures by ¹H NMR, and the analytically pure dimers 2a-2h can be isolated by fractional distillation directly from the reaction mixtures (Table 1, Scheme 2). Conversion of allylbenzene (1g) to the corresponding dimer 2g is slower than its aliphatic congeners; 100 equiv. are dimerized to 2g in 2 days. Chromatographic workup of this reaction also yields two by-products: isomerization product 6 and the alkene 7. The latter gives as an homologue of 1g an important hint to the mechanism involved in this process (see below). Although the dimerization reaction seems to be general for allylic and aromatic 1-alkenes, the absence of an α-branch seems to be necessary: conversion of the α-substituted alkene 1e gives the dimer 2e only as a by-product; isomerization leading to the isopentenes 4 and 5 is the main reaction pathway in this case. Under the same reaction conditions styrene is not converted to any product at all; also, internal olefins and 1,1-disubstituted olefins, such as the dimers 2h themselves, seem to be stable under the reaction conditions.

We decided to investigate whether this dimerization catalyst might cyclize α,ω-dienes ⁴, e.g. to form a seven-membered carbocycle ⁵, reaction of ³iallylbenzene (8) with Cp₂ZrCl₂/MAO (3 days, r.t., 1 mol% Zr, Al/Zr = 4:1) does indeed give the benzannulated methylenecycloheptane (9), which was separated from non-volatile by-products by distillation and purified by chromatography. However, a starting material structure that holds the cyclizing olefinic groups in proximity to one another appears to be required to achieve intramolecular cyclization, because simple dienes like 1,7-octadiene lead to linear oligomers rather than rings, which is the result of an intermolecular process. These polycondensation products will be the subject of a separate paper.

We believe that chloro ligands are responsible for the different catalytic properties of systems with low and high Al/Zr ratios. Treating Cp₂ZrCl₂ with a very large excess of MAO should lead to a complete displacement of Cl⁻ by CH₃⁻ ligands (at least for statistical reasons all Cl-atoms are transferred to Al-centers); the resulting Cp₂Zr(CH₃)₂-MAO adduct 11

Table 1

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<tr>
<th>Educt</th>
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<tr>
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<td>2g (81), 6 (3), 7 (3) c, (72) d</td>
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<tr>
<td>8</td>
<td>9 (70)</td>
</tr>
</tbody>
</table>

*a* Isolated yields, if nothing else stated.

*b* By ¹H NMR of the crude reaction mixture.

*c* Based on 1d.

*d* Based on MAO.

³ The reaction between Cp₂ZrCl₂ and MAO in 1:1 ratio, without alkene present, has been reported before, see Ref. [24].

⁴ There are only very few examples of transition metal mediated seven-membered carbocycle formations, for a review see Ref. [26].
(Scheme 3) (or a dissociated 14-electron Zr–CH₃ species) [27] is the likely olefin polymerization catalyst. When only 1 equiv. or a small excess of MAO is used instead, it seems reasonable that a substantial number of Cl-ligands will be retained at the Zr-centers (10). In support of this hypothesis, we observe that when treated with 1-hexene (1c), the systems Cp₂Zr(CH₃)Cl [28]/MAO and Cp₂Zr(CH₃)₂/LiCl/MAO also give only dimeric product, whereas Cp₂Zr(CH₃)₂/MAO and Cp₂ZrCl₂/(large excess MAO) form mixtures of higher oligomeric products.

We propose that the actual catalyst is a zirconium-hydrido species 13 (Scheme 3), formed in situ by addition of the Zr–CH₃ complex 10 to a 1-alkene, followed by β-hydride elimination of 2-methyl-1-alkene from the resulting Zr-alkyl complex 12. In support of this postulate, in reactions starting from 1-hexene (1c) and allylbenzene (1g) we were able to isolate the β-H elimination products from intermediate 12; the by-products 3 and 7 could be separated from the crude reaction mixtures by either fractional distillation or chromatography. Moreover, we observe that Cp₂Zr(H)Cl/MAO (1:1) also selectively dimerizes 1-hexene (1c) to give 2c. However, activation by MAO is necessary, as neither Cp₂Zr(H)Cl itself nor this chloride activated by AlCl₃ or Al(CH₃)₃ performs the dimerization. Reactions of 1-hexene catalyzed by Cp₂ZrCl₂/MAO and Cp₂Zr(H)Cl/MAO were monitored by ¹H NMR: plots of the ratio [dimer]/[Zr] versus time are shown in Fig. 1. After an induction period (of ~60 min), the turnover number (TON) in the case of Cp₂ZrCl₂/MAO catalysis becomes ~6 min⁻¹. Catalysis of Cp₂Zr(H)Cl is more efficient: the induction period is significantly shorter (~5 min), and the TON is ~30 min⁻¹. Both of these differences in induction period and TON strongly indicate that a Zr–hydrido complex, 13, is the actual catalyst, which has to be generated first in situ in the case of Cp₂ZrCl₂ from a Zr–CH₃ species, 10, as described above.

In view of our evidence that a Zr–H complex, 13, is the actual catalyst, we suggest the overall mechanism shown in Scheme 4. All elementary steps are well known for the olefin oligomerization process using zirconocene–alumoxane catalysis [29]. Insertion of a 1-alkene 1 into the Zr–C bond of complex 14 gives a Zr–alkyl complex, 14, which can either regenerate alkene 1 and complex 13 in a β-H elimination reaction, or undergo further insertion of another equivalent of alkene 1 into the Zr–C bond of complex 14 to give the new Zr–alkyl species 15. β-H elimination from 15 gives the dimeric alkene product 2, and regenerates 13. We believe that the presence of a chloro-ligand in the coordination sphere of Zr makes the β-elimination process more favorable than further insertion steps and thus is the cause of selective dimer formation rather than formation of higher oligomers. This requires the equilibrium between complexes 13 and 14 to be relatively fast compared to the insertion reaction leading to complex 15. Once compound 15 is formed, a rapid β-H elimination process gives dimer 2 before another equivalent of alkene 1 can insert into the Zr–C bond of 15 to give higher oligomers. This mechanism does conform with one suggested for the dimerization reaction of α-olefins catalyzed by a scandium-hydrido complex [1d], although this system (TON less than 1 min⁻¹ for 1-butene) is not as efficient as the Cp₂ZrCl₂/MAO catalysis introduced in this paper.

Isotope tracer studies provide support for the mechanism in Scheme 4. Starting from a 2-deutero-1-alkene, the cataly-
ically active species generated in situ is a Zr–D complex analogous to 13. Insertion of the deuterated alkene into either a Zr–D bond of complex 13 or a Zr–C bond of complex 14 followed by β-D elimination steps would regenerate the Zr catalyst 13. The dimeric product 2 is predicted to be selectively deuterated in the four-position.

We prepared 2-deutero-1-hexene (1h) from 2-bromo-1-hexene (16) (Scheme 5), and conversion of this material (1h) under our dimerization conditions using Cp2ZrCl2/MAO catalysis gives the 4,4-dideuterated product 2h. Also, by GC, 2-methyl-1-hexene (3) could be detected. The selective deuterated incorporation was proved by 1H, 2H and 13C NMR spectroscopy and EI-mass spectrometry: in the 1H NMR spectrum, the broad triplet structure at about 2 ppm in compound 2c is replaced by a triplet + singlet pattern in compound 2h. The integral of the multiplet between 1.27 and 1.44 ppm has decreased by an equivalent of 2H. Also, in the 13C NMR spectrum, apart from small changes in some of the chemical shifts, the replacement of the resonance at 27.91 ppm for 2c by a pentet at 27.12 ppm for the CD2 carbon atom in 2h is obvious. All other 13C resonances for compound 2h remain singlets. Moreover, when a sample of 1h with only 75% deuterium incorporation is used, the 1H NMR spectrum of 2h shows only a broad singlet at 1.44 ppm. The proposed mechanism for the overall vinyl dimerization reaction incorporates elementary C–C double bond insertion and β-hydride elimination steps. Evidence for this mechanism was provided by the identification of by-products and by a deuterium tracer experiment. Responsibility for the chemo-selective dimer formation can be ascribed to chloro ligands remaining in the coordination sphere of the Zr-catalyst, which make β-H elimination steps more favorable than insertion reactions.

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