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

Jens Christoffers, Robert G. Bergman *

Department of Chemistry, University of California, Berkeley, CA 94720-1460, USA

Abstract

A well known catalytic system for the oligomerization of 1-alkenes is zirconocene dichloride (Cp_2ZrCl_2), when activated by a large excess of methylalumoxane (MAO). Surprisingly, when activated by only 1 equiv. of MAO, Cp_2ZrCl_2 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 *o*-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. © 1998 Elsevier Science S.A.

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
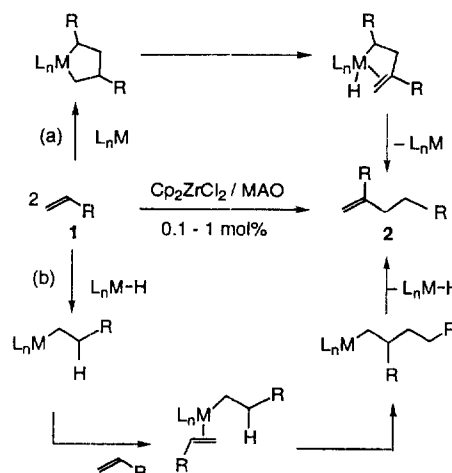
Scheme 1. Selective dimerization of 1-alkenes using a zirconocene–alumoxane (1:1) catalyst.

Ziegler-Natta polymerization catalysts might under some conditions be useful as dimerization or oligomerization catalysts. This does appear to be the case for bis-cyclopentadienylzirconium (zirconocene) complexes, one of the most important modern classes [4,5] of Ziegler-Natta catalysts. It is generally understood that methylalumoxane (MAO) is required to activate precursors such as Cp_2ZrCl_2 for catalysis, and that a large alumoxane excess (e.g. Al/Zr ratios of 500:1 up to 10 000:1) is most favorable for this polymerization

* Corresponding author. Tel.: + 1-510-642 2156; fax: + 1-510-642 7714; e-mail: bergman@cchem.berkeley.edu

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

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, in which the remaining C–C double bond allows further functionalization. Compared to other α-olefin dimerization reactions [10], the high regioselectivity of the zirconocene-catalyzed dimerization 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 CaH_2 and freshly distilled in flame dried glassware from CaH_2 under an Ar-atmosphere before use. A sample of **7** was prepared from phenylacetone and methyltriphenylphosphonium bromide using a standard procedure [12]; 2-bromo-1-hexene (**16**) was prepared from 2,3-dibromopropene and n-propylmagnesium bromide [13]; spectroscopic data for **7** [14] and **16** [15] were in agreement with literature values. Authentic samples of **3** and **6** were commercially available. Compound **8** was prepared following a literature procedure [16]. Zirconocene dichloride and zirconocene hydrido chloride 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] (40 g SiO_2, 80 g H_2O, 5.0 g $AgNO_3$). Elemental analyses were performed by the Microanalytical Laboratory and mass spectra were obtained by the Mass Spectrometry Laboratory at the University of California, Berkeley. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer. ^1H, ^2H and ^{13}C NMR spectra were obtained with a Bruker AMX-400 Fourier transform spectrometer. Assignments of ^{13}C-resonances were made using DEPT experiments. GC experiments were carried out on a HP 5890 gas chromatograph with FI detection and HP 3396A integrator. A 50 m capillary column containing 95:5 dimethylsilicone/methyl-

phenylsilicone (DB-5) as the stationary phase and helium carrier gas was used for the separation.

2.1. 2-Ethyl-1-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-butene (**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, $CDCl_3$): δ 0.92 (t, $J = 7.2$ Hz, 3H; CH_3), 1.04 (t, $J = 7.4$ Hz, 3H; CH_3), 1.28–1.37 (m, 2H; CH_2), 1.38–1.46 (m, 2H; CH_2), 2.00–2.06 (m, 4H; CH_2), 4.70 (s, 2H; $=CH_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 12.34 (CH_3), 13.96 (CH_3), 22.57 (CH_2), 28.77 (CH_2), 30.16 (CH_2), 36.04 (CH_2), 107.34 ($=CH_2$), 151.61 ($=C$) ppm. IR (neat): 3082(m), 3026(m), 2980(vs), 2933(vs), 2870(vs), 2733(w), 1782(w), 1645(s), 1460(vs), 1377(m), 1107(w), 887(s), 729(s), 694(m), 463(m) cm^{-1}. MS (EI, 70 eV): m/z (%): 112 (20) [M^+], 83 (7), 70 (100), 55 (72). Anal. Calc. for C_8H_{12} (108.18): C, 85.63; H, 14.37. Found: C, 85.81; H, 14.22%.

The alkenes **2b–2d** and **2f** are prepared analogously:

2.2. 2-Propyl-1-heptene (2b) [20]

From 1-pentene (**1b**) (7.53 g, 107 mmol), Cp_2ZrCl_2 (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, $CDCl_3$): δ 0.89 (t, $J = 7.0$ Hz, 3H; CH_3), 0.90 (t, $J = 7.3$ Hz, 3H; CH_3), 1.27–1.37 (m, 4H; CH_2), 1.38–1.50 (m, 4H; CH_2), 1.97–2.01 (m, 4H; CH_2), 4.69 (s, 2H; $=CH_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.84 (CH_3), 14.04 (CH_3), 20.97 (CH_2), 22.69 (CH_2), 27.61 (CH_2), 31.79 (CH_2), 36.08 (CH_2), 38.30 (CH_2), 108.59 ($=CH_2$), 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 (EI, 70 eV): m/z (%): 140 (28) [M^+], 97 (18), 84 (40), 69 (33), 58 (59), 56 (100). Anal. Calc. for $C_{10}H_{20}$ (140.27): C, 85.63; H, 14.37. Found: C, 85.66; H, 14.62%.

2.3. 2-Butyl-1-octene (2c) [21]

From 1-hexene (**1c**) (10.1 g, 120 mmol), Cp_2ZrCl_2 (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, $CDCl_3$): δ 0.90 (t, $J = 7.0$ Hz, 3H; CH_3), 0.91 (t, $J = 7.3$ Hz, 3H; CH_3), 1.27–1.45 (m, 12H; CH_2), 1.99–2.03 (m, 4H; CH_2), 4.70 (s, 2H; $=CH_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.99 (CH_3), 14.09 (CH_3), 22.60 (CH_2), 22.76 (CH_2), 27.91

(CH$_2$), 29.26 (CH$_2$), 30.14 (CH$_2$), 31.94 (CH$_2$), 35.87 (CH$_2$), 36.18 (CH$_2$), 108.44 (=CH$_2$), 150.11 (=C) ppm. IR (neat): 3072(m), 2958(vs), 2929(vs), 2858(s), 1645(m), 1460(s), 1379(m), 1115(w), 887(s), 728(m) cm^{-1}. MS (EI, 70 eV): m/z (%): 168 (20) [M^+], 126 (7), 111 (15), 98 (11), 84 (7), 83 (10), 70 (32), 56 (100). *Anal.* Calc. for C$_{12}$H$_{24}$ (168.32): C, 85.63; H, 14.37. Found: C, 85.39; H, 14.48%.

2.4. 2-Pentyl-1-nonene (2d)

From 1-heptene (**1d**) (5.90 g, 60.1 mmol), Cp$_2$ZrCl$_2$ (45 mg, 0.15 mmol), MAO (0.72 mmol, 1.05 g of a 4% solution in toluene), b.p. 71°C/0.20 mm, colorless liquid, yield: 4.84 g (24.6 mmol, 82%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.89 (t, $J = 7.0$ Hz, 3H; CH$_3$), 0.90 (t, $J = 7.0$ Hz, 3H; CH$_3$), 1.25–1.37 (m, 12H; CH$_2$), 1.38–1.47 (m, 4H; CH$_2$), 2.00 (t, $J = 7.6$ Hz, 4H; CH$_2$), 4.70 (s, 2H; =CH$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 14.06 (CH$_3$), 14.09 (CH$_3$), 22.66 (CH$_2$), 22.75 (CH$_2$), 27.57 (CH$_2$), 27.90 (CH$_2$), 29.34 (CH$_2$), 29.51 (CH$_2$), 31.75 (CH$_2$), 31.96 (CH$_2$), 36.10 (CH$_2$), 36.14 (CH$_2$), 108.39 (=CH$_2$), 150.25 (=C) ppm. IR (neat): 3073(w), 2956(s), 2927(vs), 2856(s), 1782(vw), 1645(m), 1461(m), 1379(w), 887(m), 725(w) cm^{-1}. MS (EI, 70 eV): m/z (%): 196 (21) [M^+], 140 (10), 125 (11), 112 (22), 97 (19), 84 (20), 70 (16), 69 (41), 56 (100). *Anal.* Calc. for C$_{14}$H$_{28}$ (196.38): C, 85.63; H, 14.37. Found: C, 85.98; H, 14.44%.

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

Zirconocene dichloride (220 mg, 0.75 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 r.t. 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$_3$): δ 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), 4.79 (s, 1H; =CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 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 (%): 140 (27) [M^+],

97 (7), 84 (67), 69 (100), 55 (35). *Anal.* Calc. for C$_{10}$H$_{20}$ (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) [1c]

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 14.4% 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$_3$): δ 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$_2$), 1.95 (t, $J = 7.6$ Hz, 2H; CH$_2$), 4.67 (m, 1H; =CH), 4.72–4.73 (m, 1H; =CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 22.57 (CH$_3$), 22.68 (CH$_3$), 25.61 (CH$_2$), 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). *Anal.* Calc. for C$_{12}$H$_{24}$ (168.32): C, 85.63; H, 14.37. Found: C, 85.48; H, 14.43%.

2.7. 5-Phenyl-2-(phenylmethyl)-1-pentene (2g) [22]

Zirconocene dichloride (214 mg, 0.73 mmol) was mixed with MAO (2.67 mmol, 3.88 g of a 4% solution in toluene), allylbenzene (**1g**) (7.80 g, 66 mmol) was added and the mixture was stirred at r.t. 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$_3$): δ 1.95–2.03 (m, 2H; CH$_2$), 2.27 (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; C$_6$H$_5$) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 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 (4CH), 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), 2979(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 (32), 132 (13), 117 (24), 104 (100), 91 (39), 65 (7). *Anal.* Calc. for C$_{18}$H$_{20}$ (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 $AgNO_3$ (pentane/Et_2O 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 Na_2SO_4. The Na_2SO_4 was washed with portions of pentane (3 × 10 ml) and the solvent was removed from the combined pentane solutions by rotary evaporation at r.t. The residual oil was heated to 150°C and transferred under high vacuum into a $N_2(l)$-cooled trap. Chromatography of this condensate (SiO_2, pentane) yielded analytically pure **9**, R_F (SiO_2, pentane) = 0.50, b.p. 89°C/13 mm, colorless liquid, yield: 2.46 g (15.5 mmol, 70%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.76–1.81 (m, 2H; 6-CH_2), 2.52 (t, $J = 6.2$ Hz, 2H; 7-CH_2), 2.92–2.94 (m, 2H; 5-CH_2), 3.51 (s, 2H; 3-CH_2), 4.77 (s, 1 H; C=CHH), 4.82 (s, 1H; C=CHH), 7.13–7.25 (m, 4H; Ar–H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 28.42 (6-CH_2), 35.20 (7-CH_2), 40.02 (5-CH_2), 44.03 (3-CH_2), 110.92 (=CH_2), 126.14 (Ar–CH), 126.35 (Ar–CH), 128.09 (Ar–CH), 128.92 (Ar–CH), 140.24 (Ar–C), 141.57 (Ar–C), 147.06 (=C) ppm. IR (neat): 3070(m), 3018(m), 2929(vs), 2840(s), 2247(m), 1643(s), 1490(s), 1448(s), 908(s), 735(vs), 642(m) cm^{-1}. MS (EI, 70 eV): m/z (%): 158 (87) [M^+], 143 (54), 129 (100), 115 (35), 91 (19). *Anal.* Calc. for $C_{12}H_{14}$ (158.24): C, 91.08; H, 8.92. Found: C, 91.01; H, 9.18%.

2.10. 2-Methyl-1-hexene (3)

As described for the preparation of **2c**, 1-hexene (2.85 g, 33.9 mmol), Cp_2ZrCl_2 (288 mg, 0.99 mmol) and MAO (3.87 mmol, 1.56 g of a 14.4% solution in toluene) were converted to the dimer. From the reaction crude, at 95–103°C a mixture containing E- and Z-2-hexene and 2-methyl-1-hexene (**3**) was obtained by fractional distillation through a 10 cm Vigreux column at 760 mm. Compound **3** was identified by ^1H NMR and by comparison with an authetic sample by GC.

2.11. Determination of turnover numbers

Cp_2ZrCl_2 (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 $CDCl_3$ and 0.1 g D_2O. Conversion values were obtained by integration of ^1H NMR spectra versus internal toluene (from MAO solution) standard. The reaction of $Cp_2Zr(H)Cl$ (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 (1h) [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 D_2O (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 **1h** (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, $CDCl_3$): δ 0.90 (t, $J = 7.2$ Hz, 3H; CH_3), 1.29–1.47 (m, 4H; CH_2), 2.04 (t, broad, 2H; CH_2), 4.95 (s, broad, 1H; =CHH), 5.01 (s, broad, 1H; =CHH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.72 (CH_3), 22.19 (CH_2), 31.18 (CH_2), 33.42 (CH_2), 113.8 (=CH_2), 138.5 (t, $J(^{13}C,^2H) = 23$ Hz; =CD) ppm. ^2H NMR (61.4 MHz, $CDCl_3$): δ 5.83 (s, broad) ppm. 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 **2c**, deuterated 1-hexene (**1h**) (2.93 g, 24.4 mmol), Cp_2ZrCl_2 (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 **2c** ($m/z = 168$) was detectable, and the ratio of mono-deuterated **2i** ($m/z = 169$) 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, CDCl$_3$): δ 0.89 (t, $J = 7.2$ Hz, 3H; CH$_3$), 0.91 (t, $J = 7.3$ Hz, 3H; CH$_3$), 1.27–1.42 (m, 10H; CH$_2$), 1.98 (s, broad, 2H; α-CH$_2$), 2.00 (t, broad, $J = 7.6$ Hz, 2H; α-CH$_2$), 4.69 (s, 2H; =CH$_2$) ppm. ^{2}H NMR (61.4 MHz, CHCl$_3$): δ 1.44 (s, broad, CD$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 13.96 (s, CH$_3$), 14.06 (s, CH$_3$), 22.60 (s, CH$_2$), 22.76 (s, CH$_2$), 27.12 (pentet, $J(^{13}$C,^{2}H) = 19.2 Hz, 4-CD$_2$), 29.07 (s, 5-CH$_2$), 30.15 (s, 2'-CH$_2$), 31.90 (s, 6-CH$_2$), 35.89 (s, 1'-CH$_2$), 36.00 (s, 3-CH$_2$), 108.44 (s, 1-CH$_2$), 150.04 (s, 2-C) ppm. IR (neat): 3072(m), 2958(s), 2925(s), 2862(s), 2187(m) [n(C–D)], 2106(m) [n(C–D)], 1645(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.: 170.2004; found: 170.1999.

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 ^{1}H NMR) was converted to a mixture of the dimers **2c**, **2i** 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 ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum, apart from resonances for **2c** and **2h**, the following signals are observed for the monodeuterated compound **2i**: δ 13.96 (s, CH$_3$), 14.06 (s, CH$_3$), 22.60 (s, CH$_2$), 22.76 (s, CH$_2$), 27.52 (t, $J(^{13}$C,^{2}H) = 19.2 Hz, 4-CHD), 29.27 (s, 5-CH$_2$), 30.15 (s, 2'-CH$_2$), 31.92 (s, 6-CH$_2$), 35.89 (s, 1'-CH$_2$), 36.09 (s, 3-CH$_2$), 108.44 (s, 1-CH$_2$), 150.04 (s, 2-C) ppm. HR MS (70 eV, EI): calc.: 169.1941; found: 169.1937.

3. Results and discussion

A catalyst prepared by mixing Cp$_2$ZrCl$_2$ 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 ^{1}H NMR, and the analytically pure dimers **2a–d** and **2f** 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 aliphatic 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
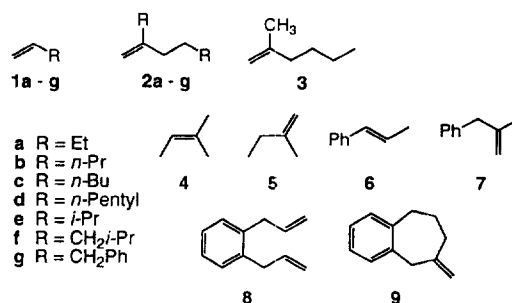
Table 1
Dimerization of 1-alkenes; yields and by-products

Educt	Product (yield (%)) [a]
1a	**2a** (75)
1b	**2b** (89)
1c	**2c** (90), **3**
1d	**2d** (82)
1e	**2e** (3), **4** (77) [b], **5** (17) [b]
1f	**2f** (90)
1g	**2g** (81), **6** (3), **7** (3) [c], (72) [d]
8	**9** (70)

[a] Isolated yields, if nothing else stated.
[b] By ^{1}H NMR of the crude reaction mixture.
[c] Based on **1d**.
[d] Based on MAO.

Scheme 2. Formulae of compounds listed in Table 1.

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 **2** themselves, seem to be stable under the reaction conditions.
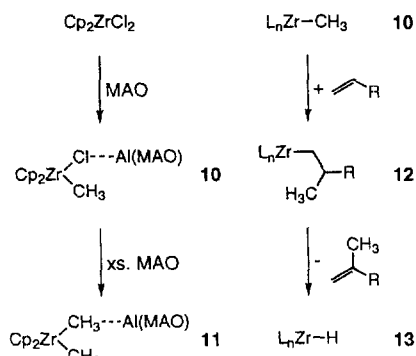
We decided to investigate whether this dimerization catalyst might cyclize α,ω-dienes [4], e.g. to form a seven-membered carbocycle [5]: reaction of o-diallylbenzene (**8**) with Cp$_2$ZrCl$_2$/MAO (3 days, r.t., 1 mol% Zr, Al/Zr = 4:1) does indeed give the benzannulated methylenecycloheptane (**9**), 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 Cp$_2$ZrCl$_2$ with a very large excess of MAO should lead to a complete displacement of Cl- by CH$_3$-ligands (at least for statistical reasons all Cl-atoms are transferred to Al-centers); the resulting Cp$_2$Zr(CH$_3$)$_2$–MAO adduct **11**

[3] The reaction between Cp$_2$ZrCl$_2$ and MAO in 1:1 ratio, without alkene present, has been reported before, see Ref. [24].

[4] 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 [25].

[5] There are only very few examples of transition metal mediated seven-membered carbocycle formations, for a review see Ref. [26].

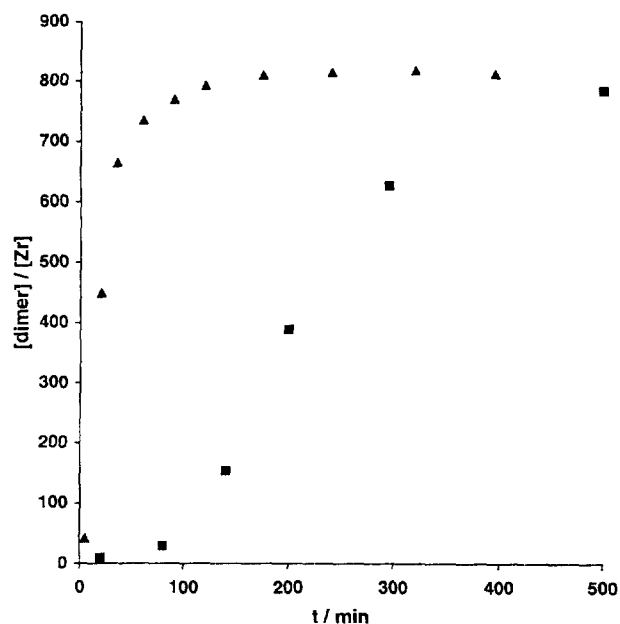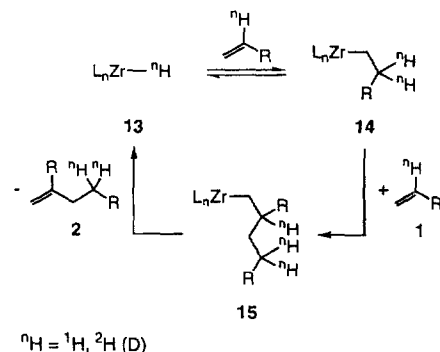Scheme 3. Formation of the catalytically active Zr–H complex.

Fig. 1. Plots of the ratio [dimer] / [Zr] vs. time for the catalytic dimerization of about 1700 equiv. of 1-hexene at 25°C: (■) Cp_2ZrCl_2/MAO catalysis; (▲) $Cp_2Zr(H)Cl/MAO$ catalysis.

(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 $Cp_2Zr(CH_3)Cl$ [28]/MAO and $Cp_2Zr(CH_3)_2/LiCl/MAO$ also give only dimeric product, whereas $Cp_2Zr(CH_3)_2/MAO$ and $Cp_2ZrCl_2/$ (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 $Cp_2Zr(H)Cl/MAO$ (1:1) also selectively dimerizes 1-hexene (1c) to give 2c. However, activation by MAO is necessary, as neither $Cp_2Zr(H)Cl$ itself nor this chloride activated by $AlCl_3$ or $Al(CH_3)_3$ performs the dimerization. Reactions of 1-hexene catalyzed by Cp_2ZrCl_2/MAO and $Cp_2Zr(H)Cl/MAO$ 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 Cp_2ZrCl_2/MAO catalysis becomes ~ 6 min⁻¹. Catalysis of $Cp_2Zr(H)Cl$ 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 Cp_2ZrCl_2 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–H bond of 13 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 Cp_2ZrCl_2/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 catalyt-

$^nH = {}^1H, {}^2H$ (D)

Scheme 4. Mechanism and catalytic cycle for the α-olefin dimer formation.

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–D catalyst **13**. The dimeric product **2** is predicted to be selectively dideuterated 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 Cp_2ZrCl_2/ MAO catalysis gives the 4,4-dideuterated product **2h**. Also, by GC, 2-methyl-1-hexene (**3**) could be detected. The selective dideutero incorporation was proved by ^1H, ^2H and ^{13}C 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 ^2H NMR spectrum of **2h**, a broad singlet at 1.44 ppm can be observed. In the ^{13}C 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 CD_2 carbon atom in **2h** is obvious. All other ^{13}C resonances for compound **2h** remain singlets. Moreover, when a sample of **1h** with only 75% deuterium incorporation in the two-position is dimerized, a mixture of non-deuterated **2c**, mono-deuterated **2i** and di-deuterated **2h** is obtained. Ratios of **2c**, **2i**, **2h** (determined by EI MS) in this case are close to the expected statistical values (see Section 2 for details). In the EI MS spectrum, **2h** shows the expected M^+-signal, and also signals at $m/z = 98$ and 128 for the McLafferty rearrangement [30] can be observed ($m/z = 98$ and 126 in case of **2c**).

The regio- and chemo-selective formation of α-olefin dimers with a Cp_2ZrCl_2/MAO ($\sim 1:1$) catalyst is different from and complementary to the olefin oligomerization process observed using larger Al/Zr ratios. Since simple 1-alkenes are readily available and since the C–C double bond functionality in the products allows further functionalization, the described process is a catalytic C–C bond forming reaction that can be used to prepare small building blocks for organic synthesis. Moreover, the intramolecular version of this reaction provides access to certain seven-membered carbocyclic products. Only 1-alkenes without an α-branch are reactive towards this dimer formation.

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 chemoselective dimer formation can be ascribed to chloro ligands remaining in the coordination sphere of the Zr-cata-

lyst, which make β-H elimination steps more favorable than insertion reactions.

Acknowledgements

References

[1] For recent examples of papers that discuss alkene dimerization, see: (a) A.M. Al-Jarallah, J.A. Anabtawi, M.A.B. Siddiqui, A.M. Aitani and A.W. Al-sa'doun, Catal. Today, 14 (1992) 1; (b) A.W. Al-Sa'doun, Appl. Catal. A: Gen., 105 (1993) 1; (c) S.J. McLain, J. Sancho and R.R. Schrock, J. Am. Chem. Soc, 102 (1980) 5610; (d) W.E. Piers, P.J. Shapiro, E.E. Bunel and J.E. Bercaw, Synlett. (1990) 74; (e) E. Hauptman, S. Sabo-Etienne, P.S. White, M. Brookhart, J.M. Garner, P.J. Fagan and J.C. Calabrese, J. Am. Chem. Soc., 116 (1994) 8038.

[2] (a) A. Andresen, H.-G. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Sinn and H.-J. Vollmer, Angew. Chem., 88 (1976) 689; Angew. Chem., Int. Ed. Engl., 15 (1976) 630; (b) H. Sinn, W. Kaminsky, H.-J. Vollmer and R. Woldt, Angew. Chem., 92 (1980) 396; Angew. Chem., Int. Ed. Engl., 19 (1980) 396.

[3] Review: H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R.M. Waymouth, Angew. Chem., 107 (1995) 1255; Angew. Chem., Int. Ed. Engl., 34 (1995) 1143.

[4] (a) J.A. Ewen, J. Am. Chem. Soc., 106 (1984) 6355; (b) W. Kaminsky, K. Külper, H.H. Brintzinger and F.R.W.P. Wild, Angew. Chem., 97 (1985) 507; Angew. Chem., Int. Ed. Engl., 24 (1985) 507; (c) J.A. Ewen, R.L. Jones, A. Razavi and J.D. Ferrara, J. Am. Chem. Soc., 110 (1988) 6255; (d) G. Erker, R. Nolte, Y.-H. Tsay and C. Krüger, Angew. Chem., 101 (1989) 642; Angew. Chem., Int. Ed. Engl., 28 (1989) 628; (e) Review: J. Okuda, Angew. Chem., 104 (1992) 49; Angew. Chem., Int. Ed. Engl., 31 (1992) 47.

[5] W. Kaminsky, A. Ahlers and N. Möller-Lindenhof, Angew. Chem., 101 (1989) 1304; Angew. Chem., Int. Ed. Engl., 28 (1989) 1216.

[6] (a) S. Jüngling and R. Mülhaupt, J. Organomet. Chem., 497 (1995) 27; (b) C. Janiak, U. Versteeg, K.C.H. Lange, R. Weimann and E. Hahn, J. Organomet. Chem., 501 (1995) 219.

[7] L.H. Slaugh and G.W. Schoenthal (Shell Oil Co.), US Patent No. 4 658 078 (1987) (Chem. Abstr., 107 (1987) P39178s).

[8] (a) J.C.W. Chien and B.-P. Wang, J. Polym. Sci. Part A: Polym. Chem., 26 (1988) 3089; (b) J. Polym. Sci. Part A: Polym. Chem., 27 (1989) 1539; (c) T. Tsutsui and N. Kashiwa, Polym. Comm., 29 (1988) 180; (d) B.W.S. Kolthammer, D.J. Mangold and D.R. Gifford, J. Polym. Sci. Part A: Polym. Chem., 30 (1992) 1017.

[9] J. Christoffers and R.G. Bergman, J. Am. Chem. Soc., 118 (1996) 4715.

[10] S.J. McLain, J. Sancho and R.R. Schrock, J. Am. Chem. Soc., 101 (1979) 5451.

[11] (a) D.Y. Kondakov and E. Negishi, J. Am. Chem. Soc., 117 (1995) 10771; (b) J. Am. Chem. Soc., 118 (1996) 1577.

[12] J. Kurze, D.J. Stein, P. Simak and R. Kaiser, Angew. Makromol. Chem., 12 (1970) 25.

[13] G.J. Martin and N. Naulet, Bull. Soc. Chim. Fr., (1970) 4001.

[14] R. Knorr and E. Lattke, Chem. Ber., 114 (1981) 2116.

[15] R.-J. Binnewirtz, H. Klingenberger, R. Welte and P. Paetzold, Chem. Ber., 116 (1983) 1271.

[16] A.M. Echavarren and J.K. Stille, J. Am. Chem. Soc., 110 (1988) 1557.
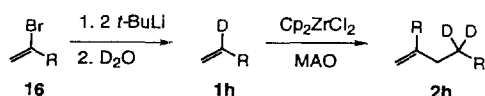
Scheme 5. Synthesis and dimerization of 2-deutero-1-alkene (R = n-Bu).

[17] L. Resconi, S. Boss and L. Abi, Macromolecules, 23 (1990) 4489.

[18] B.M. Lawrence, J. Chromatogr., 38 (1968) 535.

[19] A. Onopchenko, B.L. Cupples and A.N. Kresge, Ind. Eng. Chem. Prod. Res. Dev., 22 (1983) 182.

[20] H.J. Bestmann, P. Rösel and O. Vostrowsky, Liebigs Ann. Chem., (1979) 1189.

[21] H.Q. Liu, A. Deffieux and P. Sigwalt, Makromol. Chem., 192 (1991) 2111.

[22] M.E. Kuehne and P.J. Shannon, J. Org. Chem., 42 (1977) 2082.

[23] (a) R. Lazzaroni, G. Uccello-Barretta and M. Benetti, Organometallics, 8 (1989) 2323; (b) G. Sirokman, A. Molnar and M. Bartok, J. Lab. Comp. Radiopharm., 27 (1989) 439.

[24] D. Cam and U. Giannini, Makromol. Chem., 193 (1992) 1049.

[25] K.H. Shaughnessy and R.M. Waymouth, J. Am. Chem. Soc., 117 (1995) 5873.

[26] G. Dyker, Angew. Chem., 107 (1995) 2407; Angew. Chem., Int. Ed. Engl., 34 (1995) 2223.

[27] M. Bochmann, A.J. Jaggar and J.C. Nicholls, Angew. Chem., 102 (1990) 830; Angew. Chem., Int. Ed. Engl., 29 (1990) 780.

[28] R.F. Jordan, J. Organomet. Chem., 294 (1985) 321.

[29] (a) K. Soga, D.H. Lee and Y. Morikawa, Polymer, 33 (1992) 2408; (b) L. Resconi, F. Piemontesi, G. Franciscono, L. Abis and T. Fiorani, J. Am. Chem. Soc., 114 (1992) 1025.

[30] M. Hesse, H. Meier and B. Zeeh, Spektroskopische Methoden in der Organischen Chemie, Thieme, Stuttgart, 3rd edn., 1987, p. 213.