APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 316–324 (2000)

Zirconium-chelate and Mono-η-cyclopentadienyl Zirconium-chelate/methylalumoxane Systems as Soluble Ziegler–Natta Olefin Polymerization Catalysts

Christoph Janiak,[1]* Katharina C. H. Lange[2] and Tobias G. Scharmann[2]
[1]Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany
[2]Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany

Zirconium-chelate and mono-η-cyclopentadienyl zirconium-chelate complexes were tested as ethene and propene polymerization catalysts in combination with methylalumoxane (MAO) as a co-catalyst: in particular (acac)$_n$ZrCl$_{4-n}$ (1a–c) (acac = acetylacetonato), (dbm)$_n$ZrCl$_{4-n}$ (2a–2c) (dbm = dibenzoylmethanato = 1,3-diphenylpropanedionato) (n = 2–4) and (dbm)$_2$ZrCl$_2$(thf) (3) (thf = tetrahydrofuran), (η-C$_5$H$_5$)[H$_2$B(C$_3$H$_3$N$_2$)$_2$]ZrCl$_2$ (4), (η-C$_5$H$_5$)[HB (C$_3$H$_3$N$_2$)$_3$]ZrCl$_2$ (5) and (η-C$_5$H$_5$)[(Me$_3$SiN)$_2$ CPh]ZrCl$_2$ (6). Polymerization productivities comparable with the (η-C$_5$H$_5$)$_2$ZrCl$_2$ reference system were observed towards ethene for all of the above complexes. In addition, compound 6 showed some minor polymerization activity towards propene. Ethylalumoxane or isobutylalumoxane did not exhibit a co-catalytic activity for these chelate complexes; in combination with MAO these higher alumoxanes were even found to be deactivating ^{91}Zr NMR data are reported for 1b, 1c, 4 and 5. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: metallocene catalysis; single-site catalysts; chelate complexes; Ziegler–Natta catalysis; ethene polymerization; ^{91}Zr NMR

Received 13 September 1999; accepted 15 November 1999

INTRODUCTION

Homogeneous, single-site metallocene/methylalumoxane catalysts are of high academic and industrial interest as a new generation of Ziegler–Natta catalysts.[1] Despite the ongoing research on metallocene catalysts,[2] the search for yet another generation of olefin polymerization catalysts has already started. Such new-generation catalysts are coordination complexes with nitrogen-chelate ligands.[3] As further examples of polymerization catalysts beyond the metallocenes, we report here the catalytic behavior of molecular zirconium β-diketonato complexes (**1**–**3**),[4] cyclopentadienyl-[poly(pyrazolyl)borato]zirconium dichloride (**4** and **5**) and cyclopentadienyl[bis(trimethylsilyl)benzamidinato]zirconium dichloride, (**6**). The β-diketonato ligands employed were acetylacetonato = pentane-2,4-dionato (acac, in **1a**–**c**) and dibenzoylmethanato = 1,3-diphenylpropanedionato (dbm, in **2a**–**2c** and **3**). Dihydrobis(pyrazolyl)borato [H$_2$B(pz)$_2$ in **4**] and hydrotris(pyrazolyl)borato [HB(pz)$_3$, in **5**] were the poly(pyrazolyl)borato ligands used (Figure 1). The complexes were activated with methylalumoxane (MAO)[5] as a co-catalyst.

The use of these chelate ligands or complexes was based on the notion that compounds with two or more bis-chelate ligands can assume chiral Δ and Λ forms due to the relative orientation of the chelate ligands.[6] Chiral catalytic centers are a prerequisite for the tailored stereoregular coordination polymerization of prochiral α-olefins.[1,7] Furthermore, tetrakis(acetylacetonato)titanium, and acetylacetone itself, have been included in the early patent literature for the polymerization of α-olefins with alkylaluminum compounds as co-catalysts.[8] Claims in a patent on olefin polymerizations and a report on

---

* Correspondence to: Christoph Janiak, Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr: 21, 79104 Freiburg, Germany.
E-mail: janiak@uni-freiburg.de

Contract/grant sponsor: Deutsche Forschungsgemeinschaft; Contract/grant number: Ja466/3-1.
Contract/grant sponsor: Fonds der Chemischen Industrie.
Contract/grant sponsor: ‘Metal catalysts’ graduate college, TU Berlin.

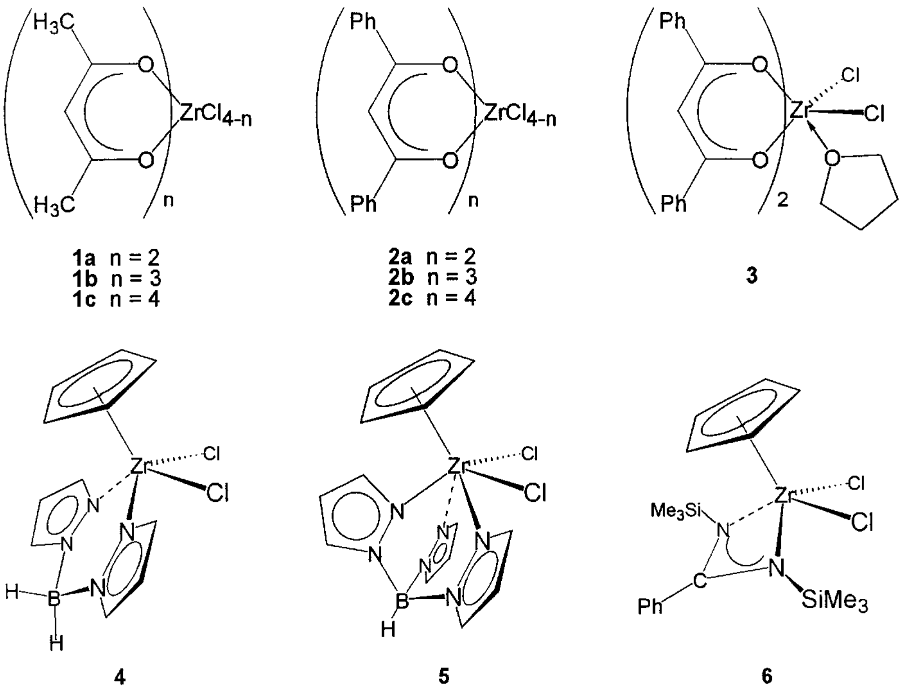

Figure 1

the polymerization of styrene with L_2ZrCl_2/MAO (L = β-diketonato; see **1b**, **2b**)[9,10] as well as a patent on styrene polymerization with **5**/MAO[11] indicate the interest in new ligand environments for soluble Ziegler–Natta olefin polymerization catalysts.[3,12,13] Of specific interest have become half-sandwich titanium and zirconium complexes containing an amido ligand linked to the cyclopentadienyl moiety by a dimethylsilylene bridge, **7** (Figure 2).[14] The mono-cyclopentadienyl zirconium-chelate complexes **4, 5** and **6** follow along the line of these *ansa*-cyclopentadienyl-amido catalysts **7**. In addition, the hydrotris(pyrazolyl)borato[15] and the benzamidinato ligands[16] are often seen as electronic or steric equivalents to the cyclopentadienyl ligand. As such, the mono-cyclopentadienyl zirconium-chelate complexes **5** and **6** can be viewed as metallocene mimics,[17] i.e. as closely related variations of the prototypical zirconocene dichloride Cp_2ZrCl_2 (Cp = cyclopentadienyl, C_5H_5) (**8**). Lanthanide complexes of the hydrotris(pyrazolyl)-borato ligand have been reported as ethene

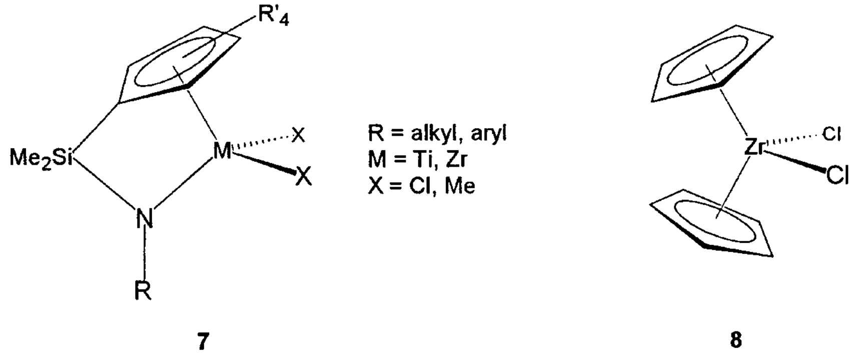

Figure 2

Table 1 Polymerization of ethene with zirconium-chelate complexes (**1**, **2** and **3**) and MAO[a]

Compound	Yield (g PE)	Activity (kg PE(g Zr^{-1})$h^{-1}bar^{-1}$)	M_w[b]	M_n[c] (g mol^{-1})	M_w/M_n
Cp_2ZrCl_2 (**8**)	29.9	21.9[d]	78 900	27 800	2.84
$(acac)_2ZrCl_2$ (**1a**)	14.5	10.6	563 200	215 300	2.62
$(acac)_3ZrCl$ (**1b**)	14.8	10.8	438 700	156 800	2.80
$(acac)_4Zr$ (**1c**)	15.6	11.4	414 500	136 000	3.05
$(dbm)_2ZrCl_2$ (**2a**)	17.0	12.4	242 500	82 600	2.94
$(dbm)_3ZrCl$ (**2b**)	12.7	9.3	391 000	124 100	3.15
$(dbm)_4Zr$ (**2c**)	16.2	11.8	301 000	82 000	3.67
$(dbm)_2ZrCl_2(thf)$ (**3**)	16.7	12.2	336 500	97 600	3.45

[a] Polymerization conditions: 300 ml toluene with 3×10^{-6} mol complex, and 12×10^{-3} mol MAO, equivalent to $[Zr] = 10^{-5}$ mol l^{-1} and a molar ratio of Al/Zr = 4000:1; $T = 70$ °C, $p = 5$ bar ethene.

[b] Weight-average molar mass.

[c] Number-average molar mass.

[d] The polymerization activities reported here for Cp_2ZrCl_2/MAO are lower than those given by Kaminsky *et al.*[20,21] This is due to the higher metallocene concentration and lower Al/Zr molar ratio employed here (see also Ref. 22)

polymerization catalysts.[18] Bis(trimethylsilyl) benzamidinatozirconium dichlorides have also been described as active polymerization catalysts.[13,19]

RESULTS AND DISCUSSION

Polymerization of complexes 1–3

The catalytic activities and polymer properties of the polyethenes obtained upon activation of **1**–**3** with MAO are listed in Table 1.

The activities of the zirconium chelates are somewhat lower than that of zirconocene dichloride, yet the molar masses of the polymers obtained are considerably higher. This suggests a slow and/or different chain-transfer reaction relative to the chain propagation. The polymer dispersity is rather narrow, thus indicating a close uniformity or single-site character of the active species. The slight broadening of the molar mass distribution can be ascribed to polymer precipitation which rapidly leads to a heterogeneous phase, i.e. a diffusion-controlled reaction. Thus, the polymerization is truly homogeneous only at the very beginning.[22]

When part of the MAO co-catalyst is replaced by trimethylaluminum (TMA), a strong increase in activity can be observed, with many of the zirconium-chelate complexes thereby approaching the activity of the Cp_2ZrCl_2 reference. The polymerization results upon activation with MAO and TMA are summarized in Table 2.

A similar MAO/TMA replacement in the Cp_2ZrCl_2/MAO system did not lead to appreciable changes in the polymer yield.[23] We note that compounds **1**, **2** and **3** cannot be activated by TMA alone towards the polymerization of ethene.

Table 2 Polymerization of ethene with zirconium-chelate complexes (**1**, **2** and **3**) and MAO/TMA[a]

Compound	Yield (g PE)	Activity (kg PE(g Zr^{-1})$h^{-1}bar^{-1}$)	M_w[b]	M_n[c] (g mol^{-1})	M_w/M_n
Cp_2ZrCl_2 (**8**)	31.3	22.9[d]	170 200	53 600	3.18
$(acac)_2ZrCl_2$ (**1a**)	14.8	10.8	494 000	187 300	2.64
$(acac)_3ZrCl$ (**1b**)	24.7	18.1	144 000	66 300	2.17
$(acac)_4Zr$ (**1c**)	24.9	18.2	401 500	130 000	3.09
$(dbm)_2ZrCl_2$ (**2a**)	19.6	14.3	519 200	166 600	3.12
$(dbm)_3ZrCl$ (**2b**)	36.7	26.8	238 600	85 700	2.78
$(dbm)_4Zr$ (**2c**)	25.4	18.6	188 000	80 600	2.33
$(dbm)_2ZrCl_2(thf)$ (**3**)	18.1	13.2	414 000	142 300	2.91

[a] Polymerization conditions: 300 ml toluene with 3×10^{-6} mol complex, 6×10^{-3} mol MAO and 6×10^{-3} mol TMA equivalent to $[Zr] = 10^{-5}$ mol l^{-1} and a molar ratio of $Al_{MAO}/Al_{TMA}/Zr$ = 2000:2000:1; $T = 70$ °C, $p = 5$ bar ethene.

[b,c,d] See corresponding footnotes in Table 1.

Table 3 Polymerization of ethene with zirconium-chelate complexes (**2**) and various alumoxanes[a]

Compound	Co-catalyst[b] (molar ratio to Zr)	Yield (g PE)	Activity (kg PE(g Zr^{-1})$h^{-1}$$bar^{-1}$)
$(dbm)_4Zr$ (**2c**)	EAO or IBAO (4000:1)	—	—
$(dbm)_4Zr$ (**2c**)	(EAO or IBAO)+TMA (4000:2000:1)	—	—
$(dbm)_2ZrCl_2$ (**2a**)	EAO or IBAO (4000:1)	—	—
$(dbm)_2ZrCl_2$ (**2a**)	(EAO or IBAO)+TMA (4000:2000:1)	—	—
$(dbm)_2ZrCl_2$ (**2a**)	EAO+MAO+TMA (4000:2000:2000:1)	6.9	5.0
$(dbm)_2ZrCl_2$ (**2a**)	IBAO+MAO+TMA (4000:2000:2000:1)	1.9	1.0

[a] Polymerization conditions: 300 ml toluene with 3×10^{-6} mol complex, equivalent to $[Zr] = 10^{-5}$ mol l^{-1}; $T = 70$ °C, $p = 5$ bar ethene

[b] EAO, ethylalumoxane; IBAO, isobutylalumoxane; MAO, methylalumoxane; TMA, trimethylaluminum.

The tetrakis(β-diketonato) complexes **1c** and **2c** are coordinatively saturated and do not contain any chloride ligands, yet they are catalytically active. Therefore, it must be assumed that the chelate ligands can be replaced by methyl groups from MAO or TMA to give an active species with an opening in the coordination sphere for the ethene monomer. While activation with MAO gives catalysts which differ only slightly in activity, a greater diversity is achieved in combination with TMA. Attempts to understand the origin of this diversity and the nature of the active species on the basis of ^{91}Zn NMR data were futile in our hands due to the very broad linewidths over 10 000 Hz together with very rapid relaxation times of the β-diketonato complexes. In toluene solution at an Al/Zr ratio of 1000:1 the ^{91}Zr NMR signals were as follows: $(acac)_2ZrCl_2$ (**1a**)/MAO 9.2 ppm, $(acac)_3ZrCl$ (**1b**)/MAO 156.6 ppm, $(acac)_4Zr$ (**1c**)/MAO 147.5 ppm and $(dbm)_3ZrCl$ (**2b**)/MAO 35.7 ppm.

In view of the apparent ease of β-diketonato ligand replacement in compounds **1**, **2** and **3**, experiments were undertaken with other alumoxanes such as ethylalumoxane (EAO) or isobutylalumoxane (IBAO) as activators. Alumoxanes other than the methyl derivative have so far failed to function as co-catalysts towards metallocenes, the reasons being still unclear. Economically it would, however, be extremely advantageous to replace the expensive MAO, as the meanwhile major cost factor in metallocene polymerization catalysis, by the much cheaper higher alumoxanes.[1] Also, the molecular structure of these higher alumoxanes is known,[24] whereas MAO is still ill-defined and therefore its functionality is not fully understood.[5]

The polymerization results with EAO and IBAO in a mixture with the zirconium-chelate complexes are summarized in Table 3. It is evident that EAO and IBAO alone, and even together with TMA, are inactive as co-catalysts. Furthermore, when EAO or IBAO are added to a zirconium complex activated with MAO/TMA the activity is decreased (cf. Table 2), thereby clearly demonstrating a deactivating effect of these higher alumoxanes. This is in contrast to reports on Cp_2ZrCl_2 with EAO or IBAO as a co-catalyst, where an activity could be observed.[21,25]

We note that in our hands, the zirconium-chelate complexes **1**, **2** and **3** did not exhibit polymerization activities towards propene or styrene, when activated with MAO. For propene the conditions chosen were similar to those in the ethene polymerization experiments. For styrene the monomer was freshly distilled from CaH_2 under reduced pressure, and 0.05 mmol of a catalyst from **1**, **2** or **3** was added to a solution of 100 ml of toluene, 33 ml of MAO (50 mmol of Al) and 20 ml of styrene (0.175 mol). Stirring at room temperature or 45 °C for several hours did not yield any polystyrene after hydrolysis. To explain the inactivity towards propene we suggest the formation of a stable adduct with the catalyst, possibly an allyl complex, which is no longer susceptible to monomer insertions. Evidence for formation, of an adduct is provided by feeding ethene to the reactor after venting off the propene, without hydrolysis of the catalyst. Then, no further ethene polymerization activity, which is normally encountered under these conditions, could be observed.

Polymerization of complexes 4, 5 and 6

The catalytic activities and polymer properties of the polyethenes obtained from the monocyclopentadienyl zirconium complexes with the nitrogen-

Table 4 Polymerization of ethene with catalytic systems consisting of monocyclopentadienyl zirconium complexes with nitrogen-chelate ligands (**4**, **5** and **6**) and MAO[a]

Compound	Al/Zr (mol mol^{-1})	Activity (kg PE(g Zr^{-1})$h^{-1}$$bar^{-1}$)	M_w[b]	M_n[c] (g mol^{-1})	M_w/M_n
Cp_2ZrCl_2 (**8**)	4000:1	19.7[d,e]	67 700	25 900	2.6
$Cp[H_2B(py)_2]ZrCl_2$ (**4**)	4000:1	19.3	87 800	39 100	2.2
$Cp[HB(py)_3]ZrCl_2$ (**5**)	4000:1	18.7	100 200	52 400	1.9
Cp_2ZrCl_2 (**8**)	4000:1	23.9[d,e]	107 000	36 900	2.9
$Cp[(Me_3SiN)_2CPh]ZrCl_2$ (**6**)	4000:1	20.9	111 000	40 000	2.8
$Cp[H_2B(py)_2]ZrCl_2$ (**4**)	8000:1	29.7	Not determined		
Cp_2ZrCl_2 (**8**)	10000:1	41.2[d,e]	71 900	34 500	2.1
$Cp[H_2B(py)_2]ZrCl_2$ (**4**)	10000:1	40.7	73 700	32 500	2.3
$Cp[HB(py)_3]ZrCl_2$ (**5**)	10000:1	47.7	74 800	32 600	2.3

[a] Polymerization conditions: 300 ml toluene with 3×10^{-6} mol complex, equivalent to [Zr] = 10^{-5} mol l^{-1} and different molar Al/Zr ratios (T = 80 °C).

[b,c,d] See corresponding footnotes in Table 1.

[e] The activities for Cp_2ZrCl_2 were determined directly before or after the comparative experiments given for **4** and **5** or **6**.

chelate rings upon activation with MAO are listed in Table 4.

The activities of the monocyclopentadienyl zirconium-chelate compounds are generally very similar, if not identical (within experimental error), to that of zirconocene dichloride. In addition, the polymer characteristics (M_w, M_n and M_w/M_n) are very similar. A slight increase in the molecular mass of polyethene from Cp_2ZrCl_2 (**8**) over $Cp[H_2B(py)_2]ZrCl_2$ (**4**) to $Cp[HB(py)_3]ZrCl_2$ (**5**) can be noted. The similarities are probably due to a closely related steric situation at the metal center in the complexes **4**, **5**, **6** and **8**. The electronic situation may also be similar, although it is known from other studies that changes in the electronic situation have a less pronounced effect on the activity than changes in the steric environment.[26] A polymerization activity of compound **6** towards ethene and propene has been reported,[13] but it has not been set in perspective to a reference system, e.g. Cp_2ZrCl_2. A comparison of the activities at different Al/Zr ratios for **4**, **5** and **8** shows the expected increase which is typical for most metallocene/MAO systems.[27]

The polymerization activity of **1a**–**1c**, **2a**–**2c**, **5** and **6** in combination with MAO was tested for propene. Among these systems, only the benzamidinato compound showed a measurable activity. The products were oily oligomers with number-average molar masses below 1000 g mol^{-1}.[28] Under the same conditions the activity of **6**/MAO was 0.3×10^3 g oligopropene/(g Zr)h, while Cp_2ZrCl_2 (**8**)/MAO gave 2.4×10^3 g oligopropene/(g Zr)h.

Conclusions

Comparative polymerization experiments with ethene as a monomer show that zirconium-chelate and monocyclopentadienyl zirconium-chelate complexes activated with MAO can reach the same catalytic activity as a zirconocene reference system. Furthermore, the important single-site character of metallocene catalysts is fully retained by the introduction of chelate ligands, as can be seen by the same narrow polymer dispersity. With β-diketonato zirconium complexes, the molar mass of the polymer can be increased considerably in comparison with the metallocene catalyst under the same conditions.

EXPERIMENTAL

Instruments

For CHN analysis a Perkin-Elmer Series II CHNS/O Analyzer 2400 and for IR spectroscopy a Nicolet Magna 750 instrument, were used.

NMR spectroscopy was carried out with a Bruker WP 80 SY, ARX 200 or ARX 400. ^1H and ^{13}C chemical shifts were referenced to TMS. ^{91}Zr NMR spectra were measured at ambient temperature against Cp_2ZrCl_2 as external reference (dissolved in a 1:1 mixture of CH_2Cl_2/CD_2Cl_2) with $\delta = -113$ ppm from Cp_2ZrBr_2.[29]

Mass spectrometry was performed with a Varian MAT 311A/AMD instrument. Mass spectrometry peaks given refer to the most abundant isotope combination, which comprises ^{90}Zr and ^{35}Cl, except when two chlorines are present. In this case, the peak arising from ^{90}Zr^{35}Cl^{37}Cl and ^{92}Zr^{35}Cl$_2$ is of maximum intensity, as was proven by an isotope simulation.

Molar masses and molar mass distributions of the polyethenes were determined by gel-permeation chromatography (GPC, Waters 150 chromatography) at 135 °C in 1,2,4-trichlorobenzene.

Materials

The zirconium chelate complexes were prepared according to the literature procedures, as indicated below. The purity was checked by melting points, elemental analysis, ^{1}H and ^{13}C NMR, and mass spectrometry (analytical data are summarized below). Biscyclopentadienylzirconium dichloride (Cp_2ZrCl_2) and anhydrous zirconium tetrachloride were purchased from Merck; dibenzoylmethane (dbmH) and tetrakis(acetylacetonato)zirconium-(IV) (**1a**) were from Aldrich and used as such. Acetylacetone was distilled prior to use. Methylalumoxane (MAO) was obtained from Witco (Bergkamen, Germany) as a 10 wt% toluene solution (4.92 wt% aluminum, density ≈ 0.9 g ml^{-1}, average molar mass of the MAO oligomers 900–1100 g mol^{-1}) unless noted otherwise. Ethylalumoxane and isobutylalumoxane were 10 and 15 wt% heptane solutions (3.34 and 3.71 wt% Al), respectively, from Witco. Trimethylaluminum (TMA) was used as a 2 M toluene solution from Aldrich. Solvents were dried over sodium metal (toluene and benzene), sodium benzophenone ketyl (pentane and diethyl ether) or potassium metal (hexane and thf) followed by distillation and storage under argon. Ethene and propene (BASF AG) were polymerization grade and used without further purification. All experiments were carried out under argon with standard Schlenk techniques.

In the following, besides melting point and CHN analysis as purity indicators, analytical data are given which could not be found in the original references.

Bis(acetylacetonato)zirconium dichloride, $(acac)_2ZrCl_2$ (1a)[30]

M.p. 183–185 °C (Lit. 180.5–182 °C,[31] 233–235 °C[32]). Found: C 32.99, H 3.71; $C_{10}H_{14}Cl_2O_4Zr$ requires C 33.33, H 3.92%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ (ppm) = 2.14 (s, 6H, CH_3), 5.98 (s, 1H, CH). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ/ppm = 26.49 (CH_3), 107.33 (CH), 193.46 (CO). EI MS: *m/z* (160 °C) 387 (9, $[(acac)_3Zr]^+$), 360 (6, $[M]^{+\cdot}$), 342 (9, $[M{-}CH_3]^+$), 323 (95, $[M{-}Cl]^+$), 307 (100, $[M{-}CH_3{-}Cl{-}H]^+$), 261 (13, $[M{-}acac]^+$), 242 (25, $[M{-}acac{-}OH]^{+\cdot}$) and 227 (25%, $[M{-}acac{-}CH_3{-}OH]^+$).

Tris(acetylacetonato)zirconium chloride, $(acac)_3ZrCl$ (1b)[30]

M.p. 165–167 °C (Lit. 159.5–161 °C[31]). Found: C 42.29, H 5.00; $C_{15}H_{21}ClO_6Zr$ requires C 42.49, H 4.99%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ(ppm) = 2.05 (s, 6H, CH_3), 5.78 (s, 1H, CH). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ(ppm) = 26.59 (CH_3), 104.82 (CH), 191.19 (CO). ^{91}Zr NMR (37.3 MHz, CH_2Cl_2/CD_2Cl_2): δ(ppm) = 77 ($\omega_{1/2}$ = 12600 Hz). EI MS: *m/z* (100 °C) 387 (100, $[M{-}Cl]^+$), 323 (5, $[M{-}acac]^+$), 305 (17, $[(acac)_2Zr(OH)]^+$), 287 (5, $[(acac)_2Zr{-}H]^+$), 225 (9, $[(acac)ZrCl(H)]^{+\cdot}$), 205 (9, $[(acac)Zr(O)]^+$) and 186 (6%).

Tetrakis(acetylacetonato)zirconium, $(acac)_4Zr$ (1c)

^{91}Zr NMR (37.3 MHz, CH_2Cl_2/CD_2Cl_2): δ(ppm) = −46 ($\omega_{1/2}$ = 13600 Hz).

Bis(dibenzoylmethanato)zirconium dichloride, $(dbm)_2ZrCl_2$ (2a)

To a slurry of $ZrCl_4$ (3.2 g, 13.7 mmol) in diethyl ether (25 ml) was added dropwise a solution of dibenzoylmethane (6.2 g, 27.6 mmol) in diethyl ether (60 ml). The resulting mixture was stirred for 40 h at room temperature, followed by refluxing for 6 h. The green–yellow precipitate obtained upon cooling was separated by filtration and dried *in vacuo* to yield a fine powder (8.0 g, 96%), m.p. 280 °C (dec.). The compound was only sparingly soluble in boiling toluene or benzene. Found: C 59.18, H 3.58; $C_{30}H_{22}Cl_2O_4Zr$ requires C 59.20, H 3.64%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ(ppm) = 7.37 (s, 1H, CH), 7.56 ('tt', 2H, *m*-C_6H_5, '$^{2/3}J_{H,H}$ = 7/2 Hz'), 7.69 ('tt', 1H, *p*-C_6H_5, '$^{2/3}J_{H,H}$ = 7/2 Hz'), 8.15 ('td', 2H, *o*-C_6H_5, '$^{2/3}J_{H,H}$ = 7/2 Hz'). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ(ppm) = 99.30 (CH), 128.47, 128.87, 128.96 129.33, 132.93 (*o*-, *m*-, *p*-C_6H_5), 134.34, 135.55 (*i*-C_6H_5), 185.33 (CO); the compound was not volatile enough for mass-spectrometrical investigations. [The quotation marks around the splitting pattern and the coupling constants are meant to indicate the superficial appearance. The hindered rotation of the phenyl rings actually gives rise to an AA′BB′C coupling system.]

Tris(dibenzoylmethanato)zirconium chloride, $(dbm)_3ZrCl$ (2b)[33]

M.p. 280–282 °C (Lit. 256–258 °C[32]). Found: C 67.52, H 4.11; $C_{45}H_{33}ClO_6Zr$ requires C 67.87, H 4.18%.

Tetrakis(dibenzoylmethanato)zirconium, $(dbm)_4Zr$ (2c)[34]

M.p. 250–252 °C (Lit. 245–246 °C[34]). Found: C 73.22, H 4.34; $C_{60}H_{44}O_8Zr$ requires C 73.22, H 4.51%. ^1H NMR (200 MHz, CD_2Cl_2): δ(ppm) = 6.93 (s, 1H, CH), 7.36 ('tt', 2H, *m*-C_6H_5, '$^{2/3}J_{H,H}$ = 7/2 Hz'), 7.48 ('tt', 1H, *p*-C_6H_5, '$^{2/3}J_{H,H}$ = 7/2 Hz'), 8.05 ('td', 2H, *o*-C_6H_5, '$^{2/3}J_{H,H}$ = 7/2 Hz'). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ(ppm) = 95.98 (CH), 128.23, 128.54, 131.78 (*o*-, *m*-, *p*-C_6H_5), 138.76 (*i*-C_6H_5, 183.21 (CO). EI MS: *m/z* (300 °C) 759 (100, $[M{-}\text{dbm}]^+$), 329 (20, $[(\text{dbm})Zr(O)]^+$), 267 (36), 223 (59, $[\text{dbm}]^+$), 165 (21), 147 (27, $[C_6H_5COCH_2CHO]^+$) and 105 (72%, $[C_6H_5CO]^+$).

Bis(dibenzoylmethanato)zirconium dichloride–tetrahydrofuran adduct, $(dbm)_2ZrCl_2(thf)$ (3)

Tetrahydrofuran (thf, 60 ml) was added to **2a** (8.0 g, 13.1 mmol). The solid initially dissolved completely to a clear solution from which a green–yellow precipitate was obtained after a few minutes. This precipitate was dissolved again almost completely upon warming to 50 °C, and the solution was filtered. Storing the clear, yellow solution at 2 °C overnight gave yellow needle-shaped crystals. The mother liquor was decanted and discarded, the crystals dried *in vacuo* (yield 7.1 g, 80%, not optimized). Found: C 59.63, H 4.30; $C_{34}H_{30}Cl_2O_5Zr$ requires C 59.99, H 4.44%. ^1H NMR (200 MHz, CD_2Cl_2): δ (ppm) 1.83 (m, 4H, thf), 3.75 (m, 4H, thf), 7.37 (s, 2H, CH), 7.51 ('tt', 8H, *m*-C_6H_5, '$^{2/3}J_{H,H}$ = 7/2 Hz'), 7.63 ('tt', 4H, *p*-C_6H_5, '$^{2/3}J_{H,H}$ = 7/2 Hz'), 8.10 ('td', 2H, *o*-C_6H_5, '$^{2/3}J_{H,H}$ = 7/2 Hz'). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ(ppm) = 25.90 (thf), 68.90 (thf), 99.37 (CH), 128.85, 129.31, 134.31 (*o*-, *m*-, *p*-C_6H_5), 135.55 (*i*-C_6H_5), 185.30 (CO). EI MS: *m/z* (300 °C) 759 (10, $[(\text{dbm})_3Zr]^+$), 606 (7, $[M{-}\text{thf}]^{+}\cdot$), 571 (100, $[M{-}\text{dbm}{-}\text{thf}]^+$), 555 (14), 267 (26), 129 (18, $[C_6H_5COCC]^+$), 105 (84%, $[C_6H_5CO]^+$).

Cyclopentadienyl[dihydrobis(pyrazolyl)borato]-zirconium dichloride, $(\eta\text{-}C_5H_5)[H_2B(C_3H_3N_2)_2]ZrCl_2$ (4)[35]

Found: C 35.23, H 3.52, N 14.72; $C_{11}H_{13}BCl_2N_4Zr$ requires C 35.31, H 3.50, N 14.97%. ^{91}Zr NMR (37.3 MHz, CH_2Cl_2/CD_2Cl_2, c = 80 mg ml^{-1}): δ(ppm) = 53 ($\omega_{1/2}$ = 1060 Hz).

Cyclopentadienyl[hydrotris(pyrazolyl)borato]-zirconium chloride, $(\eta\text{-}C_5H_5)[HB(C_3H_3N_2)_3]ZrCl_2$ (5)[35]

Purified by sublimation. Found: C 39.03, H 3.42, N 20.17; $C_{14}H_{15}BCl_2N_6Zr$ requires C 38.19, H 3.43, N 19.09%. ^{91}Zr NMR (37.3 MHz, CH_2Cl_2/CD_2Cl_2, c = 35 mg ml^{-1}): δ (ppm) = 22 ($\omega_{1/2}$ = 1280 Hz).

Cyclopentadienyl[bis(trimethylsilyl)benzamidinato]zirconium dichloride, $(\eta\text{-}C_5H_5)[(Me_3SiN)_2CPh]ZrCl_2$ (6)[13]

From $(\eta\text{-}C_5H_5)ZrCl_3(dme)$[36] and $Li[(Me_3SiN)_2CPh]$.[37] Found: C 44.02, H 5.44, N 5.89; $C_{18}H_{28}Cl_2N_2Si_2Zr$ requires C 44.06, H 5.75, N 5.71%. EI MS: *m/z* (180 °C) 490 (6, $[M]^{+}\cdot$), 475 (20, $[M{-}CH_3]^+$), 425 (100, $[M{-}C_5H_5]^+$), 263 (10, $[(Me_3SiN)_2CPh]^+$), 176 (17, $[Me_3SiNCPh]^{+}\cdot$), 146 (16, $[MeSiNCPh]^{+}\cdot$), 73 (83, $[Me_3Si]^+$).

Polymerizations

Polymerizations were carried out in a 1-liter Büchi-glass autoclave, thermostated to the chosen temperature (70 or 80 °C) and charged with 300 ml toluene, MAO (or another alumoxane), alone or with TMA, and the transition metal complex. The catalyst amount, concentration and Al/Zr ratio are specified in the respective Tables. After a pre-activation (ageing) time of 10 min the autoclave was pressurized with 5 bar ethene or propene and after 1 h the reaction was stopped by draining the toluene/polyethene slurry into acidified water. The polymer was separated by filtration, washed with hexane and dried at 80 °C. To ensure reproducibility, polymerizations were carried out at least twice with each zirconium complex.

For propene the autoclave was charged with the monomer up to a pressure of 5 bar at 50 °C. The concentrations of the zirconium complexes were 10^{-4} mol l^{-1}; the Al/Zr molar ratio was 4000:1.

Acknowledgements This work was supported by the Deutsche Forschungsgemeinschaft (grant Ja466/3-1), the Fonds der Chemischen Industrie, and the 'metal catalysts' graduate college at TU Berlin. Generous gifts of chemicals and analyses of polymers by BASF AG, Ludwigshafen, are highly appreciated.

REFERENCES

1. Reviews: Janiak C. Chapter 9. In *Metallocenes*, Vol. 2, Togni A, Halterman RL (eds). Wiley–VCH: Weinheim, 1998; 547; Alt HG. *J. Chem. Soc., Dalton Trans.* 1999; 1703. Kaminsky W. *Chem. Br.* 1998; February: 43. Kaminsky W. *J. Chem. Soc., Dalton Trans.* 1998; 1413. Kashiwa N, Imuta J-I. *Catal. Surveys Jpn.* 1997; **1**: 125. Brintzinger HH, Fischer D, Mülhaupt R, Rieger B, Waymouth RM. *Angew. Chem., Int. Ed. Engl.* 1995; **34**: 1143.
2. Recent examples: Green ML, Saßmannshausen J. *Chem. Commun.* 1999; 115. Leclerc MK, Waymouth RM. *Angew. Chem., Int. Ed. Engl.* 1998; **37**: 922. Ewen JA, Jones RL, Elder MJ, Rheingold AL, Liable-Sands LM. *J. Am. Chem. Soc.* 1998; **120**: 10786. Schaverier CJ, Ernst R, Schut P, Skiff WM, Resconi L, Barbassa E, Balboni D, Dubitsky YA, Orpen AG, Mercandelli P, Moret M, Sironi A. *J. Am. Chem. Soc.* 1998; **120**: 9945. Chen Y-X, Metz MV, Li L, Stern CL, Marks TJ. *J. Am. Chem. Soc.* 1998; **120**: 6287. Karl J, Dahlmann M, Erker G, Bergander K. *J. Am. Chem. Soc.* 1998; **120**: 5643. Resconi L, Piemontesi F, Camurati I, Sudmeijer O, Nifant'ev IE, Ivchenko PV, Kuz'mina LG. *J. Am. Chem. Soc.* 1998; **120**: 2308. Margl P, Deng L, Ziegler T. *Organometallics* 1998; **17**: 933. Roscoe SB, Fréchet JMJ, Walzer JF, Dias AJ. *Science* 1998; **280**: 270.
3. Britovsek GJP, Gibson VC, Kimberley BS, Maddox PJ, McTavish SJ, Solan GA, White AJP, Williams DJ, *Chem. Commun.* 1998; 849. Small BL, Brookhart M, Bennett AMA. *J. Am. Chem. Soc.* 1998; **120**: 4049. Britovsek GJ, Gibson VC, Wass DF. *Angew. Chem., Int. Ed. Engl.* 1999; **38**: 428. Haggin J. *Chem. Eng. News*, 1996; 5 February: 6.
4. For a preliminary report on part of this work, see Janiak C, Scharmann TG, Lange KCH. *Macromol. Rapid Commun.* 1994; **15**: 655.
5. Janiak C, Rieger B, Voelkel R, Braun HG. *J. Polym. Sci. A: Polym. Chem.* 1993; **31**: 2959.
6. See, for example: Greenwood NN, Earnshaw A. *Chemistry of the Elements*. Pergamon Press: Oxford, 1984; 1079–1080. Shriver DF, Atkins PW, Langford CH. *Inorganic Chemistry*, 2nd ed., Oxford University Press: Oxford, 1994; 242–244. Huheey JE, Kreiter EA, Kreiter RL. *Inorganic Chemistry*, 4th ed., HarperCollins: New York, 1993; 492–496.
7. Kaminsky W, Külper K, Brintzinger HH, Wild FRWP. *Angew. Chem., Int. Ed. Engl.* 1985; **24**: 507. Rieger B, Mu X, Mallin DT, Rausch MD, Chien JCW. *Macromolecules* 1990; **23**: 3559.
8. Ziegler K, Breil H, Martin H, Holzkamp E. US Patent 3257332, 1954; *Chem. Abstr.* 1966; **65**: 7308d. Meyer G, Siggel E, Roesener W. (Glanzstoff AG). German Patent 1236790, 1967; *Chem. Abstr.* 1967; **67**: 11947y. Zuech FA. (Phillips Petroleum Co.) US Patent 3393245, 1968; *Chem. Abstr.* 1968; **69**: 51519h.
9. Ueki S, Furubashi H, Murata M, Toki S. US Patent (Tonen Corporation) 5223465, 1993; *Chem. Abstr.* 1990; **116**: 7090b.
10. Longo P, Proto A, Oliva L. *Macromol. Rapid Commun.* 1994; **15**: 151.
11. Wang SJ, Chen Y-C, Chan S-H, Tsai J-C, Shen Y-HE, US Patent 5519099 1996. Hlatky GG. *Coord. Chem. Rev.* 1999; **181**: 243. Newman TH. (Dow Chemical Co.) EP 482934, 1992; *Chem. Abstr.* 1992; **117**: 172275u.
12. van der Linden A, Schaverien CJ, Mejiboom N, Ganter C, Orpen AG. *J. Am. Chem. Soc.* 1995; **117**: 3008. Mu Y, Piers WE, Macgillivrary LR, Zaworoko MJ. *Polyhedron* 1995; **14**: 1. Mitani M, Oouchi K, Hayakawa M, Yamada T, Mukaiyama T. *Polym. Bull.* 1995; **34**: 199.
13. Chernega AN, Gómez R, Green MLH. *J. Chem. Soc., Chem. Commun.* 1993; 1415. Gómez R, Duchateau R, Chernaga AN, Meetsma A, Edelmann FT, Teuben JH, Green MLH. *J. Chem. Soc., Dalton Trans.* 1995; 217. Gómez R, Duchateau R, Chernaga AN, Teuben JH, Edelmann FT, Green MLH. *J. Organomet. Chem.* 1995; **491**: 153.
14. Okuda J, Eberle T. Chapter 7. In *Metallocenes*, Vol. 1, Togni A, Halterman RL, (eds). Wiley–VCH, 1998; 415. McKnight AL, Waymouth RM. *Chem. Rev.* 1998; **98**: 2587. Okuda J, Schattenmann FJ, Wocadlo S, Massa W. *Organometallics*, 1995; **14**: 789. Herrmann WA, Morawietz MJA. *J. Organomet. Chem.* 1994; **482**: 169. Shapiro PJ, Cotter WD, Schaefer WP, Labinger JA, Bercaw JE. *J. Am. Chem. Soc.* 1994; **116**: 4623. Böhme U, Thiele K-H. *J. Organomet. Chem.* 1994; **472**: 39.
15. Trofimenko S. *Scorpionates— Polypyrazolylborate Ligands and their Coordination Chemistry*. Imperial College Press: London, 1999. Trofimenko S. *Chem. Rev.* 1993; **93**: 943.
16. Hagen C, Reddmann H, Amberger H-D, Edelmann FT, Pegelow U, Shalimoff GV, Edelstein NM. *J. Organomet. Chem.* 1993; **462**: 69, and references therein.
17. Barnhart RW, Bazan GC, Mourey T. *J. Am. Chem. Soc.* 1998; **120**: 1082.
18. Long DP, Bianconi PA. *J. Am. Chem. Soc.* 1996; **118**: 12453.
19. Herskovics-Korine D, Eisen MS. *J. Organomet. Chem.* 1996; **503**: 307. Walther D, Fischer R, Görls H, Koch J, Schweder B. *J. Organomet. Chem.* 1996; **508**: 13.
20. Sinn Hj., Kaminsky W, Vollmer H-J, Woldt R. *Angew. Chem., Int. Ed. Engl.* 1980; **19**: 390. Kaminsky W, Schlobohm M. *Makromol. Chem., Makromol. Symp.* 1986; **4**: 103.
21. Kaminsky W, Miri M, Sinn H, Woldt R. *Makromol. Chem., Rapid Commun.* 1983; **4**: 417.
22. Rieger B, Janiak C. *Angew. Makromol. Chem.* 1994; **215**: 35.
23. Chien JCW, Wang B-P. *J. Polym. Sci., Part A: Polym. Chem.* 1988; **26**: 3089.
24. Reviews: *Macromolecular Symp.* 1995; **97**: 1, with the lectures of the macromolecular colloquium on alumoxanes in Hamburg, 1994. Pasynkiewicz S. *Polyhedron* 1990; **9**: 429.
25. Kaminsky W, Steiger R. *Polyhedron* 1988; **7**: 2375.
26. Janiak C, Lange KCH, Versteeg U, Lentz D, Budzelaar PHM. *Chem. Ber.* 1996; **129**: 1517. Janiak C, Versteeg U, Lange KCH, Weimann R, Hahn E. *J. Organomet. Chem.* 1995; **501**: 219.
27. Rieger B, Janiak C. *Angew. Makromol. Chem.* 1994; **215**: 35. Rieger B, Mu X, Mallin DT, Rausch MD, Chien JCW. *Makromolecules* 1990; **23**: 3559. Chien JCW, Wang BP. *J.*

Polym. Sci: Part A, Polym. Chem. 1990; **28**: 15. Ewen JA. *J. Am. Chem. Soc.* 1984; **106**: 6355.
28. Janiak C, Lange KCH, Marquardt P. *Macromol. Rapid Commun.* 1995; **16**: 643.
29. Benn R, Rufinska A. *Angew. Chem., Int. Ed. Engl.* 1986; **25**: 861.
30. Pinnavaia TJ, Fay RC. *Inorg. Synth.* 1970; **12**: 88.
31. Pinnavaia TJ, Fay RC. *Inorg. Chem.* 1968; **7**: 502.
32. Cox M, Lewis J, Nyholm RS. *J. Chem. Soc.* 1964; 6113.
33. Janiak C, Scharmann TG. *Acta Crystallogr. Sect. C* 1998; **54**: 210.
34. Chun HK, Steffen WL, Fay RC. *Inorg. Chem.* 1979; **18**: 2458.
35. Reger DL, Mahtab R, Baxter JC, Lebioda L. *Inorg. Chem.* 1986; **25**: 2046.
36. Lund EC, Livinghouse T. *Organometallics* 1990; **9**: 2426.
37. Boeré RT, Oakley RT, Reed RW. *J. Organomet. Chem.* 1987; **331**: 161. Roesky HW, Meller B, Noltemeyer M, Schmidt H-G, Scholz U, Sheldrick GM. *Chem. Ber.* 1988; **121**: 1403.