Journal of Organometallic Chemistry 658 (2002) 242–250

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and cyclic voltammetry of 1,2,3-trisubstituted bis(cyclopentadienyl)zirconium dichlorides

Bernhard J. Rausch, Rolf Gleiter *, Frank Rominger

Organisch-Chemisches Institut, Universität Heidelberg, INF 270, D-69120 Heidelberg, Germany

Received 18 March 2002; accepted 7 June 2002

Abstract

The synthesis of the 1,2,3-trisubstituted cyclopentadienes **3**–**10** and their corresponding zirconocene dichlorides **11**–**18** from commercially available internal alkynes is presented. The solid state structures of the differently substituted zirconocenes **11**–**13** and **15**–**17** were examined by means of X-ray analysis. The bite angles have shown not to be dependent on the substitution pattern of the cyclopentadienyl ligand. Cyclic voltammetry was used to measure the effect of introducing electron withdrawing and donating groups at the five membered ligand on the Lewis acidity of the zirconium central atom. © 2002 Published by Elsevier Science B.V.

Keywords: Zirconocene dichloride; Cyclic voltammetry; Cyclopentadiene; Pauson–Khand reaction

1. Introduction

The synthesis of substituted cyclopentadienyls, which were often used as ligands in organometallic chemistry, is strongly connected with the search for modified stereospecific and highly versatile metallocene catalysts for olefin polymerization. The substitution pattern of the ligand core has proven to be crucial for the reactivity of metallocene dichlorides (Cp_2MCl_2) [1] like zirconocene [2,3b] or titanocene [3] derivatives.

The stability of the active species in the polymerization reaction can be mainly attributed to steric and electronic effects. Especially, the steric influence of cyclopentadienyl ring substituents on the stereospecificity of olefin polymerization by zirconocenes has been extensively examined in experimental studies [4] as well as model calculations [5]. To investigate the electronic effects of the substitution pattern at the ligand core of metallocenes ESCA [6] as well as cyclic voltammetry [7] have been used. For instance, it has been shown that the redox potential of zirconocene dichlorides is depending on the number of trimethylsilyl-groups [7c] at the cyclopentadienyl ligand.

However, most zirconocene based catalysts incorporate many different substituents at the same time at the cyclopentadienyl unit and therefore we found it of interest to take a closer look at the influence of the specific electronic nature of each substituent at the five-membered ligand. Since especially the stereoselective synthesis of bis(trisubstituted) metallocenes has seen rising attention in recent publications [8], we envisioned to elucidate the effect of the electronic nature of the substituents in these kind of catalyst systems.

In this work we report the synthesis of several 1,2,3-trisubstituted cyclopentadienes and their zirconocene dichlorides. Additionally, the study of the redoxpotentials of the corresponding metallocenes by means of cyclic voltammetry is presented.

2. Results

To generate an easy access to 1,2,3-trisubstituted cyclopentadienes we had to develop a straight forward synthesis of 1,2-disubstituted *cyclo*pentenones which are allowed to react with differently substituted aryllithium reagents in a Grignard type reaction to yield the corresponding cyclopentadienes. Even though many methods have been reported in the literature for the synthesis of cyclopentenones, they often suffer from not

---

* Corresponding author. Tel.: +49-6221-548-400; fax: +49-6221-544-205

E-mail address: rolf.gleiter@urz.uni-heidelberg.de (R. Gleiter).

PII: S0022-328X(02)01665-0

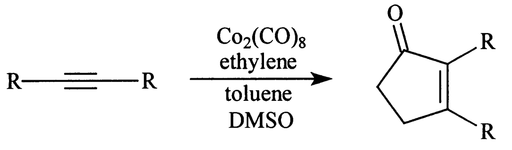
being general [9] as well as from producing mostly moderate yields [10] or isomeric mixtures [11]. Therefore, we synthesized the ketones from commercially available twofold substituted alkynes (2-butyne and 3-hexyne) and applied the Pauson–Khand [12] protocol using ethylene [13] as olefin component in toluene solution in the presence of DMSO as promotor (Scheme 1). The cyclopentenones **1** and **2** were isolated in 68–99% yield.

To generate the corresponding cyclopentadienes, **1** and **2** were allowed to react with several aryllithium reagents [14] in diethyl ether at −78 °C and after mild acidic hydrolysis the cyclopentadienes **3**–**10** were isolated in very high yields (Scheme 2).

Treatment of **3**–**10** in toluene solution with 1 equivalent of *n*-butyllithium yielded the corresponding 1,2,3-trisubstituted cyclopentadienyl ligands. Subsequently, 0.5 equivalents of $ZrCl_4(thf)_2$ were added and after 3 days stirring under reflux the corresponding zirconocene dichlorides **11**–**18** were obtained as mixtures of stereoisomeres (*rac*/*meso*, 85–70% yield of crude metallocene products). By iterative recrystallization from mixtures of *n*-hexane and toluene the isomerically pure metallocenes were isolated in 2–21% yield (Scheme 3). Increasing solubility of the zirconocenes in *n*-hexane led to decreasing yields obtained after purification, e.g. rather unpolar **18** could only be isolated in poor yield (2%), while isomerically pure **11** was isolated in 21% yield after recrystallization.

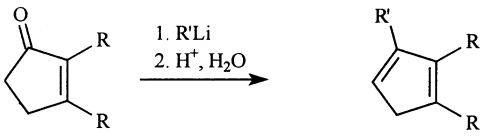
The stereochemistry of **11**–**13** and **15**–**17** was deduced by X-ray analysis on single crystals, for the *p*-$(Me_3C)C_4H_4$-substituted derivatives **14** and **18** no single crystals could be obtained. For **15** the *meso*-metallocene and for **12**, **13**, **16** and **17** the *rac*-compounds were isolated isomerically pure. Only for **11** both stereoisomers could be separated.

Fig. 1 shows the solid state structures of the 1-naphthyl- (*rac*-**13**) and the *o*-fluorphenyl-substituted zirconocenes (*meso*-**15**). The bite angles α, Cp(centroid)–Zr–Cp(centroid), are 130.3 and 129.7°, respectively, thus only slightly depending on the substitution pattern at the cyclopentadienyl ligand and on differences of the electronic nature of the substituents. Similar bite angle values have been reported in the literature [8,15]. Further selected angles and bond lengths are given in Table 1.



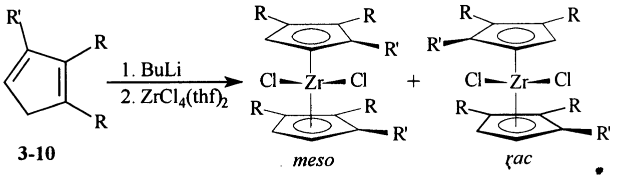
1 R = Me (99 %)
2 R = Et (68 %)

Scheme 1.



1 R = Me
3 R = Me, R' = Ph (95 %)
4 R = Me, R' = p-MeC$_4$H$_4$ (91 %)
5 R = Me, R' = 1-naphthyl (99 %)
6 R = Me, R' = p-(Me$_3$C)C$_4$H$_4$ (90 %)
7 R = Me, R' = o-FC$_4$H$_4$ (90 %)
2 R = Et
8 R = Et, R' = Ph (99 %)
9 R = Et, R' = p-MeC$_4$H$_4$ (99 %)
10 R = Et, R' = p-(Me$_3$C)C$_4$H$_4$ (97 %)

Scheme 2.



11 R = Me, R' = Ph (21 %, *meso*)
12 R = Me, R' = p-MeC$_4$H$_4$ (19 %, *rac*)
13 R = Me, R' = 1-naphthyl (18 %, rac)
14 R = Me, R' = p-(Me$_3$C)C$_4$H$_4$ (10 %, single isomer)
15 R = Me, R' = o-FC$_4$H$_4$(17 %, *meso*)
16 R = Et, R' = Ph (14 %, *rac*)
17 R = Et, R' = p-MeC$_4$H$_4$ (7 %, *rac*)
18 R = Et, R' = p-(Me$_3$C)C$_4$H$_4$ (2 %, single isomer)

Scheme 3.

To substantiate the view that each substituent at the cyclopentadienyl ligand influences the Lewis acidity of the zirconium metal center, we examined the reduction peak potentials of compounds **11**–**13** and **15**–**17** by means of cyclic voltammetry [16]. This correlation between Lewis acidity and reduction peak potential is based on the results of quantum chemical calculations which predict a large 4d character of the lowest unoccupied molecular orbital (LUMO) of zirconocene dichloride [17]. In Table 2 we list the results obtained at a scan rate of 100 mV s^{-1} in tetrahydrofuran. The reduction peak potentials (E_{red}) were scaled to the standard potential of ferrocene (Fc) which was found to be 0.58 ± 0.01 V (Fc/Fc^+). Additionally, we refer to unsubstituted zirconocene dichloride **19** as standard compound [7c,18] to assure comparability of data.

Fig. 2 shows a shift of the reduction peak potentials towards more negative values from the unsubstituted zirconocene dichloride (**19**) to bis(1,2-diethyl-3-(4-methylphenyl)cyclopentadienyl)zirconium dichloride (**17**). We ascribe this shift to the ability of the alkyl substituents to donate electron density. In view of this interpretation, it is interesting to compare the various

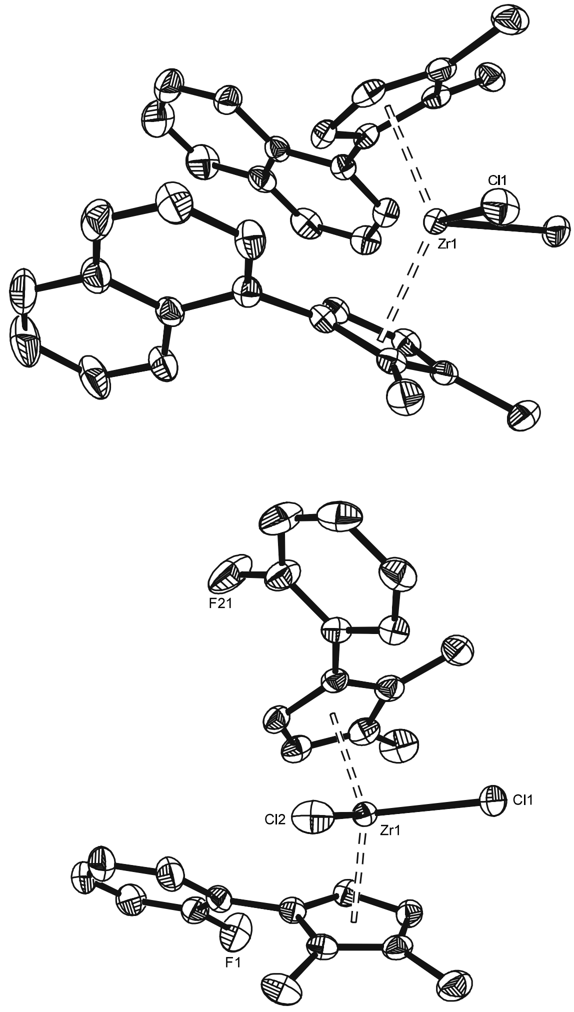


Fig. 1. Molecular structures of **13** (top) and **15** (bottom), hydrogen atoms are omitted for the sake of clarity. Plots are presented at 50% probability level of the thermal ellipsoids.

Table 1
Selected structural data for **11**, **12**, **13**, **15**, **16** and **17**

Compound	Angles (°)		Bond lengths (pm)	
	α [a]	Cl–Zr–Cl	Zr–C	Zr–Cl
meso-**11**	131.3	93.8	247.3–256.5	244.0
rac-**11**	130.7	94.8	245.3–261.6	242.9–244.9
rac-**12**	130.3	97.6	246.1–259.9	245.6
rac-**13**	130.3	96.3	246.1–262.3	243.2–243.6
meso-**15**	129.7	97.9	246.6–260.9	242.1–244.0
rac-**16**	132.4	95.7	246.9–262.1	243.8–244.2
rac-**17**	131.5	96.4	246.4–260.6	244.1–245.5

[a] Bite angle α, Cp(centroid)–Zr–Cp(centroid).

Table 2
Reduction peak potentials (E_{red}) for **11**, **12**, **13**, **15**, **16**, **17** and zirconocene dichloride **19** (Cp_2ZrCl_2)

Compound	R	R′	E_{red} [a] [−V]
11	Me	Ph	2.35 ± 0.01
12	Me	*p*-MeC_4H_4	2.36 ± 0.01
13	Me	1-naphthyl	2.33 ± 0.01
15	Me	*o*-F–C_4H_4	2.31 ± 0.01
16	Et	Ph	2.40 ± 0.01
17	Et	*p*-MeC_4H_4	2.44 ± 0.01
19	H	H	2.28 ± 0.01

[a] Scan rate 100 mV s^{-1}, concentration 1 mmol l^{-1} in tetrahydrofuran.

substituents in a more detailed fashion. A shift towards smaller reduction potential is anticipated and found when one methyl group at the aromatic ring in **12** is replaced by the more electronegative fluorine (**15**, $\Delta E =$ 50 mV). A similar shift is encountered when a hydrogen atom at the aryl substituent in **11** is replaced by a fluorine atom (**15**, $\Delta E = 40$ mV). A comparison between **11** and **16** as well as **12** and **17** reveals that the replacement of two methyl groups by two stronger electron donating ethyl groups at the Cp ligand shows a shift to more negative values ($\Delta E = 50$–80 mV). These examples demonstrate that the Lewis acidity of the metal center can not only be tuned by the number of substituents introduced at the ligand core, but also by varying the donor capacity or acceptors at the cyclopentadienyl ring.

3. Conclusion

In this paper, we present an easy access to 1,2,3-trisubstituted cyclopentadienes via the Pauson–Khand reaction of an alkyne with ethylene and subsequent treatment with organolithium compounds. These ligands could be transformed into 1,2,3-substituted bis(cyclopentadienyl)zirconium dichlorides by reaction with $ZrCl_4(thf)_2$. The stereochemistry of six out of eight zirconocene dichlorides could be deduced by X-ray analysis. Investigations by means of cyclic voltammetry suggest that the Lewis acidity of zirconocene dichlorides can be tuned by introducing electron withdrawing or electron donating substituents not only at the cyclopentadienyl ring itself but also at the aryl substituent. We have demonstrated that the magnitude of the electronic interaction of the differently 1,2,3-trisubstituted ligands can be compared by cyclic voltammetry. This might enable us to predict the changes in reactivity of the metallocenes and therefore to help us to modify specifically metallocene based catalyst for olefin polymerization in the future.

4. Experimental

4.1. General remarks

All melting points are uncorrected. The NMR spectra were measured with a Bruker Avance 500 (^{1}H-NMR at

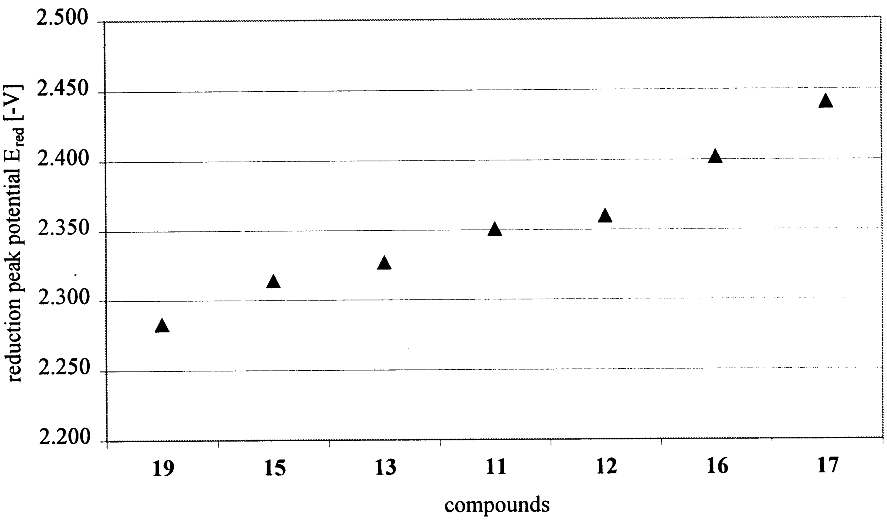


Fig. 2. Dependencies of the reduction peak potentials (E_{red}) [−V] of **11**–**13**, **15**–**17** and **19** at a scan rate of 100 mV s^{-1} in tetrahydrofuran.

500 MHz and ^{13}C-NMR at 125 MHz) and a Bruker Avance 300 (^{1}H-NMR at 300 MHz and ^{13}C-NMR at 75 MHz) using the solvent as internal standard (δ). The mass spectra refer to data from a JEOL JMS-700 instrument. IR spectra were recorded with a Bruker Vector 22. UV light absorption data were recorded using a Hewlett Packard 8452A spectrometer. All reactions were carried out in dried glassware under argon atmosphere using dried and oxygen-free solvents. The aryllithium reagents were synthesized according to literature known procedures [14] except for phenyllithium (Fluka).

4.2. Syntheses of cyclopentenones

4.2.1. Standard procedure

The alkyne was dissolved in 175 ml of toluene and 1.71 g of octacarbonyl dicobalt as well as 1.4 ml of DMSO were added. The mixture was poured in a steel vessel and pressurized with 50 bar of ethylene. After 40 h at 110 °C the gas pressure was released, the solvent was removed and the crude product was freed from cobalt clusters by filtration through a thin layer of silica eluting with light petroleum. Vacuum distillation yielded the pure oily products.

4.2.2. 2,3-Dimethylcyclopent-2-en-1-one (1)

Starting materials: 0.39 ml (5.0 mmol) of 1-butyne, 1.71 g (5.0 mmol) of octacarbonyl dicobalt and 1.4 ml (20 mmol) of DMSO. Yield: 99%. Colorless oil. B.p. 102 °C/18 mbar. ^{1}H-NMR ($CDCl_3$): δ 2.30–2.27 (m, 2H, CH_2), 2.16–2.14 (m, 2H, CH_2), 1.86 (s, 3H, CH_3), 1.48 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 210.0 (CO), 170.3 (C=C), 136.5 (C=C), 34.5 (CH_2), 31.8 (CH_2), 17.5 (CH_3), 8.1 (CH_3). For additional analytical data see literature [10b].

4.2.3. 2,3-Diethylcyclopent-2-en-1-one (2)

Starting materials: 0.41 ml (5.0 mmol) of 1-hexyne, 1.71 g (5.0 mmol) of octacarbonyl dicobalt and 1.4 ml (20 mmol) of DMSO. Yield: 68%. Colorless oil. B.p. 119 °C/18 mbar. ^{1}H-NMR ($CDCl_3$): δ 2.49–2.48 (m, 2H, CH_2), 2.45–2.41 (m, 2H, CH_2), 2.35–2.33 (m, 2H, CH_2), 2.18–2.16 (m, 2H, CH_2), 1.13 (s, 3H, CH_3), 0.96 (s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 210.6 (CO), 175.4 (C=C), 141.9 (C=C), 34.9 (CH_2), 29.2 (CH_2), 24.8 (CH_2), 16.9 (CH_2), 14.0 (CH_3), 12.8 (CH_3). For additional analytical data see literature. [9]

4.3. Syntheses of cyclopentadienes

4.3.1. Standard procedure

A solution of the cyclopentenone in 100 ml of diethyl ether was treated with the aryllithium reagent at −78 °C. The reaction mixture was allowed to warm up to room temperature (r.t.) over night and was hydrolysed by adding 50 ml of water. The organic phase was separated and the aqueous phase was subsequently extracted with diethyl ether (3 × 50 ml). The combined organic phases were treated with 5 ml of 3 M HCl, vigorously stirred for 10 minutes and neutralized by washing with $NaHCO_3$-solution (2 × 50 ml). After drying ($MgSO_4$) the solvent was removed and the crude product was purified by filtration through a thin layer of alumina (neutral, grade III) using light petroleum to yield the desired oily product.

4.3.2. 1,2-Dimethyl-3-phenylcyclopentadiene (3)

Starting materials: 0.75 g (6.8 mmol) of 2,3-dimethylcyclopent-2-en-1-one (**1**) and 7.5 mmol of phenyllithium (1.6 M in hexane solution). Yield: 95%. Colorless oil. MS(EI) 170 [M^+], 155 [$M^+ - CH_3$]. HRMS(EI) Anal. Calc. for [$C_{13}H_{14}$]: 170.1095. Found: 170.1074.

4.3.3. 1,2-Dimethyl-3-(4-methylphenyl)cyclopentadiene (**4**)

Starting materials: 0.5 g (4.5 mmol) of 2,3-dimethylcyclopent-2-en-1-one (**1**) and 4.7 mmol of *p*-methylphenyllithium. Yield: 91%. Colorless oil. MS(EI) 184 [M^+], 169 [$M^+ - CH_3$]. HRMS(EI) Anal. Calc. for [$C_{14}H_{16}$]: 184.1252. Found: 184.1231.

4.3.4. 1,2-Dimethyl-3-(1-naphthyl)cyclopentadiene (**5**)

Starting materials: 0.5 g (4.5 mmol) of 2,3-dimethylcyclopent-2-en-1-one (**1**) and 4.7 mmol of 1-naphthyllithium. Yield: 99%. Colorless oil. MS(EI) 220 [M^+], 205 [$M^+ - CH_3$]. HRMS(EI) Anal. Calc. for [$C_{17}H_{16}$]: 220.1252. Found: 220.1256%.

4.3.5. 1,2-Dimethyl-3-(4-tert-butylphenyl)cyclopentadiene (**6**)

Starting materials: 0.5 g (4.5 mmol) of 2,3-dimethylcyclopent-2-en-1-one (**1**) and 4.7 mmol of *p*-(*tert*-butyl)phenyllithium. Yield: 90%. Colorless oil. MS(EI) 226 [M^+], 211 [$M^+ - CH_3$]. HRMS(EI) Anal. Calc. for [$C_{17}H_{22}$]: 226.1722. Found: 226.1717.

4.3.6. 1,2-Dimethyl-3-(2-fluorphenyl)cyclopentadiene (**7**)

Starting materials: 0.5 g (4.5 mmol) of 2,3-dimethylcyclopent-2-en-1-one (**1**) and 4.7 mmol of *o*-fluorphenyllithium. Yield: 90%. Colorless oil. MS(EI) 189 [$M^+ + H$]. HRMS(EI) Anal. Calc. for [$C_{13}H_{14}F$]: 189.1079. Found: 189.1069.

4.3.7. 1,2-Diethyl-3-phenylcyclopentadiene (**8**)

Starting materials: 0.62 g (4.5 mmol) of 2,3-diethylcyclopent-2-en-1-one (**2**) and 5.0 mmol of phenyllithium (1.6 M in hexane solution). Yield: 99%. Colorless oil. MS(EI) 198 [M^+], 183 [$M^+ - CH_3$], 169 [$M^+ - C_2H_5$]. HRMS(EI) Anal. Calc. for [$C_{15}H_{18}$]: 198.1408. Found: 198.1407.

4.3.8. 1,2-Diethyl-3-(4-methylphenyl)cyclopentadiene (**9**)

Starting materials: 0.62 g (4.5 mmol) of 2,3-diethylcyclopent-2-en-1-one (**2**) and 4.7 mmol of *p*-methylphenyllithium. Yield: 99%. Colorless oil. MS(EI) 212 [M^+], 197 [$M^+ - CH_3$], 183 [$M^+ - C_2H_5$]. HRMS(EI) Anal. Calc. for [$C_{16}H_{20}$]: 212.1565. Found: 212.1571%.

4.3.9. 1,2-Diethyl-3-(4-tert-butylphenyl)cyclopentadiene (**10**)

Starting materials: 0.62 g (4.5 mmol) of 2,3-diethylcyclopent-2-en-1-one (**2**) and 4.7 mmol of *p*-(*tert*-butyl)phenyllithium. Yield: 97%. Colorless oil. MS(EI) 254 [M^+], 239 [$M^+ - CH_3$]. HRMS(EI) Anal. Calc. for [$C_{19}H_{26}$]: 254.2034. Found: 254.2014.

4.4. Syntheses of zirconocene dichlorides

4.4.1. Standard procedure

The cyclopentadiene was dissolved in toluene, cooled to −78 °C and treated with 1 equivalent of *n*-butyllithium (1.6 M solution in hexane) in a dropwise fashion. After warming up to room temperature a white slurry had formed, which was again cooled down to −78 °C. Addition of the solid $ZrCl_4(thf)_2$ complex and stirring for an additional 3 days under reflux led to the formation of a yellow-brownish reaction mixture. After filtration through a pad of Celite the solvent was removed and the crude product (*rac*/*meso*-mixture) was isolated in 85–70% yield. Recrystallization from mixtures of *n*-hexane and toluene yielded the isomerically pure product (either *rac*- or *meso*-complex). The yields given below refer to the isomerically pure zirconocenes as determined by NMR spectra.

4.4.2. Bis(1,2-Dimethyl-3-phenylcyclopentadienyl)-zirconium dichloride (**11**)

Starting materials: 1.2 g (6.8 mmol) of 1,2-dimethyl-3-phenylcyclopentadiene (**3**), 4.25 ml (6.8 mmol) of *n*-butyllithium and 1.28 g (3.4 mmol) of $ZrCl_4(thf)_2$ complex in 180 ml of toluene. Yield: 21% (*meso*). Yellow solid. M.p. 179 °C. ^1H-NMR ($CDCl_3$): δ 7.29–7.23 (m, 10H, PhH), 6.07 (d, 2H, CpH), 5.74 (d, 2H, CpH), 2.20 (s, 6H, CH_3), 2.13 (s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 134.5 (PhC), 130.1 (CpC), 128.7 (PhC), 128.5 (PhC), 128.5 (CpC), 128.0 (CpC), 127.4 (PhC), 112.6 (CpC), 109.3 (CpC), 14.1 (CH_3), 13.0 (CH_3). IR (KBr): 3102, 2920, 2092, 2056, 1630, 1508, 1482, 1446, 1381 cm^{-1}. UV–vis (CH_2Cl_2, 0.02 mg ml^{-1}) λ [nm] (log ε): 242 (4.48), 344 (3.65). Elemental Anal. Calc.: C, 62.38; H, 5.24; Cl, 14.16. Found: C, 62.56; H, 5.39; Cl, 14.15%.

4.4.3. Bis(1,2-Dimethyl-3-(4-methylphenyl)cyclopentadienyl)zirconium dichloride (**12**)

Starting materials: 0.58 g (3.14 mmol) of 1,2-dimethyl-3-(4-methylphenyl)cyclopentadiene (**4**), 1.96 ml (3.14 mmol) of *n*-butyllithium and 0.59 g (1.57 mmol) of $ZrCl_4(thf)_2$ complex in 120 ml of toluene. Yield: 19% (*rac*). Yellow solid. M.p. 128 °C. ^1H-NMR ($CDCl_3$): δ 7.13–7.08 (m, 4H, PhH), 7.07–7.04 (m, 4H, PhH), 6.04 (d, 2H, CpH), 5.71 (d, 2H, CpH), 2.34 (s, 6H, $PhCH_3$), 2.18 (s, 6H, CH_3), 2.12 (s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 137.1 (PhC), 131.6 (CpC), 129.7 (PhC), 129.1 (PhC), 128.5 (CpC), 128.5 (PhC), 127.9 (CpC), 112.3 (CpC), 109.1 (CpC), 21.3 ($PhCH_3$), 14.4 (CH_3), 12.9 (CH_3). IR (KBr): 3022, 2919, 1622, 1524, 1449, 1380 cm^{-1}. UV–vis (CH_2Cl_2, 0.027 mg ml^{-1}) λ [nm] (log ε): 244 (4.81), 278 (4.52), 348 (4.08), 362 (4.07). Elemental Anal. Calc.: C, 63.61; H, 5.72; Cl, 13.41. Found: C, 63.39; H, 5.81; Cl, 13.61%.

*4.4.4. Bis(1,2-Dimethyl-3-(1-naphthyl)cyclopentadienyl)zirconium dichloride (**13**)*

Starting materials: 1.0 g (4.54 mmol) of 1,2-dimethyl-3-(1-naphthyl)cyclopentadiene (**5**), 2.83 ml (4.54 mmol) of *n*-butyllithium and 0.85 g (2.27 mmol) of $ZrCl_4(thf)_2$ complex in 180 ml of toluene. Yield: 18% (*rac*). Yellow solid. M.p. 234 °C. ^{1}H-NMR ($CDCl_3$): δ 7.84–7.83 (m, 4H, ArH), 7.58–7.55 (m, 4H, ArH), 7.54–7.51 (m, 2H, ArH), 7.27–7.23 (m, 4H, ArH), 5.93 (d, 2H, CpH), 5.86 (d, 2H, CpH), 2.31 (s, 6H, CH_3), 2.04 (s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 134.8 (ArC), 134.3 (ArC), 132.7 (ArC), 132.1 (CpC), 128.6 (ArC), 128.6 (ArC), 128.5 (CpC), 127.5 (CpC), 126.5 (ArC), 126.2 (ArC), 125.9 (ArC), 125.3 (ArC), 124.5 (ArC), 114.8 (CpC), 113.1 (CpC), 14.1 (CH_3), 12.5 (CH_3). IR (KBr): 3053, 2918, 1623, 1594, 1510, 1442, 1388 cm^{-1}. UV–vis (CH_2Cl_2, 0.026 mg ml^{-1}) λ [nm] (log ε): 294 (4.25), 358 (3.66). Elemental Anal. Calc.: C, 67.98; H, 5.03; Cl, 11.80. Found: C, 67.97; H, 5.07; Cl, 11.65%.

*4.4.5. Bis(1,2-Dimethyl-3-(4-tert-butylphenyl)cyclopentadienyl)zirconium dichloride (**14**)*

Starting materials: 0.92 g (4.0 mmol) of 1,2-dimethyl-3-(4-*tert*-butylphenyl)cyclopentadiene (**6**), 2.54 ml (4 mmol) of *n*-butyllithium and 0.77 g (2.0 mmol) of $ZrCl_4(thf)_2$ complex in 150 ml of toluene. Yield: 10% (single isomer). Yellow solid. M.p. 144 °C. ^{1}H-NMR ($CDCl_3$): δ 7.30–7.28 (m, 4H, PhH), 7.18–7.15 (m, 4H, PhH), 6.04 (d, 2H, CpH), 5.74 (d, 2H, CpH), 2.19 (s, 6H, CH_3), 2.12 (s, 6H, CH_3), 1.32 (s, 18H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 150.3 (PhC), 131.7 (PhC), 129.5 (CpC), 128.9 (PhC), 128.5 (CpC), 128.2 (CpC), 125.4 (PhC), 112.2 (CpC), 109.2 (CpC), 34.7 (C), 31.5 (CCH_3), 14.5 (CH_3), 13.0 (CH_3). IR (KBr): 2962, 2867, 1628, 1526, 1464, 1364 cm^{-1}. UV–vis (CH_2Cl_2, 0.015 mg ml^{-1}) λ [nm] (log ε): 244 (4.42), 362 (3.49). HRMS(EI) Anal. Calc. for [$C_{34}H_{42}{}^{35}Cl_2{}^{92}Zr$]: 612.1714. Found: 612.1697%.

*4.4.6. Bis(1,2-dimethyl-3-(2-fluorphenyl)cyclopentadienyl)zirconium dichloride (**15**)*

Starting materials: 0.85 g (4.5 mmol) of 1,2-dimethyl-3-(2-fluorphenyl)cyclopentadiene (**7**), 2.8 ml (4.5 mmol) of *n*-butyllithium and 0.85 g (2.25 mmol) of $ZrCl_4(thf)_2$ complex in 120 ml of toluene. Yield: 17% (*meso*). White solid. M.p. 188 °C. ^{1}H-NMR ($CDCl_3$): δ 7.36–7.33 (m, 2H, PhH), 7.31–7.26 (m, 2H, PhH), 7.15–7.09 (m, 4H, PhH), 6.23 (d, 2H, CpH), 5.90 (d, 2H, CpH), 2.14 (s, 6H, CH_3), 2.12 (s, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 161.0 (PhCF), 159.0 (PhC), 132.0 (CpC), 129.6 (PhC), 129.5 (CpC), 125.9 (CpC), 124.2 (PhC), 123.1 (PhC), 116.2 (PhC), 113.6 (CpC), 111.7 (CpC), 14.2 (CH_3), 12.9 (CH_3). IR (KBr): 2958, 2921, 1629, 1509, 1453, 1382 cm^{-1}. UV–vis (CH_2Cl_2, 0.013 mg ml^{-1}) λ [nm] (log ε): 256 4.26), 280 (3.99), 340 (3.56). Elemental Anal. Calc.: C, 58.20; H, 4.51; Cl, 13.21. Found: C, 58.28; H, 4.61; Cl, 13.00%.

*4.4.7. Bis(1,2-Diethyl-3-phenylcyclopentadienyl)-zirconium dichloride (**16**)*

Starting materials: 1.1 g (5.4 mmol) of 1,2-diethyl-3-phenylcyclopentadiene (**8**), 3.4 ml (5.4 mmol) of *n*-butyllithium and 1.0 g (2.75 mmol) of $ZrCl_4(thf)_2$ complex in 180 ml of toluene. Yield: 14% (*rac*). Yellow solid. M.p. 138 °C. ^{1}H-NMR ($CDCl_3$): δ 7.27–7.24 (m, 10H, PhH), 6.09 (d, 2H, CpH), 5.80 (d, 2H, CpH), 2.69–2.65 (s, 4H, CH_2), 2.56–2.49 (s, 4H, CH_2), 1.15 (t, 6H, CH_3), 0.83 (t, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 134.8 (PhC), 134.3 (CpC), 134.2 (PhC), 128.5 (PhC), 128.4 (CpC), 128.2 (PhC), 127.4 (CpC), 110.5 (CpC), 109.7 (CpC), 21.7 (CH_2), 20.2 (CH_2). 15.0 (CH_3), 13.6 (CH_3). IR (KBr): 3061, 2969, 2934, 2873, 2019, 1631, 1507, 1458, 1376 cm^{-1}. UV–vis (CH_2Cl_2, 0.017 mg ml^{-1}) λ [nm] (log ε): 238 (4.25), 348 (3.45). Elemental Anal. Calc.: C, 64.72; H, 6.16; Cl, 12.74. Found: C, 64.52; H, 6.15; Cl, 12.57%.

*4.4.8. Bis(1,2-Diethyl-3-(4-methylphenyl)cyclopentadienyl)zirconium dichloride (**17**)*

Starting materials: 0.96 g (4.5 mmol) of 1,2-diethyl-3-(4-methylphenyl)cyclopentadiene (**9**), 2.84 ml (4.5 mmol) of *n*-butyllithium and 0.86 g (2.25 mmol) of $ZrCl_4(thf)_2$ complex in 180 ml of toluene. Yield: 7% (*rac*). Yellow solid. M.p. 196 °C. ^{1}H-NMR ($CDCl_3$): δ 7.22–7.16 (m, 8H, PhH), 5.64 (d, 2H, CpH), 5.47 (d, 2H, CpH), 2.89-2.74 (m, 4H, CH_2), 2.65–2.51 (s, 4H, CH_2), 2.40 (s, 6H, $PhCH_3$), 1.18 (t, 6H, CH_3), 0.79 (t, 6H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 137.3 (PhC), 136.2 (CpC), 133.6 (CpC), 132.6 (PhC), 129.7 (PhC), 127.7 (CpC), 124.2 (PhC), 110.5 (CpC), 109.7 (CpC), 21.4 ($PhCH_3$), 21.3 (CH_2), 20.4 (CH_2). 15.3 (CH_3), 13.8 (CH_3). IR (KBr): 3022, 2969, 2934, 2873, 1622, 1524, 1455, 1376, 1305 cm^{-1}. UV–vis (CH_2Cl_2, 0.038 mg ml^{-1}) λ [nm] (log ε): 236 (4.81), 260 (4.70), 362 (4.04). HRMS(EI) Anal. Calc. for [$C_{32}H_{38}{}^{35}Cl_2{}^{92}Zr$]: 584.1401. Found: 584.1397%. Elemental Anal. Calc.: C, 65.72; H, 6.55; Cl, 12.13. Found: C, 65.04; H, 6.48; Cl, 11.94%. HRMS(EI) Anal. Calc. for [$C_{32}H_{38}{}^{35}Cl_2{}^{92}Zr$]: 584.1401. Found: 584.1397.

*4.4.9. Bis(1,2-Diethyl-3-(4-tert-butylphenyl)cyclopentadienyl)zirconium dichloride (**18**)*

Starting materials: 1.0 g (4.0 mmol) of 1,2-diethyl-3-(4-*tert*-butylphenyl)cyclopentadiene (**10**), 2.5 ml (4.0 mmol) of *n*-butyllithium and 0.75 g (2.0 mmol) of $ZrCl_4(thf)_2$ complex in 150 ml of toluene. Yield: 2% (single isomer). White solid. M.p. 198 °C. ^{1}H-NMR ($CDCl_3$): δ 7.40–7.37 (m, 4H, PhH), 7.22–7.18 (m, 4H, PhH), 5.67 (d, 2H, CpH), 5.46 (d, 2H, CpH), 2.90–2.73 (m, 4H, CH_2), 2.67–2.45 (m, 4H, CH_2), 1.35 (s, 18H, CH_3), 1.16 (t, 6H, CH_3), 0.79 (t, 6H, CH_3). ^{13}C-NMR

Table 3
Crystal data and structure refinement for **11**, **12**, **13**, **15**, **16** and **17**

	rac-**11**	meso-**11**	*rac*-**12**	*rac*-**13**	meso-**15**	*rac*-**16**	*rac*-**17**
Chemical formula	$C_{26}H_{26}Cl_2Zr$	$C_{26}H_{26}Cl_2Zr$	$C_{28}H_{30}Cl_2Zr$	$C_{34}H_{30}Cl_2Zr$	$C_{28}H_{30}Cl_2F_2Zr$	$C_{30}H_{34}Cl_2Zr$	$C_{32}H_{36}Cl_2Zr$
Formula weight	500.59	500.59	528.64	600.70	536.57	556.69	582.73
Crystal size (mm)	0.22 × 0.17 × 0.16	0.55 × 0.20 × 0.10	0.32 × 0.32 × 0.16	0.23 × 0.15 × 0.13	0.50 × 0.24 × 0.21	0.35 × 0.21 × 0.04	0.28 × 0.24 × 0.22
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$Aba2$	$P\bar{1}$	$C222_1$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
Z	4	4	4	2	4	4	4
Unit cell dimensions							
a (Å)	17.0512(1)	10.7936(2)	11.0679(1)	10.2720(1)	9.5599(1)	10.9449(2)	11.8597(4)
b (Å)	20.4376(1)	12.2936(2)	20.6220(2)	11.5260(1)	12.3663(1)	12.6688(3)	12.3449(4)
c (Å)	6.6458(1)	16.6320(3)	11.1717(2)	12.8450(1)	19.7561(3)	19.4841(3)	19.6320(6)
α (°)	90	84.542(1)	90	77.067(1)	90	90	90
β (°)	90	84.298(1)	90	74.037(1)	94.574(1)	100.503(1)	90
γ (°)	90	88.822(1)	90	73.706(1)	90	90	90
V (Å^3)	2315.97(4)	2185.92(7)	2549.85(6)	1385.58(2)	2328.14(5)	2656.38(9)	2874.26(2)
D_{calc} (g cm^{-3})	1.436	1.521	1.377	1.440	1.531	1.392	1.347
Absorption coefficient, μ (mm^{-1})	0.715	0.758	0.654	0.611	0.729	0.631	0.587
Min./max. transmission	0.81 and 0.91	0.81 and 0.94	0.79 and 0.91	0.83 and 0.93	0.42 and 0.88	0.85 and 0.98	0.83 and 0.89
Index ranges	$-22 < h < 21$, $-26 < k < 26$, $-8 < l < 8$	$-13 < h < 14$, $-15 < k < 15$, $-21 < l < 21$	$-14 < h < 14$, $-26 < k < 26$, $-14 < l < 14$	$-13 < h < 13$, $-14 < k < 14$, $-16 < l < 16$	$-12 < h < 12$, $-15 < k < 16$, $-25 < l < 25$	$-14 < h < 14$, $-16 < k < 16$, $-25 < l < 25$	$-15 < h < 15$, $-15 < k < 16$, $-25 < l < 25$
Reflections collected	11623	22632	13259	21613	23435	26960	30005
Independent reflections	2650	9908	2936	21613	5328	6082	6582
Observed reflections	2476	8195	2840	16700	4681	4590	6018
Parameters	134	531	144	339	284	302	322
Goodness-of-fit on F^2	1.05	1.03	1.14	1.04	1.07	1.04	1.03
$R(F)$	0.019	0.026	0.022	0.039	0.026	0.030	0.026
$R_w(F^2)$	0.048	0.059	0.062	0.088	0.066	0.066	0.060
($\Delta\rho$) max, min (e Å^{-3})	0.21, −0.29	0.40, −0.48	0.48, −0.32	0.85, −0.42	0.34, −0.39	0.72, −0.47	0.45, −0.30

($CDCl_3$): δ 150.2 (PhC), 135.7 (PhC), 133.4 (CpC), 132.1 (PhC), 127.1 (CpC), 125.3 (CpC), 124.0 (PhC), 112.9 (CpC), 111.7 (CpC), 34.3 (C), 31.1 (CCH_3), 21.0 (CH_2), 20.0 (CH_2), 14.9 (CH_3), 13.5 (CH_3). IR (KBr): 2966, 2872, 1628, 1521, 1462, 1365 cm^{-1}. UV–vis (CH_2Cl_2, 0.066 mg ml^{-1}) λ [nm] (log ε): 238 (4.49), 262 (4.67), 360 (3.81). HRMS(EI) Anal. Calc. for [$C_{38}H_{50}^{35}Cl_2^{92}Zr$]: 668.2340. Found: 668.2350%.

4.5. Cyclic voltammetry

The electrochemical measurements were performed with the METROHM potentiostat system PGSTAT20. As working electrode a METROHM disc electrode was used (radius ~0.3 cm, glassy carbon). The Ag/AgCl reference electrode was separated from the solution by a fine grid and a luggin capillary. A 0.1 M solution of n-Bu_4PF_6 in THF was used as electrolyte. The potential of ferrocene/ferrocenium (Fc/Fc^+) was recorded at 580 mV with an error of ± 10 mV vs. Ag/AgCl. All measurements were recorded at a scan rate of 100 mV s^{-1}. Samples were measured at a concentration of 1 mmol l^{-1} in tetrahydrofuran at room temperature. Oxygen was removed from the solution by purging argon through the cell.

4.6. X-ray crystallography and structure solution

The crystallographic data were recorded with a Bruker Smart CCD diffractometer at 200 K at a wavelength λ of 0.71073 Å. Relevant crystal and data collection parameters are given in Table 3. The structures were solved by using direct methods, least-squares refinement and Fourier techniques. Structure solution and refinement were performed with SHELXTL [19]. An empirical absorption correction was carried out using SADABS [20] based on the Laue symmetry of the reciprocal space. Hydrogen atoms were included at calculated positions. The crystal of **13** was a partially merohedrical twin, which could be treated successfully with an appropriate twinning model.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 181334 (*rac*-**11**), 181335 (*meso*-**11**), 181336 (**12**), 181337 (**13**), 181338 (**15**), 181339 (**16**) and 181340 (**17**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF Aktiengesellschaft, Ludwigshafen, for financial support.

References

[1] P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1 and references cited therein.

[2] (a) M.F. Lappert, C.J. Pickett, P.I. Riley, P.I.W. Yarrow, J. Chem. Soc. Dalton Trans. (1981) 805;
(b) G. Erker, R. Nolte, R. Aul, S. Wilker, C. Krüger, R. Noe, J. Am. Chem. Soc. 113 (1991) 7594;
(c) G. Fink, R. Mühlhaupt, H.-H. Brintzinger (Eds.), Ziegler Catalysts, Springer, Berlin, 1995;
(d) H.-H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger, R. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143;
(e) E. Negishi, J.-L. Montchamp, in: A. Togni, R.L. Halterman (Eds.), Metallocenes, VCH, Weinheim, 1998, pp. 241–319;
(f) H.G. Alt, E. Samuel, Chem. Soc. Rev. 27 (1998) 323;
(g) W. Kaminsky, Pure Appl. Chem. 70 (1998) 1229;
(h) G.G. Hlatky, Coord. Chem. Rev. 181 (1999) 243;
(i) W. Kaminsky, Catal. Today 62 (2000) 23;
(j) G.G. Hlatky, Coord. Chem. Rev. 199 (2000) 235.

[3] (a) R. Beckhaus, in: A. Togni, R.L. Halterman (Eds.), Metallocenes, VCH, Weinheim, 1998, pp. 153–239;
(b) R.L. Halterman, in: A. Togni, R.L. Halterman (Eds.), Metallocenes, Weinheim: VCH, 1998, pp. 455–544;
(c) R.J. Maldanis, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 599 (2000) 107 (and references cited therein).

[4] (a) W. Kaminsky, K. Külper, H.-H. Brintzinger, F.R.W.P. Wild, Angew. Chem. Int. Ed. Engl. 24 (1985) 507;
(b) P. Courtot, R. Pichon, J.Y. Salaun, L. Toupet, Can. J. Chem. 69 (1991) 661;
(c) C. Janiak, U. Versteeg, K.C.H. Lange, R. Weimann, E. Hahn, J. Organomet. Chem. 501 (1995) 219;
(d) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255;
(e) S. Mansel, U. Rief, M.-H. Prosenc, R. Kirsten, H.-H. Brintzinger, J. Organomet. Chem. 512 (1996) 225;
(f) P. Witte, T.K. Lai, R.M. Waymouth, Organometallics 18 (1999) 4147;
(g) H. Yamazaki, K. Kimura, M. Nakano, T. Ushioda, Chem. Lett. (1999) 1311;
(h) E.J. Thomas, J.C.W. Chien, M.D. Rausch, Organometallics 18 (1999) 1439;
(i) Y.K. Kang, K.S. Shin, S.-G. Lee, I.S. Lee, Y.K. Chung, Organometallics 18 (1999) 180;
(j) E.J. Thomas, J.C.W. Chien, M.D. Rausch, Macromolecules 33 (2000) 1546.

[5] (a) P. Montag, Y. v. d. Leek, K. Angermund, G. Fink, J. Organomet. Chem. 497 (1995) 201;
(b) J.C. Green, Chem. Soc. Rev. 27 (1998) 263;
(c) M. Toto, L. Cavallo, P. Corradini, G. Moscardi, L. Resconi, G. Guerra, Macromolecules 31 (1998) 3431;
(d) K. Thorshaug, J.A. Støvneng, E. Rytter, Macromolecules 33 (2000) 8136;
(e) A. Maiti, M. Sierka, J. Andzehm, J. Golab, J. Sauer, J. Phys. Chem. A 104 (2000) 10932;
(f) J.N. Harvey, Organometallics 20 (2001) 4887;
(g) E. Zwek, T. Ziegler, Organometallics 21 (2002) 83 (and references cited therein).

[6] (a) P.G. Gassmann, D.W. Macomber, J.W. Hershberger, Organometallics 2 (1983) 1470;
(b) P.G. Gassmann, C.H. Winter, Organometallics 10 (1991) 1592;
(c) P.G. Gassmann, P.A. Deck, C.H. Winter, D.A. Dobbs, D.H. Cao, Organometallics 11 (1992) 959.

[7] (a) M.F. Lappert, C.J. Pickett, P.I. Riley, P.I.W. Yarrow, J. Chem. Soc. Dalton Trans. (1981) 805;
(b) J. Langmaier, Z. Samec, V. Varga, M. Horácek, K. Mach, J. Organomet. Chem. 579 (1999) 348;
(c) J. Langmaier, Z. Samec, V. Varga, M. Horácek, R. Choukroun, K. Mach, J. Organomet. Chem. 584 (1999) 323.

[8] (a) K. Kimura, K. Takaishi, T. Matsukawa, T. Yoshimura, H. Yamazaki, Chem. Lett. (1998) 571;
(b) B.Y. Lee, J.W. Han, Y.K. Chung, S.W. Lee, J. Organomet. Chem. 587 (1999) 181;
(c) F. Zhang, Y. Mu, L. Zhao, Y. Zhang, W. Bu, C. Chen, H. Zhai, H. Hong, J. Organomet. Chem. 613 (2000) 68.

[9] T. Takahashi, Z. Xi, Y. Nishihara, S. Huo, K. Kasai, K. Aoyagi, V. Denisov, E. Negishi, Tetrahedron 53 (1997) 9123. (This method cannot be used to synthesize 2,3-dimethylcyclopent-2-en-1-one).

[10] (a) J. Ficini, J.-P. Genêt, Tetrahedron Lett. 12 (1971) 1565;
(b) M.A. Baig, D.V. Banthorpe, G. Carr, D. Whittaker, J. Chem. Soc. Perkin Trans. 2 (1989) 1981;
(c) M.L.F. Cadman, L. Crombie, S. Freeman, J. Mistry, J. Chem. Soc. Perkin Trans. 1 (1995) 1397.

[11] (a) S. Hirano, T. Hiyama, H. Nozaki, Tetrahedron Lett. 15 (1974) 1429;
(b) S. Hirano, S. Tagaki, T. Hiyama, H. Nozaki, Bull. Chem. Soc. Jpn. 53 (1980) 169.

[12] (a) P.L. Pauson, Tetrahedron 41 (1985) 5855;
(b) P.L. Pauson, in: A. de Meijere, H. tom Dieck (Eds.), Organometallics in Organic Synthesis, Springer, Berlin, 1988, pp. 233–246;
(c) N.E. Schore, in: B.M. Trost (Ed.), Comprehensive Organic Synthesis, vol. 5, Pergamon, Oxford, 1991, pp. 1037–1064;
(d) N.E. Schore, Org. React. 40 (1991) 1;
(e) N.E. Schore, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, pp. 703–739;
(f) O. Geis, H.G. Schmalz, Angew. Chem. Int. Ed. Engl. 37 (1998) 911;
(g) Y.K. Chung, Coord. Chem. Rev. 188 (1999) 297;
(h) K.M. Brummond, J.L. Kent, Tetrahedron 56 (2000) 3263;
(i) A.J. Fletcher, S.D.R. Christie, J. Chem. Soc. Perkin Trans. 1 (2000) 1657.

[13] (a) J.G. Donkervoort, A.R. Gordon, C. Johnstone, W.J. Kerr, U. Lange, Tetrahedron 52 (1996) 7391;
(b) B.J. Rausch, R. Gleiter, Tetrahedron Lett. 42 (2001) 1651.

[14] L. Brandsma, H.D. Verkruijsse, Preparative Polar Organic Chemistry, vol. 1, Springer, New York, 1987.

[15] (a) For further X-ray structures of substituted unbridged zirconocene dichlorides see: J.L. Petersen, J.W. Egan, Jr, Inorg. Chem. 22 (1983) 3571;
(b) R.G. Rodgers, M.M. Benning, L.K. Kurihara, K.J. Moriarty, M.D. Rausch, J. Organomet. Chem. 293 (1985) 51–60;
(c) R. Bortolin, V. Patel, I. Munday, N.J. Taylor, A.J. Carty, J. Chem. Soc. Chem. Commun. (1985) 456;
(d) R.A. Howie, G.P. McQuillan, D.W. Thompson, G.A. Lock, J. Organomet. Chem. 303 (1986) 213;
(e) J.C. Gallucci, B. Gautheron, M. Gugelchuk, P. Meunier, L.A. Paquette, Organometallics 6 (1987) 15;
(f) A. Antiñolo, M.F. Lappert, A. Singh, D.W. Winterborn, L.M. Engelhardt, C.L. Raston, A.H. White, A.J. Carty, N.J. Taylor, J. Chem. Soc. Dalton Trans. (1987) 1463;
(g) P.B. Hitchcock, M.F. Lappert, G.A. Lawless, H. Olivier, E.J. Ryan, J. Chem. Soc. Chem. Commun. (1992) 474;
(h) R. Choukroun, F. Dahan, Organometallics 13 (1994) 2097;
(i) M.T. Reetz, H. Brümmer, M. Kessler, J. Kuhnigk, Chimia 49 (1995) 501;
(j) E. Polo, M.L.H. Green, F. Benetollo, G. Prini, S. Sostero, O. Traverso, J. Organomet. Chem. 527 (1997) 173;
(k) A.S. Batsanov, B.M. Bridgewater, J.A.K. Howard, A.K. Hughes, C. Wilson, J. Organomet. Chem. 590 (1999) 169;
(l) J. Pflug, A. Bertuleit, G. Kehr, R. Fröhlich, G. Erker, Organometallics 18 (1999) 3818;
(m) O.W. Lofthus, C. Slebodnick, P.A. Deck, Organometallics 18 (1999) 3702;
(n) P.L. Chirik, M.W. Day, J.E. Bercaw, Organometallics 18 (1999) 1873.

[16] J. Heinze, Angew. Chem. Int. Ed. Engl. 23 (1984) 831 (and references cited therein).

[17] (a) J.L. Petersen, L.F. Dahl, J. Am. Chem. Soc. 97 (1975) 6422;
(b) J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.

[18] (a) E. Samuel, D. Guery, J. Vedel, F. Basile, Organometallics 4 (1985) 1073;
(b) A. Antiñolo, G.S. Bristow, G.K. Campbell, A.W. Duff, P.B. Hitchcock, R.A. Kamarudin, M.F. Lappert, R.J. Norton, N. Sarjudeen, D.J.W. Winterborn, J.L. Atwood, W.E. Hunter, H. Zhang, Polyhedron 8 (1989) 1601.

[19] G.M. Sheldrick, Bruker Analytical X-ray Division, Madison, WI, 1997.

[20] G.M. Sheldrick, Bruker Analytical X-ray Division, Madison, WI, 1996.