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The reaction of $[\eta^5{:}C_5H_4{-}(CH_2)_n{-}C_6H_5]_2MCl_2$ complexes ($n = 1–5$; $M = Zr$, Hf) with EtLi

Helmut G. Alt *, Christine E. Denner, Wolfgang Milius

Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 101251, Universitätsstrasse 30, NW I, D-95440 Bayreuth, Germany

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Dedicated to Professor Helmut Werner on the occasion of his 70th birthday (19.4.2004)

Abstract

The reaction of metallocene complexes of the type $[\eta^5{:}C_5H_4{-}(CH_2)_n{-}C_6H_5]_2MCl_2$ ($n = 1–5$; $M = Zr$, Hf) with EtLi gives the mono nuclear ethyl derivatives $[\eta^5{:}C_5H_4{-}(CH_2)_n{-}C_6H_5]_2M(Et)Cl$ and the metallacycles $[\eta^5{:}C_5H_4{-}(CH_2)_n{-}C_6H_5][\eta^5{:}C_5H_4{-}(CH_2)_n{-}\eta^1{:}C_6H_4]MEt$. A large excess of EtLi affords the dinuclear species $[\eta^5{:}C_5H_4{-}(CH_2)_n{-}\eta^6{:}C_6H_5]_2M_2Cl_2$ ($n = 2–5$). All types of complexes can be activated with methylalumoxane (MAO) and then be used for catalytic polymerization of ethylene.

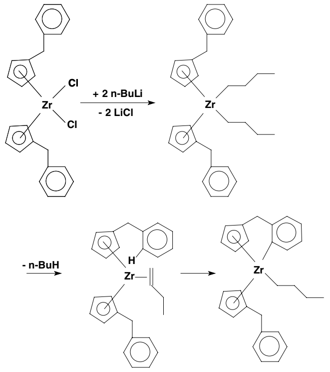
Keywords: Metallocene complexes; Metallacycles; Dinuclear complexes; Ethylene polymerization

1. Introduction

The reaction of ω-phenylalkyl substituted metallocene complexes of the type $[\eta^5{:}C_5H_4{-}(CH_2)_n{-}C_6H_5]_2MCl_2$ ($n = 1–3$; $M = Zr$, Hf) with BuLi gives a variety of reaction products depending on n [1–4].

The first step is the formation of a dibutyl complex and lithium chloride. The dibutyl complex can undergo reductive β-H elimination to give butane and the butene complex $[\eta^5{:}C_5H_4{-}(CH_2)_n{-}C_6H_5]_2ZrC_4H_8$. This olefin complex can form a metallacyclic butyl complex via *ortho*-metallation and oxidative addition.

In order to investigate this reaction further, we varied the parameters n and the lithium alkyl. Depending on the various parameters, different reaction products could be identified and characterized.



2. Results and discussion

2.1. Synthesis and characterization of the ω-phenylalkyl substituted zirconocene and hafnocene dichloride complexes 1–10

Metallocene dichloride complexes with substituted cyclopentadienyl ligands have been synthesized in large numbers in recent years [1,5–8].

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* Corresponding author. Tel.: +49-921-55-2555; fax: +49-921-55-2157.
E-mail address: helmut.alt@uni-bayreuth.de (H.G. Alt).

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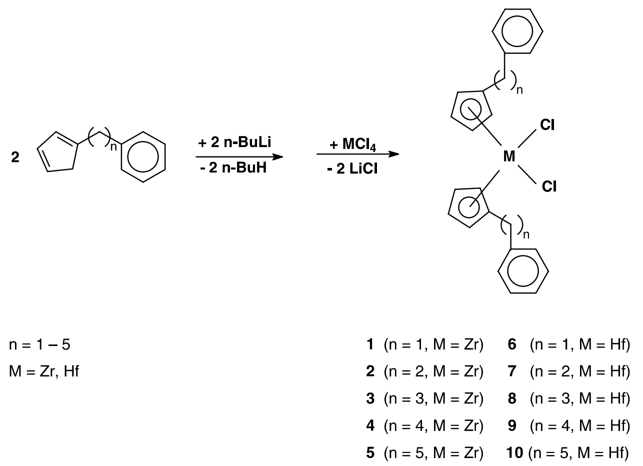


Scheme 1. Synthesis of complexes **1**–**10**.

The reaction of a substituted cyclopentadienyl alkali metal salt [9] with zirconium and hafnium tetrachloride in diethyl ether gave the corresponding zirconocene and hafnocene complexes **1**–**10** (Scheme 1).

The synthesized ω-phenylalkyl substituted hafnocene complexes **7**–**10** are new. They were characterized by ^{1}H and ^{13}C NMR spectroscopy (Table 1, Figs. 1 and 2).

The symmetric complexes **7**–**10** show two multiplet signals between $\delta = 5.89$ and 5.56 ppm for the eight protons of the cyclopentadienyl ligands.The protons of the phenyl ligands are found at $\delta = 7.18$–7.00 ppm. The aliphatic CH_2 bridges give proton signals at $\delta =$ 2.98–0.95 ppm.

In the ^{13}C NMR spectrum the signals for the phenyl carbon atoms appear at $\delta = 128.8$–125.9 ppm, while the carbon atoms of the cyclopentadienyl ligands are found in the region of $\delta = 116.3$–109.0 ppm.

2.2. X-ray structure of the ω-phenylalkyl substituted hafnocene dichloride complex $[\eta^5{:}C_5H_4{-}(CH_2)_3{-}C_6H_5]_2HfCl_2$ (**8**)

The X-ray structural analysis of a single crystal of **8** reveals important bond lengths (pm) and angles (°) (Table 2).

Table 1
^{1}H and ^{13}C NMR data for the metallocene complexes **1**–**10**

Compound	^{1}H NMR[a] δ (ppm)	^{13}C NMR[b] δ (ppm)
1	7.46–7.12 (m, 10H), 6.39–6.32 (m, 4H), 6.28–6.16 (m, 4H), 3.98 (s, 4H)	(Cq): 141.1, 134.2 (CH): 128.6, 128.2, 128.3, 116.8, 112.4 (CH2): 35.7
2	7.47–7.14 (m, 10H), 6.39–6.29 (m, 4H), 6.26–6.16 (m, 4H), 3.14–2.90 (m, 8H)	(Cq): 141.0, 133.9 (CH): 128.5, 128.3, 128.2, 116.6, 112.1 (CH2): 36.6, 32.0
3	7.36–7.18 (m, 10H), 6.30–6.21 (m, 8H), 2.75–2.64 (m, 8H), 1.95–1.89 (m, 4H)	(Cq): 141.8, 134.5 (CH): 128.5, 128.2, 128.1, 116.6, 112.0 (CH2): 35.4, 32.0, 30.0
4	7.39–7.17 (m, 10H), 6.29 (m, 4H), 6.21 (m, 4H), 2.68 (m, 8H), 1.67 (m, 8H)	(Cq): 142.3, 134.6 (CH): 128.3, 128.2, 125.6, 116.6, 112.1 (CH2): 35.5, 30.9, 30.1, 29.9
5	7.39–7.24 (m, 10H), 6.34 (m, 4H), 6.25 (m, 4H), 2.71 (m, 4H), 1.78–1.42 (m, 16H)	(Cq): 142.5, 134.8 (CH): 128.3, 128.1, 128.0, 116.6, 112.1 (CH2): 35.7, 31.1, 30.4, 29.9, 28.8
6	7.15–7.03 (m, 10H), 5.78–5.75 (m, 4H), 5.62–5.59 (m, 4H), 3.92 (s, 4H)	(Cq): 141.5, 132.3 (CH): 128.7, 128.4, 128.1, 115.5, 111.1 (CH2): 35.1
7	7.13–7.00 (m, 10H), 5.70–5.68 (m, 4H), 5.58–5.56 (m, 4H), 2.98–2.67 (m, 8H)	(Cq): 141.3, 131.6 (CH): 128.6, 128.4, 126.0, 115.0, 110.3 (CH2): 36.8, 31.9
8	7.18–7.03 (m, 10H), 5.89–5.87 (m, 4H), 5.64–5.62 (m, 4H), 2.76–1.72 (m,8H),	(Cq): 141.9, 130.9 (CH): 128.5, 128.4, 125.9, 116.3, 110.1 (CH2): 35.6, 32.7, 30.4
9	7.15–7.01 (m, 10H), 5.75–5.72 (m, 4H), 5.63 – 5.61 (m, 4H), 2.49 (m, 8H), 1.15 (m, 8H)	(Cq):141.5, 131.1 (CH):128.7, 128.4, 126.2, 115.7, 110.5 (CH2): 35.3, 30.5, 29.8, 29.0
10	7.14–7.00 (m, 10H), 5.78–5.73 (m, 4H), 5.64 – 5.60 (m, 4H), 2.56 (m, 4H), 1.26–0.95 (m, 16H)	(Cq): 141.8, 131.5 (CH): 128.8, 128.6, 127.0, 115.9, 109.9 (CH2): 35.7, 31.0, 30.8, 29.3, 28.7

[a] 25 °C, in chloroform-d_1, rel. chloroform (7.24).

[b] 25 °C, in chloroform-d_1, rel. chloroform-d_1 (77.0).

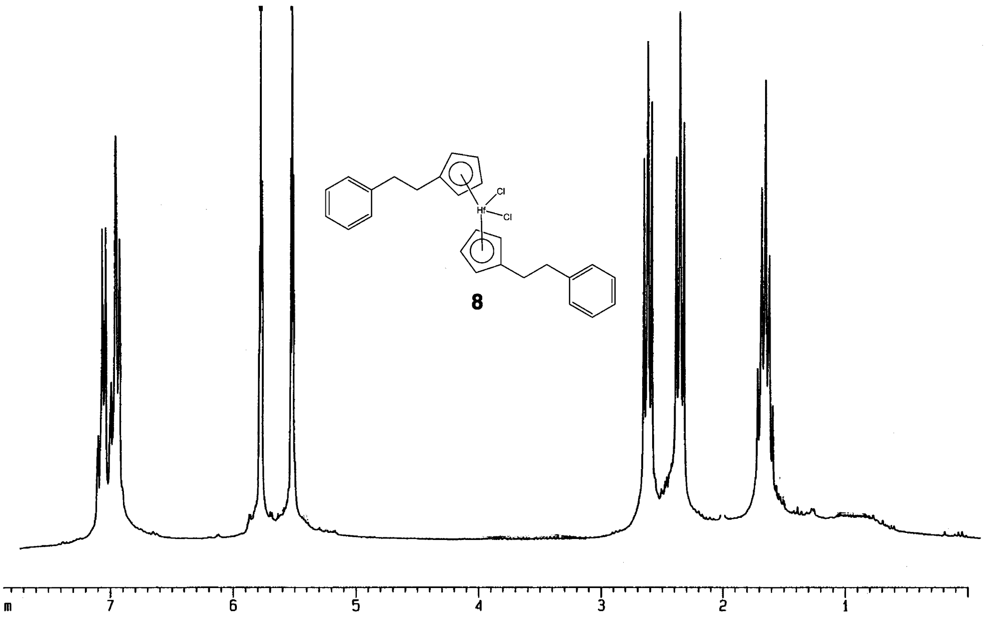


Fig. 1. ^{1}H NMR spectrum of **8**.

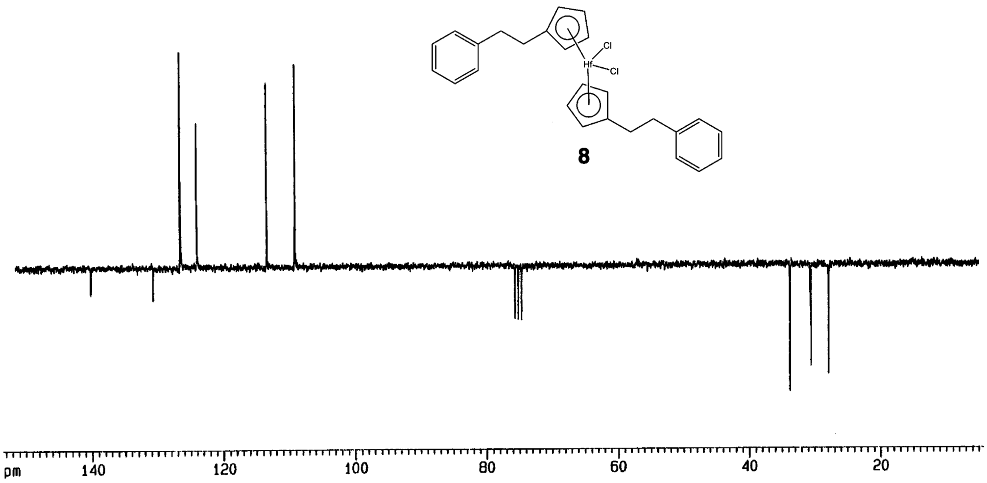


Fig. 2. ^{13}C NMR spectrum of **8**.

Table 2
Important bond distances (pm) and angles (°) of complex **8**

Hf–C(1)#1	255.1	C(9)–C(10)	139.0	C(12)–C(13)	146.0
Hf–C(1)	255.1	C(9)–C(14)	140.0	C(13)–C(14)	136.0
Hf–Cl	257.3	C(10)–C(11)	142.0	C(6)–C(7)	157.0
Hf–Cl#1	257.3	C(11)–C(12)	132.0	C(7)–C(8)	153.0
Cl–Hf–Cl#1	93.31	C(8)–C(7)–C(6)	113.0	C(3)–C(2)–C(1)	121.0
C(1)–C(6)–C(7)	109.9	C(1)–C(5)–C(4)	93.0	C(5)–C(1)–C(2)	111.0
C(9)–C(8)–C(7)	116.0	C(3)–C(4)–C(5)	119.0		

Both substituted cyclopentadienyl ligands are tilted and the bond lengths between the central metal and the cyclopentadienyl carbon atoms vary from 242 to 255.1 pm.

The carbon–carbon distances in the phenyl groups are in the range from 139.0 to 146.0 pm. The carbon–carbon distances between the bridging CH_2 groups differ from 150.0 to 157.0 pm.

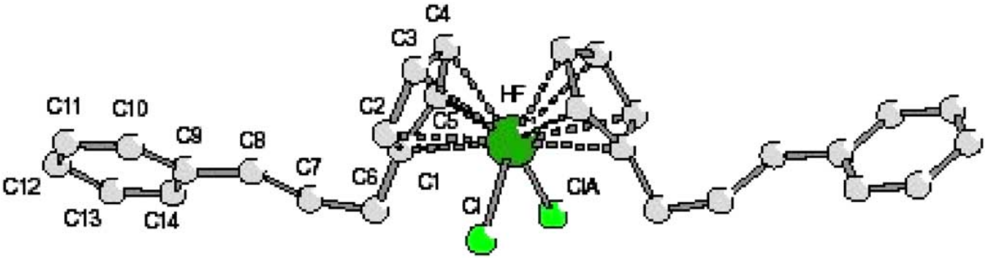


Fig. 3. Molecular structure of **8**; hydrogen atoms omitted for clarity.

Slight differences can be found for the Hf–Cl bond length and Cl–Hf–Cl bond angles observed in the structures of [η^5:C_5H_4–$(CH_2)_3$–η^5:C_5H_4]$HfCl_2$ (242.3 pm, 95.87°) [10], [η^5:$C_5(CH_3)_5$]$_2HfCl_2$ (241.5 pm, 96.04°) [11] and [η^5:C_5H_4–$(CH_2)_3$–C_6H_5]$_2HfCl_2$ (257.3 pm, 93.91°) (**8**).

The structure of the molecule is given in Fig. 3.

2.3. Synthesis and characterization of ω-phenylalkyl substituted zirconocene and hafnocene ethyl chloride complexes

The dichloride complexes **1**–**10** were dissolved in toluene and treated with one equivalent of EtLi in ether. After stirring over night at 0 °C, the ethyl chloride complexes **11**–**20** could be isolated (Scheme 2).

The ethyl chloro zirconocene complexes **11**–**15** are stable at 0 °C, the corresponding hafnocene complexes **16**–**20** could be handled at room temperature without decomposition.

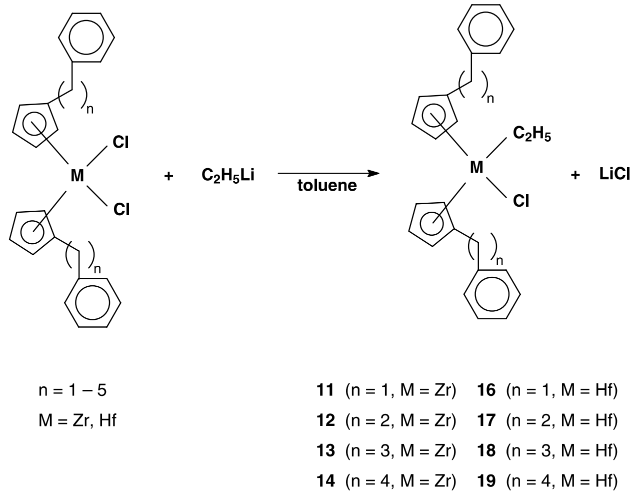
Complexes **11**–**20** were characterized by ^{1}H and ^{13}C NMR spectroscopy (see Table 3, Figs. 4 and 5).

Due to the asymmetry of complexes **11**–**20**, the 8 protons of the ω-phenyl substituted cyclopentadienyl ligands give four resonance signals in the region of $\delta = 5.23$–6.00 ppm. In the ^{1}H NMR spectrum of **17** the ethyl group shows a triplet signal for the methyl group at $\delta = 1.5$ ppm [^3J(H,H) = 7.7 Hz] and a quadruplet signal for the methylene group at $\delta = 0.9$ ppm [^3J(H,H) = 7.7 Hz].

The signals for the aliphatic CH_2 groups of the ω-alkenyl substituent are found as multiplets between $\delta = 2.3$–3.6 ppm. The signals for the two phenyl groups appear as multiplets at $\delta = 7.00$–7.20 ppm.

In the ^{13}C NMR spectrum of **17** the quarternary carbon atom of the phenyl group is observed at $\delta = 141.8$ ppm, while the quarternary carbon atom of the cyclopentadienyl substituent appears at $\delta = 131.5$ ppm.

Further data are listed in Table 3.



Scheme 2. Synthesis of the ω-phenylalkyl substituted zirconocene and hafnocene complexes **11**–**20**.

2.4. Synthesis and characterization of metallacyclic zirconocene ethyl complexes

The reaction between [η^5:C_5H_4–$(CH_2)_n$–C_6H_5]$_2MCl_2$ ($n = 1$–5; M = Zr, Hf) and 2EtLi in toluene results in the formation of the metallacyclic complexes **21**–**22** (M = Zr, $n = 1, 2$) and the formation of the diethyl complexes **23**–**27** (M = Hf, $n = 1$–5) (Scheme 3).

Under CH bond activation the ω-phenyl substituted cyclopentadienyl substituent reacts with 2EtLi.

In the first step a zirconocene diethyl complex is the intermediate that is stable for a few minutes in solution at low temperatures (−60 °C). Under ethane elimination via β-H-transfer a further intermediate, a reactive ethylene complex, is formed that gives the corresponding metallacycles **21** and **22** (Scheme 3).

With two equivalents of EtLi the ω-phenyl substituted hafnocene dichloride complexes **6**–**10** form the corresponding hafnocene diethyl complexes **23**–**27** (Scheme 4).

Metallocene dichloride complexes with C3, C4 or C5$^-$ spacers also react with 2EtLi to give product mixtures that have not yet been completely identified.

Complexes **23**–**27** were isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy (see Table 4).

^{1}H NMR and ^{13}C NMR of the complexes **21**–**27** are listed in Table 4.

Table 3
^1H and ^{13}C NMR data for the metallocene complexes **11**–**20**

Compound	^1H NMR[a] δ (ppm)	^{13}C NMR[b] δ (ppm)
11	7.18–7.05 (m, 10H), 6.00 (m, 2H), 5.73 (m, 2H), 5.46 (m, 2H), 5.31 (m, 2H), 3.58 (s, 4H)	(Cq): 141.7, 131.0 (CH): 128.7, 128.4, 126.2, 115.7, 112.2, 110.5, 108.0 (CH2): 45.3, 34.9 (CH3): 18.9
12	7.17–7.05 (m, 10H), 5.98 (m, 2H), 5.69 (m, 2H), 5.43 (m, 2H), 5.27 (m, 2H), 2.87–2.69 (m, 8H), 1.42 (t, 3H), 1.10 (q, 4H)	(Cq): 141.5, 130.6 (CH): 128.6, 128.4, 126.1, 115.5, 111.9, 110.3, 107.3 (CH2): 45.1, 37.7, 33.1 (CH3): 18.7
13	7.15–7.05 (m, 10H), 6.04 (m, 2H), 5.75 (m, 2H), 5.52 (m, 2H), 5.35 (m, 2H), 2.68–1.77 (m, 12H), 1.46 (t, 3H), 1.11 (q, 4H)	(Cq): 142.1, 131.1 (CH): 128.6, 128.5, 125.9, 115.3, 112.1, 109.5, 107.5 (CH2): 45.1, 35.6, 32.9, 29.8 (CH3): 18.2
14	7.15–7.04 (m, 10H), 6.00 (m, 2H), 5.71 (m, 2H), 5.49 (m, 2H), 5.37 (m, 2H), 2.51 (m, 8H), 1.62 (m, 8H), 1.43 (t, 3H), 1.14 (q, 4H)	(Cq): 141.8, 131.5 (CH): 128.4, 128.2, 125.7, 115.4, 112.4, 109.2, 107.9 (CH2): 44.8, 35.1, 33.2, 30.2 (CH3): 18.2
15	7.14–7.03 (m, 10H), 5.99 (m, 2H), 5.71 (m, 2H), 5.43 (m, 2H), 5.34 (m, 2H), 2.57 (m, 8H), 1.52 (m, 8H), 1.42 (t, 3H), 1.07 (q, 4H)	(Cq): 141.9, 131.2 (CH): 128.7, 128.5, 126.2, 115.5, 112.2, 109.6, 108.3 (CH2): 45.5, 35.4, 31.3, 30.5, 29.6, 28.5 (CH3): 18.5
16	7.15–7.05 (m, 10H), 6.04 (m, 2H), 5.75 (m, 2H), 5.52 (m, 2H), 5.35 (m, 2H), 2.68–1.77 (m, 12H), 1.46 (t, 3H), 1.11 (q, 4H)	(Cq): 142.1, 131.1 (CH): 128.6, 128.5, 125.9, 115.3, 112.1, 109.5, 107.5 (CH2): 45.1, 35.6, 32.9, 29.8 (CH3): 18.2
17	7.15–7.04 (m, 10H), 6.00 (m, 2H), 5.71 (m, 2H), 5.49 (m, 2H), 5.37 (m, 2H), 2.51 (m, 8H), 1.62 (m, 8H), 1.43 (t, 3H), 1.14 (q, 4H)	(Cq): 141.8, 131.5 (CH): 128.4, 128.2, 125.7, 115.4, 112.4, 109.2, 107.9 (CH2): 44.8, 35.1, 33.2, 30.2 (CH3): 18.2
18	7.14–7.03 (m, 10H), 5.99 (m, 2H), 5.71 (m, 2H), 5.43 (m, 2H), 5.34 (m, 2H), 2.57 (m, 8H), 1.52 (m, 8H), 1.42 (t, 3H), 1.07 (q, 4H)	(Cq): 141.9, 131.2 (CH): 128.7, 128.5, 126.2, 115.5, 112.2, 109.6, 108.3 (CH2): 45.5, 35.4, 31.3, 30.5, 29.6, 28.5 (CH3): 18.5
19	7.18–7.03 (m, 10H), 5.92 (m, 2H), 5.66 (m, 2H), 5.42 (m, 2H), 5.28 (m, 2H), 3.21 (s, 4H), 1.67 (t, 3H), 0.0.95 (q, 4H)	(Cq): 141.7, 129.6 (CH): 128.6, 128.5, 125.9, 113.9, 110.8, 108.5, 107.2 (CH2): 46.7, 37.5 (CH3): 18.2
20	7.17–7.03 (m, 10H), 5.88 (m, 2H), 5.64 (m, 2H), 5.38 (m, 2H), 5.24 (m, 2H), 2.86–2.68 (m, 8H), 1.63 (t, 6H), 0.86 (q, 8H)	(Cq): 141.6, 129.7 (CH): 128.6, 128.4, 126.0, 114.1, 110.9, 108.8, 106.8 (CH2): 45.2, 37.3, 31.9 (CH3): 17.0

[a] 25 °C, in benzene-d_6, rel. benzene (7.15).

[b] 25 °C, in benzene-d_6, rel. benzene-d_6 (128.0).

The metallacycles **21**, **22** and the hafnocene diethyl complexes **23**–**27** were characterized by ^1H and ^{13}C NMR spectroscopy. NMR data is listed in Table 4.

The reaction of Cp_2ZrCl_2 and two equivalents of EtMgCl as alkylating reagent leads to the formation of the dinuclear complex $[Cp_2ZrEt]_2(\mu\text{-ethene})$ [12,13].

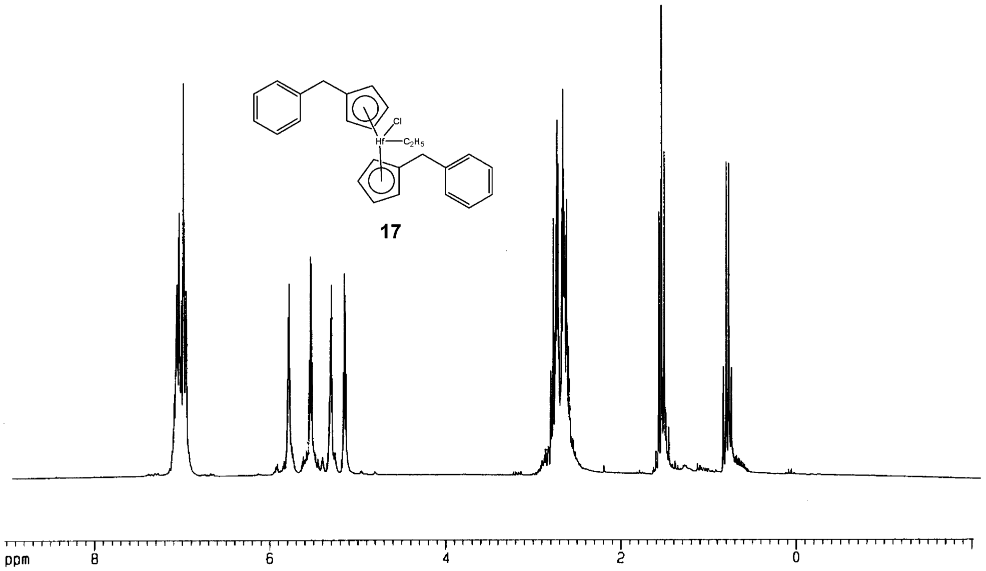


Fig. 4. (a) ^{1}H NMR spectrum of complex **17**. (b) ^{13}C NMR spectrum of complex **17**.

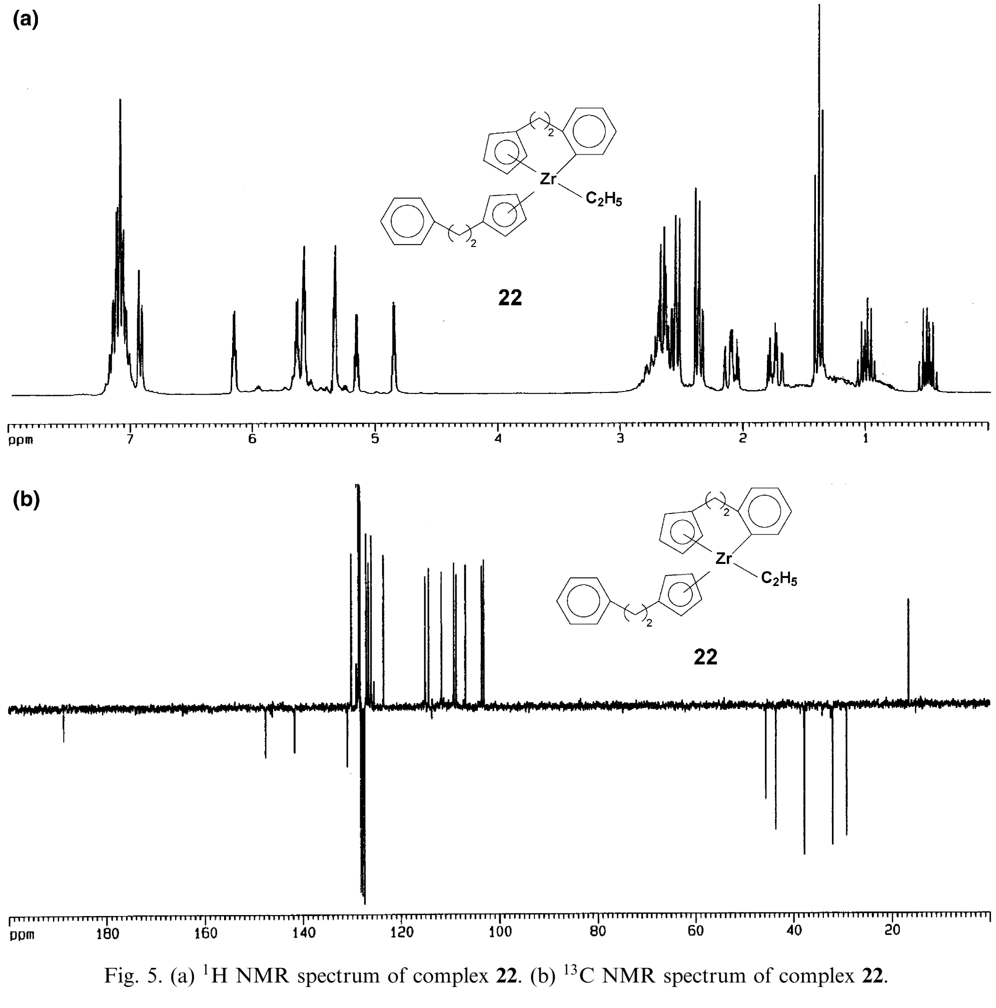
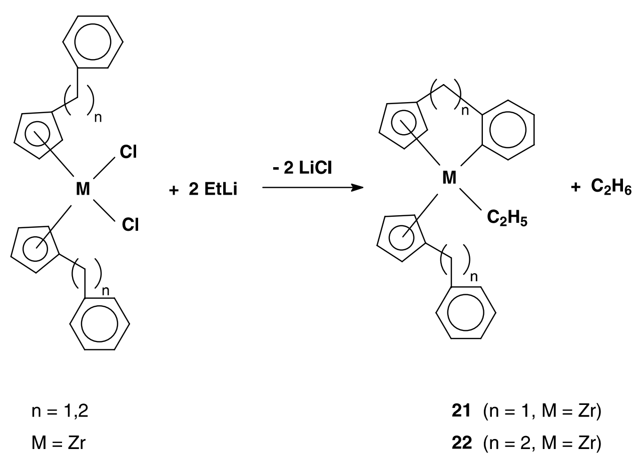
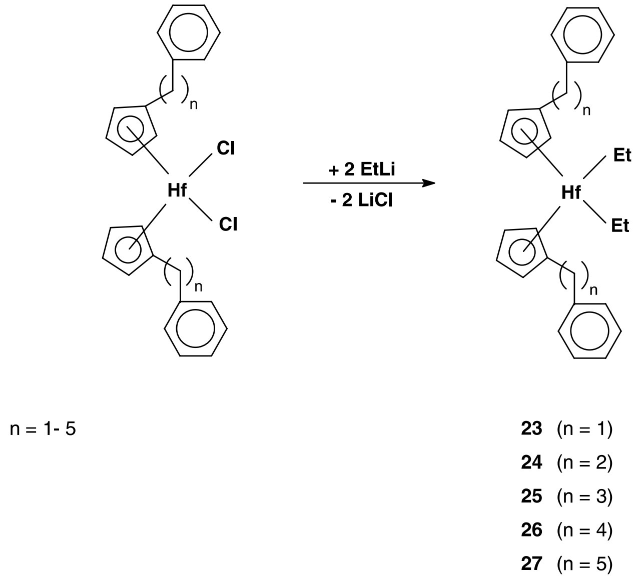


Fig. 5. (a) ^{1}H NMR spectrum of complex **22**. (b) ^{13}C NMR spectrum of complex **22**.



Scheme 3. Synthesis of the metallacyclic zirconocene ethyl complexes **21** and **22**.



Scheme 4. Synthesis of the hafnocene diethyl complexes **23**–**27**.

In the ^{1}H NMR spectrum of **22** (Fig. 5) the eight cyclopentadienyl protons show six different signals in the area of $\delta = 6.17$–4.48 ppm.

This indicates a dissymmetric metallocene complex structure.

The hydrogen atoms of the ethyl group are diastereotopic and show two multiplets at $\delta = 1.06$–0.52 ppm (CH_2) and a triplet at $\delta = 1.40$ ppm (CH_3).

The signals for the phenyl groups appear in the region of $\delta = 7.17$–6.90 ppm.

The protons of the C2 spacer of the metal bonded phenyl groups are diastereotopic and form 4 multiplet signals in the range of $\delta = 2.72$–1.75 ppm, while the protons of the C2 spacer of the free phenyl group appear as two multiplet signals between $\delta = 2.60$–2.34 ppm.

In the ^{1}H NMR spectrum of **21** the fixed C1 spacer shows two doublet signals at $\delta = 3.95$ and 3.82 ppm and the "free" C1 spacer a singlet signal at $\delta = 3.49$ ppm.

The ^{13}C NMR spectrum of the metallacycle **22** shows eight different tertiary carbon signals for both cyclopentadienyl ligands in the region of $\delta = 115.0$–103.2 ppm. The two differently shielded C2-spacers give four different resonance signals at $\delta = 45.7$, 43.6, 32.0 and 29.2 ppm.

Separated signals are observed for the carbon atoms of the non-bonded and the bonded phenyl groups in the region of $\delta = 130.9$–129.5 ppm.

The shift for the zirconium bonded, quarternary carbon atom of the phenyl group is observed at $\delta = 189.0$ ppm.

The resonance signals for the ethyl group are observed at $\delta = 45.7$ (CH_2) and 16.5 ppm (CH_3).

2.5. Synthesis and characterization of dinuclear zirconium and hafnium chloride complexes

Surprisingly the reaction of the ω-phenyl substituted cyclopentadienyl zirconium or hafnium complexes **1**–**10** with an excess of lithium ethyl in diethyl ether (Scheme 5) gives dinuclear complexes with η^5-cyclopentadienyl ligands, η^6-phenyl ligands and bridging chloro ligands. Obviously the metal prefers the η^6-coordination of an arene ligand instead of a phenylalkyl substituted cyclopentadienyl ligand.

The reducing agent EtLi leads to a change of the oxidation number of zirconium and hafnium from IV to II.The composition of the complexes has been established by elemental analysis, mass spectroscopy and NMR spectroscopy.

Similar mononuclear complexes containing η^6-bonded arene ligands have been described in the literature [8,14–19]. Typical examples are complexes like $[(\eta^5{:}C_5H_4{-}CMe_2{-}\eta^6{:}C_6H_5)MMe_2]^+$ (M = Ti, Zr) and $[(\eta^5{:}C_5H_4{-}CMe_2{-}CH_2{-}\eta^6{:}C_6H_5)MMe_2]^+$ [8,16] that are stabilized by perfluorated anions like $[B(C_6F_5)_4]^-$.

Also dinuclear dications are known such as the dimethyl bridged η^6-toluene ligands containing complexes $[(\eta^5{:}C_5H_3R_2)(\eta^6{:}C_6H_5Me)Hf(\mu{-}Me)]_2^+$ (R = $SiMe_3$) [17].

Neutral complexes with η^6-bonded arene ligands like $(\eta^6{:}C_6H_6)_2Ti$ are also known from cocondensation reactions [18,19] and prove this type of bonding mode.

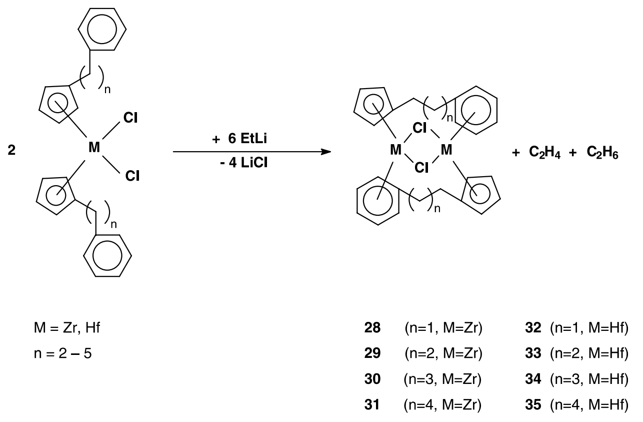
The apparently strong coordination of the phenyl groups to the metal is an indication for the fact that the solvent can play an important role in olefin polymerization when metallocene complexes are applied as catalysts.

It is not possible to obtain these dinuclear complexes **28**–**35** with an excess of BuLi instead of EtLi. The products of this reaction are a mixture and not yet identified. Different from this reaction, Cp_2ZrCl_2 and BuLi give butane, butene and Cp_2ZrBu_2 that reacts immediately under decomposition [7,20–26].

Table 4
^{1}H and ^{13}C NMR data for complexes **21**–**27**

Compound	^{1}H NMR^{a} δ (ppm)	^{13}C NMR^{b}s δ (ppm)
21	7.36–7.13 (m, 9H), 6.37 (m, 1H), 6.04 (m, 1H), 5.92 (m, 2H), 5.86 (m, 2H), 5.46 (m, 1H), 5.02 (m, 1H), 3.96 (d, 1H), 3.76 (d, 1H), 3.46 (s, 2H) 1.41 (t, 3H), 1.26–0.85 (m, 2H)	(Cq): 186.1, 162.5, 141.9, 138.5 (CH):138.4, 128.9, 128.5, 128.0, 127.0, 125.2, 123.3, 115.8, 113.9, 111.7, 110.3, 109.2, 107.5, 104.2, 103.9 (CH2): 56.2, 38.1, 37.7, 30.0 (CH3): 17.2
22	7.16–6.93 (m, 9H), 6.17 (m, 1H), 5.67 (m, 1H), 5.62 (m, 2H), 5.36 (m, 2H), 5.18 (m, 1H), 4.88 (m, 1H), 2.72–2.54 (m, 6H), 2.41–2.12 (m, 2H), 1.41 (t, 3H), 1.06–0.52 (m, 2H)	(Cq): 189.3, 147.5, 141.6, 130.9 (CH):130.0, 128.5, 128.3, 127,3 127.0, 125.9, 123.5, 115.0, 114.3, 111.7, 109.2, 108.7, 106.8, 103.6, 103.1 (CH2): 45.7, 43.6, 37.8, 32.0 29.2 (CH3): 16.6
23	7.19–7.00 (m, 10H), 5.58 (m, 8H), 3.19 (s, 4H), 1.49 (t, 6H), 0.14 (q, 8H)	(Cq): 141.8, 126.0 (CH): 128.8, 128.6, 126.1, 110.5, 108.7 (CH2): 50.0, 36.5 (CH3): 16.2
24	7.17–7.02 (m, 10H), 5.54 (m, 8H), 2.75–2.54 (m, 8H), 1.46 (t, 6H), 0.13 (q, 8H)	(Cq): 141.6, 125.7 (CH): 128.6, 128.4, 125.9, 110.0, 108.1 (CH2): 49.2, 38.5, 31.8 (CH3): 15.8
25	7.16–7.02 (m, 10H), 5.49 (m, 8H), 2.62–2.31 (m, 12H), 1.47 (t, 6H), 0.14 (q, 8H)	(Cq): 141.4, 125.1 (CH): 128.6, 128.3, 125.8, 109.8, 107.9 (CH2): 49.0, 38.3, 31.5, 30.1 (CH3): 15.3
26	7.17–7.01 (m, 10H), 5.50 (m, 8H), 2.21 (m, 8H), 1.46 (t, 6H), 1.00 (m, 8H) 0.13 (q, 8H)	(Cq): 141.6, 125.4 (CH): 128.8, 128.6, 126.0, 110.3, 107.9 (CH2): 48.9, 38.2, 34.8, 33.0, 31.9 (CH3): 15.8
27	7.17–7.02 (m, 10H), 5.48 (m, 8H), 2.69 (m, 4H), 1.46 (t, 6H), 1.10– 0.75 (m, 16H), 0.14 (q, 8H)	(Cq): 141.1, 126.2 (CH): 128.7, 128.4, 126.1, 110.2, 108.3 (CH2): 48.7, 37.5, 35.8, 33.3, 32.2, 29.9 (CH3): 15.9

[a] 25 °C, in benzene-d_6, rel. benzene (7.15)
[b] 25 °C, in benzene-d_6, rel. benzene-d_6 (128.0).



Scheme 5. Synthesis of the dinuclear complexes **28**–**35**.

Dinuclear zirconium or hafnium complexes are often synthesized as μ-oxo [27–31], μ-halo [32–37] or μ-hydrido bridged compounds [38–45].

For the formation of complexes **28**–**35**, the length of the CH_2 spacers is the decisive factor. For steric reasons $(\eta^5{:}C_5H_4{-}CH_2{-}C_6H_5)_2ZrCl_2$ cannot form a corresponding dinuclear compound. The distance between the Cp ligand and the Ph group is not long enough for a dinuclear species.

In the zirconocene complexes **2**–**5** and hafnocene complexes **7**–**10,** with more than one CH_2 spacer, the steric conditions are sufficient for the formation of complexes **28**–**35**.

Complexes **28**–**35** were characterized by ^{1}H and ^{13}C NMR spectroscopy (see Table 5). Fig. 6 shows the ^{1}H NMR spectrum of complex **29**.

Four different resonance signals at $\delta = 6.19$, 6.05, 5.81 and 5.74 ppm are assigned to the eight cyclopentadienyl protons. This is in accordance with the asymmetry of the complex. The resonance signals for the three CH_2 spacer groups are found as multiplets at $\delta = 2.69$, 2.57 and 1.85 ppm. The two phenyl groups appear as a multiplet at $\delta = 7.19$–7.08 ppm.

Fig. 7 represents the ^{13}C NMR spectrum of the dinuclear complex **29**. The four different, tertiary carbon resonance signals for the cyclopentadienyl ligands appear at

Table 5
^{1}H and ^{13}C NMR data for the dinuclear complexes **28**–**43**

Compound	^{1}H NMR^{a} δ (ppm)	^{13}C NMR^{b} δ (ppm)
28	7.16–7.00 (m, 10H), 5.94 (vq, 2H), 5.88 (vq, 2H), 5.77 (vq, 2H), 5.73 (vq, 2H), 2.94 (m, 4H), 2.68 (m, 4H)	(Cq): 141.1, 133.0 (CH): 129.0, 128.6, 126.0, 116.5, 113.4, 112.9, 108.7 (CH2): 37.5, 32.7
29	7.19–7.08 (m, 10H), 6.20 (vq, 2H), 6.06 (vq, 2H), 5.80 (vq, 2H), 5.74 (vq, 2H), 2.72–2.55 (m,8H), 1.85 (vq, 4H)	(Cq): 142.1, 130.5 (CH): 128.6, 128.5, 125.9, 116.7, 113.4, 113.2, 108.9 (CH2): 35.6, 33.1, 30.1
30	7.19–7.03 (m, 10H), 6.21 (vq, 2H), 6.06 (vq, 2H), 5.81 (vq, 2H), 5.72 (vq, 2H), 2.69 (m, 4H), 2.53 (m, 4H), 1.58 (m, 8H)	(Cq): 142.4, 130.7 (CH): 128.5, 128.3, 125.7, 117.5, 113.2, 113.1, 108.7 (CH2): 35.8, 31.2, 31.0, 30.5
31	7.18–7.06 (m, 10H), 6.23 (vq, 2H), 6.08 (vq, 2H), 5.84 (vq, 2H), 5.73 (vq, 2H), 2.72 (m, 4H), 2.61 (m, 8H), 1.57–1.35 (m, 8H)	(Cq): 142.4, 130.7 (CH): 128.5, 128.3, 125.7, 116.8, 113.2, 113.1, 108.7 (CH2): 35.8, 31.2, 31.1, 30.5, 30.4
32	7.16–7.03 (m, 10H), 6.11 (vq, 2H), 5.83 (vq, 2H), 5.77 (vq, 2H), 5.55 (vq, 2H), 2.96 (m, 4H), 2.70 (m, 4H)	(Cq): 141.2, 131.0 (CH): 128.6, 128.4, 126.0, 116.4, 114.7, 110.4, 109.9 (CH2): 36.9, 32.3
33	7.19–7.08 (m, 10H), 6.14 (vq, 2H), 6.02 (vq, 2H), 5.75 (vq, 2H), 5.64 (vq, 2H), 2.75–2.51 (m, 8H), 1.82 (vq, 4H)	(Cq): 142.1, 128.7 (CH): 128.5, 128.3, 125.9, 115.5, 112.3, 107.4 (CH2): 35.6, 33.2, 30.0
34	7.19–7.03 (m, 10H), 6.18 (vq, 2H), 6.06 (vq, 2H), 5.87 (vq, 2H), 5.62 (vq, 2H), 2.71 (m, 4H), 2.57 (m, 4H), 1.61 (m, 8H)	(Cq): 142.2, 129.1 (CH): 128.5, 128.3, 125.7, 115.8, 112.5, 107.9 (CH2): 35.8, 32.9, 31.0, 30.2
35	7.17–7.02 (m, 10H), 6.19 (vq, 2H), 6.08 (vq, 2H), 5.92 (vq, 2H), 5.69 (vq, 2H), 2.70 (m, 4H), 2.59 (m, 8H), 1.60–1.41 (m, 8H)	(Cq): 142.4, 129.0 (CH): 128.6, 128.2, 126.1, 116.0, 112.8, 112.7, 108.0 (CH2): 36.2, 33.2, 31.1, 30.5, 30.2
36	7.19–7.09 (m, 10H), 5.70 (vq, 2H), 5.65 (vq, 2H), 5.58 (vq, 2H), 5.36 (vq, 2H), 2.78 (m, 4H), 2.62 (m, 4H), 0.20 (s, 6H)	(Cq): 141.8, 127.0 (CH): 128.6, 128.5, 126.0, 111.4, 110.5, 110.0, 106.9 (CH2): 38.1, 32.2 (CH3): 22.5
37	7.18–7.07 (m, 10H), 5.72 (m, 4H), 5.65 (vq, 2H), 5.46 (vq, 2H), 2.57 (m, 4H), 2.36 (m, 4H), 1.84 (m, 4H), 0.18 (s, 6H)	(Cq): 142.4, 126.9 (CH): 128.8, 128.7, 126.9, 111.8, 110.8, 110.3, 107.4 (CH2): 35.9, 33.6, 29.7 (CH3): 22.7
38	7.17–7.06 (m, 10H), 5.69 (vq, 2H), 5.67 (vq, 2H), 5.65 (vq, 2H), 5.41 (vq, 2H), 2.53 (m, 4H), 2.62 (m, 4H), 1.62 (m, 8H), 0.18 (s, 6H)	(Cq): 142.6, 127.1 (CH): 128.9, 128.8, 127.2, 112.5, 111.1, 110.9, 107.6 (CH2): 36.2, 32.6, 32.2, 29.7 (CH3): 22.9
39	7.18–7.06 (m, 10H), 5.63 (m, 4H), 5.59 (vq, 2H), 5.39 (vq, 2H), 2.42 (m, 4H), 2.29 (m, 8H), 1.50–1.32 (m, 8H)	(Cq): 142.7, 126.8 (CH): 128.7, 128.6, 126.7, 111.9, 111.8, 110.9, 108.5 (CH2): 36.1, 32.2, 31.5, 31.1, 29.9 (CH3): 23.1
40	7.17–7.06 (m, 10H), 5.96 (vq, 2H), 5.63 (vq, 2H), 5.58 (vq, 2H), 5.35 (vq, 2H), 2.76 (m, 4H), 2.51 (m, 4H), 0.20 (s, 6H)	(Cq): 141.3, 126.5 (CH): 128.6, 128.5, 126.1, 111.2, 110.3, 109.6, 107.9 (CH2): 37.5, 32.4 (CH3): 22.5
41	7.18–7.08 (m, 10H), 5.64 (m, 4H), 5.48 (vq, 2H), 5.36 (vq, 2H), 2.37–2.20 (m, 8H), 1.81 (m, 4H), 0.18 (s, 6H)	(Cq): 141.4, 126.9 (CH): 128.8, 128.7, 126.2, 111.8, 111.7, 110.5, 107.6 (CH2): 35.7, 33.6, 29.7 (CH3): 21.9
42	7.19–7.08 (m, 10H), 5.69 (vq, 2H), 5.67 (vq, 2H), 5.35 (vq, 2H), 5.21 (vq, 2H), 2.51 (m, 4H), 2.41 (m, 4H), 1.59 (m, 8H), 0.21 (s, 6H)	(Cq): 141.6, 127.1 (CH): 128.9, 128.8, 126.7, 112.1, 111.9, 110.7, 107.5 (CH2): 36.2, 33.2, 32.7, 29.9 (CH3): 22.9

Table 5 (*continued*)

Compound	^{1}H NMR^{a} δ (ppm)	^{13}C NMR^{b} δ (ppm)
43	7.18–7.06 (m, 10H), 5.63 (m, 4H), 5.31 (vq, 2H), 5.22 (vq, 2H), 2.42 (m, 4H), 2.27 (m,8H), 1.49–1.30 (m, 8H), 0.20 (s, 6H)	(Cq): 141.5, 126.8 (CH): 128.7, 128.6, 126.5, 111.6, 111.4, 110.9, 107.6 (CH2): 36.1, 32.5, 31.9, 31.1, 29.9 (CH3): 22.5

[a] 25 °C, in benzene-d_6, rel. benzene (7.15).

[b] 25 °C, in benzene-d_6, rel. benzene-d_6 (128.0).

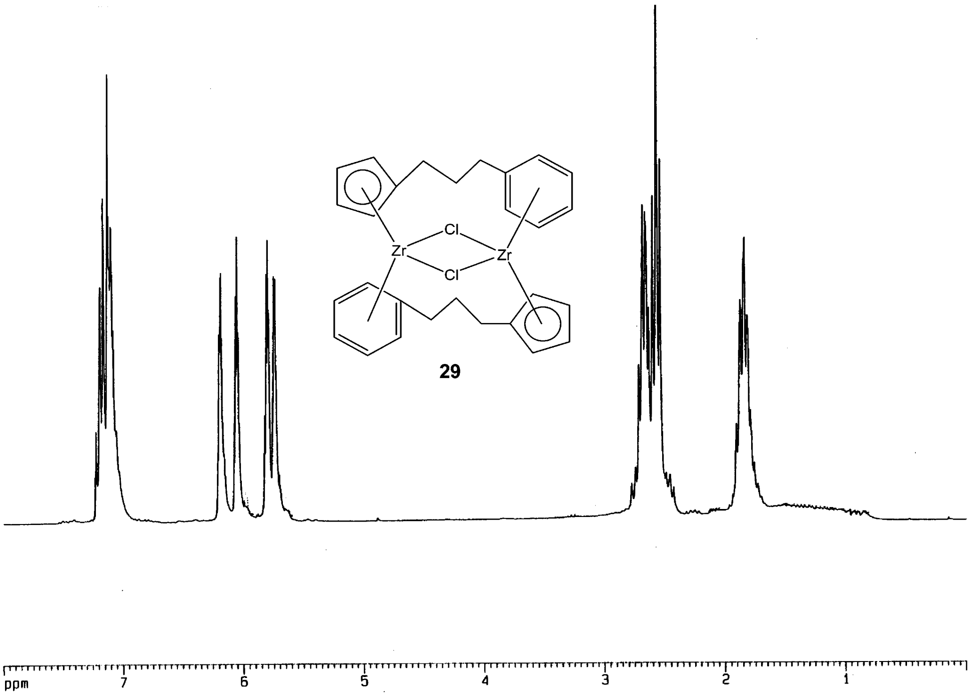


Fig. 6. ^{1}H NMR spectrum of complex **29**.

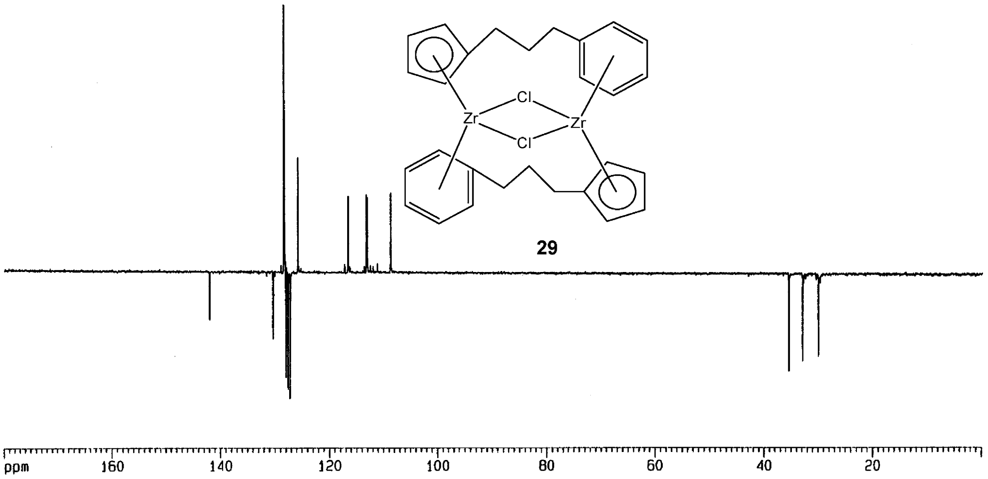
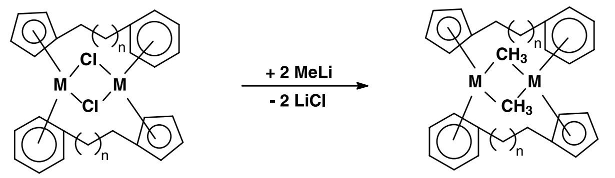


Fig. 7. ^{13}C NMR spectrum of complex **29**.

$\delta = 116.8$, 113.4, 113.2 and 108.8 ppm, the quarternary carbon atom at $\delta = 130.5$ ppm. The three CH_2 spacer groups give resonance signals at $\delta = 35.6$, 33.1 and 30.1 ppm, the ten carbon atoms of the phenyl groups at $\delta = 128.5$, 128.4 and 125.9 ppm. The quarternary carbon atom of the phenyl group is found at $\delta = 142.1$ ppm.



Scheme 6. Synthesis of complexes **36**–**43**.

2.6. Synthesis and characterization of methyl bridged dinuclear ω-phenyl substituted cyclopentadienyl complexes of zirconium(II) and hafnium(II)

The reaction of the dinuclear chloro bridged complexes **28**–**35** and two equivalents of MeLi gives the dinuclear methyl bridged zirconium(II) and hafnium(II) complexes **36**–**43** (Scheme 6).

Like the corresponding chloro complexes **28**–**35,** the methyl substituted compounds **36**–**43** are characterized by ^{1}H and ^{13}C NMR spectroscopy (Table 5).

2.7. Polymerization reactions

2.7.1. Homogeneous ethylene polymerization

Complexes **7**–**43** were dissolved in toluene solution, activated with MAO (Al:Zr = 2500:1) and used for homogeneous polymerization of ethylene at 60 °C, 10 bar ethylene pressure in pentane solution, for 1 h. The results of the activity of the catalysts for the polymerization of ethylene will be published later.

3. Experimental

3.1. NMR spectroscopy

The instrument Bruker ARX 250 was available for recording NMR spectra. The organometallic samples were transferred into NMR tubes under argon and measured at 25 °C. The chemical shifts in the ^{1}H NMR spectra are referenced to the residual proton signal of the solvent ($\delta = 7.24$ ppm for chloroform, $\delta = 7.15$ ppm for benzene) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform-d$_1$, $\delta = 128.0$ ppm for benzene-d$_6$).

3.2. Gas chromatography

Organic compounds were analyzed with a Perkin–Elmer Auto System Gas Chromatograph with flame ionization detector. The gas chromatograph was equipped with a 30 m J&W Fused Silica Column (DB 1, film thickness 0.25 μm). Carrier gas was helium, flow through the column was 4 ml min^{-1} (split 1:15, 60 ml min^{-1}).

3.3. Mass spectroscopy

Routine measurement were performed using a Varian MAT CH7 instrument (direct inlet, electron impact ionization 70 eV) in the Central Analytical Department at the University of Bayreuth.

3.4. Elemental analysis

The micro analyses were conducted by the Mikroanalytisches Labor Pascher, Remagen.

3.5. X-ray data analysis

The crystal data and structure refinements were conducted with a Siemens P4-diffractometer at the University of Bayreuth.

Crystal data and structure refinements of complex **8**:

Colourless crystals from toluene with a monoclinic crystal system and a C_2/c space group. The unique cell dimension are $a = 2879.0$ pm, $b = 714.4$ pm and $c = 1255.4$ pm. $V = 250180.0$ pm^3, $Z = 4$, $d_{\mathrm{calc}} = 1.635$ Mg/m^3, absorption coefficient: 4.396 mm^{-1}, $F(000) = 1216$, reflections collected: 2236, independent reflections: 2236, Goodness-of-fit on $F^2 = 1.159$, R indices (all data): $R_1 = 0.1020$, $wR_2 = 0.2893$.

The crystal was measured at a temperature of 293 K.

3.6. General synthesis procedure for the cyclopentadienyl derivatives

Sodium cyclopentadienyl (160 mmol) was placed in a reaction flask and 100 ml ammonia were condensed into it at −78 °C. Within 1 h, 100.0 mmol of the corresponding α-phenylalkylbromide, dissolved in 100 ml *n*-pentane, were added dropwise to the dark brown solution at −78 °C. The reaction mixture was stirred for 2 h at −78 °C and then slowly warmed up to room temperature (r.t). Ammonia was allowed to evaporate. The residue was mixed with 200 ml *n*-pentane, the suspension filtered over sodium sulfate and silica gel and the solvent evaporated in vacuo. The products were obtained as colourless to light yellow oils in 80–90% yields.

3.7. General synthesis procedure for the metallocene dichloride complexes $[\eta^5{:}C_5H_4{-}(CH_2)_n{-}C_6H_5]_2MCl_2$ *[M = Zr, n = 1–5 (**1**–**5**); M = Hf, n = 1–5 (**6**–**10**)]*

The ligand precursor (10.0 mmol) was dissolved in 100 ml diethyl ether at −78 °C and reacted with 6.3 ml (10.0 mmol) *n*-butyllithium (1.6 M in *n*-hexane). Then zirconium tetrachloride or hafnium tetrachloride (5.0 mmol) were added at −78 °C and the reaction mixture was stirred over night at r.t.

The suspension was filtered over sodium sulfate and the solution evaporated. The residue was washed twice with *n*-pentane and freed from solvent residues in vacuo. The yields were 70–80%. The complexes are characterized in Table 1.

3.8. General synthesis procedure for the metallocene ethyl chloride complexes [η^5:C_5H_4–$(CH_2)_n$–C_6H_5]$_2$M(C_2H_5)Cl [M = Zr, n = 1–5 (**11–15**); M = Hf, n = 1–5 (**16–20**)]

EtLi (5.0 mmol, 3.13 ml, 1.6 M in ether) was added to 5.0 mmol of the metallocene dichloride complexes in toluene at 0 °C. The reaction mixture was stirred for 15 h at 0 °C. After filtration over sodium sulfate, the toluene/ether solvent was removed in vacuo. The residue was extracted twice with 50 ml pentane, the solution was filtered over sodium sulfate and the solvent was evaporated again in vacuo. The yields were 65–70%.

3.9. General synthesis procedure for the metallacyclic complexes [η^5:C_5H_4–$(CH_2)_n$–C_6H_5] [η^5:C_5H_4–$(CH_2)_n$–η^1:C_6H_4]$_2$MC_2H_5 [M = Zr, n = 1 (21); M = Zr, n = 2 (22)]

The corresponding metallocene complex (3.0 mmol) was dissolved in toluene and 6.0 mmol (3.75 ml) of EtLi (1.6 M in ether) were added at −78 °C. The reaction mixture was warmed to r.t. and stirred over night. It was filtered over sodium sulfate and the solvent was removed in vacuo. The yields were 75–85%.

3.10. General synthesis procedure for the diethyl complexes [η^5:C_5H_4–$(CH_2)_n$–C_6H_5]$_2$Hf$(C_2H_5)_2$ (n = 1–5; **23–27**)

To a solution of 3.0 mmol of the corresponding hafnocene dichloride complex in 100 ml toluene 6.0 ml (3.75 ml) of EtLi (1.6 M in ether) were added at r.t. After stirring over night, the solvents were evaporated in vacuo. The residue was extracted twice with 50 ml pentane, the pentane solution was filtered over sodium sulfate and the solution was evaporated in vacuo. The yields were 85–90%.

3.11. General synthesis procedure for the dinuclear complexes [η^5:C_5H_4–$(CH_2)_n$–η^6:C_6H_5]$_2$$M_2Cl_2$ [M = Zr, n = 2–5 (**28–31**); M = Hf, n = 2–5 (**32–35**)]

EtLi (9.0 mmol, 5.63 ml, 1.6 M in ether) was added at 0 °C to a solution of the corresponding metallocene complex (6.0 mmol) in 100 ml toluene.

The reaction mixture was stirred for 15 h at 0 °C and then filtered over sodium sulfate. The solvent was evaporated in vacuo and the residue was extracted twice with 30 ml pentane. After evaporation of the solvents the yields were 35–40%.

Elemental analysis of complex **29**: Calc. C, 54.35; H, 4.85; Cl, 11.45. Found: C, 57.20; H, 5.21; Cl, 11.8%.

The mass spectrum of complex **29** shows the molecular peak at M^+ 618.

3.12. General synthesis procedure for the dinuclear complexes [η^5:C_5H_4–$(CH_2)_n$–η^6:C_6H_5]$_2$$M_2(CH_3)_2$ [M = Zr, n = 2–5 (**36–39**); M = Hf, n = 2–5 (**40–43**)]

3.0 mmol (1.9 ml) of MeLi (1.6 M in ether) were added to a solution of 3.0 mmol of the corresponding dinuclear chloride complex in toluene at 0 °C. After stirring over night, the reaction mixture was filtered over sodium sulfate and the solvents were evaporated in vacuo. The residue was extracted twice with 50 ml pentane. After filtration over sodium sulfate, the solvent was removed in vacuo. The yields were 70–80%.

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