ELSEVIER

Journal of Organometallic Chemistry 512 (1996) 51–60

Journal of Organometallic Chemistry

C_2-symmetric bis(fluorenyl) complexes: four complex models as potential catalysts for the isospecific polymerization of propylene

Helmut G. Alt *, Roland Zenk

Laboratorium für Anorganische Chemie der Universität Bayreuth, Box 10 12 51, D-95440 Bayreuth, Germany

Received 23 May 1995; in revised form 6 October 1995

Abstract

Four possible structures of C_2-symmetric bis(fluorenyl)zirconium complexes are presented. Three bis(fluorenyl)zirconocene complexes have been prepared and tested for the polymerization of propylene and ethylene. *rac*/*meso*-Dichloro[η^{10}-(1,2-ethanediyl)bis(7*H*-benzo[c]fluoren-7-ylidene)zirconium (**10**/**10** *) seems to be the most active polymerization catalyst for ethylene.

Keywords: Zirconium; Iron; Metallocenes; Propylene; Catalysis; Polymerization

1. Introduction

Many examples of C_2-symmetric zirconium complexes are known in the art, bearing substituted cyclopentadienyl and indenyl ligands. On activation with methyl aluminoxane (MAO) these catalysts produce isotactic polypropylene [1–25]. In contrast, there are only a few substituted bis(fluorenyl)zirconium complexes [26–30] and only a small number thereof are C_2-symmetric [28,30]. The goal of this work was to explore the ability of C_2-symmetric bis(fluorenyl) complexes for isospecific polymerization of propylene. Four new complex models are presented which have a structure that may satisfy this principle.

2. Results and discussion

There are many examples of C_2-symmetric racemic *ansa*-bis(cyclopentadienylidene) and *ansa*-bis(indenylidene) metal dichloride complexes showing good isospecificity in the polymerization of α-olefins. In the case of bis(fluorenyl) metal dichloride complexes the higher degree of symmetry must be lowered to obtain potential isospecific polymerization catalysts. This could be achieved by introducing suitable substituents or a stereorigid bridge twisting both fluorenylidene fragments with respect to each other (Fig. 1).

Fig. 2 schematically shows four different models that fulfil these criteria. In model 1 a (biphenyl)ylene bridge produces a helical arrangement of the fluorenyl fragments. Model 2 contains a 1,1'-disubstituted ferrocene joint. Model 3 is the racemate of a twofold benzene anellated dichloro-[η^{10}-(1,2-ethanediyl)bis(9*H*-fluoren-9- ylidene)zirconium [29]. In model 4 large substituents R and R' are preventing the unbridged fluorenyl ligands from rotation.

2.1. Synthesis of 2,2'-(biphenyl)ylene-bridged bisfluorenes (2, 4)

2,2'-Substituted biphenyl seemed to be a good ligand precursor owing to the fact that no meso complex could be formed.

The synthesis of **2** proceeds in two steps and with good yield. 2,2'-Dibromobiphenyl [31–33] is dissolved in ether, lithiated by addition of two equivalents of *n*-butyllithium and then allowed to react with two equivalents of fluorenone. Intermediate **1** is soluble in ether and can be reduced by heating with hydriodic acid in acetic acid.

Unreacted **1** can be extracted with ether and the remaining solid recrystallized from boiling toluene. Al-

* Corresponding author.

SSDI 0022-328X(95)06008-1

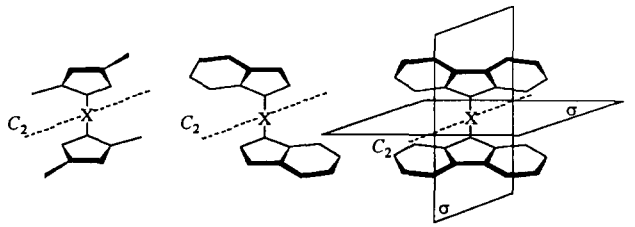


Fig. 1. Comparison of C_2-symmetric isospecific complexes and highly symmetric aspecific bis(fluorenyl) complexes (schematically).

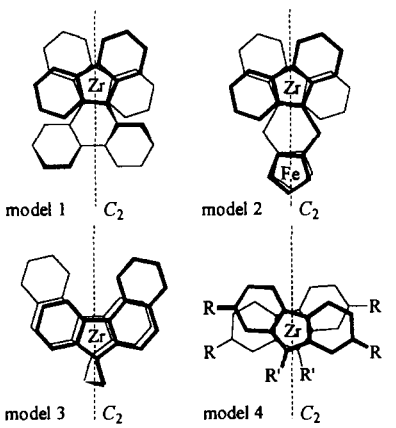
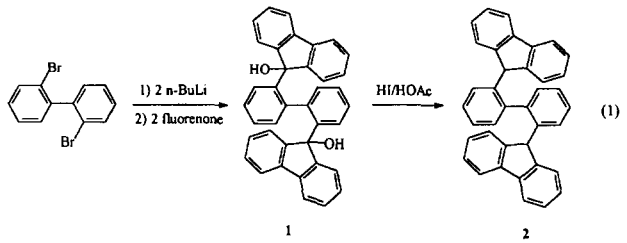


Fig. 2. Four C_2-symmetric complex models.

ternatively, biphenyl may be dilithiated by two equivalents of *n*-butyllithium in the presence of TMEDA [34].

On adding two equivalents of *n*-butyllithium to a slurry of **2** in ether no fluorenyl lithium salt is formed, even after several days. This can be concluded from the colour of the slurry, which does not change from white to red or orange as fluorenyl compounds normally do. No lithium salt is formed, even under forced conditions such as heating a mixture of **2** in toluene, ether and *n*-butyllithium in a pressure tube to 80°C.

In order to exclude the possibility that the poor solubility of the ligand precursor in ether is responsible



for this effect, we synthesized derivative **4** with two additional tert-butyl substituents. Here the preparation of 4,4′-di-*tert*-butyl-2,2′-diiodobiphenyl (**3**) seems worth mentioning. According to the literature [35,36], the monoiodo derivative can be prepared in 97% yield, but the diiodo compound **3** is not accessible by this route. We found that a twofold iodination of 4,4′-di-*tert*-butylbiphenyl is possible when heating with a three- or fourfold excess of iodine and periodic acid in acetic acid for several days. No isomers or by-products could be detected.

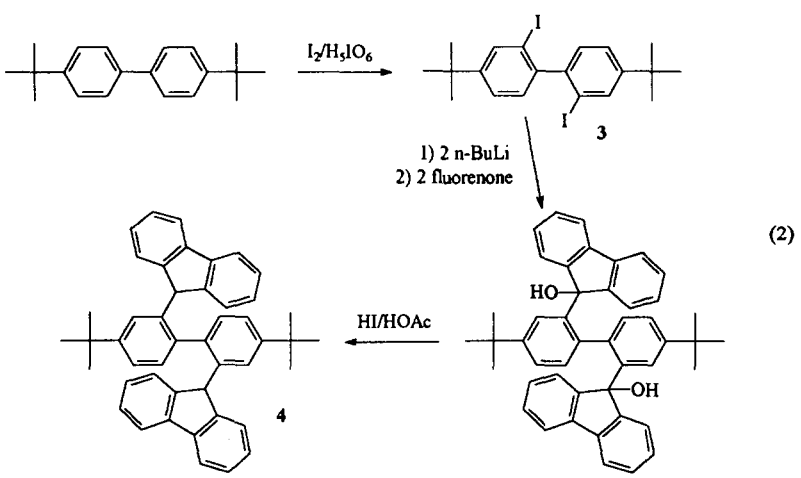
Compound **4** dissolves easily in ether, but no lithium salt is formed even in this case.

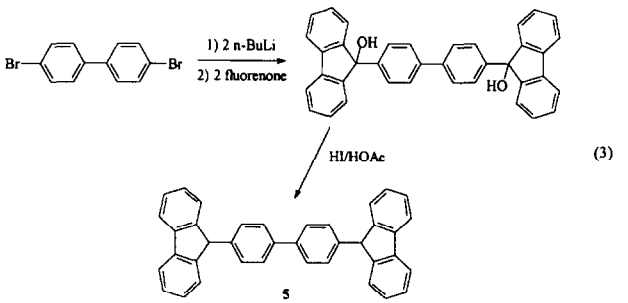
In contrast to this, **5** in ether immediately forms a deep red solution on adding *n*-butyllithium. The preparation of compound **5** is analogous to that of compound **2**. The results suggest the assumption that the lithium salts of **2** and **4** do not form for steric reasons.

2.2. Synthesis of 1,1′-ferrocenylidene-bridged bisfluorenes

As known in the art [37], [1.1]ferrocenophanes bearing methyl groups on each bridge carbon can exist in two isomeric forms: exo–exo and exo–endo. The endo–endo isomer does not exist owing to the steric repulsion of the methyl groups (Fig. 3).

Therefore, we tried to synthesize bimetallic complexes containing iron and zirconium from the ferrocene





(3)

derivatives **7** and **8**. Owing to the steric repulsion of the two carbon bridges, the racemic form of the zirconocene complex should be the only product.

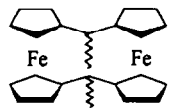
Fluorenyllithium reacts with 6-dimethylaminofulvene in tetrahydrofuran with elimination of dimethylamine to give a deep red solution. The fulvenoide lithium salt reacts with $FeCl_2 \cdot 2THF$ [38] to form the ferrocene derivative **6**. This compound is a dark red solid which can be hydrogenated quantitatively to the orange compound **7** using palladium on charcoal as a catalyst.

The tetramethyl derivative **8** can easily be synthesized by the reaction shown in Eq. (5).

On adding two equivalents of *n*-butyllithium to a slurry of **7** or **8** in ether, the orange colour changes to dark orange. Zirconium tetrachloride reacts with the lithium salts formed and the colour of the slurry turns red. A number of efforts have been made to isolate one of the ferrocenylidene-bridged zirconium complexes [39]. The crude product was extracted with toluene or methylene chloride, but no pure product could be obtained. ^1H NMR measurements of the crude products suggest the formation of oligomeric complexes.

2.3. Synthesis of rac / meso-dichloro[η^{10}-(1,2-ethanediyl)bis(7H-benzo[c]fluoren-7-ylidene)zirconium (10 / 10 *)

7*H*-Benzo[c]fluorenyllithium [40–43] reacts with 1,2-dibromoethane to form the ligand precursor **9/9*** in very good yield. As we can see from the ^1H and ^{13}C NMR spectra, it consists of a mixture of the racemate and the meso form. It does not make sense to separate these isomers at this stage because the chiral information of carbon 7 gets lost when forming the lithium salt. The zirconium dichloride complex can be isolated in good yield as an isomeric mixture. Here again, racemic and meso isomers are formed in about 1:1 ratio, as one can see from the intensities of corresponding resonance signals in the ^{13}C NMR spectra. We have not succeeded in enriching one of the isomers by crystallization from methylene chloride. In the second crystal fraction, the ratio is still 1:1.



exo-exo
exo-endo
not endo-endo

Fig. 3. Conformations of methylsubstituted [1.1]ferrocenophanes (schematically) [37].

2.4. Synthesis of unbridged complexes of the formula Flu'_2ZrCl_2 (Flu' = substituted fluorenyl) with hindered rotation of the ligands (11, 12)

Several authors have shown that the bridge between the aromatic π-ligands is not necessary for stereospecificity, but normally the polymerization temperature must be very low to generate isotactic polypropylene for example [44–46]. Dichlorobis(1-methyl-9*H*-fluorenyl-zirconium [27] was the first unbridged bis(fluorenyl) zirconium complex to produce isotactic polypropylene at 60 °C after activation with MAO. Its activity is low, but the stereoselectivity is unexpectedly high (92% meso-diads) [28]. The complexes dichloro(9-cyclohexyl-9*H*-fluorenyl)zirconium, dichloro(9-phenyl-9*H*-fluorenyl)zirconium and dichloro-bis(1-methyl-9-phenyl-9*H*-fluorenyl)zirconium show very low activities for propylene polymerization and only slightly higher activities for ethylene polymerizations [30].

Two unbridged bis(fluorenyl) zirconium dichloride complexes bearing very large substituents in the positions 2, 7 and 9 have been synthesized for reasons of comparison. NMR data and the results of polymerization experiments are presented. 2,7-Di-*tert*-butyl-9-cyclohexylfluorene can easily be prepared from an ethereal solution of 2,7-di-*tert*-butylfluorene by adding one equivalent of butyllithium and bromocyclohexane [47]. The synthesis of 2,7-dimesitylfluorene starts from 2,7-diiodofluorene which is reacted with two equivalents of mesityl magnesium bromide in the presence of $Ni(dppp)Cl_2$ ($dppp = Ph_2PCH_2CH_2CH_2PPh_2$) [48].

Complex **11** (Fig. 4) can be obtained from methylene

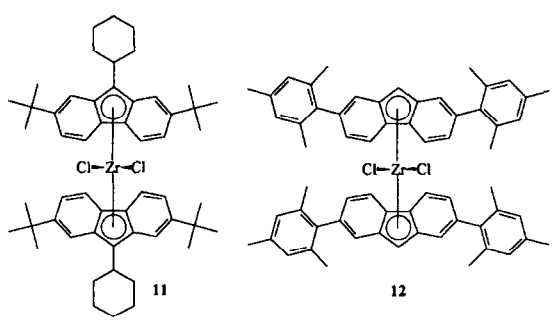


Fig. 4. Structures of the metallocene complexes **11** and **12**.

dichloride in the form of red crystals. At room temperature, the ^{1}H NMR spectrum shows only sharp signals for the tert-butyl groups, the cyclohexyl fragment and the aromatic hydrogen atoms (Fig. 5). At temperatures below 0°C the line width of the signals increases due to the slower rotational movements of the bulky ligands. The substituents of the fluorenyl ligands are too small to freeze the dynamic behaviour of the catalyst precursors. This has been proved by experimentation: polymerization of 400 ml of liquid propylene with 2 mg **11** and 2 ml of MAO (30%) at 60°C gave only atactic polymer in low yield.

The mass spectrum of **11** (Fig. 6) clearly shows the molecule ion at $m/e = 880$ and the main fragmentation product at $m/e = 521$, formed by the loss of one substituted fluorenyl ligand.

Complex **12** has four large mesityl substituents and their methyl groups prevent the free rotation. Even the bulkiness of these ligands is insufficient to hinder the fluorenyl ligands from rotating about the axis between the zirconium atom and the centre of the five-membered rings. Here again, the resonance signals of the methyl groups and the aromatic protons are very sharp in the ^{1}H NMR spectrum at room temperature (Fig. 7).

2.5. Polymerization of ethylene and propylene

Complexes **10/10***, **11** and **12** have been activated with MAO and tested for the polymerization of ethylene and propylene. The activity of all three catalysts is low towards propylene and the polymer is almost completely atactic. Towards ethylene, a slurry of **11** and MAO in pentane has an activity of only 3.8 kg PE (mmol h)$^{-1}$ (10 bar ethylene, 30°C). This could be due to the thermal instability of the unbridged bis(fluorenyl) complexes.

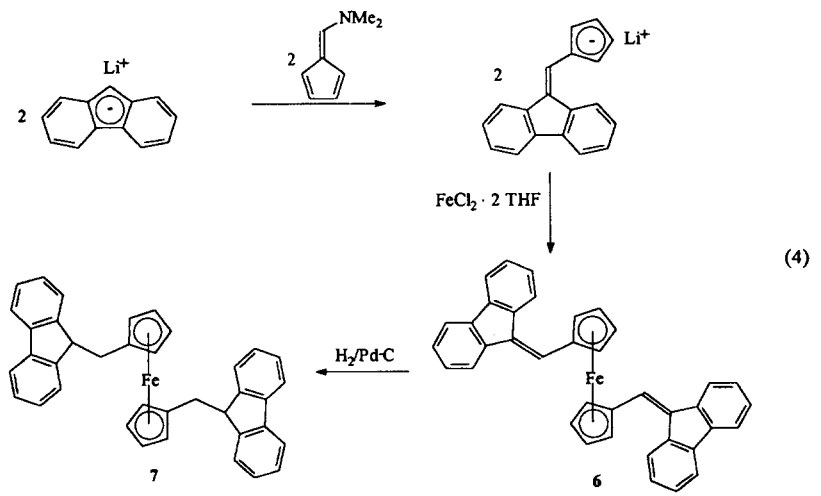
It is known from the literature that bridged bis(fluorenyl) zirconium complexes such as dichloro[η^{10}-(1,2-ethanediyl)bis(9*H*-fluoren-9-ylidene)zirconium [29] are extremely active in the polymerization of ethylene. In toluene at 60°C and 10 bar ethylene, 1 mol of this catalyst produces 4900 tons of polyethylene in 1 h. In hexane, the activity is about 1% of the activity in toluene.

We found, that complex **10/10***/MAO is even more active than the unsubstituted catalyst. In hexane, its activity is about eight times higher, and the molecular weight of the polyethylene produced is about the same (ca. 400 kg mol^{-1}) (Table 1). We speculate that the higher activity is due to the steric repulsion of the large MAO counterions which stabilize the cationic catalytic species. Perhaps, the flat anellated benzene rings increase the distance between the cationic catalyst and the MAO anion, thus making the coordination and the insertion of the ethylene molecules easier.

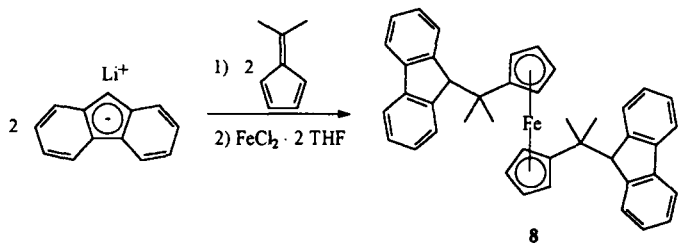
3. Experimental

3.1. 9,9'-[2,2'-(1,1'-Biphenyl)ylene]bis(9H-fluoren-9-ol) (1)

Route A: 0.5 g (1.6 mmol) of 2,2'-dibromobiphenyl are dissolved in 10 ml ether and treated at 0°C with 2.0 ml (3.2 mmol) of *n*-butyllithium (1.6 M in hexane). The light yellow solution is brought to ambient temperature, stirred for 2 h, and then allowed to react at −78 °C with 0.6 g (3.3 mmol) of fluorenone in 20 ml of ether.



(4)



8 (5)

The solution is stirred at −78°C for an additional hour and at room temperature for 2 h. The reaction mixture is then hydrolyzed with dilute hydrochloric acid and extracted with ether. The solvent is evaporated and the crude product isolated. Further purification is not required.

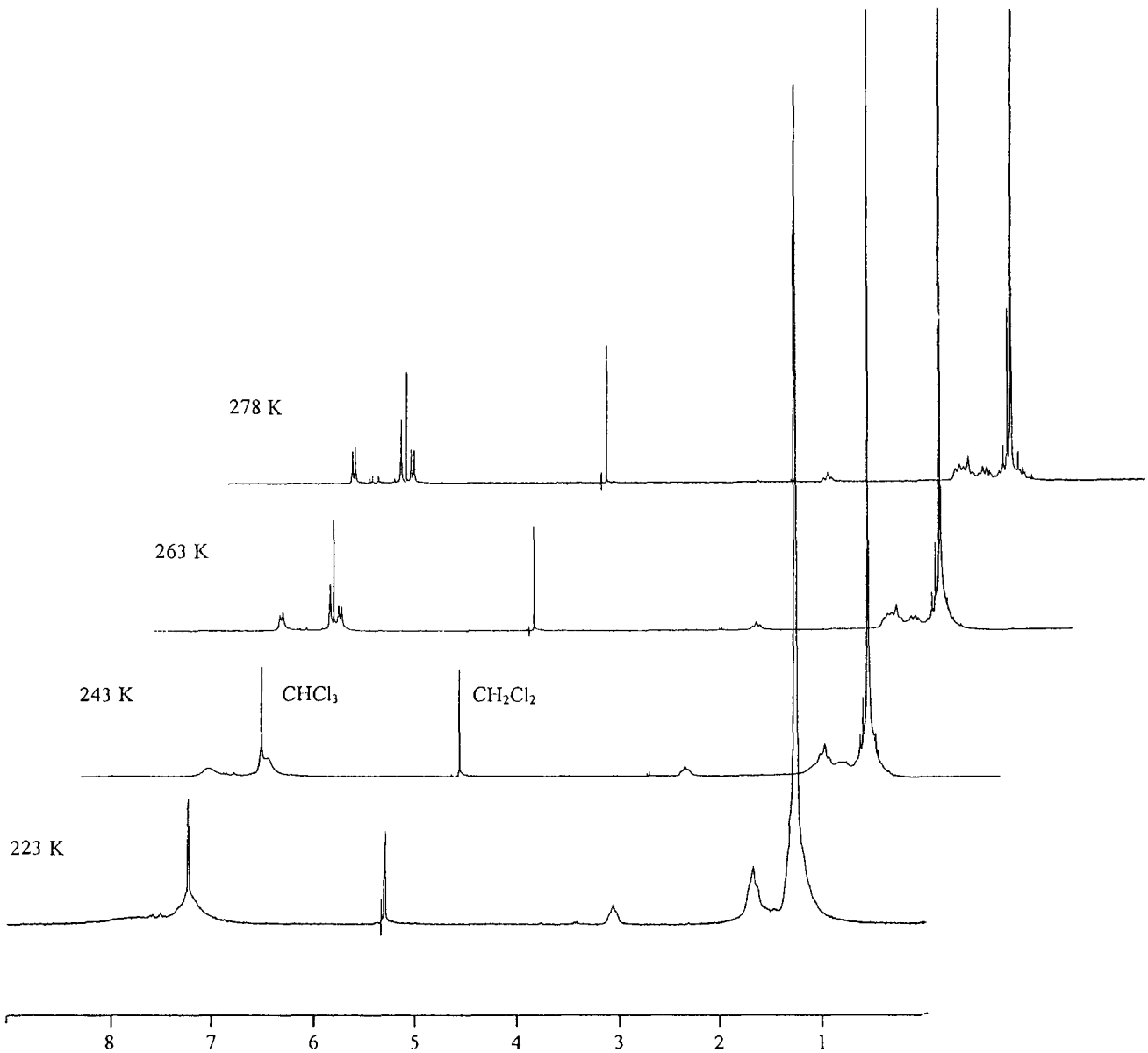


Fig. 5. Temperature-dependent ^{1}H NMR spectra of **11** ($CDCl_3$).

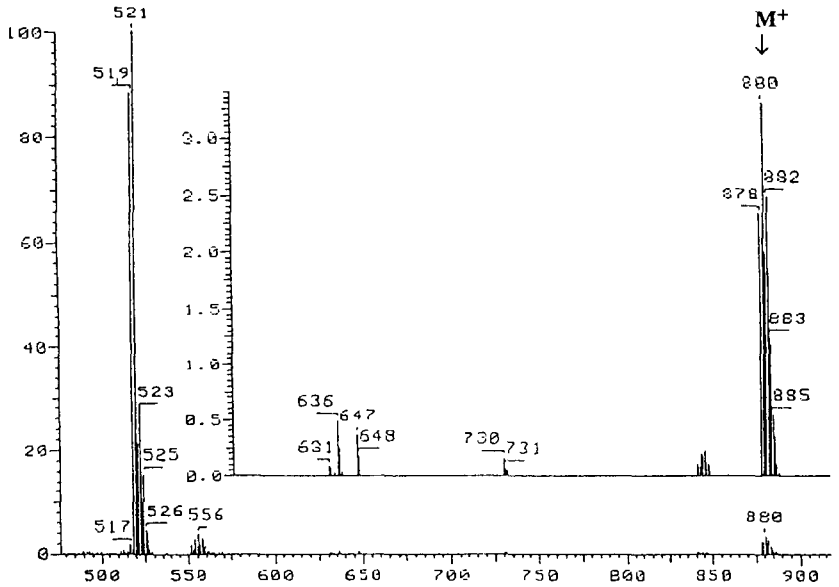


Fig. 6. Mass spectrum of **11**.

Route B: (preparation of the dilithium salt follows Ref. [34]): 45 ml (72 mmol) of *n*-butyllithium (1.6 M in hexane), 11 ml (72 mmol) of TMEDA and 4.7 g (31 mmol) of biphenyl are heated for 90 min at 60°C and the resulting dark brown solution cooled to −20°C. Orange crystals having the formula $C_{12}H_8Li_2 \cdot$ TMEDA are separated from the solution and dried under reduced pressure (yield ca. 70%). Next 4.0 g (14.2 mmol) of $C_{12}H_8Li_2 \cdot$ TMEDA are dissolved in 50 ml of ether and treated with 5.4 g (30 mmol) of fluorenone in 50 ml of ether at −78 °C. The greenish solution is stirred overnight at room temperature, then hydrolyzed and extracted with ether. The crude product can be used without purification. Pure **1** can be obtained by the following procedure: the ethereal solution is dried over sodium sulphate, the solvent evaporated and the yellow

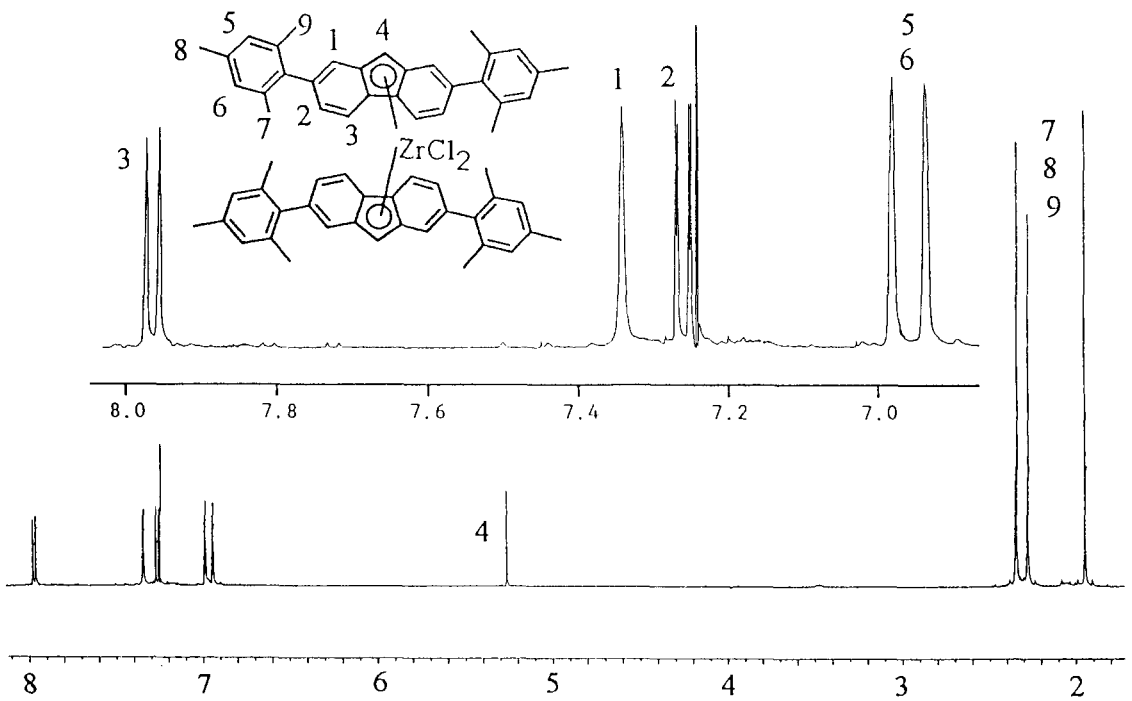
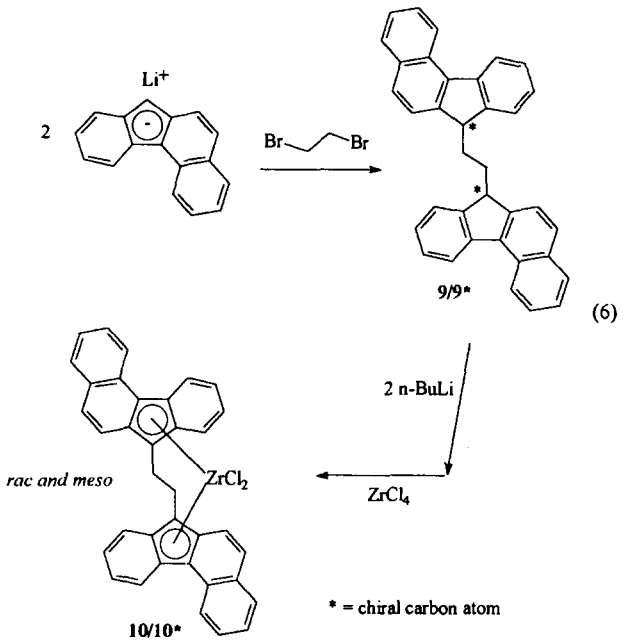


Fig. 7. ^{1}H NMR spectrum of **12** ($CDCl_3$, 25°C).



residue extracted with pentane using ultrasound. The product is almost insoluble in pentane and the colourless flakes can be separated by filtration and recrystallization from ether. Yield 5.0 g (33%). ^{1}H NMR ($CDCl_3$) δ 3.98 (s, 2 H), 6.58 (d, $^3J(^1H,^1H)$ 8.7 Hz, 2 H), 7.04 (m, 2 H), 7.15–7.25 (m, 4 H), 7.26–7.50 (m, 12 H), 7.67 (m, 4 H); ^{13}C NMR δ 25.5, 45.2, 67.8, 87.0, 119.7, 120.2, 124.9, 125.0, 125.9, 126.7, 128.2, 128.3, 128.7, 128.8, 128.8, 132.4, 139.2, 140.0, 140.5, 142.4 (br), 150.9, 150.9, 152.7, 152.8. M.p. 276–277°C. MS, *m/e* 514 (M^+).

3.2. 9,9'-[2,2'-(1,1'-Biphenyl)ylene]bis(9H-fluorene) (2)

2.5 g (ca. 5 mmol) of **1** (crude) are dissolved in 100 ml of acetic acid and refluxed with 2.8 ml of hydriodic acid (67%, 25 mmol) for 2 h. The reaction mixture is poured into ice-water, the product separated by filtration and washed with aqueous sodium sulphite and ether. The product is almost insoluble in ether and can be recrystallized from hot toluene. Colourless crystals. Yield 1.7 g (71% over two steps). ^{1}H NMR ($CDCl_3$) δ 5.74 (d, $^3J(^1H,^1H)$ 7.8 Hz, 2 H), 5.99 (d, $^3J(^1H,^1H)$ 7.8 Hz, 2 H), 6.67 (m, 2 H), 6.92–7.09 (m, 6 H), 6.98 (s, 2 H), 7.24 (m, 4 H), 7.33 (d, $^3J(^1H,^1H)$ 7.8 Hz, 2 H), 7.42 (m, 2 H), 7.49 (d, $^3J(^1H,^1H)$ 8.0 Hz, 2 H), 8.12 (d, $^3J(^1H,^1H)$ 8.0 Hz, 2 H); ^{13}C NMR δ 62.7 (*C*(9)), 118.7, 119.6, 124.2, 125.4, 125.5, 125.8, 126.9, 127.1, 127.4, 127.8, 128.1, 128.2, 135.3, 139.9, 140.8, 141.8, 144.7, 148.9. M.p. > 360°C. MS, *m/e* 482 (M^+).

Table 1
Comparison of activities of **10/10*** and unsubstituted catalyst

	10/10*	$(FluC_2H_4Flu)ZrCl_2$
Activity (kg PE (mmol h^{-1}))	420	51
M_η (kg mol^{-1})	410	ca. 400
$T_{i,max}$ (°C)	63.0	60.3

Suspension polymerization in hexane, 10 bar ethylene.

3.3. 2,2'-Diiodo-4,4'-bis(1,1-dimethylethyl)-1,1'-biphenyl (3)

10.0 g (37.5 mmol) of 4,4'-di-*tert*-butylbiphenyl [35], 11.0 g (43.3 mmol) of iodine, 8.0 g (35.1 mmol) of periodic acid, 35 ml of tetrachloromethane, 5 ml of water and 2.5 ml of sulphuric acid were heated to reflux temperature. After 14 h, 80% mono- and 18% diiodoproduct **3** were detected by gas chromatography. The product ratio was 60:35 after 3 days and 35:63 after 11 days. The reaction was stopped by addition of water and sodium sulphite. The product was isolated by extraction with ether and crystallization from hot acetone. ^{1}H NMR ($CDCl_3$) δ 1, 35 (s, 18 H), 7.10 (d, $^3J(^1H,^1H)$ 8.0 Hz, 2 H), 7.40 (dd, $^3J(^1H,^1H)$ 8.0/$^4J(^1H,^1H)$ 2.0 Hz, 2 H), 7.90 (d, $^4J(^1H,^1H)$ 2.0 Hz, 2 H); ^{13}C NMR δ 31.3 ($C(CH_3)_3$), 34.5, 99.9, 125.9, 129.6, 135.7, 146.0, 152.5. M.p. 140–141°C. GC 2488 s. MS, *m/e* 512 (M^+).

3.4. 9,9'-[4,4'-bis(1,1-dimethylethyl)-2,2'-(1,1'-biphenyl)ylene]bis(9H-fluoren-9-ol)

The preparation is analogous to 3.1A. The reaction product can be reacted to **4** without purification.

3.5. 9,9'-[4,4'-Bis(1,1-dimethylethyl)-2,2'-(1,1'-biphenyl)ylene]bis(9H-fluorene) (4)

The preparation of **4** is analogous to 3.2. The product is soluble in ether and can be crystallized from this solvent. Colourless crystals (43% yield, not optimized) formed. ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 18 H), 5.69 (d, $^3J(^1H,^1H)$ 7.8 Hz, 2 H), 6.62 (d, $^4J(^1H,^1H)$ 2.0 Hz, 2 H), 6.69 (m, 2 H), 6.93 (s, 2 H), 6.94 (m, 2 H), 7.04 (m, 2 H), 7.25 (m, 2 H), 7.32 (d, $^3J(^1H,^1H)$ 7.5 Hz, 2 H), 7.43 (d, $^3J(^1H,^1H)$ 8.2 Hz, 2 H), 7.48 (d, $^3J(^1H,^1H)$ 7.6 Hz, 2 H), 8.00 (d, $^3J(^1H,^1H)$ 8.2 Hz, 2 H); ^{13}C NMR δ 31.1 ($C(CH_3)_3$), 34.5, 63.4 (*C*(9)), 118.6, 119.4, 123.6, 124.4, 124.8, 125.5 (br), 126.6, 127.2, 127.5, 132.9, 138.8, 141.0, 141.8, 144.9, 149.1, 150.5. MS, *m/e* 594 (M^+).

3.6. 9,9'-[4,4'-(1,1'-Biphenyl)ylene]bis(9H-fluorene) (5)

The preparation of **5** is analogous to 3.1A–3.2. ^{1}H NMR ($CDCl_3$) δ 5.07 (s, 2 H), 7.12 (d, $^3J(^1H,^1H)$ 8.3 Hz, 4 H), 7.25 (m, 4 H), 7.30–7.42 (m, 8 H), 7.43 (m, 4 H), 7.80 (d, $^3J(^1H,^1H)$ 7.5 Hz, 4 H); ^{13}C NMR δ 54.0

(*C*(9)), 119.9, 125.3, 127.3, 127.3, 127.3, 128.7, 139.4, 140.5, 141.0, 147.8. M.p. 188–190°C. MS, *m/e* 482 (M^+).

3.7. 1,1'-Bis(9H-fluoren-9-ylidenemethyl)ferrocene (6)

A solution of fluorenyllithium from 10.0 g (60.2 mmol) of fluorene and 37.6 ml (60.2 mmol) of *n*-butyllithium (1.6 M in hexane) in 50 ml of tetrahydrofuran is added dropwise to 7.3 g (60.2 mmol) of 6-dimethylaminofulvene in 50 ml of tetrahydrofuran and the resulting dark violet solution stirred for 5 h at 60°C. After addition of 8.2 g $FeCl_2 \cdot 2THF$ the colour of the solution changes to dark red. The mixture is stirred for another 2 h at room temperature and the solvent evaporated. The residue is air stable and can be extracted with hot toluene and filtered over silica. At −25°C dark red crystals are separated. Yield: 11.9 g (73%). ^1H NMR ($CDCl_3$) δ 2.40 (s, 2 H), 4.50 (m, 4 H), 4.78 (m, 4 H), 7.12–7.40 (m, 8 H), 7.49 (d, $^3J(^1H,^1H)$ 7.5 Hz, 2 H), 7.73 (m, 4 H), 8.16 (d, $^3J(^1H,^1H)$ 8.1 Hz, 2 H); ^{13}C NMR δ 34.6, 49.6, 68.4 (br, C_5H_4), 70.6 (br, C_5H_4), 119.7, 124.9, 126.5, 127.0, 140.8, 146.9. M.p. 164–165 °C. MS, *m/e* 538 (M^+).

3.8. 1,1'-Bis(9H-fluoren-9-ylmethyl)ferrocene (7)

6.4 g (11.8 mmol) of **6** are dissolved in 250 ml of tetrahydrofuran and hydrogenated in the presence of 0.5 g of palladium on charcoal (10% Pd) at ambient temperature. After about 24 h, the stoichiometric volume of hydrogen gas (about 530 ml) is consumed. The catalyst is separated by filtration over silica, the orange solution evaporated and the orange solid crystallized from toluene. Orange crystals. Yield 5.4 g (85%). ^1H NMR ($CDCl_3$) δ 2.88 (d br, $^3J(^1H,^1H)$ 7.1 Hz, 4 H), 3.91 (t br, $^3J(^1H,^1H)$ 7.1 Hz, 2 H), 3.99 (m br, 8 H), 7.15–7.38 (m br, 12 H), 7.68 (d br, $^3J(^1H,^1H)$ 7.4 Hz, 4 H); ^{13}C NMR δ 34.5, 49.4, 69.0 (br, C_5H_4), 71.2 (br, C_5H_4), 119.7, 125.0, 126.5, 127.0, 140.8, 146.9. M.p. 207–209 °C. MS, *m/e* 542 (M^+).

3.9. 1,1'-Bis[1-(9H-fluoren-9-yl)-1-methylethyl]ferrocene (8)

Route A: 3.0 g (18.0 mmol) of fluorene are dissolved in 50 ml of tetrahydrofuran, treated with 11.3 ml (18.0 mmol) of *n*-butyllithium (1.6 M in hexane) and stirred at room temperature for 2 h. Then 2.2 ml (18.0 mmol) of 6,6-dimethylfulvene are added, and the solution stirred for another 2 h. The pale yellow solution of the monolithium salt is treated with 2.5 g of $FeCl_2 \cdot 2THF$ and stirred for 3 h. Within a few minutes an orange slurry is formed. The solvent is evaporated, the residue extracted with hot toluene and the solution filtered over silica. Orange crystals are formed in 70–80% yields.

Route B: 3.0 g (11.0 mmol) of 9-[1-(1,3-cyclopentadien-1-yl)-1-methylethyl]-9H-fluorene are dissolved in 50 ml of tetrahydrofuran and transformed to the monolithium salt by adding 6.9 ml (11.0 mmol) of *n*-butyllithium (1.6 M in hexane). After 30 min 1.6 g (5.7 mmol) of $FeCl_2 \cdot 2THF$ are added, and the orange suspension stirred for 3 h at room temperature. The workup is the same as described under 3.9A. Yield: 70–80 %. ^1H NMR ($CDCl_3$) δ 1.27 (s, 12 H), 3.71 (s, 2 H), 3.95 (m, 4 H), 4.12 (m, 4 H), 6.94 (d, *J* 7.6 Hz, 4 H), 7.06 (m, 4 H), 7.24 (m, 4 H), 7.58 (d, *J* 7.5 Hz, 4 H); ^{13}C NMR δ 26.2 (CH_3), 38.3, 60.5 (C_5H_4), 67.6 (C_5H_4), 68.2 (C_5H_4), 100.6, 119.1, 125.5, 126.9, 127.0, 142.1, 145.5. M.p. 257–258°C (decomp.). MS, *m/e* 598 (M^+).

3.10. rac / meso-7,7'-(1,2-Ethanediyl)bis(7H-benzo[c]fluorene) (9/9*)

3.0 g (13.9 mmol) of **8** are dissolved in 100 ml ether and treated with 8.7 ml (13.9 mmol) of *n*-butyllithium (1.6 M in hexane). After 3 h, 0.6 ml (6.9 mmol) of 1,2-dibromoethane are added dropwise and stirred for another 4 h. Then, the mixture is hydrolyzed with a small amount of water, the solid product is separated by filtration and washed with water, ether and pentane. A colourless solid is crystallized from toluene. Yield: 2.5 g (80%). ^1H NMR ($CDCl_3$) δ 1.69 (m, 4 H), 3.85 (m, 2 H), 7.30–7.45 (m, 6 H), 7.45–7.60 (m, 4 H), 7.66 (m, 2 H), 7.83 (d, $^3J(^1H,^1H)$ 8.3 Hz, 2 H), 7.99 (d, $^3J(^1H,^1H)$ 8.3 Hz, 2 H), 8.38 (d, $^3J(^1H,^1H)$ 7.7 Hz, 2 H), 8.78 (d, $^3J(^1H,^1H)$ 8.4 Hz, 2 H); ^{13}C NMR δ 25.0 (br) (CH_2), 47.0, 122.2, 122.2, 122.8, 123.8, 123.9, 123.91, 125.0, 126.0, 126.5, 127.1, 127.9, 129.2, 129.5, 133.6, 135.8, 142.5, 145.7, 145.7, 147.7, 147.7. M.p. 198–200°C. MS, *m/e* 458 (M^+).

3.11. rac / meso-Dichloro[η^{10}-(1,2-ethanediyl)bis(7H-benzo[c]fluoren-7-ylidene)zirconium (10/10*)

1.0 g (2.2 mmol) of **9/9*** in 30 ml of ether is treated with 2.7 ml (4.4 mmol) of *n*-butyllithium (1.6 M in hexane) and stirred for 6 h at room temperature. To the red slurry are added 0.52 g (2.3 mmol) of zirconium tetrachloride. After another 2 h the solvent is evaporated and the red residue extracted with methylene dichloride and filtered over sodium sulphate. At −25°C a mixture of the rac- and meso-forms crystallizes (ca. 1:1). From the mother liquor, a second fraction of crystals can be obtained (ca. 1:1). ^1H NMR ($CDCl_3$) δ 4.48 (m, 4 H), 7.20 (m, 2 H), 7.32–7.56 (m, 8 H), 7.65–7.77 (m, 4 H), 7.97 (d, $^3J(^1H,^1H)$ 8.7 Hz, 2 H), 8.02 (d, $^3J(^1H,^1H)$ 8.7 Hz, 2 H), 8.21 (d, $^3J(^1H,^1H)$ 8.6 Hz, 2 H), 8.30 (d, $^3J(^1H,^1H)$ 7.8 Hz, 2 H); ^{13}C NMR (DEPT) δ 77.2 (CH_2), 102.0, 119.3, 119.6, 122.7, 123.2, 124.2, 124.3, 125.7, 125.9, 126.1, 126.1, 126.3, 126.4, 126.6, 128.1,

128.2, 129.3, 129.3, 130.2, 130.5. M.p. ca. 235°C (decomp.). MS, *m/e* 618 (M^+).

3.12. General procedure for the preparation of unbridged substituted bis(fluorenyl) zirconium dichloride complexes 11, 12

About 1.0 g of the substituted fluorene is dissolved or suspended in 30 ml of ether and treated with an equivalent amount of *n*-butyllithium (1.6 M in hexane). After 4 h, a half equivalent of solid zirconium tetrachloride is added, and the slurry stirred for another 2 h. The workup procedures of the mixtures are different:

3.12.1. Dichlorobis[2,7-bis(1,1,dimethylethyl)-9-cyclohexyl-9H-fluorenyl]zirconium (11)

The solvent is evaporated and the residue extracted with a small amount of methylene dichloride and filtered over sodium sulphate. At −25°C **11** crystallizes as red platelets. ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 36 H), 1.10–1.95 (m, 20 H), 3.16 (m, 2 H), 7.19 (d, $^3J(^1H,^1H)$ 9.0 Hz, 4 H), 7.33 (s, 4 H), 7.76 (d, $^3J(^1H,^1H)$ 9.0 Hz, 4 H); ^{13}C NMR δ 26.8, 27.6, 31.2 ($C(CH_3)_3$), 32.2, 35.1, 38.4, 112.9, 115.3, 118.8, 122.3, 123.5, 133.1, 149.0. MS, *m/e* 880 (M^+).

3.12.2. Dichlorobis[2,7-bis(2,4,6-trimethylphenyl)-9H-fluorenyl]zirconium (12)

Complex **12** is very soluble in methylene dichloride. Therefore, the ethereal slurry of compound **12** is filtered over sodium sulphate and washed with ether. The product is extracted with a small amount of methylene dichloride and then ether is added to this solution. At −25 or −78°C an orange microcrystalline powder can be obtained. ^{1}H NMR ($CDCl_3$) δ 1.94 (s, 12 H), 2.27 (s, 12 H), 2.34 (s, 12 H), 5.26 (s, 2 H), 7.30 (s, 4 H), 7.34 (s, 4 H), 7.62 (d, $^3J(^1H,^1H)$ 8.6 Hz, 4 H), 7.70 (s, 4 H), 8.32 (d, $^3J(^1H,^1H)$ 8.6 Hz, 4 H); ^{13}C NMR δ 20.9 (CH_3), 21.0 (CH_3), 21.7 (CH_3), 90.7, 122.2, 124.6, 125.4, 128.2, 128.3, 128.5, 128.5, 136.0, 136.4, 137.1, 138.2, 141.6, 145.9. MS, *m/e* 965 (M^+).

Acknowledgements

We thank the Deutschen Forschungsgemeinschaft and Phillips Petroleum Company (Bartlesville, OK, USA) for financial support of this research.

References

[1] F.R.W.P. Wild, L. Zsolnai, G. Huttner and H.H. Brintzinger, *J. Organomet. Chem., 232* (1982) 233.
[2] F.R.W.P. Wild, M. Wasincionek, G. Huttner and H.H. Brintzinger, *J. Organomet. Chem., 288* (1985) 63.
[3] W. Kaminsky, K. Külper, H.H. Brintzinger and F.R. W.P. Wild, *Angew. Chem. Int. Ed. Engl., 24* (1985) 507.
[4] W. Kaminsky, *Angew. Makromol. Chem., 145–146* (1986) 149.
[5] J.A. Ewen, L. Haspeslagh, J.L. Atwood and H. Zhang, *J. Am. Chem. Soc., 109* (1987) 6544.
[6] A. Schäfer, E. Karl, L. Zsolnai, G. Huttner and H.H. Brintzinger, *J. Organomet. Chem., 328* (1987) 87.
[7] K. Soga, T. Shiono, S. Takemura and W. Kaminsky, *Makromol. Chem. Rapid Commun., 8* (1987) 305.
[8] H. Wiesenfeldt, A. Reinmuth, E. Barsties, K. Evertz and H.H. Brintzinger, *J. Organomet. Chem., 369* (1989) 359.
[9] S. Gutmann, P. Burger, H.U. Hund, J. Hofmann and H.H. Brintzinger, *J. Organomet. Chem., 369* (1989) 343.
[10] W. Röll, H.H. Brintzinger, B. Rieger and R. Zolk, *Angew. Chem. Int. Ed. Engl., 29* (1990) 279.
[11] S. Collins, Y. Hong, R. Ramachandran and N. Taylor, *J. Organomet., 10* (1991) 2349.
[12] P. Burger, K. Hortmann, J. Diebold and H.H. Brintzinger, *J. Organomet. Chem., 417* (1991) 9.
[13] K. Hortmann and H.H. Brintzinger, *New J. Chem., 16* (1992) 51.
[14] B. Rieger, *J. Organomet. Chem., 428* (1992) C33.
[15] W. Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, R. Behm and W.A. Herrmann, *Angew. Chem., Int. Ed. Engl., 31* (1992) 1347.
[16] P. Burger, J. Diebold, S. Gutmann, H.U. Hund and H.H. Brintzinger, *Organometallics, 11* (1992) 1319.
[17] Z. Chen and R.L. Halterman, *J. Am. Chem. Soc., 114* (1992) 2276.
[18] M.E. Huttenloch, J. Diebold, U. Rief, H.H. Brintzinger, A.M. Gilbert and T.J. Katz, *Organometallics, 11* (1992) 3600.
[19] R.L. Halterman, *Chem. Rev., 92* (1992) 965.
[20] J. Okuda, *Nachr. Chem. Tech. Lab., 41* (1993) 8.
[21] R.L. Halterman and T.M. Ramsey, *Organometallics, 12* (1993) 2879.
[22] W.A. Herrmann, R. Anwander, H. Riepl, W. Scherer and C.R. Whitaker, *Organometallics, 12* (1993) 4342.
[23] W. Spaleck, F. Küber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle and E.F. Paulus, *Organometallics, 13* (1994) 954.
[24] U. Stehling, J. Diebold, R. Kirsten, W. Röll, H.H. Brintzinger, S. Jüngling, R. Mülhaupt and F. Langhauser, *Organometallics, 13* (1994) 964.
[25] Y.X. Chen, M.D. Rausch and J.C.W. Chien, *Organometallics, 13* (1994) 748.
[26] E. Samuel, H.G. Alt, D.C. Hrncir and M.D. Rausch, *J. Organomet. Chem., 113* (1976) 331.
[27] S.J. Palackal, *Dissertation*, Universität Bayreuth, 1991.
[28] A. Razavi and J.L. Atwood, *J. Am. Chem. Soc., 115* (1993) 7529.
[29] H.G. Alt, W. Milius and S.J. Palackal, *J. Organomet. Chem., 472* (1994) 113.
[30] K. Patsidis, *Dissertation*, Universität Bayreuth, 1993.
[31] H. Gilman and B.J. Gaj, *J. Org. Chem., 22* (1957) 447.
[32] S.A. Kandil and R.E. Dessy, *J. Am. Chem. Soc., 88* (1966) 3027.
[33] T.K. Dougherty, K.S.Y. Lau and F.L. Hedberg, *J. Org. Chem., 48* (1983) 5273.
[34] W. Neugebauer, A.J. Kos and P. Ragué Schleyer, *J. Organomet. Chem., 228* (1982) 107.
[35] M. Tashiro and T. Yamato, *J. Org. Chem., 44* (1979) 3037.
[36] R.E. Buckles, E.A. Hausman and N.G. Wheeler, *J. Am. Chem. Soc., 72* (1950) 2494.
[37] A. Cassens, P. Eilbracht, A. Nazzal, W. Prössdorf and U.T. Mueller-Westerhoff, *J. Am. Chem. Soc., 103* (1981) 6367.
[38] G. Wilkinson, N.J. Leonard, K.L. Rinehart, D.J. Casey, R. Woo and S. Moon, *Org. Synth. Coll., 4* (1963) 473.

[39] Compare: P. Scott, U. Rief, J. Diebold and H.H. Brintzinger, *Organometallics, 12* (1993) 3094.
[40] R.G. Harvey, J. Pataki, C. Cortez, R. Di Raddo and C.X. Yang, *J. Org. Chem., 56* (1991) 1210.
[41] W.S. Rapson and R.G. Shuttleworth, *J. Chem. Soc.*, (1940) 636.
[42] G. Saint-Ruf, N.P. Buu-Hoi and P. Jacquignon, *J. Chem. Soc.*, (1960) 2690.
[43] J.W. Cook, A. Dansi, C.L. Hewett, J. Iball, M.V. Mayneord and E. Roc, *J. Chem. Soc.*, (1935) 1319.
[44] G. Erker, M. Aulbach, M. Knickmeier, D. Wingbermühle, C. Krüger, M. Nolte and S. Werner, *J. Am. Chem. Soc., 115* (1993) 4590.
[45] G. Erker, R. Nolte, Y.H. Tsay and C. Krüger, *Angew. Chem. Int. Ed. Engl., 28* (1989) 628.
[46] J.A. Ewen, *J. Am. Chem. Soc., 106* (1984) 6355.
[47] M. Schmid, *Dissertation*, Universität Bayreuth, 1994.
[48] H.G. Alt and R. Zenk, submitted to *J. Organomet. Chem.*