

Synthesis and characterization of the catalytic isotactic-specific metallocene complex ($\eta^5\text{-C}_5\text{H}_3\text{C}_4\text{H}_9\text{-CMe}_2\text{-}\eta^5\text{-C}_{13}\text{H}_8$) ZrCl_2 Mechanistic aspects of the formation of isotactic polypropylene, the stereoregulative effect of the distal substituent and the relevance of C_2 symmetry¹

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Abstract

The reaction of ZrCl_4 with the dilithium salt of 2-(tertiarybutyl-3-cyclopentadienyl)-2-(fluorenyl)propane in pentane leads to the formation of the complex ($\eta^5\text{-C}_5\text{H}_3\text{C}_4\text{H}_9\text{-CMe}_2\text{-}\eta^5\text{-C}_{13}\text{H}_8$) ZrCl_2 . The complex is fully characterized by single crystal X-ray diffraction and different NMR methods. When activated with methylaluminumoxane or other appropriate ionizing agents the title complex catalyzes the stereospecific polymerization of propylene to isotactic polypropylene.

Keywords: Zirconium; Isotactic propylene polymerization; Stereoregulative effects

1. Introduction

The molecular structures and polymerization behavior of the syndiotactic-specific metallocene complexes, isopropyl(cyclopentadienyl-fluorenyl) MCl_2 $\text{M} = \text{Zr, Hf}$ as catalyst systems have been reported in several papers [1]. In these articles, the significance of the bilateral symmetry (C_s) of the chelating ligand and the prochirality of the metallocene complex molecule, as well as the relevance of the chain migratory insertion mechanism for the formation of syndiotactic polypropylene with the incipient active species have been discussed in length.

Similarly, the molecular structures and polymerization behavior of the C_1 symmetric metallocenes, isopropyl(3-methylcyclopentadienyl-fluorenyl) MCl_2 $\text{M} = \text{Zr, Hf}$ have been reported [2]. It was shown that the mere introduction of a methyl group in one of the distal positions of the cyclopentadienyl moiety of the ligand provokes profound changes in the secondary structural features of the metallocene molecules, such as elimina-

tion of the bilateral symmetry and prochirality. These symmetry modifications have, in turn, dramatic consequences for the stereospecificity of the final activated catalyst. As a result of this structural modification, a syndio-iso stereoblock-type (hemitactic [3]) polymer has been obtained with the methyl-modified catalysts. In this communication we report the formation, crystal structure and catalytic behavior of the complex isopropyl(3-^tbut-cyclopentadienyl-fluorenyl) ZrCl_2 [4] and elaborate on the impact of the size of the β -substituent and its role in the formation of the isotactic polypropylene.

2. Results and discussion

The bridged 2-(^tbut-cyclopentadienyl)-2-(fluorenyl)propane (1) can be prepared according to the reactions shown in Scheme 1.

Double deprotonation of 1 with two equivalents of methyllithium in THF solution gives the corresponding dianion 2. The reaction of 2 with one equivalent of ZrCl_4 in pentane yields the red complex 3.

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¹ In memory of Professor Hidemasa Takaya.

The identity of **3** has been confirmed by its ^1H NMR spectrum and its molecular structure determined by single crystal X-ray diffraction.

2.1. ^1H NMR spectrum

Fig. 1 presents the ^1H NMR spectrum of **3** in methylene chloride at room temperature. The proton signal assignments have been made following a procedure using ^1H and ^{13}C NMR correlated spectroscopy. Three groups of signals belonging to the protons of the methyl (aliphatic region), cyclopentadienyl (olefinic/aromatic region) and fluorenyl (aromatic region) moieties of the ligand are observed. The corresponding chemical shifts are within the range of $\delta = 1\text{--}2.5$ ppm for the methyl, $\delta = 5.6\text{--}6.2$ ppm for the cyclopentadienyl and $\delta = 7.2\text{--}8.2$ ppm for the fluorenyl protons. There is nothing unusual about this spectrum except for the singlet pattern for the six protons of the two methyl substituents in the bridge. In the ^1H NMR spectrum of the corresponding methyl-substituted metallocene complex [2] two singlets had been observed for each methyl group. The phenomenon was rationalized as being related to the loss of the local symmetry of the isopropylidene bridge.

2.2. The X-ray structure of **3**

Two perspective views of the molecular structure of **3** are shown in Fig. 2. Important bond distances and bond angles are given in Table 1. As in similar metallocene complexes having a $(\text{C}_5\text{H}_3\text{R}')\text{CR}_2(\text{C}_{13}\text{H}_8)$ ($\text{R}' = \text{H, Me}$; $\text{R} = \text{Me, Ph}$) chelating ligand system [1,2], the least squares planes defined by the two C5 fragments in **3** are inclined toward the transition metal with respect to $\text{C}(6)\text{--}\text{C}(5)$ and $\text{C}(6)\text{--}\text{C}(7)$ vectors. The effect is more pronounced for the cyclopentadienyl ring than for the fluorenyl group. Similarly, the angle formed by the two centroid zirconium connections, $\text{Flu}\text{--}\text{Zr}\text{--}\text{Cp}$, of 118.38° and the $\text{Cl}\text{--}\text{Zr}\text{--}\text{Cl}$ angle of 96.23° are within the expected range of angles observed for ansa metallocene molecules with a single carbon as the bridging atom [1,2]. The fluorenyl ligand is η^5 -bonded to the zirconium and the progressive increase in the $\text{Zr}\text{--}\text{C}$ bond distances from the bridge head carbon ($\text{C}(7)$ (2.411 Å) to $\text{C}(8)$ (2.554 Å), $\text{C}(13)$ (2.677 Å), $\text{C}(14)$ (2.650 Å), and $\text{C}(19)$ (2.514 Å) should be attributed to the repulsive non-bonding interactions between the two chlorine atoms and the closer carbon and hydrogen atoms of the fluorenyl six-membered rings rather than to any haptoc-

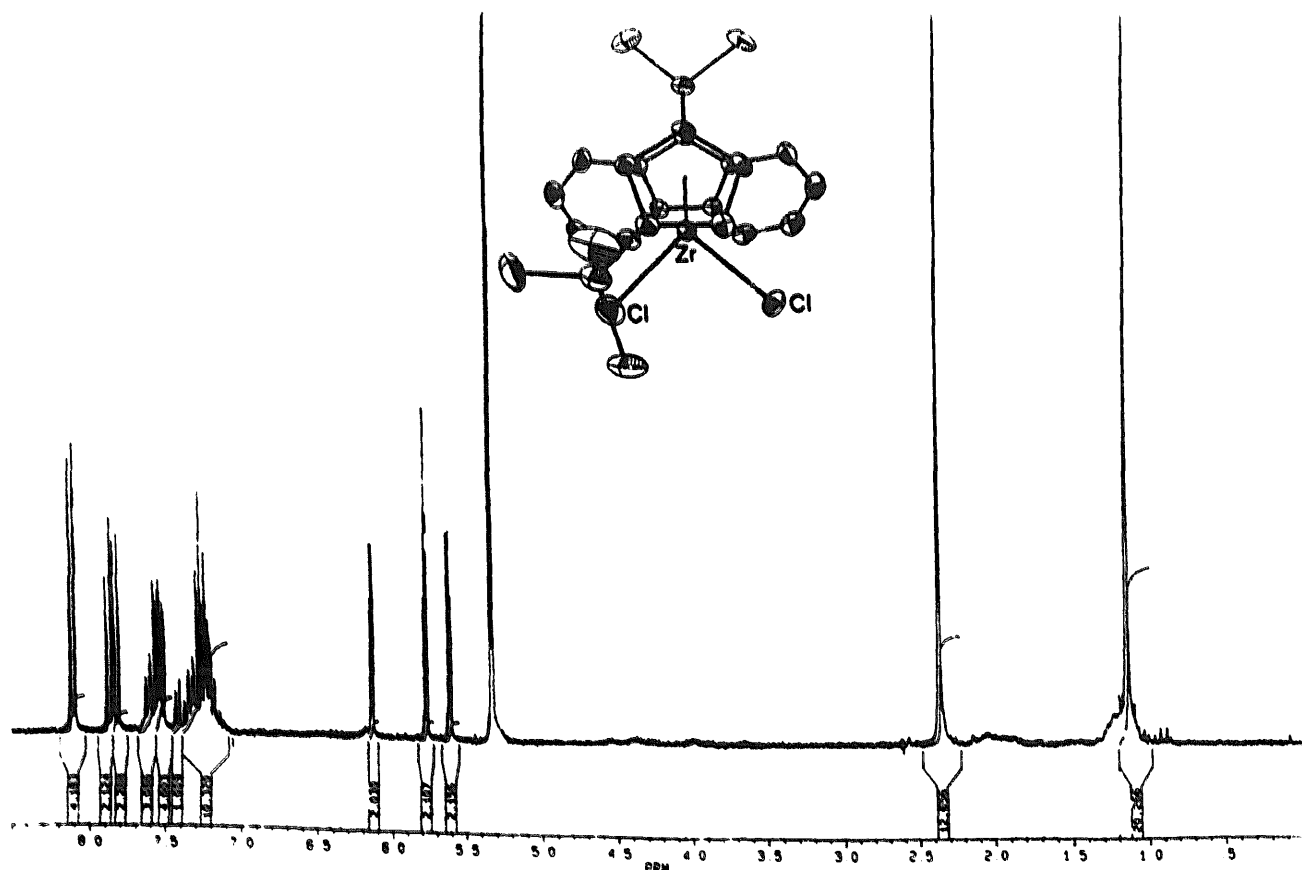


Fig. 1. 300 MHz ^1H NMR spectrum of **3** in methylene chloride at room temperature.

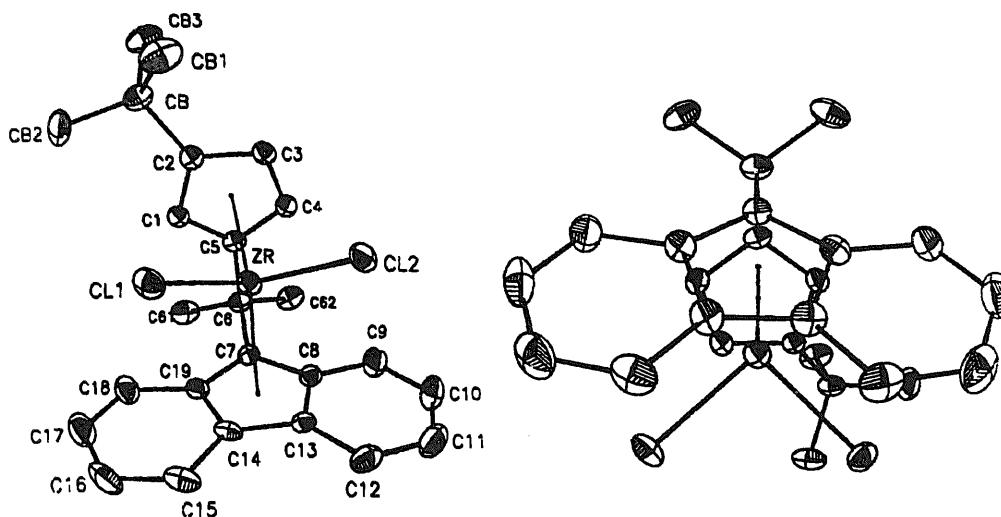


Fig. 2. Two perspective views of the molecular structure of **3** with atom numbering scheme.

ity modification. The lop-sided character of the bonding is due to the bulky tertiarybutyl β -substituent of the cyclopentadienyl moiety. The large size of this substituent is also at the origin of the very long Zr–C2 bond distance of 2.618 Å due to the very strong non-bonding interaction with the chlorine atom positioned just below it. This strong interaction is primordial for the stereoselectivity of the activated catalyst suspected to be a cationic species [5].

2.3. Polymerization behavior

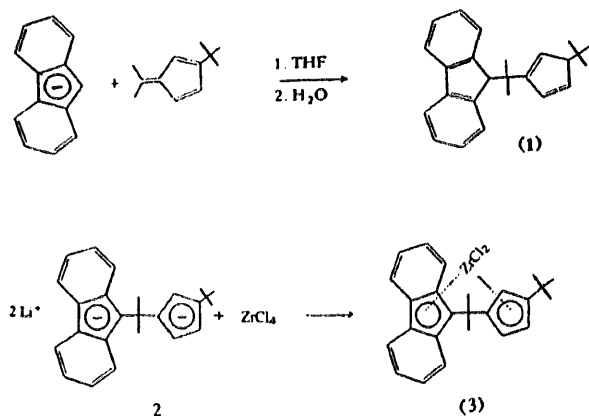
When combined with methylaluminoxane (MAO) or any other appropriate ionizing agent, **3** promotes the polymerization of propylene to isotactic polypropylene (Fig. 3). The polymerization conditions and results are summarized in Table 2. The data presented in this table indicate clearly a low sensitivity of the polymer's stereoregularity to the increase of polymerization temperature while the molecular weights of the polymers, fol-

lowing the expected trend, decrease sharply with increasing polymerization temperature.

2.4. Mechanistic aspects of polymerization

The mechanism of the polymerization and the reasons for the unexpected catalytic performance of **3** can be most elegantly explained by taking into consideration the following widely accepted principles about the origin of stereospecific polymerization of α -olefins with metallocene-based catalysts [6].

(1) The chirality and electron configuration of the



Scheme 1.

Table 1
Important bond lengths (Å) and bond angles (deg) for **3** with estimated standard deviations

Bond distances	
Zr–Cl(1)	2.422(2)
Zr–Cl(2)	2.427(2)
Zr–C(1)	2.472(6)
Zr–C(2)	2.618(6)
Zr–C(3)	2.548(6)
Zr–C(4)	2.427(6)
Zr–C(5)	2.428(5)
Zr–C(7)	2.411(6)
Zr–C(8)	2.554(6)
Zr–C(13)	2.677(6)
Zr–C(14)	2.650(6)
Zr–C(19)	2.514(6)
Cp–Zr ^a	2.182
Flu–Zr ^a	2.234
Bond angles	
Cp–Zr–Flu	118.38
Cl(1)–Zr–Cl(2)	96.23(7)

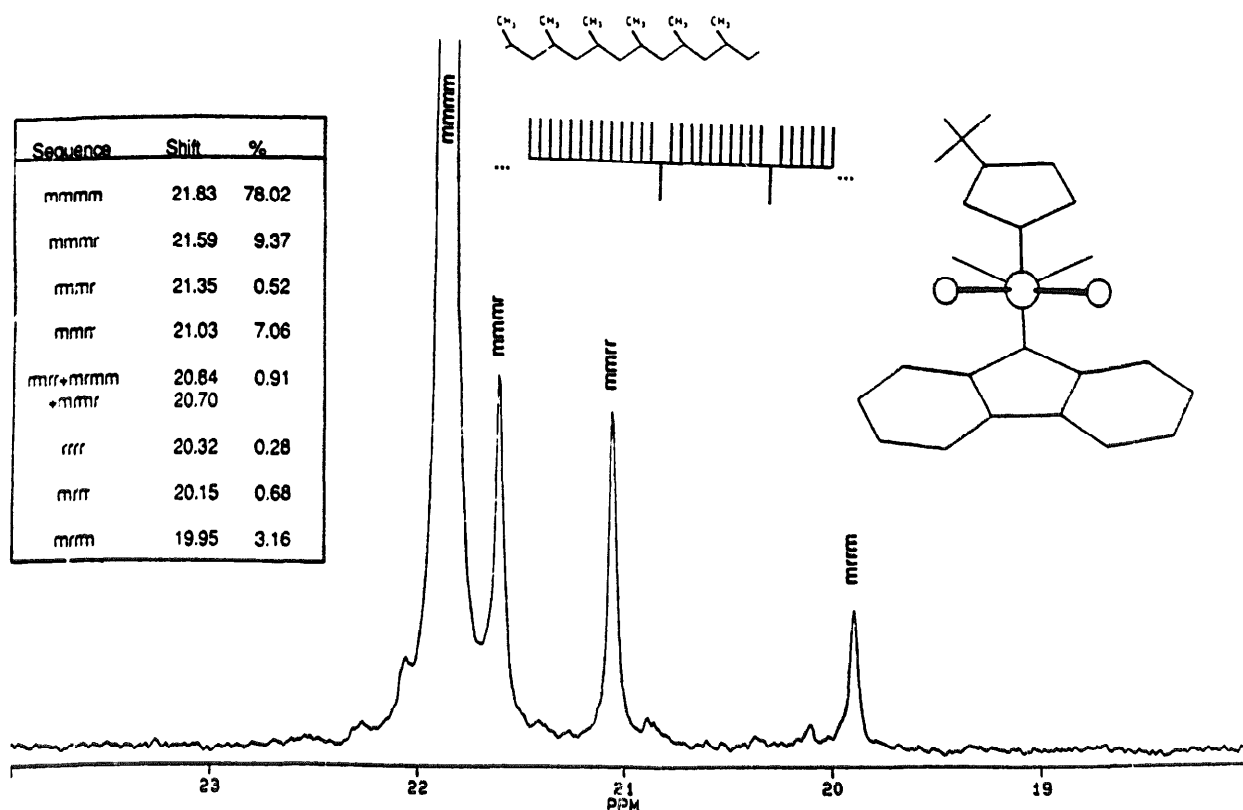


Fig. 3. ^{13}C NMR spectrum of the methyl region of isotactic propylene produced with 3 at 40°C .

cationic active site and the unique steric arrangement of the organic ligand surrounding it, dictate the stereochemistry of insertion [7]. This particular geometry (combined stereo-electronic requirements) of the site matches only one of the two possible conformations of the helically growing polymer chain. In this unique configuration the chain in turn steers the facial coordination mode of the monomer through a concerted, repulsive and non-bonding interaction.

(2) The formation of a hypothetical metalacyclobutane complex, comprising the $\text{M}-\text{C}$ and $\text{C}=\text{C}$ bonds in the transition state, occurs after the monomer coordination and prior to the monomer insertion.

(3) The dynamic behavior of the chain and the frequency of its migration (its side-to-side swing and

back swing) is crucial for the type of the stereospecificity of the final polymeric chain [8].

Thus, by introducing sizable substituents in the relevant positions of the cyclopentadienyl ligands of a highly syndiospecific catalyst, and by intentionally tampering with the migratory mechanism of the chain, we can restrict or block its periodic migration and manipulate the reaction mechanism to arrive at polymers with different microstructures and varying proportion of syndio/iso block sequence lengths.

Table 2

Polymerization conditions ^a and polymer analyses for $^i\text{Pr}(\text{3-}^i\text{Bu}(\text{CpFlu})\text{ZrCl}_2\text{-MAO}$ catalyst system

Cat. (mg)	Polymerization temperature ($^\circ\text{C}$)	Act. (kg g^{-1})	$\text{M}_w \times 10^{-1}$	M.p. ($^\circ\text{C}$)	mmmm (%)
8	20	10	175	133	79.17
2	40	18	75	129	78.02
2	60	48	62	127	77.47
2	80	20	48	127	76.80

^a Polymerizations were performed in a pressure reactor in liquid propylene with 10 ml of a 10 wt.% solution of MAO in toluene.

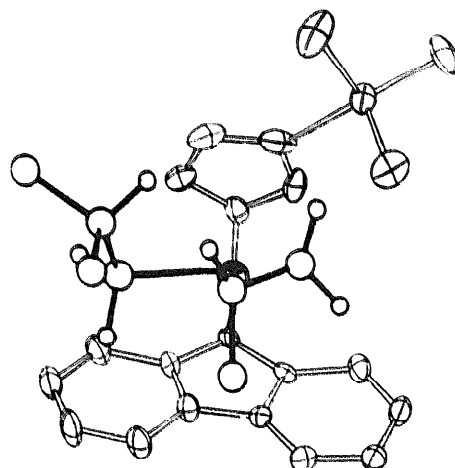


Fig. 4. The structure of putative active site with growing chain and coordinated polymer.

Table 3
Crystal data and summary of data collection for $[(C_{13}H_8-\mu-CMe_2-C_5H_3CMe_3)_2ZrCl_2] \cdot CH_2Cl_2$

Mol wt.	573.5
Space group	$P\bar{1}$
Cell constants	
a (Å)	10.510(1)
b (Å)	10.737(2)
c (Å)	11.567(2)
α (deg)	98.92(2)
β (deg)	98.70(1)
γ (deg)	99.11(1)
V (Å ³)	1252
Molecules/unit cell	2
D_c (g cm ⁻³)	1.53
Radiation	Mo K α
Max crystal dimensions (mm ³)	0.30 × 0.35 × 0.40
Scan width (deg)	0.80 + 0.20 tan θ
Decay of stds (%)	< 2
2 θ range (deg)	2–50
No. reflections collected	4552
No. of obsd reflections	3301
No. of parameters varied	280
R	0.048
R_w	0.061

Complex **3** is an excellent example for the demonstration of this property. A close inspection of the top view perspective of the molecular structure of **3** displayed in Fig. 2 provides a clue to the understanding of its seemingly unexpected catalytic behavior. The bulky tertiary group that resides on one of the cyclopentadienyl's distal (β to the bridge head carbon C5) positions is hovering exactly above one of the prospective coordination positions. During the polymerization process it interacts strongly with the growing polymer chain in a non-bonding, repulsive manner in the event of an intended approach of the latter, and would block its migration (Fig. 4). Thus, throughout the polymerization process two coordination sites with differing degrees of steric environment will exist and persist at each active center. The site underneath the *t*-butyl group is prohibitively congested to accommodate the sterically demanding polymer chain and will be vacant for monomer coordination only. The opposite site is the only position where the growing polymer chain, by avoiding the *t*-butyl group, can grow without being exposed to excessive steric perturbation exerted from the environment. The blockage of the chain migratory insertion and the exclusive availability of only one position for propylene coordination at each active center and its preference for only one of the propylene prochiral faces (*re* or *si*) are the reasons for the formation of isotactic polypropylene with a C_1 symmetric-type catalyst.

3. Experimental details

All experiments were conducted under purified nitrogen by standard glove box and Schlenk techniques. Tetrahydrofuran (THF) was purified by distillation under nitrogen over sodium benzophenone, and pentane and methylene chloride were distilled under nitrogen from calcium chloride.

3.1. Preparation of the 2-(*t*-butyl-cyclopentadienyl)-2-fluorenylpropane **1**

In a 500 ml round bottom flask was placed 60 mmol (10 g) of fluorene dissolved in 100 ml of THF. To this

Table 4
Final fractional coordinates for $[(C_{13}H_8-\mu-CMe_2-C_5H_3CMe_3)_2ZrCl_2] \cdot CH_2Cl_2$

Atom	x	y	z	U_{eq}
Zr	0.12085(6)	0.73230(6)	0.26275(5)	0.038
Cl(1)	0.3449(2)	0.7273(2)	0.3477(2)	0.047
Cl(2)	0.0391(2)	0.5040(2)	0.2418(1)	0.047
C(1)	0.1832(7)	0.8818(6)	0.1297(5)	0.035
C(2)	0.2166(6)	0.7684(6)	0.0719(5)	0.034
C(3)	0.0983(7)	0.6780(6)	0.0374(5)	0.036
C(4)	-0.0046(7)	0.7364(7)	0.0696(5)	0.037
C(5)	0.0469(7)	0.8665(6)	0.1254(5)	0.037
C(6)	-0.0247(7)	0.9502(7)	0.1998(6)	0.044
C(61)	0.0361(9)	1.0955(7)	0.2161(7)	0.065
C(62)	-0.1710(8)	0.9313(9)	0.1420(7)	0.062
C(7)	-0.0018(6)	0.8971(6)	0.3171(5)	0.035
C(8)	-0.0808(7)	0.7858(6)	0.3439(6)	0.039
C(9)	-0.2063(8)	0.7095(8)	0.2917(7)	0.054
C(10)	-0.2518(9)	0.6093(9)	0.3422(9)	0.069
C(11)	-0.183(1)	0.5742(9)	0.4395(8)	0.070
C(12)	-0.0635(9)	0.6427(8)	0.4918(7)	0.058
C(13)	-0.0098(7)	0.7479(7)	0.4445(5)	0.040
C(14)	0.1113(7)	0.8379(7)	0.4834(5)	0.041
C(15)	0.2168(8)	0.8442(8)	0.5776(6)	0.055
C(16)	0.3216(9)	0.937(1)	0.5954(7)	0.064
C(17)	0.3272(9)	1.0303(9)	0.5209(8)	0.062
C(18)	0.2289(8)	1.0271(7)	0.4303(7)	0.050
C(19)	0.1158(7)	0.9312(6)	0.4075(6)	0.037
CB	0.3438(7)	0.7516(7)	0.0313(6)	0.048
CB(1)	0.3747(9)	0.6159(8)	0.0398(8)	0.075
CB(2)	0.4597(8)	0.8553(9)	0.1032(9)	0.065
CB(3)	0.3229(9)	0.7644(9)	-0.1023(7)	0.071
C	-0.349(1)	0.620(1)	0.7033(9)	0.085
CLS(1)	-0.4662(3)	0.6710(3)	0.6095(3)	0.098
CLS(2)	-0.3254(3)	0.7041(3)	0.8500(2)	0.095
H(1)	0.2477(7)	0.9616(6)	0.1686(5)	0.050
H(3)	0.0896(7)	0.5872(6)	-0.0038(5)	0.050
H(4)	-0.0987(7)	0.6937(7)	0.0561(5)	0.050
H(9)	-0.2594(8)	0.7300(8)	0.2201(7)	0.050
H(10)	-0.3406(9)	0.5573(9)	0.3066(9)	0.050
H(11)	-0.221(1)	0.4984(9)	0.4718(8)	0.050
H(12)	-0.0134(9)	0.6185(8)	0.5629(7)	0.050
H(15)	0.2123(8)	0.7793(8)	0.6310(6)	0.050
H(16)	0.3962(9)	0.942(1)	0.6617(7)	0.050
H(17)	0.4067(9)	1.0993(9)	0.5352(8)	0.050
H(18)	0.2365(8)	1.0936(7)	0.3789(7)	0.050
HC(1)	-0.376(1)	0.526(1)	0.7022(9)	0.090
HC(2)	-0.264(1)	0.635(1)	0.6740(9)	0.090

solution an equimolar amount of methyl lithium in diethyl ether (1.6 M) was added over 30 min at room temperature. The resulting red solution was stirred for 4 h until the gas evolution had completely ceased and the reaction was completed. To this solution 60 mmol (9.72 g) of 6,6-dimethyl-3-tertiarybutyl fulvene in 50 ml THF was added at ambient temperature. After stirring for 4 h at this temperature the solution was hydrolyzed by adding 30 ml of an aqueous solution of saturated ammonium chloride. The organic phase was extracted with ether and dried over magnesium sulfate. After evaporation of the ether a white solid was obtained that was recrystallized from a chloroform–ethanol mixture to yield 17.13 g (87%) of white crystals. Anal. Found: C, 90.85; H, 8.45. $C_{25}H_{28}$. Calc.: C 91.409; H, 8.591%.

3.2. Preparation of the dianion 2

A 500 ml round-bottom flask equipped with side arm, addition funnel, and magnetic stirring bar was charged with 0.035 mol of **1** in 200 ml of THF. To this solution two molar equivalents of methyl lithium in ether (1.6 M) were added dropwise at room temperature. The resulting red solution was stirred overnight. The evaporation of the solvents yielded the dianion quantitatively as an orange powder. The product was used without further purification.

3.3. Preparation of 3

To a suspension of 0.035 mol of **2** in 200 ml of dry pentane in a 1 l round bottom-flask equipped with a magnetic stirring bar was added a suspension of 0.035 mol of $ZrCl_4$ powder in 200 ml of pentane. The mixture was stirred for 6 h during which the suspension became red and the reaction went to completion. The pentane was decanted and the remaining red solid was extracted with methylene chloride and separated from LiCl. Cooling of the extract to $-20^\circ C$ gave analytically-pure red crystals in quantitative yield. Anal. Found: C, 60.86; H, 5.52; Cl, 14.11; Zr, 18.31. $C_{25}H_{26}ZrCl_2$. Calc.: C, 61.455; H, 5.363; Cl, 14.512; Zr, 18.670%.

3.4. X-ray data collection, solution and refinement for 3

Single crystals of **3** were sealed under N_2 in thin-walled glass capillaries as a precaution, although the crystals appear rather stable in air. Data were collected on an Enraf–Nonius CAD4 diffractometer by the θ – 2θ scan technique as previously described [9]. The struc-

ture was solved by the application of the standard Patterson methods. The crystals diffracted well. All non-hydrogen atoms were treated with anisotropic thermal parameters. Hydrogen atoms were located on a difference Fourier map, but their parameters were not refined. A final difference Fourier map showed no unaccounted electron density. A summary of data collection parameters and positional parameters are given in Tables 3 and 4. Calculations were carried out with the SHELX system of computer programs [10].

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