Synthesis of bis-cyclopentadienyl compounds with a 9,9-fluorenylidene bridge. Crystal and molecular structure of [μ-9,9-Flu(η^5-Cp)$_2$]ZrCl$_2$

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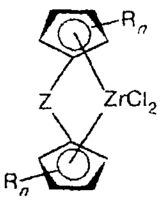
An efficient synthetic approach to 9,9-bis(cyclopentadienyl)fluorenes was developed. The two corresponding *ansa*-zirconocenes were synthesized. The structure of one of these compounds was established by X-ray diffraction analysis.

Key words: nickelocenes, 9,9-dichlorofluorene, *ansa*-zirconocenes, X-ray diffraction analysis.

Sandwich complexes of Group IV metals (primarily, of zirconium) are recognized as the most promising homogeneous catalysts of polymerization of α-olefins.[1] Substituted *ansa*-zirconocenes **1** containing short bridges between cyclopentadienyl fragments (Z = $-CH_2CH_2-$ or $-SiR_2-$) attract the major attention. In the presence of methylalumoxane (MAO), these complexes efficiently catalyze polymerization of terminal olefins, yielding products with a broad spectrum of physicochemical properties. A large number of various *ansa*-zirconocenes have already been synthesized, some of which are used in the industrial preparation of polymers. The catalytic activity of *ansa*-metallocenes is determined by the nature, positions, and number of substituents in the cyclopentadienyl rings.



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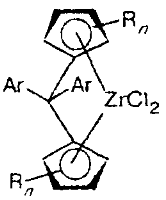


2

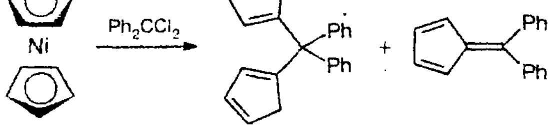
It was demonstrated[2-4] that the presence of aryl substituents in the bridge often has a beneficial effect on the catalytic activity of zirconocene and the properties of the resulting polymers. In addition, many *ansa*-metallocenes containing the one-membered carbon bridge exhibit high activity in polymerization of olefins.[5] In this connection, the preparation of the previously unknown compounds **2** containing the diarylmethylene bridge is an urgent problem.

Results and Discussion

Attempt to prepare bis(cyclopentadienyl)diarylmethanes

Previously, it has been demonstrated[6] that the simplest representative of bis-cyclopentadienyl compounds containing the diarylmethylene bridge, *viz.*, Cp_2CPh_2 (**3**), can be prepared by the reaction of Ph_2CCl_2 with CpCu—PEt$_3$. An attempt to synthesize compound **3** by the reaction of Ph_2CCl_2 with nickelocene in benzene was also described[7]; however, the authors failed to identify the reaction products. We reproduced the reaction of Ph_2CCl_2 with nickelocene described in Ref. 7 under different conditions (Scheme 1). In all cases, 6,6-diphenylfulvene (**4**) was obtained in high yields instead of the expected bis-cyclopentadienyl compound **3**; Cp_2CPh_2 was not detected even in trace amounts (control by ^{1}H NMR spectroscopy).

Scheme 1



3 **4**

Conditions and yields: THF, 0% **3**, 48% **4**; C_6H_6/Ph_3P, 0% **3**, 81% **4**; Et_2O/Ph_3P, 0% **3**, 84% **4**; THF/Ph_3P, 0% **3**, 94% **4**.

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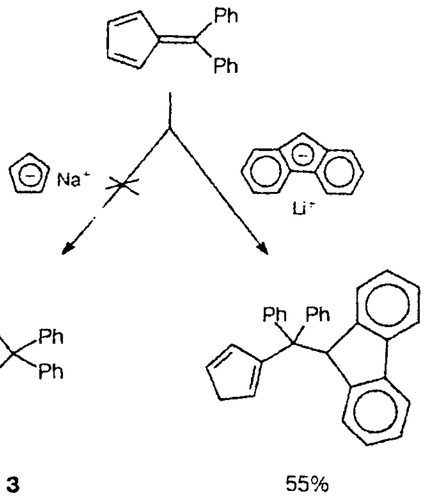
The reaction of Ph_2CCl_2 with the cyclopentadienyl copper complex afforded a complex mixture of unidentified products. In this case also, compound **3** was not detected.

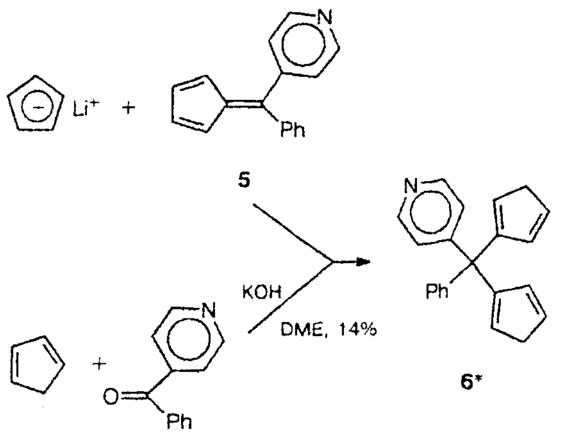
The second possible procedure for the preparation of bis-cyclopentadienyl compounds containing the diarylmethylene bridge involves the reaction of diarylfulvene with sodium cyclopentadienylide. Previously, this procedure has been successfully used[4] for the synthesis of the only known representative of the class of compounds of interest, *viz.*, Cp—CPh_2—Flu (Flu is fluoren-9-yl). However, in this case also the target bis-cyclopentadienyl compound **3** was not found even in trace amounts (Scheme 2).

Scheme 2



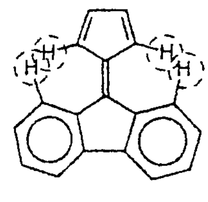
Previously, we have demonstrated[8—10] that bis-cyclopentadienyl-bridged compounds are often formed in reactions of various carbonyl compounds with cyclopentadienes or indenes in the KOH/DME system. Taking into account this fact, we carried out the reaction of cyclopentadiene with benzophenone. However, in this case, too, 6,6-diphenylfulvene (**4**) was isolated in virtually quantitative yield. Apparently, 6,6-diphenylfulvene is so much more thermodynamically and kinetically stable that it cannot react with the cyclopentadienyl anion. We supposed that the reactivity of diarylfulvene with respect to nucleophiles can be governed by electronic factors. If so, the presence of the electron-withdrawing aromatic substituent in the fulvene molecule can promote the nucleophilic attack on position 6. To verify this hypothesis, we chose 6-(4-pyridyl)-6-phenylfulvene (**5**) as the model compound. It was detected by ^{1}H NMR spectroscopy that fulvene **5** actually reacted with lithium cyclopentadienylide to form the target product **6*** (Scheme 3). Moreover, condensation of cyclopentadiene with 4-benzoylpyridine in the two-phase KOH/DME system also afforded bis-cyclopentadienyl compound **6**; however, its yield was only 14% (Scheme 3). The low yield of the target product is attributable to side processes resulting from the ability of the pyridine fragment to react with strong bases.

Scheme 3



Synthesis of 9,9-bis(cyclopentadienyl)fluorenes

We demonstrated that the simplest representative of bis(cyclopentadienyl)diarylmethanes, *viz.*, Cp_2CPh_2 (**3**), is difficult to prepare due to the high stability of 6,6-diphenylfulvene. We suggested that the introduction of diarylketone, which cannot form fulvene, into the reaction has promise for the preparation of bis-cyclopentadienyl compounds containing the diarylmethylene bridge. Fluorenone is the most readily accessible compound of this type. In this case, steric hindrances due to interactions between the protons of the cyclopentadienyl and fluorenyl rings prevent the formation of the corresponding fulvene.



However, it appeared that fluorenone did not react with cyclopentadiene in the KOH/DME system.

Taking into account that nickelocene can react with some alkyl halides, we introduced 9,9-dichlorofluorene into the reaction with nickelocene and 1,1′-di-*tert*-butylnickelocene (Scheme 4). As a result, the corresponding bis-cyclopentadienyl compounds **7** and **8** were obtained, the maximum yield being achieved when the reaction was carried out in ether in the presence of PPh_3.

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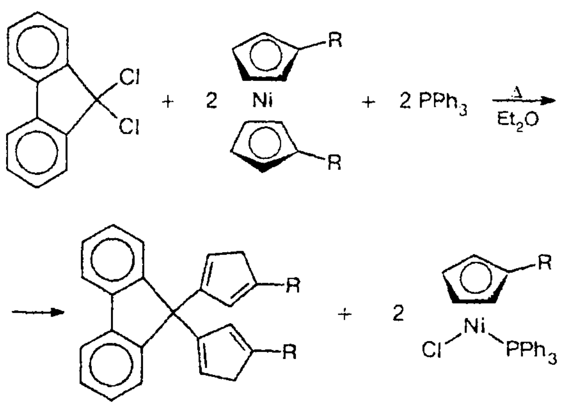
* In a mixture with an insignificant amount of two isomers with other positions of double bonds.

Scheme 4

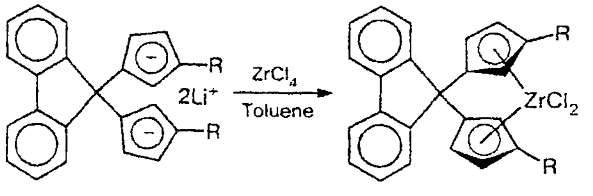


7*, R = H, 79%
8*, R = Bu^t, 81%

Synthesis of ansa-zirconocenes with the fluorenylidene bridge

We synthesized the corresponding *ansa*-zirconocenes based on compounds **7** and **8**. The maximum yields of metallocenes **9** and **10** were obtained when the reactions of dilithium derivatives **7a** and **8a** with ZrCl$_4$ were performed in toluene (Scheme 5).

Scheme 5



7a, R = H
8a, R = Bu^t

9, R = H, 68%
10, R = Bu^t, 80%

We failed to synthesize the zirconium complex from compound **6**. Apparently, this is associated with the fact that the corresponding dilithium derivative cannot be formed because the reaction of compound **6** with butyllithium is accompanied by competitive metallation of the pyridine fragment.

X-ray diffraction study of compound 9

The molecular and crystal structure of compound **9** was established by X-ray diffraction analysis (Fig. 1).

It was found that toluene molecules are involved in the crystal lattice of metallocene **9** in an equimolar ratio (Fig. 2), resulting, apparently, in stabilization of the crystal packing. The metallocene molecule has a rather high symmetry group (C_2) in spite of the fact that it is located in the monoclinic unit cell ($P2_1/n$).

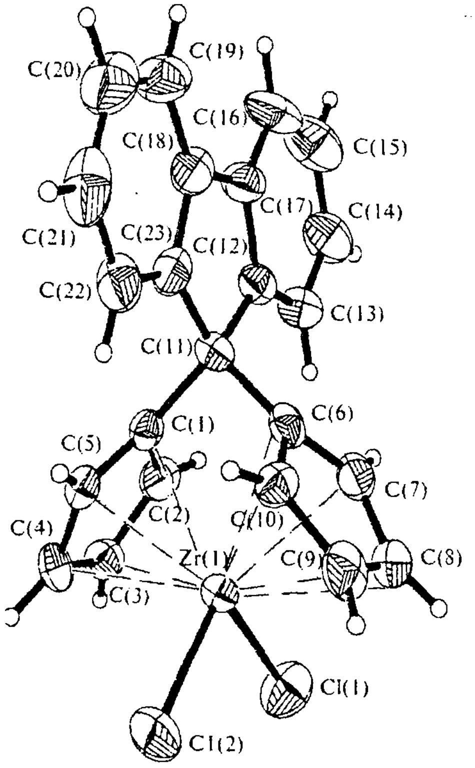


Fig. 1. Molecular structure of compound **9**.

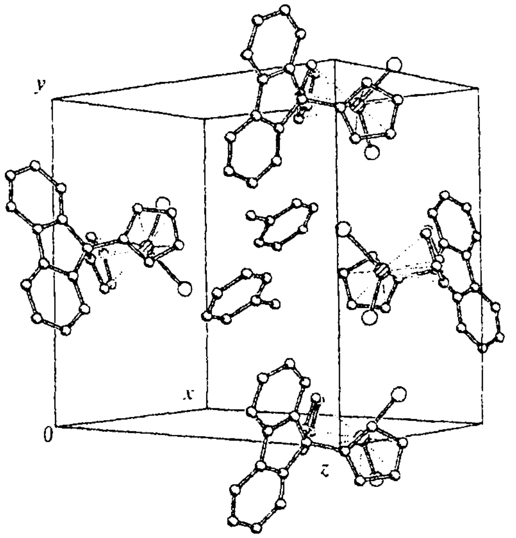


Fig. 2. Crystal unit cell of compound **9**.

In *ansa*-complex **9**, the zirconium atom is η^5-coordinated by the cyclopentadienyl fragments and two chlorine atoms. The distortions of the molecule are typical of *ansa*-metalocenes and are caused by the presence of a short bridge between two cyclopentadienyl fragments. Thus, the dihedral angle between the planes of the Cp rings (109.5°) is substantially smaller than the value characteristic of nonbridged zirconocenes (~125°).

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* In a mixture with an insignificant amount of two isomers with other positions of double bonds.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in molecule **9**

Bond	*d*/Å	Bond	*d*/Å
Zr(1)—Cl(1)	2.432(2)	Zr(1)—C(9)	2.551(6)
Zr(1)—Cl(2)	2.422(2)	C(1)—C(2)	1.408(8)
Zr(1)—C(1)	2.448(6)	C(1)—C(11)	1.543(7)
Zr(1)—C(6)	2.456(5)	C(6)—C(7)	1.408(8)
Zr(1)—C(5)	2.458(6)	C(6)—C(11)	1.533(8)
Zr(1)—C(10)	2.459(5)	C(11)—C(23)	1.526(8)
Zr(1)—C(7)	2.463(6)	C(11)—C(12)	1.544(8)
Zr(1)—C(2)	2.467(6)	C(12)—C(17)	1.404(8)
Zr(1)—C(4)	2.540(6)	C(17)—C(18)	1.444(9)
Zr(1)—C(8)	2.546(6)	C(18)—C(23)	1.405(9)
Zr(1)—C(3)	2.550(6)		

Angle	ω/deg	Angle	ω/deg
Cl(2)—Zr(1)—Cl(1)	100.92(8)	C(23)—C(11)—C(1)	114.9(5)
C(2)—C(1)—C(5)	106.8(5)	C(6)—C(11)—C(1)	99.2(4)
C(2)—C(1)—C(11)	124.6(5)	C(23)—C(11)—C(12)	101.8(4)
C(5)—C(1)—C(11)	125.3(5)	C(6)—C(11)—C(12)	113.2(4)
C(3)—C(2)—C(1)	108.6(6)	C(1)—C(11)—C(12)	114.2(4)
C(7)—C(6)—C(10)	106.6(5)	C(17)—C(12)—C(11)	109.4(5)
C(7)—C(6)—C(11)	124.8(5)	C(12)—C(17)—C(18)	109.3(5)
C(10)—C(6)—C(11)	125.1(5)	C(23)—C(18)—C(17)	109.7(5)
C(6)—C(7)—C(8)	108.7(6)	C(18)—C(23)—C(11)	109.7(5)
C(23)—C(11)—C(6)	114.2(4)		

A distinguishing feature of the complex under study is the presence of the rather bulky fluorenyl bridging fragment. This fact may be responsible for some chemical properties of the metallocene because two hydrogen atoms are located rather close to the zirconium atom. Although the corresponding distances are large enough (>4 Å) to exclude nonbonding agostic interactions, these atoms can exert a direct effect on the coordination sphere about the zirconium atom and, clearly, on the catalytic properties of the metallocene.

The selected bond lengths and bond angles for molecule **9** are given in Table 1.

Experimental

All operations were carried out under an atmosphere of argon. Lithium derivatives and zirconium complexes were prepared in a completely sealed evacuated glass apparatus of the Schlenk vessels type. The ether solvents were kept and distilled over KOH and then over sodium benzophenone ketyl. Dichloromethane was successively washed with water, concentrated H_2SO_4, and water until the reaction became neutral, dried over $CaCl_2$, and distilled over P_2O_5. The ^1H and ^{13}C NMR spectra were recorded on Varian VXR-400 and Varian VXR-300 instruments. We failed to obtain reliable data of elemental analysis for the resulting zirconocenes because the sample obtained after combustion contained impurities of zirconium carbides.

4-[Bis(cyclopenta-1,4-dien-3-yl)(phenyl)methyl]pyridine (6) (containing an insignificant impurity of two isomers with respect to the double bond). Freshly distilled cyclopentadiene (33 mL, 0.4 mol) was added dropwise with vigorous stirring to a suspension of KOH (22.5 g, 0.4 mol) in DME (200 mL) at 0—5 °C. After 15 min, a solution of 4-benzoylpyridine (Merck) (36.6 g, 0.2 mol) in DME (50 mL) was added dropwise at this temperature (with cooling). The reaction mixture was heated to boiling and refluxed with stirring for 2 h. Then the reaction mixture was cooled and water (500 mL) was added. The organic layer was separated and the aqueous layer was extracted with benzene. The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was extracted with heptane (5×100 mL), from which compound **6** precipitated as a brown crystalline powder in a yield of 8.3 g (14%). The powder decomposed at a temperature higher than 120 °C. Found (%): C, 88.80; H, 6.51. $C_{22}H_{19}N$. Calculated (%): C, 88.85; H, 6.44. ^1H NMR of the major component (~90%) ($CDCl_3$, 30 °C), δ: 2.94 (br.s, 4 H, CH_2); 5.90, 6.17, and 6.30 (all m, 6 H, —CH=); 6.95—7.20 and 8.38 (both m, 9 H, $C_{Ar}H$).

9,9-Bis(cyclopentadienyl)-9*H*-fluorene (7) (a mixture of three isomers with respect to the double bond in a ratio of approximately 10 : 1 : 1). A mixture of nickelocene[11] (12 g, 0.063 mol), 9,9-dichlorofluorene[12] (7.4 g, 0.032 mol), and Ph_3P (16.6 g, 0.063 mol) in ether (50 mL) was refluxed with stirring under an atmosphere of argon for 1 h. The reaction mixture was cooled. The solution was separated from the precipitate and concentrated under reduced pressure. The residue was dissolved in a minimun volume of benzene and chromatographed on 60/100-μm silica gel (benzene as the eluent) until the elution of $CpNiCl(PPh_3)$ started (a dark-claret zone). The solvent was removed under reduced pressure and compound **7** was obtained as a pale-yellow crystalline substance in a yield of 7.3 g (79%), m.p. 152 °C. Found (%): C, 93.88; H, 6.12. $C_{23}H_{18}$. Calculated (%): C, 93.84; H, 6.16. ^1H NMR ($CDCl_3$, 30 °C), δ: 2.73, 2.80, and 2.90 (three isomers, all dd, 4 H, CH_2, $J_1 = J_2 = 1.4$ Hz); 6.21, 6.31, and 6.35 (three isomers, all m, 6 H, —CH=); 7.30 (m, 4 H), 7.43 (m, 2 H), 7.72 (d, 2 H, $J = 7.5$ Hz) (C_{Ar}—H of three isomers). MS (60 eV, direct introduction): 295 $[M]^+$ (1.8); 294 [M] (24); 266 (12); 254 (18); 230 (64); 229 (79); 228 (100); 203 (31); 166 (23); 114 (18); 98 (12); 86 (18); 70 (34); 55 (44); 58 (57); 56 (64).

9,9-Bis(*tert*-butylcyclopentadienyl)fluorene (8) (a mixture of three isomers with respect to the double bond in a ratio of approximately 2 : 1 : 1). Compound **8** was synthesized analogously to compound **7** from 1,1′-di-*tert*-butylnickelocene (3.16 g, 0.011 mol), 9,9-dichlorofluorene (1.23 g, 0.053 mol), and Ph_3P (2.75 g, 0.011 mmol) as a yellow crystalline substance in a yield of 1.7 g (81%), m.p. 94 °C. Found (%): C, 91.62; H, 8.38. $C_{31}H_{34}$. Calculated (%): C, 91.57; H, 8.43. ^1H NMR ($CDCl_3$, 30 °C), δ: 0.92 (18 H); 1.05 (9 H); 1.10 (9 H); 1.14 (18 H) (three isomers, all s, CMe_3); 2.60, 2.64, 2.70, and 2.75 (three isomers, all br.s, 4 H, CH_2); 5.70—6.60 (three isomers, all m, 4 H, —CH=); 7.10, 7.25, and 7.60 (three isomers, all m, 8 H, C_{Ar}—H).

Dilithium derivative of 9,9-bis(cyclopentadienyl)fluorene (7a). A 1.6 *M* Bu^nLi solution (42 mL, an excess) in hexane (Merck) was rapidly added to a solution of compound **7** (8.6 g, 29.2 mmol) in ether (75 mL) with cooling to −40 °C. The reaction mixture turned dark and a very finely dispersed pale-brown precipitate immediately began to form. The precipitate was washed with ether (5×50 mL) and dried *in vacuo* (0.01 Torr). Compound **7a** was obtained as a very finely dispersed beige powder in a yield of 5.7 g (64%). ^1H NMR (THF-d_8, 30 °C), δ: 5.45 and 5.68 (both br.s, 4 H each, Cp ring); 7.15 (4 H), 7.60 (2 H), and 7.80 (2 H) (all m, C_{Ar}—H).

Dilithium derivative of 9,9-bis(*tert*-butylcyclopentadienyl)fluorene (8a). A 1.6 *M* Bu^nLi solution (3.7 mL) in hexane (Merck) was rapidly added to a solution of compound **8** (2 g, 5 mmol) in ether (15 mL) with cooling to −40 °C. The reaction mixture turned dark. After 1 h, a finely crystalline pale-pink precipitate began to form. The precipitate was washed with ether (3×5 mL) and dried. Compound **8a** was obtained as a virtually colorless finely crystalline powder in a yield of 1.1 g (54%). ^{1}H NMR (THF-d$_8$, 30 °C), δ: 1.13 (s, 18 H, CMe$_3$); 5.40 (t, 2 H, J = 2.5 Hz); 5.62 (dt, 4 H, Cp ring, J_1 = 2.5 Hz, J_2 = 7.9 Hz); 7.13 (m, 4 H), 7.58 (dd, 2 H, J_1 = 6.66 Hz, J_2 = 1.5 Hz), 7.86 (d, 2 H, J = 6.5 Hz) (C$_{Ar}$—H). ^{13}C NMR (THF-d$_8$, 30 °C), δ: 15.7 (CH$_3$); 32.3 and 33.8 (>C<); 98.6, 100.8, 102.5, 119.3, 125.4, 126.2, and 127.9 (=CH—); 123.6, 128.2, 140.3, and 158.8 (=C<).

[Fluoren-9,9-ylidene(η^5-cyclopentadienyl)]dichlorozirconium(IV) (9). ZrCl$_4$ (1.94 g, 8.33 mmol) was added with stirring and cooling to −70 °C to a suspension of dilithium derivative **7a** (2.55 g, 8.33 mmol) in CH$_2$Cl$_2$ (20 mL). The mixture was allowed to warm to −20 °C with stirring over 2 h. The solution was decanted from the precipitate of LiCl and the solvent was removed. The residue was recrystallized from toluene and compound **9** was obtained as pale-yellow well-faceted crystals in a yield of 3.1 g (68%). The crystals of the product are composed of clathrates with toluene (according to the data of ^{1}H NMR spectroscopy and X-ray diffraction study, the **9**/toluene ratio was 1 : 1). ^{1}H NMR (CD$_2$Cl$_2$, 30 °C), δ: 6.42 and 6.76 (both t, 4 H each, Cp ring, J = 3 Hz); 7.25 (4 H), 7.56 (2 H), and 8.00 (2 H) (all m, C$_{Ar}$—H).

[Fluoren-9,9-ylidene(η^5-*tert*-butylcyclopentadienyl)]dichlorozirconium(IV) (10). ZrCl$_4$ (0.73 g, 3.13 mmol) was added with stirring and cooling to −20 °C to a suspension of dilithium derivative **8a** (1.31 g, 3.13 mmol) in toluene (20 mL). The mixture was allowed to warm to −20 °C, the solution was decanted from the precipitate of LiCl, and the solvent was removed. The residue was recrystallized from ether and complex **10** was obtained as a mixture of *rac*- and *meso*-forms (according to the ^{1}H NMR spectral data, the ratio was 1 : 1) in a yield of 1.4 g (80%). Attempts to separate the two forms by crystallization failed. The product is a pale-yellow finely crystalline powder, which is moderately stable in air. ^{1}H NMR of a mixture of *rac*-**10** and *meso*-**10** (CD$_2$Cl$_2$, 30 °C), δ: 1.31 and 1.32 (both s, 18 H, CMe$_3$, *rac*-**10** and *meso*-**10**); 6.15 and 6.18 (both t, 2 H, J = 2.7 Hz, *rac*-**10** and *meso*-**10**); 6.36 and 6.47 (both t, 2 H, J = 3.3 Hz, *rac*-**10** and *meso*-**10**); 6.65 and 6.59 (both dd, 2 H, Cp ring, J_1 = 2.7 Hz, J_2 = 1.4 Hz, *rac*-**10** and *meso*-**10**); 7.93, 8.03, and 8.18 (all m, 8 H, C$_{Ar}$—H, *rac*-**10** and *meso*-**10**).

Table 2. Principal crystallographic data for compound **9**

Parameter	Value
Molecular formula	$C_{30}H_{24}Cl_2Zr$
Molecular weight	546.61
Crystal dimensions/mm	0.36×0.46×0.08
System	Monoclinic
Space group	$P2_1/n$
Unit cell parameters:	
a/Å	11.386(6)
b/Å	13.555(5)
c/Å	15.947(10)
α/deg	90
β/deg	102.59
γ/deg	90
V/Å^3	2402(2)
Z	4
$d_{\text{выч}}$/g cm^{-3}	1.512
Absorption coefficient, μ/mm^{-1}	0.697
Diffractometer	Siemens SMART
Temperature/K	293.0(2)
Radiation (λ/Å)	Mo-Kα (0.71073)
Scanning technique	ω
Number of reflections	4239
Number of independent reflections	4120 (R_{int} = 0.1303)
Absorption correction	No
Procedure for the structure solution	Direct
Rrefinement procedure	Full-matrix least-squares based on F^2
Location of hydrogen atoms	From the difference Fourier synthesis, refined isotropically
R_1, wR_2 for $F > 2\sigma(F)$	0.0524, 0.1344
R_1, wR_2 using all data	0.1007, 0.1577

X-ray diffraction study of compound 9. Crystals of compound **9** suitable for X-ray diffraction study were prepared by crystallyzation of a preheated (100 °C) toluene solution. The details of X-ray diffraction study are given in Table 2. All calculations were carried out using the SHELXL76[14] and SHELXL93 program packages.[15] The molecular structure was drawn with the use of the ORTEP program. The complete tables of the bond lengths, bond angles, atomic coordinates, and thermal parameters were deposited with the Cambridge Structural Database.

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