Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 1067–1079
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and molecular structures of zirconium and hafnium complexes bearing dimethylsilandiyl-bis-2,4,6-trimethylindenyl and dimethylsilandiyl-bis-2-methyl-4,6-diisopropylindenyl ligands

Vyacheslav V. Izmer [a], Denis A. Sorokin [a], Lyudmila G. Kuz'mina [b], Andrei V. Churakov [b], Judith A.K. Howard [c], Alexander Z. Voskoboynikov [a,*]

[a] *Department of Chemistry, Moscow State University, V-234, Moscow 119899, Russian Federation*
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, 31, Leninskii pr., Moscow 119991, Russian Federation*
[c] *Department of Chemistry, Durham University, South Road, Durham DH1 3LE, United Kingdom*

Received 19 June 2004; accepted 5 October 2004

Abstract

Zirconium and hafnium *ansa*-complexes containing 2,4,6-trialkyl-substituted indenyl fragments were synthesized and unambiguously characterized. Mixtures of *rac*- and *meso*-$Me_2Si(2\text{-}Me\text{-}4,6\text{-}R_2C_9H_3\text{-}\eta^5)_2MCl_2$, where R = Me, *i*-Pr and M = Zr, Hf, were obtained by a treatment of MCl_4 by dilithium salts of the respective bis(2,4,6-trialkylindenyl)dimethylsilanes in toluene. Alternatively, better yields of the same complexes can be obtained by the reaction between metal tetrachlorides and indenyl-tin derivatives gave the desired *ansa*-metallocenes. All *rac*- and *meso*-complexes of Zr and Hf were isolated in an analytically pure form, and six of these *ansa*-metallocenes were characterized by X-ray crystal structure analysis.

Keywords: Zirconium; Hafnium; Metallocenes

1. Introduction

Among chiral *ansa*-metallocenes the silylene-bridged bis-indenyl complexes with Me in position 2 have been most intensively studied because of their application for α-olefin polymerization [1]. Catalytic properties of these complexes depend strongly on type and position of substituents in the indenyl fragment. For instance, the complexes with 4-substituted (preferably aryl) indenyl ligands were found to have outstanding catalytic properties in the propene polymerization [2]. *Ansa*-metallocenes with 4,7-disubstituted indenyl ligands have been recently described [2–4]. Complexes with benzoannelated indenyl residue were prepared as well [2–8]. Meanwile, synthesis of the compounds with 4,6-disubstituted indenyl fragments has not been described so far. In this paper we report on convenient methods for the preparation of such 4,6-disubstituted indenes, the respective dimethylsilandiyl bridged ligands, and their *ansa*-complexes of zirconium and hafnium.

* Corresponding author. Tel.: +7 095 939 4764; fax: +7 095 932 8846.
E-mail address: voskoboy@org.chem.msu.ru (A.Z. Voskoboynikov).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.10.052

2. Results and discussion

2.1. Synthesis of 2,4,6-trimethyl-, 2,5,7-trimethyl-, 2-methyl-5,7-diisopropyl-1H-indenes and the respective Me_2Si-bridged ligands

Mixtures of isomeric trialkyl-substituted indenes were prepared from the corresponding *meta*-dialkylbenzenes as shown in Scheme 1. Whereas the chloromethylation of *m*-xylene gave a mixture of 2,4- and 2,6-dimethylbenzyl chlorides in ratio of 9:2 in 43% yield *m*-diisopropylbenzene formed only 2,4-diisopropylbenzyl chloride in 58% yield. Indanone synthesis from the respective benzyl halides is a well-known procedure [1,2]. In our case, Lewis acid catalyzed intermolecular cyclization of β-substituted *iso*-butyryl chlorides gave 2,4,6-trimethyl-1-indanone and 4,6-diisopropyl-2-methyl-1-indanone with 86% and 90% yields, respectively. The overall yields of pure 2,5,7-trimethyl-1*H*-indene (**1**) and 5,7-diisopropyl-2-methyl-1*H*-indene (**2**) from *m*-xylene and *m*-diisopropylbenzene were 19% and 34%, respectively.

Alternatively, isomeric indene **3** was prepared from mesitylene as shown in Scheme 2. In this case, intermolecular cyclization of 2-(3,5-dimethylbenzyl)propionic acid gave 2,5,7-trimethylindan-1-one in 73% yield [9]; and the overall yield of **3** was 14%.

Another general procedure for the preparation of indanones is the acid-catalyzed Nazarov-like cyclization of arylvinylketones (Scheme 3) [10–13]. The respective arylvinylketones can be prepared by acylation of the arene by acryloyl chloride or other acrylic acid derivative. In the presence of excess of $AlCl_3$ electron rich arenes give the respective indanones via one-pot acylation-cyclization reaction [4,14,15] as shown in Scheme 4. We used this approach for the synthesis of the desired trialkylindenes. In this way, the overall yields of 2,4,6-trimethyl-(**3**) and 2-methyl-4,6-diisopropyl-1*H*-indenes (**4**) were 77% and 65%, respectively.

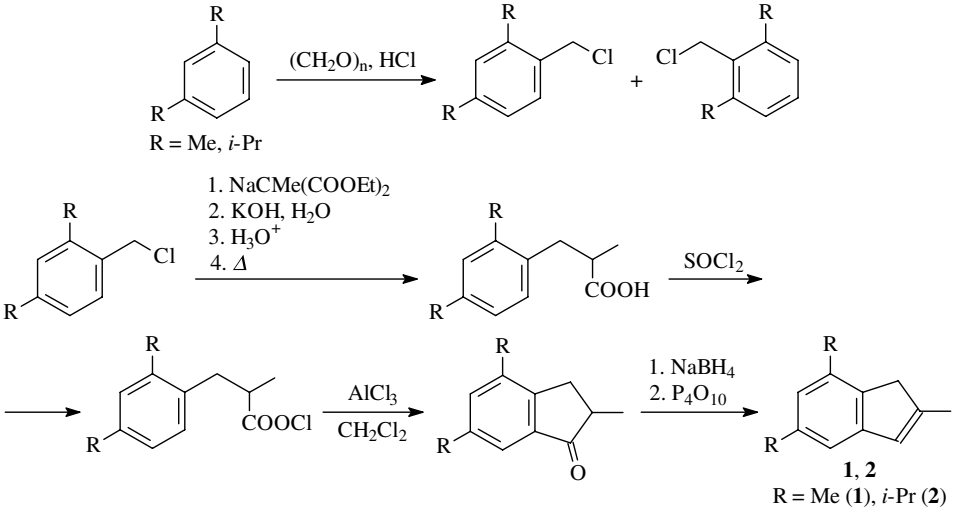
To synthesize the respective bis(trialkylindenyl)dimethylsilanes, the above-mentioned trialkylindenes were deprotonated with *n*-BuLi, and, then, treated with 0.5 equiv. of Me_2SiCl_2 as shown in Scheme 5. Pure *rac*-**5** was isolated in 40% yield by crystallization of crude product from *n*-hexane. A mixture of *rac*- and *meso*-diastereomers of **6** was obtained in 61% yield. After distilling off the starting indene, **6** was purified by flash chromatography.

2.2. Synthesis and molecular structures of ansa-metallocenes

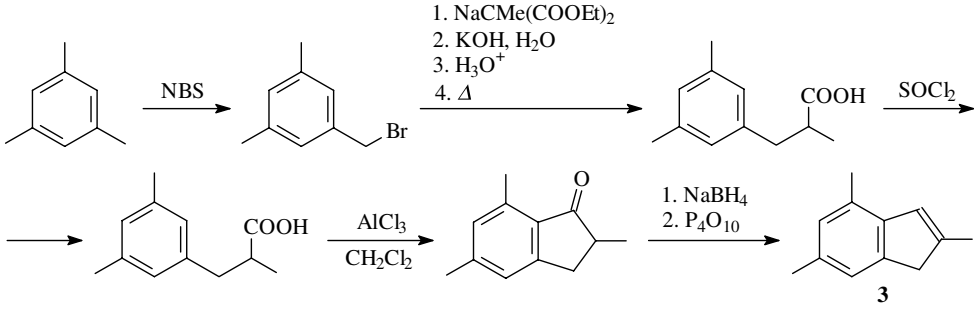
We used two general approaches to the synthesis of the desired *ansa*-metallocenes, i.e. (1) the reaction between di-lithium salts of the ligands and MCl_4, where M = Zr, Hf [1]; (2) the reaction between metal tetrachlorides and indenyl-tin derivatives [16–19].

The bridged ligands **5** and **6** were deprotonated with 2 equiv. of *n*-BuLi and the resulting dilithium bis-indenyls were treated with $ZrCl_4$ or $HfCl_4$ in toluene to give ca. 1:1 mixtures of *rac*- and *meso*-complexes of zirconium or hafnium (Scheme 6). Pure diastereomers were isolated by re-crystallization (see Section 3 below).

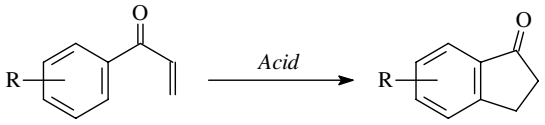
An alternative transmetallation using softer organotin reagents (Scheme 7) gave the desired complexes, particularly racemates in better yields. *Meso*- and *rac*-complexes were isolated after re-crystallization from toluene and DME, respectively. It should be noted, that in the first method using organolithium reagents the yield of *meso*-complexes was higher than the yield of the respective racemates, though in the case of organotin reagents the picture was reverse, i.e. racemates were formed and isolated in higher yield, though the respec-



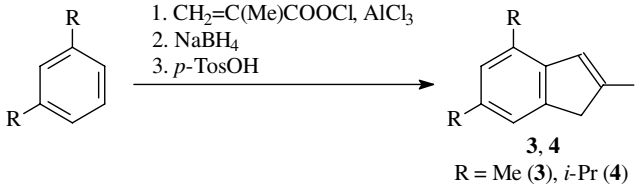
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

tive *meso*-complexes were obtained in moderate yield only. This phenomenon may be associated with sterical hindrance of the starting materials used. Actually, softer organotin reagents should give better yields of more thermodynamically stable products (presumably, racemates [1]), though analogous reactions with organolithium compounds would result in higher yield of kinetically controlled products, i.e. probably organometallic olygomers and *meso*-complexes bearing bulky 2,4,6-trisubstituted indenyls.

The structures of complexes *rac*-**7,** *meso*-**7,** *rac*-**8,** *meso*-**8,** *meso*-**9**, and *rac*-**10** were determined by X-ray analysis (see Figs. 1–6). Selected bond lengths and angles are given in Table 1. In all cases, the molecules represent bent metallosandwiches with nearly planar indenyl ligands. In general, the geometry of core metallocene fragments is close to that previously reported for other *ansa*-bis-indenyl complexes of zirconium and hafnium with dialkylsilyl bridge [1]. It should be noted that the pairs of complexes *rac*-**7**-*rac*-**8** and *meso*-**7**-*meso*-**8** are isostructural.

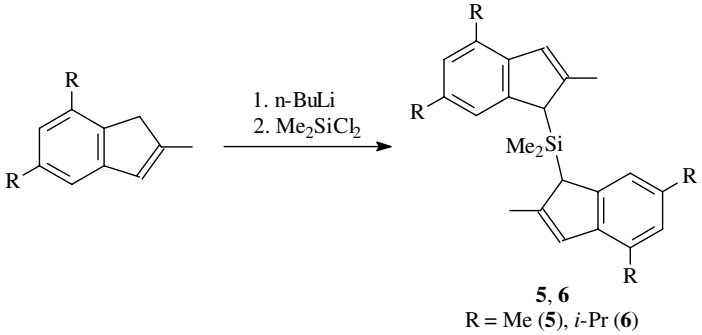
3. Experimental

3.1. General procedures

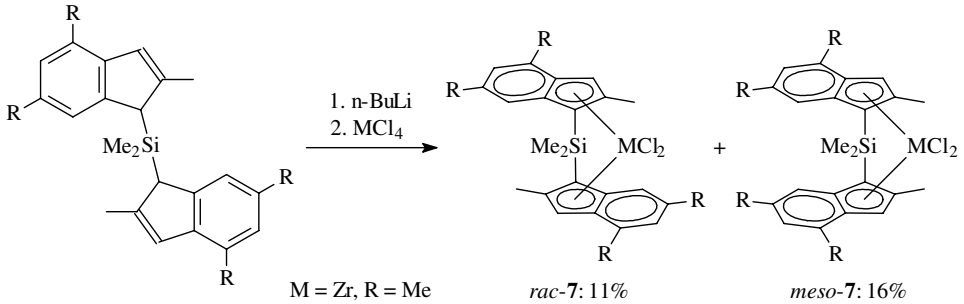
All manipulations with organometallic compounds have been done either on the high-vacuum line in an all-glass apparatus equipped with polytetrafluoroethylene stopcocks or in the atmosphere of thoroughly purified argon using the standard Shlenk technique. THF was distilled over $LiAlH_4$. Toluene and hexane were distilled over Na/K alloy and kept over CaH_2. CH_2Cl_2, as well $CDCl_3$ and CD_2Cl_2 were distilled over P_4O_{10} and kept over 3A molecular sieves. ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 360 spectrometer.

3.2. Mixture of 2,4- and 2,6-dimethylbenzylchlorides

A mixture of 200 ml of 12 M HCl, 200 ml (174 g, 1.64 mol) of *m*-xylene, 88 g of $ZnCl_2$, and 33 g (1.10 mol)

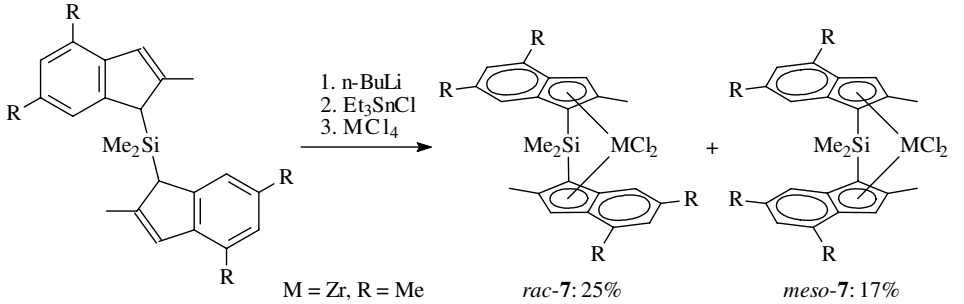


Scheme 5.



M = Zr, R = Me	*rac*-**7**: 11%	*meso*-**7**: 16%
M = Hf, R = Me	*rac*-**8**: 12%	*meso*-**8**: 16%
M = Zr, R = *i*-Pr	*rac*-**9**: 15%	*meso*-**9**: 21%
M = Hf, R = *i*-Pr	*rac*-**10**: 14%	*meso*-**10**: 20%

Scheme 6.



M = Zr, R = Me	*rac*-**7**: 25%	*meso*-**7**: 17%
M = Hf, R = Me	*rac*-**8**: 27%	*meso*-**8**: 15%
M = Zr, R = *i*-Pr	*rac*-**9**: 31%	*meso*-**9**: 20%
M = Hf, R = *i*-Pr	*rac*-**10**: 32%	*meso*-**10**: 23%

Scheme 7.

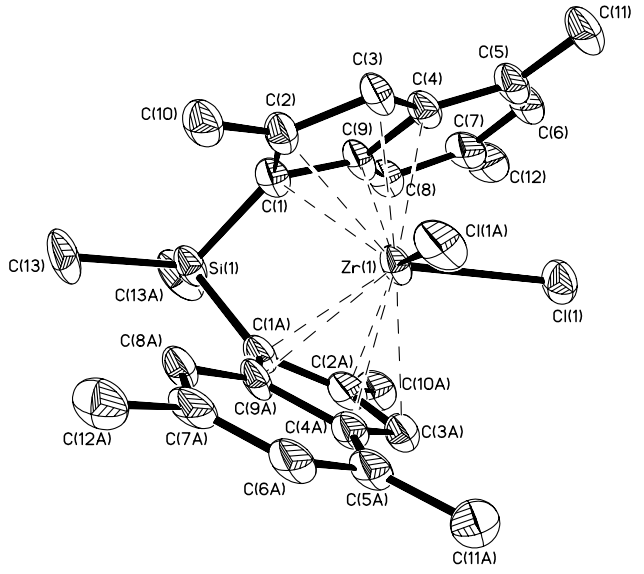


Fig. 1. Molecular structure of complex *rac*-**7**. Hydrogen atoms are omitted for clarity.

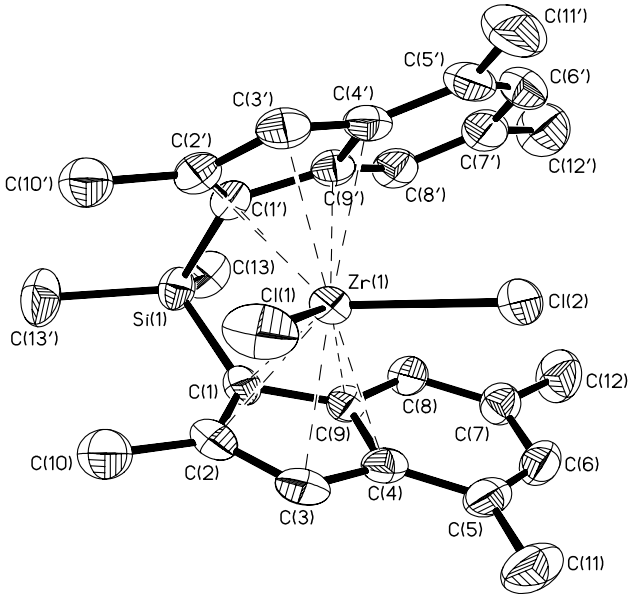


Fig. 2. Molecular structure of complex *meso*-**7**. Hydrogen atoms are omitted for clarity.

paraform was treated with HCl gas (prepared from 300 ml of 12 M HCl, 40 g of NaCl, and 300 ml of 98% of H_2SO_4) for 3.5 h at room temperature. Then, organic layer was separated and dried over K_2CO_3. Fractional distillation gave colorless product, b.p. 111 °C/18 mm Hg. Yield: 109 g (43%) of a mixture of 2,4- and

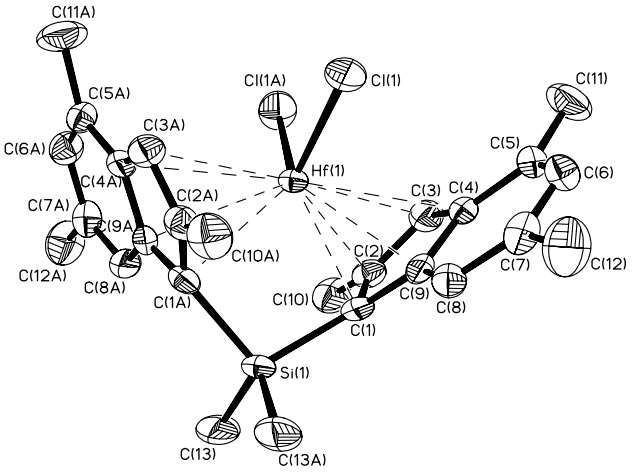


Fig. 3. Molecular structure of complex *rac*-**8**. Hydrogen atoms are omitted for clarity.

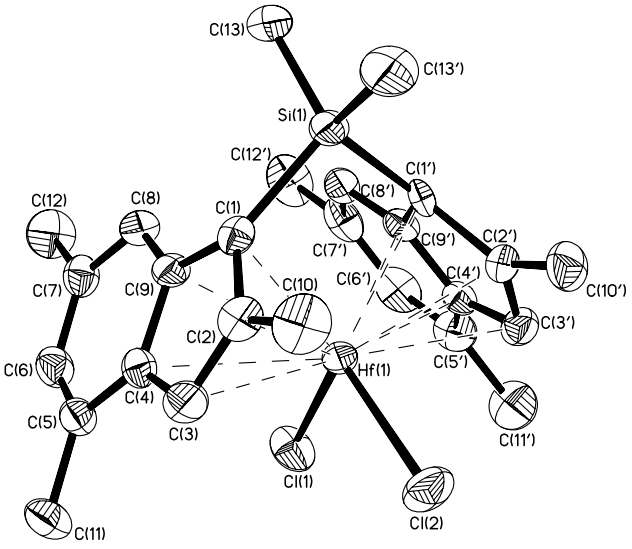


Fig. 4. Molecular structure of complex *meso*-**8**. Hydrogen atoms are omitted for clarity.

2,6-dimethylbenzylchlorides in ratio ca. 9:2. Anal. Calc. for $C_9H_{11}Cl$: C, 69.90; H, 7.17. Found: C, 69.98; H, 7.14%. ^1H NMR($CDCl_3$): 2,4-dimethylbenzylchloride, δ 7.1–7.4 (m, 3H, C_6H_3), 4.46 (s, 2H, CH_2), 2.30 (s, 3H, Me), 2.24 (s, 3H, Me); 2,6-dimethylbenzylchloride, δ 7.1–7.4 (m, 3H, C_6H_3), 4.55 (s, 2H, CH_2), 2.34 (s, 6H, 2,6-Me_2).

3.3. Mixture of 2-(2,4-dimethylbenzyl)- and 2-(2,6-dimethyl-benzyl)propionic acids

Sodium metal (15.6 g, 0.68 mol) was dissolved in 550 ml of dry ethanol. To the resulted solution 113 g (0.65 mol) of diethylmethylmalonate was added dropwise for 10 min; then, 105 g (0.68 mol) of the above-described mixture of 2,4- and 2.6-dimethylbenzyl chlorides was

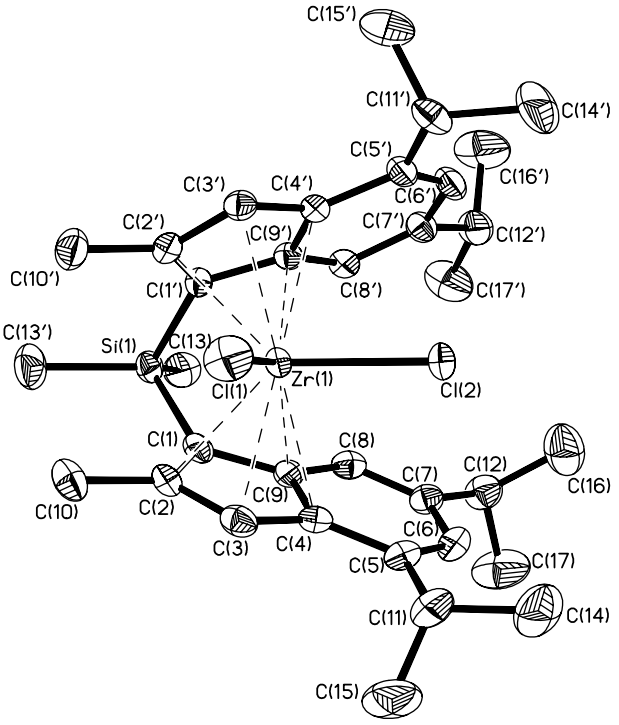


Fig. 5. Molecular structure of complex *meso*-**9**. Hydrogen atoms are omitted for clarity.

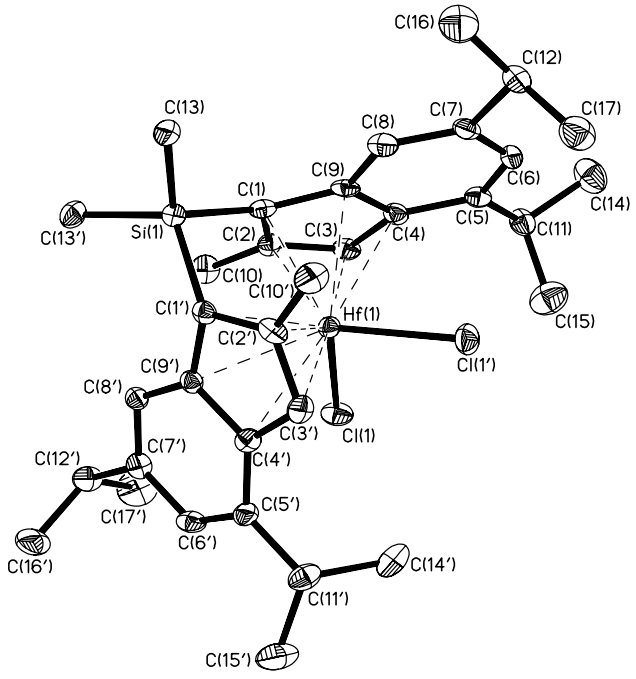


Fig. 6. Molecular structure of complex *rac*-**10**. Hydrogen atoms are omitted for clarity

added by vigorous stirring at such a rate that the reaction mixture was maintained at gentle reflux. Additionally, this mixture was refluxed for 5 h and cooled to room temperature. A solution of 135 g (2.41 mol) of

Table 1
Selected bond lengths (Å) and angles (°) for compounds *rac*-**7**, *meso*-**7**, *rac*-**8**, *meso*-**8**, *meso*-**9**, and *rac*-**10**

Complex	*rac*-**7**	*meso*-**7**	*rac*-**8**	*meso*-**8**	*meso*-**9**	*rac*-**10**
M	Zr[a]	Zr	Hf[a]	Hf	Zr	Hf
M–Cl(1)	2.420(3)	2.440(1)	2.395(2)	2.375(3)	2.435(1)	2.3983(8)
M–Cl(2)		2.410(1)		2.411(3)	2.400(1)	2.399(1)
M–C(1)	2.46(1)	2.459(2)	2.453(5)	2.434(7)	2.469(3)	2.445(4)
M–C(1′)		2.481(2)		2.479(7)	2.472(3)	2.483(4)
M–C(2)	2.50(1)	2.514(2)	2.477(6)	2.510(7)	2.526(3)	2.503(4)
M–C(2′)		2.508(2)		2.496(8)	2.502(4)	2.520(3)
M–C(3)	2.56(1)	2.580(2)	2.536(7)	2.555(8)	2.588(3)	2.579(4)
M–C(3′)		2.570(2)		2.551(8)	2.558(3)	2.582(4)
M–C(4)	2.63(1)	2.631(2)	2.632(6)	2.628(8)	2.645(3)	2.637(4)
M–C(4′)		2.646(2)		2.640(8)	2.645(3)	2.630(4)
M–C(9)	2.569(9)	2.535(2)	2.550(6)	2.518(7)	2.535(3)	2.520(4)
M–C(9′)		2.570(2)		2.548(7)	2.567(3)	2.530(4)
M–CR[b]	2.231	2.235	2.218	2.221	2.244	2.225
M–CR′[b]		2.248		2.237	2.241	2.239
Si(1)–C(1)	1.87(1)	1.877(2)	1.874(6)	1.867(8)	1.878(3)	1.876(4)
Si(1)–C(1′)		1.883(2)		1.888(8)	1.881(3)	1.886(4)
Si(1)–C(13)	1.85(1)	1.862(3)	1.870(7)	1.863(8)	1.863(4)	1.858(4)
Si(1)–C(13′)		1.870(3)		1.878(9)	1.867(4)	1.860(4)
Cl–M–Cl	98.0(2)	97.76(5)	97.2(1)	97.1(1)	98.41(3)	99.12(4)
CR–M–CR′[b]	128.4	128.1	129.0	128.4	128.1	129.2
C(1)–Si(1)–C(1′)	94.9(6)	95.29(9)	94.6(3)	95.4(3)	94.7(1)	95.0(2)
C(13)–Si(1)–C(13′)	105(1)	105.2(2)	105.9(5)	105.4(4)	104.7(2)	104.7(2)

[a] Molecule lies on crystallographic two-fold axes.
[b] CR and CR′ denote the centroids of five-membered rings C(1), C(2), C(3), C(4), C(9) and C(1′), C(2′), C(3′), C(4′), C(9′), respectively.

KOH in 350 ml of water was added. This mixture was refluxed for 4 h to saponificate the ester formed. Ethanol was distilled off. To the residue 1 liter of water and, then, 12 M HCl (to pH 1) were added. The substituted methylmalonic acid precipitated at 5 °C was separated, washed with 3 × 100 ml of cold water and dried. Crude product was obtained after decarboxilation at 130 °C. This product was used without further purification. Yield: 125 g (96%) of a mixture of 2-(2,4-dimethylbenzyl)- and 2-(2,6-dimethylbenzyl)propionic acids in ratio ca. 5:1. Anal. Calc. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.78; H, 8.22%. ^{1}H NMR($CDCl_3$): δ 12.25 (s, COOH), 7.15–6.95 (m, C_6H_3), 3.25–2.60 (m, CH and CH_2), 2.42 (s, Me), 2.34 (s, Me), 1.4–1.2 (m, Me).

3.4. 2,4,6-Trimethylindan-1-one

The above-described mixture of 2-(2,4-dimethylbenzyl)- and 2-(2,6-dimethylbenzyl)propionic acids (196 g, 1.02 mol) was stirred with 252 ml (3.50 mol) of thionyl chloride for 24 h at room temperature. Then, an excess of thionyl chloride was distilled off. Fractional distillation of the residue gave colorless liquid, b.p. 125–130 °C/1 mm Hg. Yield: 167 g (78%) of a mixture of 2-(2,4-dimethylbenzyl)- and 2-(2,6-dimethylbenzyl)propionyl chlorides. To a stirred suspension of 101 g (0.76 mol) of $AlCl_3$ in 1 liter of dry CH_2Cl_2 a solution of 106 g (0.50 mol) of the isomeric acid chlorides in 200 ml of dry CH_2Cl_2 was added dropwise for 1.5 h by vigorous stirring at 10 °C. This mixture was refluxed for 1.5 h and cooled to room temperature. Then, it was poured on 1 kg of ice, acidified with 12 M HCl to pH 1, and extracted with 3 × 200 ml of ether. The combined extracts were washed with aqueous solution of $NaHCO_3$, dried over K_2CO_3, and evaporated to dryness. The crude product was used without further purification. Yield: 75 g (86%). Anal. Calc. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.89; H, 8.23%. ^{1}H NMR ($CDCl_3$): δ 7.38 (s, 1H, 7-H), 7.22 (s, 1H, 5-H), 3.23 (dd, 1H, J = 17.3 Hz, J = 8.0 Hz, 3-H), 2.68 (m, 1H, 2-H), 2.53 (dd, 1H, J = 17.3 Hz, J = 3.6 Hz, 3′-H), 2.35 (s, 3H, 6-Me), 2.29 (s, 3H, 4-CH_3), 1.30 (d, 3H, J = 7.6 Hz, 2-Me).

3.5. 2,5,7-Trimethylindene (*1*)

To a solution of 96 g (0.55 mol) of 2,4,6-trimethylindan-1-one in 750 ml of THF/MeOH mixture (2:1) 31.2 g (0.83 mol) of $NaBH_4$ was added in small portions at 0 °C. This mixture was stirred for 24 h at room temperature and, then, poured on 700 cm^3 of ice, acidified with 12 M HCl to pH 1, and extracted with 3 × 500 ml of ether. The combined extract was washed with 2 × 200 ml of water, dried over $MgSO_4$, and evaporated to dryness. To the residue 300 ml of benzene and 102 g of P_4O_{10} was added, and this mixture was refluxed for 1 h. Then, 300 ml of water was added. An organic layer was separated, washed with water and aqueous solution of $NaHCO_3$, then, evaporated to dryness. Fractional distillation gave colorless crystallizable liquid, b.p. 96 °C/1 mm Hg. Yield: 59 g (68%) of white solid of 2,5,7-

trimethylindene. Alternatively, a mixture of 1.07 mol of the alcohol, 18 g of *p*-toluenesulfonic acid monohydrate and 1100 ml of benzene was refluxed for 3 h. Fractional distillation gave slightly yellow liquid 1, b.p. 87–89 °C/2 mm Hg. Yield: 128 g (81 %). Anal. Calc. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.20; H, 8.99%. ^{1}H NMR ($CDCl_3$): δ 6.85 (s, 1H, 4-H), 6.67 (s, 1H, 6-H), 6.35 (s, 1H, 3-H), 3.00 (s, 2H, 1-H), 2.29 (s, 3H, 5-Me), 2.20 (s, 3H, 7-Me), 2.06 (s, 3H, 2-Me).

3.6. Mixture of 3,5-dimethylbenzylbromide and 2,4,6-trimethylbromobenzene

In a three-necked round-bottom 500 ml flask equipped with reflux condenser and dropping funnel with the inlet tube reaching down to the bottom of the flask, to 250 ml (216 g, 1.8 mol) of mesitylene 102 ml (316 g, 1.98 mol) of bromine was added dropwise under exposure to 200 W medium pressure UV lamp for 6 h at 120 °C. The reaction temperature was maintained in the range of 120–135 °C. The reaction mixture was washed with 2×100 ml of water. Fractional distillation gave colorless liquid, b.p. 115–125 °C/15 mm Hg. Yield: 144 g (40%) of the mixture of 3,5-dimethylbenzylbromide (78%) and 2,4,6-trimethylbromobenzene (22%). Anal. Calc. for $C_9H_{11}Br$: C, 54.30; H, 5.57. Found: C, 54.42; H, 5.65%. ^{1}H NMR ($CDCl_3$), 3,5-dimethylbenzylbromide: δ 6.91 (s, 2H, C_6H_3), 6.83 (s, H, C_6H_3), 4.30 (s, 2H, CH_2), 2.22 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.92, 137.48, 129.61, 126.69, 33.54, 20.88.

3.7. (3,5-Dimethylbenzyl)propionic acid

Sodium metal (14.8 g, 0.64 mol) was dissolved in 400 ml of dry ethanol. To the resulting solution 107 g (0.62 mol) of diethylmethylmalonate in 100 ml of dry ethanol was added dropwise within 10 min; then, 129 g (0.65 mol) of 3,5-dimethylbenzylbromide (165 g of the above-described mixture of 3,5-dimethylbenzylbromide and 2,4,6-trimethylbromobenzene) was added by vigorous stirring at such a rate, so the reaction mixture maintained at gentle reflux. Additionally, this mixture was refluxed for 5 h and cooled to room temperature. A solution of 128 g (2.29 mol) of KOH in 350 ml of water was added. This mixture was refluxed for 4 h to saponificate the ester formed. Viscous oil of 2,4,6-trimethylbromobenzene was removed in separatory funnel. Ethanol was distilled off. To the residue 1 l of water and, then, 12 M HCl (to pH 1) were added. The substituted methylmalonic acid precipitated at 5 °C was separated, washed with 3×100 ml of cold water and dried. Crude product was obtained after decarboxilation at 130 °C. This product was used without further purification. Yield: 81 g (65%). Anal. Calc. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.11; H, 8.46%. ^{1}H NMR ($CDCl_3$): δ 12.12 (br.s, 1H, COOH), 6.83 (s, 1H, C_6H_3), 6.77 (s, 2H, C_6H_3), 3.04 (dd, 1H, $J = 13.4$ Hz, $J = 8.3$ Hz, C*H* H′), 2.76 (m, 1H, CH), 2.57 (dd, 1H, $J = 13.4$ Hz, $J = 8.2$ Hz, CH*H*′), 2.27 (s, 6H, 3,5-Me_2), 1.15 (d, 3H, $J = 6.9$ Hz, *Me*CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.85, 137.72, 127.96, 126.73, 41.17, 39.08, 21.13, 16.32.

3.8. 2,5,7-Trimethylindan-1-one

Mixture of 98 g (0.51 mol) of 2-(3,5-dimethylbenzyl)propionic acid and 126 ml of $SOCl_2$ was stirred for 24 h at room temperature. Thionyl chloride was distilled off. The residue was dried in vacuo and, then, dissolved in 200 ml of CH_2Cl_2. To a suspension of 101 g (0.76 mol) of $AlCl_3$ in 1000 ml of CH_2Cl_2 the above-mentioned solution of 2-(3,5-dimethylbenzyl)propionyl chloride was added dropwise by vigorous stirring for 1 h 0 °C. This mixture was refluxed for 1.5 h, cooled to ambient temperature, and, then, poured on 1000 cm^3 of iced water, acidified with 12 M HCl to pH 1. Organic layer was separated, washed with aqueous $NaHCO_3$, dried over K_2CO_3, and evaporated to dryness. Yield: 64.7 g (73%) of crude 2,5,7-trimethylindan-1-one. This product was used without further purification. Anal. Calc. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.90; H, 8.25%. ^{1}H NMR ($CDCl_3$): δ 7.02 (br.s, 1H, 6-H), 6.88 (br.s, 1H, 4-H), 3.26 (m, 1H, 3-H), 2.61 (m, 2H, 3-H′ and 2-H), 2.58 (s, 3H, 5-Me), 2.36 (s, 3H, 7-Me), 1.27 (d, 3H, $J = 7.3$ Hz, 2-Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 209.60, 154.36, 144.70, 138.38, 131.26, 130.10, 124.01, 42.11, 34.16, 21.53, 17.89, 16.23.

3.9. 2,4,6-Trimethylindene (**3**) (Method 1)

To a solution of 64.7 g (0.37 mol) of 2,5,7-trimethylindan-1-one in 500 ml of THF/MeOH mixture (2:1) 21 g (0.56 mol) of $NaBH_4$ was added in small portions at 0 °C. This mixture was stirred for 24 h at room temperature and, then, poured over 500 cm^3 of ice, acidified with 12 M HCl to pH 1, and extracted with 3×300 ml of ether. The combined extract was washed with 2×150 ml of water, dried over $MgSO_4$, and evaporated to dryness. To the residue 200 ml of benzene and 69 g of P_4O_{10} was added, and this mixture was refluxed for 1 h. Then, 200 ml of water was added. An organic layer was separated, washed with water and aqueous solution of $NaHCO_3$, then, evaporated to dryness. Fractional distillation gave slightly yellow liquid **3**, b.p. 73–77C/1 mm Hg. Yield: 41.4 g (71%). Alternatively, a mixture of 1.07 mol of the alcohol, 18.3 g of *p*-toluenesulfonic acid monohydrate, and 1200 ml of benzene was refluxed for 3 h. The product was isolated as described above. Yield: 165 g (71%). Anal. Calc. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.01; H, 8.93%. ^{1}H NMR ($CDCl_3$): δ 6.98 (br.s, 1H, 7-H), 6.81 (br.s, 1H, 5-H), 6.49 (br.s, 1H, 3-H), 3.19 (s, 2H, CH_2), 2.32 (s, 3H, 4-Me), 2.30 (s, 3H,

6-Me), 2.10 (s, 3H, 2-Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.03, 143.43, 141.96, 132.97, 128.32, 127.93, 125.05, 121.64, 42.65, 21.15, 18.31, 16.66.

3.10. 2,4,6-Trimethylindene (3) (Method 2)

To a suspension of 269 g (2.03 mol) of $AlCl_3$ in 1000 ml of CH_2Cl_2 121 g (1.12 mol) of methacrylchloride in 600 ml of CH_2Cl_2 was added dropwise at −70 °C. To this mixture 122 ml (106 g, 1.00 mol) of *m*-xylene was added. This mixture was refluxed for 3 h and stored for a night at room temperature. Then, this mixture was poured to 1500 cm^3 of ice and acidified with 12 M HCl to pH 1. Organic layer was separated, washed with aqueous $NaHCO_3$, dried over K_2CO_3, and evaporated to dryness. Following the procedure described for 2,5,7-trimethylindene, crude 2,5,7-trimethylindan-1-one, 1330 ml of THF/MeOH (2:1), 56.8 g (1.49 mol) of $NaBH_4$, 1100 ml of benzene, and 16.8 g of *p*-toluenesulfonic acid gave crude title indene. Fractional distillation gave yellowish **3**, b.p. 104 °C/5 mm Hg. Yield: 122 g (77%). Anal. Calc. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.15; H, 8.99%.

3.11. Bis(2,4,6-trimethylindenyl)dimethylsilane (5)

To a solution of 56.4 g (0.36 mol) of 2,4,6-trimethylindene (or 2,5,7-trimethylindene) in 650 ml of THF/toluene (1:12) 143 ml (0.36 mol) of a 2.5 M *n*-BuLi in hexane was added by vigorous stirring at room temperature. This mixture was stirred for 1 h at 80 °C, cooled to 0 °C, and 21.7 ml (23.1 g, 0.18 mol) of Me_2SiCl_2 was added dropwise. The reaction mixture was stirred for 1 h at 80 °C. Then, 100 ml of water was added. An organic layer was separated and evaporated to dryness. To the residue 200 ml of cold hexane was added. Product precipitated from this mixture was filtered (G3), washed with 2×50 ml of hexane, and dried in vacuo over P_4O_{10}. Yield: 26.6 g (40%) of *rac*-**5**. Alternatively, the product was purified by flash chromatography (Silica Gel 60, hexane/CH_2Cl_2 = 9/1) and obtained in 34% yield. Anal. Calc. for $C_{26}H_{32}Si$: C, 83.81; H, 8.66. Found: C, 83.95; H, 8.72%. ^1H NMR ($CDCl_3$): δ 7.21 (s, 2H, 7,7′-H), 6.97 (s, 2H, 5,5′-H), 6.77 (s, 2H, 3,3′-H), 3.77 (s, 2H, 1,1′-H), 2.51 (s, 6H, 4,4′-Me), 2.44 (s, 6H, 6,6′-Me), 2.30 (s, 6H, 2,2′-Me), −0.18 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.22, 145.00, 141.65, 132.17, 128.52, 127.05, 124.70, 121.51, 47.09, 21.47, 18.64, 17.87, −5.84.

3.12. Rac- and meso-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)zirconium dichlorides (rac-7 and meso-7) (Method 1)

To a solution of 26.5 g (71 mmol) of bis-(2,4,6-trimethylindenyl)dimethylsilane in 550 ml of toluene 57 ml (142 mmol) of a 2.5 M *n*-BuLi in hexanes was added at room temperature. This mixture was refluxed with vigorous stirring for 3 h, then, cooled to −40 °C, and 17.3 g (74 mmol) of $ZrCl_4$ was added. The resulted mixture was allowed to warm to room temperature over a period of 2 h (color changed from yellow to red) and, then, refluxed for 2 h. The suspension was filtered (G4), and the precipitate was washed with 100 ml of toluene, 4×100 ml of hot DME. Crystallization of the combined toluene filtrate at −30 °C gave orange-yellow crystals of *meso*-**7**. Yield: 6.05 g (16%). Then, crystallization of the combined DME filtrate at −30 °C gave yellow crystals of *rac*-**7**. Yield: 4.11 g (11%). Anal. Calc. for $C_{26}H_{30}Cl_2SiZr$: C, 58.62; H, 5.68. *meso*-**7**: Found: C, 58.71; H, 5.76%. *meso*-**7**: ^1H NMR (CD_2Cl_2): δ 7.24 (m, 2H, 7,7′-H), 6.66 (m, 2H, 5,5′-H), 6.51 (m, 2H, 3,3′-H), 2.003 (s, 3H, 4-Me), 2.001 (s, 3H, 4′-Me), 1.87 (s, 6H, 6,6′-Me), 1.802 (s, 3H, 2-Me), 1.799 (s, 3H, 2′-Me), 1.41 (s, 3H, Si*Me*Me′), 1.19 (s, 3H, SiMe*Me′*). *rac*-**7**: Found: C, 58.68; H, 5.75%. *rac*-**7**: ^1H NMR (CD_2Cl_2): δ 7.21 (m, 2H, 7,7′-H), 6.91 (m, 2H, 5,5′-H), 6.64 (m, 2H, 3,3′-H), 2.24 (s, 6H, 4,4′-Me), 2.23 (s, 6H, 6,6′-Me), 2.14 (s, 6H, 2,2′-Me), 1.24 (s, 6H, $SiMe_2$).

3.13. Rac- and meso-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)zirconium dichlorides (rac-7 and meso-7) (Method 2)

To a solution of 15.3 g (41 mmol) of bis-(2,4,6-trimethylindenyl)dimethylsilane in 140 ml of toluene 49 ml (82 mmol) of a 1.68 M MeLi in ether was added at room temperature. This mixture was stirred overnight. Then, 19.7 g (82 mmol) of Et_3SnCl (WARNING: Organotin reagents are very toxic!) was added dropwise, and the reaction mixture was stirred for 3 h at room temperature and then evaporated to dryness. The residue was treated with 170 ml of toluene. The suspension formed was filtered (G4). To the filtrate cooled to −40 °C, 9.55 g (41 mmol) of $ZrCl_4$ was added, and the resulted mixture was stirred overnight, then, additionally refluxed for 5 h. The precipitate was filtered off (G4), washed with 50 ml of toluene, then, washed with 3×100 ml of hot DME. Crystallization of the combined toluene filtrate at −30 °C gave orange-yellow crystals of *meso*-**7**. Yield: 3.71 g (17%). Then, crystallization of the combined DME filtrate at −30 °C gave yellow crystals of *rac*-**7**. Yield: 5.46 g (25%). Anal. Calc. for $C_{26}H_{30}Cl_2SiZr$: C, 58.62; H, 5.68. *rac*-**7**: Found: C, 58.44; H, 5.54%. *meso*-**7**: Found: C, 58.68; H, 5.73%.

3.14. Rac- and meso-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)hafnium dichlorides (rac-8 and meso-8) (Method 1)

Following the procedure described for *rac*- and *meso*-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)zirco-

nium dichlorides (Method 1), 8.70 g (23.3 mmol) of bis(2,4,6-trimethylindenyl)dimethylsilane, 18.9 ml (47 mmol) of 2.5 M solution of *n*-BuLi in hexanes, and 7.47 g (23.3 mmol) of $HfCl_4$ gave yellow-orange crystals of *meso*-**8** and yellow crystals of *rac*-**8**. Yields 2.31 g (16%) and 1.73 g (12%) of *meso*- and *rac*-complexes, respectively. Anal. Calc. for $C_{26}H_{30}Cl_2SiHf$: C, 50.37; H, 4.88. *meso*-**8**: Found: C, 50.48; H, 4.95%. *meso*-**8**: ^1H NMR (CD_2Cl_2): δ 7.24 (m, 2H, 7,7′-H), 6.60 (m, 2H, 5,5′-H), 6.37 (m, 2H, 3,3′-H), 2.48 (s, 6H, 4,4′-Me), 2.20 (s, 6H, 6,6′-Me), 2.16 (s, 6H, 2,2′-Me), 1.37 (s, 3H, Si*Me*Me′), 1.15 (s, 3H, SiMe*Me*′). *rac*-**8**: Found: C, 50.26; H, 4.80%. *rac*-**8**: ^1H NMR (C_6D_6): δ 7.29 (m, 2H, 7,7′-H), 6.84 (m, 2H, 5,5′-H), 6.66 (m, 2H, 3,3′-H), 2.27 (s, 6H, 4,4′-Me), 2.23 (s, 6H, 2,2′-Me), 2.19 (s, 6H, 6,6′-Me), 0.91 (s, 6H, $SiMe_2$).

3.15. Rac- and meso-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)hafnium dichlorides (rac-8 and meso-8) (Method 2)

Following the procedure described for *rac*- and *meso*-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)zirconium dichlorides (Method 2), 24.6 g (66 mmol) of bis(2,4,6-trimethylindenyl)dimethylsilane, 79 ml (132 mmol) of 1.68 M solution of MeLi in ether, 31.8 g (132 mmol) of Et_3SnCl (WARNING: Organotin reagents are very toxic!), and 21.2 g (66 mmol) of $HfCl_4$ gave yellow crystals of *rac*-**8** and yellow-orange crystals of *meso*-**8**. Yields 9.52 g (27%) and 5.27 g (15%) of *rac*- and *meso*-complexes, respectively. Anal. Calc. for $C_{26}H_{30}Cl_2SiHf$: C, 50.37; H, 4.88. *rac*-**8**. Found: C, 50.18; H, 4.75%. *meso*-**8**. Found: C, 50.45; H, 4.91%.

3.16. 2,4-Diisopropylbenzylchloride

A mixture of 400 ml of 12 M HCl, 380 ml (2.35 mol) of *m*-diisopropylbenzene, 177 g of $ZnCl_2$, and 65 g of paraform was treated with HCl gas (prepared from 250 ml of 12 M HCl, 40 g of NaCl, and 250 ml of 98% H_2SO_4) for 3 h at 80 °C. This reaction mixture was stored overnight. Then, 60 g of paraform was added, and the resulted mixture was treated one more time with HCl gas. Finally, this procedure was repeated with 40 g of paraform. Organic layer was separated and dried over K_2CO_3. Fractional distillation in the presence of 1 g of $NaHCO_3$ gave colorless oil, b.p. 90–111 °C/1 mm Hg. Yield: 250 g (58%) of the title product. Anal. Calc. for $C_{13}H_{19}Cl$: C, 74.09; H, 9.09. Found: C, 74.20; H, 9.14%. ^1H NMR($CDCl_3$): δ 7.21–7.01 (m, 3H, C_6H_3), 4.61 (s, 2H, CH_2), 3.28 (sept, 1H, $J = 6.9$ Hz, C*H*Me_2(1)), 2.88 (sept, 1H, $J = 6.6$ Hz, C*H*Me_2(2)), 1.27 (d, 6H, $J = 6.9$ Hz, CH*Me*$_2$(1)), 1.23 (d, 6H, $J = 6.6$ Hz, CH*Me*$_2$(2)).

3.17. 2-(2,4-Diisopropylbenzyl)propionic acid

Sodium metal (16.2 g, 0.71 mol) was dissolved in 400 ml of dry ethanol. To the resulted solution 117 g (0.69 mol) of diethylmethylmalonate in 125 ml of ethanol was added dropwise for 10 min; then, 150 g (0.71 mol) 2,4-diisopropylbenzyl chloride was added by vigorous stirring at such a rate, so the reaction mixture maintained at gentle reflux. Additionally, this mixture was refluxed for 5 h and cooled to room temperature. A solution of 140 g (2.50 mol) of KOH in 400 ml of water was added. This mixture was refluxed for 4 h to saponificate the ester formed. Ethanol was distilled off. To the residue 1 liter of water and, then, 12 M HCl (to pH 1) were added. The substituted methylmalonic acid precipitated at 5 °C was separated, washed with 3×100 ml of cold water and dried. Crude product was obtained after decarboxylation at 130 °C. This product was used without further purification. Yield: 163 g (92%). Anal. Calc. for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.50; H, 9.85%. ^1H NMR ($CDCl_3$): δ 11.91 (br.s, 1H, COOH), 6.87–7.32 (m, 3H, C_6H_3), 3.35–2.25 (m, 5H, C*H*Me_2, C*H*(Me)COOH, and CH_2), 1.03–1.51 (m, 15H, CH*Me*$_2$ and CH(*Me*)COOH).

3.18. 2-Methyl-4,6-diisopropylindan-1-one

Mixture of 163 g (0.66 mol) of 2-(2,4-diisopropylbenzyl)propionic acid and 162 ml of $SOCl_2$ was stirred for 24 h at room temperature. Thionyl chloride was distilled off. The residue was dried in vacuo and, then, dissolved in 200 ml of CH_2Cl_2. To a suspension of 130 g (0.98 mol) of $AlCl_3$ in 1800 ml of CH_2Cl_2 the above-mentioned solution of 2-(2,4-diisopropylbenzyl)propionyl chloride was added dropwise by vigorous stirring for 1 h at 0 °C. This mixture was refluxed for 1.5 h, cooled to ambient temperature, and, then, poured to 1500 cm^3 of iced water, acidified with 12 M HCl to pH 1. Organic layer was separated, washed with aqueous $NaHCO_3$, dried over K_2CO_3, and evaporated to dryness. Yield: 137 g (90%) of crude 2-methyl-4,6-triisopropylindan-1-one. This product was used without further purification. Anal. Calc. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.58; H, 9.76%. ^1H NMR ($CDCl_3$): δ 7.44 (d, 1H, $J = 1.44$ Hz, 7-H), 7.36 (d, 1H, $J = 1.44$ Hz, 5-H), 3.34 (dd, 1H, $J = 16.6$ Hz, $J = 7.6$ Hz, 3-H), 3.09 (sept, 1H, $J = 6.9$ Hz, 6-C*H*Me_2), 2.95 (sept, 1H, $J = 7.2$ Hz, 4-C*H*Me_2), 2.67 (m, 1H, 2-H), 2.62 (dd, 1H, $J = 16.6$ Hz, $J = 4.0$ Hz, 3′-H), 1.31–1.24 (m, 15H, 2-Me and CH*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 209.45, 148.77, 148.63, 145.76, 136.24, 129.75, 118.24, 41.89, 33.84, 32.93, 29.56, 23.80, 23.78, 22.66, 16.15.

3.19. 2-Methyl-5,7-diisopropylindene (**2**)

Following the procedure described for 2,5,7-trimethylindene, 137 g (0.60 mol) of 2-methyl-4,6-triisopropy-

lindan-1-one, 800 ml of THF/MeOH (2:1), 33.7 g (0.90 mol) of $NaBH_4$, 300 ml of benzene, and 110 g of P_4O_{10} gave the title crude indene. Fractional distillation gave yellowish liquid 2, b.p. 104–110 °C/1 mm Hg. Yield: 89 g (70%). Anal. Calc. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.73; H, 10.39%. ^{1}H NMR ($CDCl_3$): δ 7.11 (s, 1H, 4-H), 6.99 (s, 1H, 6-H), 6.57 (m, 1H, 3-H), 3.34 (s, 2H, 1-H), 3.17 (sept, 1H, J = 7.0 Hz, 5-C*H*Me$_2$), 3.03 (sept, 1H, J = 6.9 Hz, 7-C*H*Me$_2$), 2.25 (s, 3H, 2-Me), 1.42–1.38 (m, 12H, 5,7-CH*Me*$_2$).

3.20. 2-Methyl-4,6-diisopropylindene (**4**)

To a suspension of 45.3 g (0.339 mol) of $AlCl_3$ in 550 ml of CH_2Cl_2 29.0 g (0.337 mol) of methacrylchloride in 150 ml of CH_2Cl_2 was added dropwise at −70 °C. To this mixture 50.0 ml (42.8 g, 0.264 mol) of 1,3-diisopropylbenzene in 100 ml of CH_2Cl_2 was added. This mixture was refluxed for 3 h and stored for a night at room temperature. Then, this mixture was immersed in 500 cm^3 of ice and acidified with 12 M HCl to pH 1. Organic layer was separated, washed with aqueous $NaHCO_3$, dried over K_2CO_3, and evaporated to dryness. Following the procedure described for 2,5,7-trimethylindene, crude 2-methyl-5,7-diisopropylindan-1-one, 330 ml of THF/MeOH (2:1), 14.2 g (0.374 mol) of $NaBH_4$, 260 ml of benzene, and 4.2 g of *p*-toluenesulfonic acid gave the title crude indene. Fractional distillation gave yellowish liquid **4**, b.p. 101–105C/1 mm Hg. Yield: 36.7 g (65%). Anal. Calc. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.61; H, 10.31%. ^{1}H NMR ($CDCl_3$): δ 7.14 (s, 1H, 7-H), 7.00 (s, 1H, 5-H), 6.64 (s, 1H, 3-H), 3.30 (s, 2H, 1-H), 3.21 (sept, 1H, J = 6.8 Hz, 6-C*H*Me$_2$), 2.95 (sept, 1H, J = 7.1 Hz, 4-C*H*Me$_2$), 1.29 (d, 6H, J = 7.1 Hz, 4-CH*Me*$_2$), 1.33 (d, 6H, J = 6.8 Hz, 6-CH*Me*$_2$).

3.21. Bis(2-methyl-4,6-diisopropylindenyl)dimethylsilane (**6**)

To a solution of 84 g (0.39 mol) of 2-methyl-4,6-diisopropylindene in 1200 ml of THF/toluene (1:23) 156 ml (0.39 mol) of a 2.5 M *n*-BuLi in hexane was added with vigorous stirring at room temperature. This mixture was stirred for 1 h at 80 °C, cooled to 0 °C, and 23.7 ml (25.2 g, 0.195 mol) of Me_2SiCl_2 was added dropwise. The reaction mixture was stirred for 1 h at 80 °C. Then, 100 ml of water was added. An organic layer was separated and evaporated to dryness. Unreacted 2-methyl-4,6-diisopropylindene was distilled off at 150 °C/1 mm Hg. Product was purified by flash chromatography (Silica Gel 60, hexane). Yield: 58 g (61%) of *rac*-/*meso*-mixture of **6**. Anal. Calc. for $C_{34}H_{48}Si$: C, 84.23; H, 9.98. Found: C, 84.39; H, 10.11%. ^{1}H NMR ($CDCl_3$): *rac*-, δ 7.34 (s, 2H, 7,7′-H), 7.07 (s, 2H, 5,5′-H), 6.83 (s, 2H, 3,3′-H), 3.78 (s, 2H, 1,1′-H), 3.34 (sept, 2H, J = 6.9 Hz, 4,4′-C*H* Me$_2$), 3.02 (sept, 2H, J = 6.9 Hz, 6.6′-C*H* Me$_2$), 2.28 (s, 6H, 2,2′-Me), 1.38–1.25 (m, 24H, 4,4′,6,6′-CH*Me*$_2$), 0.20 (6H, SiMe$_2$); *meso*-, δ 7.21 (s, 2H, 7,7′-H), 7.09 (s, 2H, 5,5′-H), 6.85 (s, 2H, 3,3′-H), 3.75 (s, 2H, 1,1′-H), 3.34 (sept, 2H, J = 6.9 Hz, 4,4′-C*H*Me$_2$), 3.02 (sept, 2H, J = 6.9 Hz, 6,6-C*H*Me$_2$), 2.33 (s, 6H, 2,2′-Me), 1.38–1.25 (m, 24H, 4,4′,6,6′-CH*Me*$_2$), 0.13 (s, 3H, Si*Me*Me′), 0.23 (s, 3H, SiMe*Me*′).

3.22. Rac- and meso-dimethylsilandiyl-bis(2-mehyl-4,6-diisopropylindenyl)zirconium dichlorides (rac-9 and meso-9) (Method 1)

Following the procedure described for *rac*- and *meso*-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)zirconium dichlorides (Method 1), 15.1 g (31.1 mmol) of bis(2-methyl-4,6-diisopropyl-indenyl)dimethylsilane, 24.9 ml (62.3 mmol) of 2.5 M solution of butyllithium in hexanes, and 7.59 g (32.6 mmol) of $ZrCl_4$ gave yellow-orange crystals of *meso*-**9** and yellow crystals of *rac*-**9**. Yields 4.21 g (21%) and 3.02 g (15%) of *meso*- and *rac*-complexes, respectively. Anal. Calc. for $C_{34}H_{46}Cl_2SiZr$: C, 63.32; H, 7.19. *meso*-**9**: Found: C, 63.43; H, 7.26%. *meso*-**9**: ^{1}H NMR (CD_2Cl_2): δ 7.17 (s, 2H, 7,7′-H), 6.83 (s, 2H, 5,5′-H), 6.66 (s, 2H, 3,3′-H), 2.97 (sept, 2H, J = 7.0 Hz, 4,4′-C*H*Me$_2$), 2.69 (sept, 2H, J = 6.8 Hz, 6.6′-C*H*Me$_2$), 2.41 (s, 6H, 2,2′-Me), 1.38 (s, 3H, Si*Me*Me′), 1.25 (d, 3H, J = 6.8 Hz, 6-CH*Me*$_2$), 1.18 (d, 3H, J = 6.8 Hz, 6′-CH*Me*$_2$), 1.17 (s, 3H, SiMe*Me*′), 1.14 (d, 3H, J = 7.0 Hz, 4-CH*Me*$_2$), 1.06 (d, 3H, J = 7.0 Hz, 4′-CH*Me*$_2$). *meso*-**9**: ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 146.90, 145.26, 136.46, 135.37, 130.53, 129.72, 122.44, 121.54, 121.09, 35.96, 33.05, 25.04, 24.60, 24.37, 22.55, 20.10, 4.33, 4.07. *rac*-**9**: Found: C, 63.47; H, 7.22%. *rac*-**9**: ^{1}H NMR (CD_2Cl_2): δ 7.26 (s, 2H, 7,7′-H), 7.02 (s, 2H, 5,5′-H), 6.74 (s, 2H, 3,3′-H), 2.97 (sept, 2H, J = 6.8 Hz, 4,4′-C*H* Me$_2$), 2.81 (sept, 2H, J = 6.8 Hz, 6.6′-C*H* Me$_2$), 2.20 (s, 6H, 2,2′-Me), 1.29 (d, 3H, J = 6.8 Hz, 4-CH*Me*$_2$), 1.25 (s, 6H, SiMe$_2$), 1.22 (d, 3H, J = 6.8 Hz, 6-CH*Me*$_2$), 1.18 (d, 3H, J = 6.8 Hz, 6′-CH*Me*$_2$), 1.17 (d, 3H, J = 6.8 Hz, 4′-CH*Me*$_2$). *rac*-**9**: ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 147.90, 145.88, 135.61, 133.20, 129.18, 124.59, 122.21, 121.23, 120.10, 36.16, 33.21, 24.73, 24.72, 24.12, 22.79, 20.00, 4.07.

3.23. Rac- and meso-dimethylsilandiyl-bis(2-mehyl-4,6-diisopropylindenyl)zirconium dichlorides (rac-9 and meso-9) (Method 2)

Following the procedure described for *rac*- and *meso*-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)zirconium dichlorides (Method 2), 8.57 g (23 mmol) of bis(2-methyl-4,6-diisopropyl-indenyl)dimethylsilane, 27.5 ml (46 mmol) of 1.68 M solution of MeLi in ether, 11.1 g

Table 2
Crystal data, data collection, structure solution and refinement parameters for ***rac*-7**, ***meso*-7**, ***rac*-8**, ***meso*-8**, ***meso*-9**, and ***rac*-10**

Compound	*meso*-**7**	*meso*-**8**	*rac*-**7**	*rac*-**8**	*meso*-**9**	*rac*-**10**
Empirical formula	$C_{26}H_{30}Cl_2Si_1Zr_1$	$C_{26}H_{30}Cl_2Si_1Hf_1$	$C_{26}H_{30}Cl_2Si_1Zr_1$	$C_{26}H_{30}Cl_2Si_1Hf_1$	$C_{34}H_{46}Cl_2Si_1Zr_1$	$C_{34}H_{46}Cl_2Si_1Hf_1$
Formula weight	532.71	619.98	532.71	619.98	644.92	732.19
Color, habit	Red block	Orange block	Yellow block	Yellow block	Yellow block	Orange block
Crystal size (mm)	$0.6 \times 0.5 \times 0.4$	$0.5 \times 0.4 \times 0.3$	$0.4 \times 0.2 \times 0.1$	$0.3 \times 0.3 \times 0.1$	$0.3 \times 0.2 \times 0.2$	$0.3 \times 0.3 \times 0.2$
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$C2/c$	$P2_1/n$	$C2/c$
Unit cell dimensions						
a (Å)	9.106(3)	9.084(8)	14.674(6)	14.654(6)	10.104(2)	28.4346(9)
b (Å)	10.431(4)	10.408(9)	9.832(6)	9.831(6)	17.547(5)	9.8833(3)
c (Å)	14.711(7)	14.69(1)	16.972(9)	16.98(1)	18.614(4)	26.7154(8)
α (°)	107.16(3)	107.23(9)				
β (°)	94.28(3)	94.25(7)	100.68(5)	100.47(5)	90.97(2)	119.675(1)
γ (°)	110.19(3)	110.08(9)				
Volume (Å^3)	1228.6(9)	1222(2)	2406(2)	2046(2)	3300(1)	6253.1(3)
Z	2	2	4	4	4	8
Density (calc.) (g cm^{-3})	1.440	1.685	1.471	1.712	1.298	1.491
Absorption coefficient (mm^{-1})	0.725	4.548	0.740	4.620	0.552	3.420
$F(000)$	548	612	1096	1224	1352	2960
Diffractometer	Enraf-Nonius CAD4					Bruker SMART CCD
Temperature (K)	293	293	293	293	293	150.0(2)
Radiation (λ/Å)	Graphite-monochromated Mo Kα (0.71073)					
Scan mode	ω	ω	ω	ω	ω	ω
θ range (°)	2.20–26.97	2.20–24.99	2.44–25.00	2.44–24.97	3.08–25.96	1.65–27.00
Index ranges	$-11 \leqslant h \leqslant 10$, $-2 \leqslant k \leqslant 13$, $-18 \leqslant l \leqslant 18$	$-10 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 12$, $-3 \leqslant l \leqslant 17$	$-9 \leqslant h \leqslant 18$, $-11 \leqslant k \leqslant 11$, $-21 \leqslant l \leqslant 21$	$-17 \leqslant h \leqslant 17$, $-11 \leqslant k \leqslant 11$, $-4 \leqslant l \leqslant 20$	$-11 \leqslant h \leqslant 6$, $0 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 22$	$-36 \leqslant h \leqslant 36$, $-12 \leqslant k \leqslant 12$, $-34 \leqslant l \leqslant 31$
Reflections collected	6037	5560	2611	5464	5170	24208
Independent reflections	5236 [R_{int} = 0.0163]	4294 [R_{int} = 0.0312]	1593 [R_{int} = 0.0688]	2122 [R_{int} = 0.0571]	4767 [R_{int} = 0.1064]	7137 [R_{int} = 0.0589]
Data reduction	XCAD4[a]					Bruker SAINT[b]
Absorbtion correction	None		Empirical		None	Empirical
Minimum/maximum transmission		0.1041/0.5681	0.7360/1.0000	0.4066/0.7277		0.4522/0.6052
Solution method	Direct methods (SHELX-86)[c]					
Refinement method	Full-matrix least-squares on F^2 (SHELXL-93)[d]					
Data/restraints/parameter	5236/0/382	4256/0/280	1489/0/141	2103/0/142	4767/0/356	6278/0/356
Reflections with $I > 2\sigma(I)$	4836	3929	1372	1956	4259	4621
Goodness-of-fit on F^2	1.073	1.066	1.133	1.046	1.053	0.992
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0265, wR_2 = 0.0719	R_1 = 0.0465, wR_2 = 0.1396	R_1 = 0.1007, wR_2 = 0.2896	R_1 = 0.0365, wR_2 = 0.0902	R_1 = 0.0395, wR_2 = 0.1141	R_1 = 0.0336, wR_2 = 0.0713
R indices (all data)	R_1 = 0.0301, wR_2 = 0.0739	R_1 = 0.0531, wR_2 = 0.1536	R_1 = 0.1143, wR_2 = 0.3202	R_1 = 0.0414, wR_2 = 0.0931	R_1 = 0.0452, wR_2 = 0.1183	R_1 = 0.0487, wR_2 = 0.0835
Extinction coefficient	0.018(1)	0.0001(7)	—	0.0001(1)	0.0053(8)	0.00003(1)
Largest difference peak/hole (e Å^{-3})	0.501/−0.606	2.397/−2.914	1.744/−1.335	2.692/−2.163	0.848/−1.115	0.827/−0.581

[a] K. Harms, XCAD4 – Program for the Lp-Correction of Nonius CAD4 DATA, Marburg, 1997.
[b] SAINT Version 4.050, Bruker AXS, Madison, Wisconsin, USA, 1995.
[c] G.M. Sheldrick, Acta Crystallogr. Sect. A A46 (1990) 467.
[d] G.M. Sheldrick, SHELXL-93 – Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1993.

(46 mmol) of Et_3SnCl (WARNING: Organotin reagents are very toxic!), and 5.36 g (23 mmol) of $ZrCl_4$ gave yellow crystals of *rac*-**9** and yellow-orange crystals of *meso*-**9**. Yields 4.60 g (31%) and 2.97 g (20%) of *rac*- and *meso*-complexes, respectively. Anal. Calc. for $C_{34}H_{46}Cl_2SiZr$: C, 63.32; H, 7.19. *rac*-**9**: Found: C, 63.19; H, 7.04%. *meso*-**9**: Found: C, 63.45; H, 7.26%.

3.24. Rac- and meso-dimethylsilandiyl-bis(2-mehyl-4,6-diisopropylindenyl)hafnium dichlorides (rac-10 and meso-10) (Method 1)

Following the procedure described for *rac*- and *meso*-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)zirconium dichlorides (Method 1), 24.7 g (51 mmol) of bis(2-methyl-4,6-diisopropyl-indenyl)dimethylsilane, 40.8 ml (102 mmol) of 2.5 M solution of *n*-butyllithium in hexanes, and 16.3 g (51 mmol) of $HfCl_4$ gave yellow crystals of *meso*-**10** and *rac*-**10**. Yields 5.23 g (14%) and 7.47 g (20%) of *meso*- and *rac*-complexes, respectively. Anal. Calc. for $C_{34}H_{46}Cl_2SiHf$: C, 55.77; H, 6.33. *meso*-**10**: Found: C, 55.87; H, 6.45%. *meso*-**10**: ^1H NMR (CD_2Cl_2): δ 7.18 (s, 2H, 7,7′-H), 6.80 (s, 2H, 5,5′-H), 6.54 (s, 2H, 3,3′-H), 2.95 (sept, 2H, $J = 6.9$ Hz, 4,4′-C*H*Me_2), 2.71 (sept, 2H, $J = 6.9$ Hz, 6.6′-C*H*Me_2), 2.52 (s, 6H, 2,2′-Me), 1.36 (s, 3H, Si*Me*Me′), 1.23 (d, 3H, $J = 6.9$ Hz, 6-CH*Me*$_2$), 1.17 (s, 3H, SiMe*Me*′), 1.16 (d, 3H, $J = 6.9$ Hz, 6′-CH*Me*$_2$), 1.14 (d, 3H, $J = 6.9$ Hz, 4-CH*Me*$_2$), 1.06 (d, 3H, $J = 6.9$ Hz, 4′-CH*Me*$_2$). *meso*-**10**: $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 146.44, 144.89, 135.77, 135.05, 134.30, 128.47, 122.29, 121.02, 119.52, 35.85, 32.99, 25.05, 24.67, 24.35, 22.51, 19.97, 4.30, 4.02. *rac*-**10**: Found: C, 55.90; H, 6.40%. *rac*-**10**: ^1H NMR (CD_2Cl_2): δ 7.29 (s, 2H, 7,7′-H), 6.99 (s, 2H, 5,5′-H), 6.63 (s, 2H, 3,3′-H), 2.96 (sept, 2H, $J = 6.8$ Hz, 4,4′-C*H*Me_2), 2.83 (sept, 2H, $J = 7.0$ Hz, 6.6′-C*H*Me_2), 2.29 (s, 6H, 2,2′-Me), 1.28 (d, 3H, $J = 6.8$ Hz, 4-CH*Me*$_2$), 1.24 (s, 6H, $SiMe_2$), 1.21 (d, 3H, $J = 7.0$ Hz, 6-CH*Me*$_2$), 1.19 (d, 3H, $J = 7.0$ Hz, 6′-CH*Me*$_2$), 1.18 (d, 3H, $J = 6.8$ Hz, 4′-CH*Me*$_2$).

3.25. Rac- and meso-dimethylsilandiyl-bis(2-mehyl-4,6-diisopropylindenyl)hafnium dichlorides (rac-10 and meso-10) (Method 2)

Following the procedure described for *rac*- and *meso*-dimethylsilandiyl-bis(2,4,6-trimehylindenyl)zirconium dichlorides (Method 2), 5.96 g (16 mmol) of bis(2-methyl-4,6-diisopropyl-indenyl)dimethylsilane, 19.2 ml (32 mmol) of 1.68 M solution of MeLi in ether, 7.71 g (32 mmol) of Et_3SnCl (WARNING: Organotin reagents are very toxic!), and 5.13 g (16 mmol) of $HfCl_4$ gave yellow crystals of *rac*-**10** and yellow-orange crystals of *meso*-**10**. Yields: 3.75 g (32%) and 2.70 g (23%) of *rac*- and *meso*-complexes, respectively. Anal. Calc. for $C_{34}H_{46}Cl_2SiHf$: C, 55.77; H, 6.33. *rac*-**10**: Found: C, 55.60; H, 6.26%. *meso*-**10**: Found: C, 55.86; H, 6.33%.

4. X-ray diffraction experimental determination

Crystal data, data collection, structure solution and refinement parameters of *rac*-**7**, *meso*-**7**, *rac*-**8**, *meso*-**8**, *meso*-**9**, and *rac*-**10** are listed in Table 2. All non-hydrogen atoms in all structures were refined in the anisotropic approximation. In the case of complex *meso*-7 hydrogen atoms were found from difference Fourier synthesis and refined with isotropic thermal parameters. In all other cases, hydrogen atoms were placed in calculated positions and refined using a riding model. CCDC Reference Nos. 203928-203933. See Supplementary Material section for crystallographic data in CIF format.

Acknowledgements

Financial support from the International Science and Technology Center (Grant. No. 1036/99), The resident of the Russian Federation (Grant no. MD-340.2003.03) INTAS (Grant No. 00-00841) and Exxon-Mobil Chemical Company is gratefully acknowledged. L.G.K. and A.V.C. thank the Royal Society of Chemistry for the RSC Journal Grants for International Authors. A.V.C. is grateful to the grant of The President of Russian Federation for young scientists (Grant no. MK-3697.2004.03). We also thank Prof. I.P. Beletskaya.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.10.052.

References

[1] A. Togni, R.L. Halterman (Eds.), Metallocenes: Synthesis, Reactivity, Applications, Wiley-VCH, 1998, and references therein.
[2] W. Spaleck, F. Küber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E.F. Paulus, Organometallics 13 (1994) 954.
[3] W. Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, J. Behm, W.A. Herrmann, Angew. Chem. Int., Ed. Engl. 31 (1992) 1347.
[4] W. Kaminsky, O. Rabe, A.-M. Schauwienold, G.U. Schupfner, J. Hanss, J. Kopf, J. Organomet. Chem. 497 (1995) 181.
[5] U. Stehling, J. Diebold, R. Kirsten, W. Röll, S. Jüngling, R. Mülhaupt, F. Langhauser, Organometallics 13 (1994) 964.
[6] B. Thiyagarajan, R.F. Jordan, V.G. Young Jr., Organometallics 18 (1999) 5347.

[7] N. Schneider, M.E. Huttenloch, U. Stehling, R. Kirsten, F. Schaper, H.H. Brintzinger, Organometallics 16 (1997) 3413.
[8] X. Zhang, Q. Zhu, I.A. Guzei, R.F. Jordan, J. Am. Chem. Soc. 122 (2000) 8093.
[9] M. Fukuoka, K. Yoshihira, S. Natori, K. Mihashi, M. Nishi, Chem. Pharm. Bull. 31 (1983) 3113.
[10] J.H. Burckhalter, R.C. Fuson, J. Am. Chem. Soc. 70 (1948) 4184.
[11] O. Meth-Cohn, S. Gronowitz, Acta Chim. Scand. 20 (1966) 1577.
[12] E.D. Thorsett, F.R. Stermitz, Synth. Commun. 2 (1972) 375.
[13] S.H. Pines, A.W. Douglas, J. Am. Chem. Soc. 98 (1976) 8119.
[14] T.M. Frankcom, J.C. Green, A. Nagy, A.K. Kakkar, T.B. Marder, Organometallics 12 (1993) 3688.
[15] R.W. Layer, I.R. MacGregor, J. Org. Chem. 21 (1956) 1120.
[16] A.Z. Voskoboynikov, A.Yu. Agarkov, E.A. Chernishev, I.P. Beletskaya, A.V. Churakov, L.G. Kuz'mina, J. Organomet. Chem. 530 (1997) 75.
[17] I.E. Nifant'ev, P.V. Ivchenko, Organometallics 16 (1997) 713.
[18] A.Y. Agarkov, V.V. Izmer, A.N. Riabov, L.G. Kuz'mina, J.A.K. Howard, I.P. Beletskaya, A.Z. Voskoboynikov, J. Organomet. Chem. 619 (2001) 280.
[19] V.V. Izmer, A.Y. Agarkov, V.M. Nosova, L.G. Kuz'mina, J.A.K. Howard, I.P. Beletskaya, A.Z. Voskoboynikov, J. Chem. Soc., Dalton Trans. (2001) 1131.