Organometallic Chemistry

Synthesis of 1-(cyclopentadienyl)adamantane and the corresponding zirconium complexes

N. B. Ivchenko, P. V. Ivchenko, and I. E. Nifant'ev**

Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 4523. E-mail: inif@org.chem.msu.su

An effective method for the synthesis of 1-(cyclopentadienyl)adamantane based on the reaction of 1-bromoadamantane with nickelocene in the presence of PPh_3 was proposed. A number of organic derivatives and bis-cyclopentadienyl complexes of zirconium(IV) were prepared from this compound.

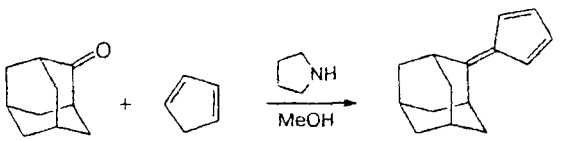
Key words: 1-bromoadamantane, nickelocene, 1-(cyclopentadienyl)adamantane, zirconocenes.

The preparation of new substituted cyclopentadienes remains an important task in organic chemistry, as these compounds are the precursors of sandwich complexes of group IV metals, which are effective catalysts for homogeneous polymerization of α-olefins.[1] This is due to the fact that variation of the structure of an organic moiety of metallocene molecule directly effects the properties of the catalytic center of the complex and thus allows control of the properties of the polymer formed.[2–4]

It seems interesting to study the opportunity of preparation of zirconocenes containing an adamant-1-yl substituent in their cyclopentadiene rings, being a structural analog of Me_3C and Me_3Si groups, conventionally used as bulky substituents.

The synthesis of 2-(cyclopentadienyl)adamantane seems to be not difficult, since adamantan-2-one was shown[5] to form the corresponding fulvene easily upon interaction with cyclopentadiene in methanol in the presence of pyrrolidine (Scheme 1). The fulvene can further be reduced into 2-(cyclopentadienyl)adamantane.

Scheme 1



However, the synthesis of 1-(cyclopentadienyl)-adamantane has failed until now. The most simple synthetic approach to the substituted cyclopentadienes is the alkylation of cyclopentadienides of alkaline metals or magnesium. At the same time the reaction of 1-halogenoadamantanes with strong nucleophiles is known[6] not to lead to the formation of substitution products.

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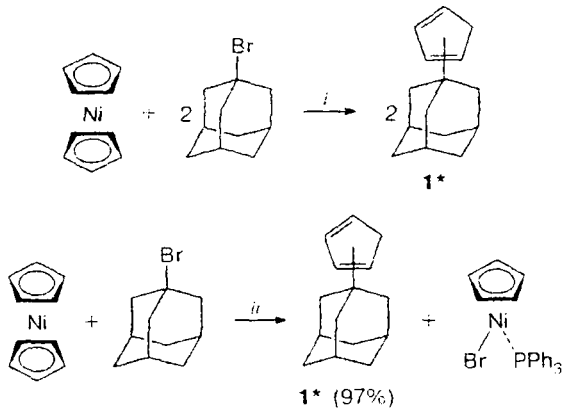
An alternative way for obtaining substituted cyclopentadienes is the interaction of halogen derivatives with nickelocene proceeding on the SET mechanism.[7] This synthetic approach was shown[7–14] to be rather effective in some cases. The range of halogen derivatives reacting with nickelocene to give substituted cyclopentadienes can be extended by the addition of an equimolar quantity of donor ligand (usually triphenylphosphine). In this case the completeness of the reaction is due to the formation of a stable 18-electronic complex $CpNiBr(PPh_3)$ of semi-sandwich type.[8,10,12–14]

We carried out the reaction of nickelocene with 1-bromoadamantane both in the presence of triphenylphosphine and without it, using earlier described procedures[7–14] (Scheme 2). In the absence of triphenylphosphine the target product was obtained in a very low yield; in the presence of an equimolar quantity of triphenylphosphine the yield of compound **1*** increased up to almost quantitative.

Scheme 2



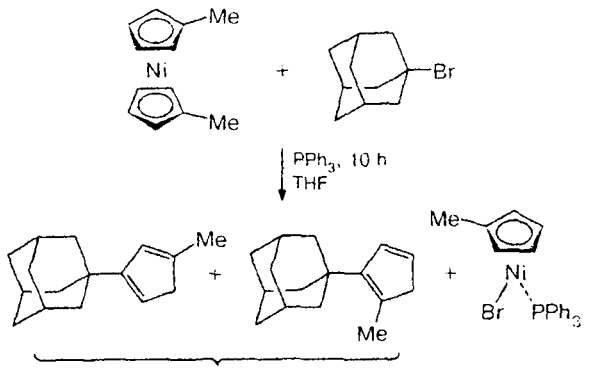
Reagents and conditions: *i*. Et_2O, refluxing, 10 h (the yield of **1** 10%), or THF, refluxing, 10 h (the yield of **1** 15%); *ii*. PPh_3, THF, refluxing, 10 h.

We succeeded in obtaining the alkyl derivatives of compound **1** too. They could be obtained either by the reaction of 1,1'-dialkylnickelocenes with 1-bromoadamantane or by the insertion of alkyl substituents into the molecule of compound **1**. However, the reaction of 1,1'-dialkylnickelocene with 1-bromoadamantane was found to give a mixture of 1,2- and 1,3-disubstituted cyclopentadienes (Scheme 3).

Therefore we chose the second approach, *viz.*, the structural modification of 1-(cyclopentadienyl)adamantane. The unique method for the selective insertion of non-bulky alkyl substituents into the molecule of monosubstituted cyclopentadiene to obtain 1,3-disubstituted cyclopentadienes is their conversion into fulvenes

* Compounds **1**, **4**, and **5** were obtained as a mixture of isomers differing in the position of the double bond.

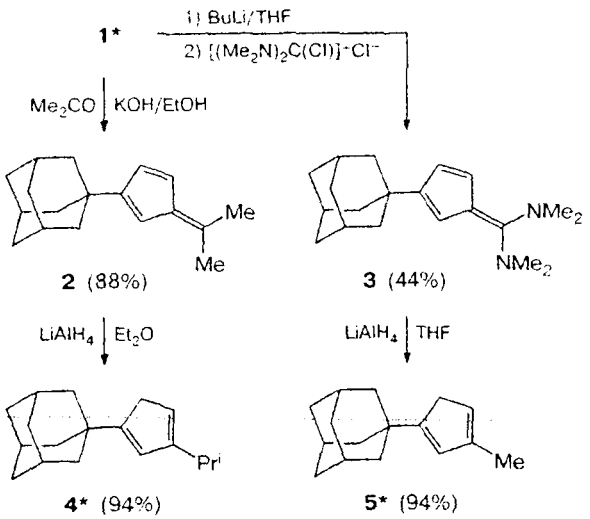
Scheme 3



Five isomers with different positions of the double bond can be formed

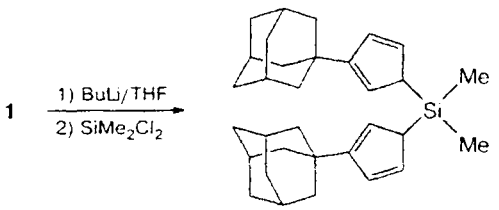
with the following reduction. To obtain methyl- and iso-propyl substituted 1-adamantylcyclopentadienes 6,6-dimethylfulvene **2** was synthesized by the interaction of cyclopentadiene **1** with acetone in ethanol medium in the presence of a base and 6,6-bis(dimethylamino)fulvene **3** was synthesized by the reaction between lithium adamantylcyclopentadienide and $[(Me_2N)_2CCl]^+Cl^-$. We succeeded in obtaining 1-(isopropylcyclopentadienyl)-adamantane **4** and 1-(methylcyclopentadienyl)adamantane **5** by reducing fulvenes **2** and **3** (Scheme 4).

Scheme 4



For another way of obtaining zirconium *ansa*-complexes we tried to insert a dimethylsilylidene bridge between the molecules of the cyclopentadienyladamantanes mentioned above. Only in the case of compound **1**, did we succeed in obtaining product **6**, with the yield being rather mediocre (Scheme 5).

Scheme 5

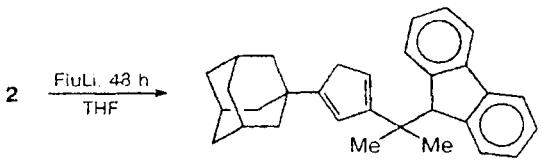


6 (33%)

We also tried to obtain bis-cyclopentadienyl compounds with a one-membered carbon bridge from cyclopentadienes **1**, **4**, **5**. However the reactions with acetone and formalin, carried out using standard procedures,[15] led to complicated mixtures of unidentified products.

At the same time it was known[16–20] that a one-membered carbon bridge can be inserted by the reaction of fluorenyllithium with substituted fulvenes. By analogy to those articles we tried to obtain a non-symmetrical bridged compound with the substituted cyclopentadienyl ring linked to a fluorenyl fragment. Working on the known procedure[19] we succeeded in obtaining compound **7** in a practically quantitative yield by the reaction of fulvene **2** with fluorenyllithium (Scheme 6).

Scheme 6



7* (96%)

Flu — fluoren-9-yl.

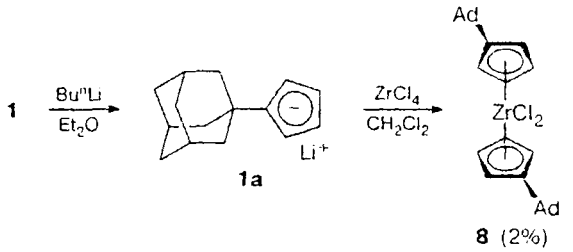
We tried to obtain the bis-cyclopentadienyl complex $(AdCp)_2ZrCl_2$ (**8**) starting from compound **1**. The reaction of the lithium derivative of cyclopentadienyladamantane with $ZrCl_4$ was studied in the following solvents: Et_2O, THF, CH_2Cl_2, toluene, and hexane. Metallocene **8** was successfully synthesized only when the reaction was carried out in CH_2Cl_2, the yield of the target product being 2% (Scheme 7).

It was shown earlier[21,22] that high yields of metallocenes can sometimes be achieved in the intermetallation reactions of organosilicon or -tin derivatives of cyclopentadienes and indenes (Scheme 8).

Based on this information we synthesized the $SnMe_3$-derivative of cyclopentadienyladamantane and brought it into reaction with $ZrCl_4$. Unfortunately we failed to separate and analyze the product of the reaction above.

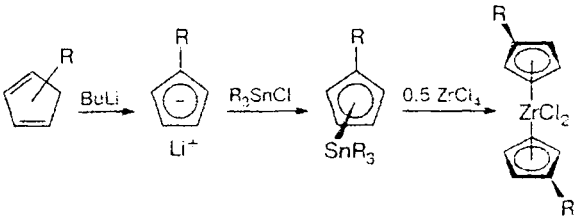
* Compound 7 was obtained as a mixture of isomers differing in the position of the double bond.

Scheme 7



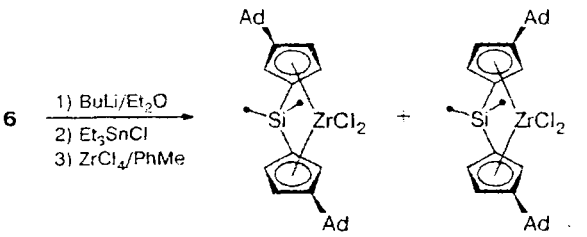
8 (2%)

Scheme 8



For the zirconocene preparation based on compound **6** we tried two approaches: the interaction of dilithium or ditin derivatives with $ZrCl_4$ in different solvents. In the first case the target compound wasn't obtained. However the reaction of ditin derivative of compound **6** with $ZrCl_4$ resulted in the formation of zirconocene **9** with a high yield: 78% (Scheme 9).

Scheme 9



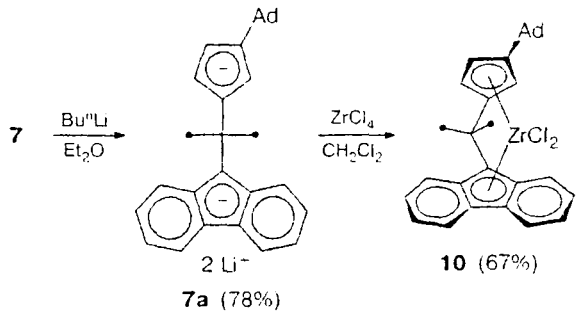
9 (78%)

Rac- and *meso*-forms of compound **9** were separated by crystallization.

In contrast to zirconocene **9** we succeeded in obtaining the composite cyclopentadienylfluorenyl complex **10** by the reaction of dilithium derivative **7a** with $ZrCl_4$ in CH_2Cl_2 (Scheme 10).

Based on the analysis of the reactions leading to metallocenes **8**, **9**, and **10**, we suggest that the low yield of the non-bridged complex **8** can be explained by the lability of 1-(cyclopentadienyl)adamantane in the presence of $ZrCl_4$, known as a strong Lewis acid. The formation of bridged complexes proceeds considerably faster than can be accounted for by the chelate effect. Consequently the competitive reaction leading to the

Scheme 10



destruction of the organic core of the bis-cyclopentadienyl ligand has no time to be realized and the yields of *ansa*-compounds **9** and **10** are enhanced by an order of magnitude in comparison with the yield of zirconocene **8**.

Experimental

All procedures were carried out under argon. The lithium derivatives and zirconium complexes were obtained using all-glass sealed systems of Schlenk flask type. The ethers were kept and distilled over KOH followed by distillation over sodium benzophenone ketyl; CH_2Cl_2 was washed with water, concentrated H_2SO_4, and water to a neutral reaction, dried over $CaCl_2$, and distilled over P_2O_5. The ^1H and ^{13}C NMR spectra were recorded using Varian VXR-400 and Varian VXR-300 spectrometers.

1-(Cyclopentadienyl)adamantane (1) (a mixture of two isomers differing in the position of the double bond). A mixture of 12.6 g of nickelocene[23] (0.067 moles), 14.3 g of 1-bromoadamantane (Fluka) (0.067 mol), and 17.5 g of triphenylphosphine (0.067 mol) in tetrahydrofuran (90 mL) was refluxed with stirring under argon for 10 h. Then the reaction mixture was evaporated in vacuum using a water aspirator pump, followed by washing of the crystalline vinous precipitate with hot hexane (6×50 mL). The extract formed was evaporated and the resulting dark-cherry oil was purified by column chromatography with hexane as eluent. Compound **1** (12.9 g, 97%) was obtained as a light-yellow oil, crystallizing at subroom temperature (m.p. 19–21 °C). Found (%): C, 84.44; H, 9.35. $C_{15}H_{20}$. M = 200.33. Calculated (%): C, 89.94; H, 10.06. ^1H NMR spectrum (benzene-d_6, 30 °C), δ: 6.64, 6.42, 6.26, 6.13, 5.93 (all m, 3 H in each, =CH—); 2.92 (m, 2 H, $-CH_2-$); 2.00 (s, 3 H), 1.77 (s, 6 H), 1.61 (s, 6 H) (adamantane).

1-(3-Isopropylidenecyclopenta-1,4-dien-1-yl)adamantane (2). 1-(Cyclopentadienyl)adamantane (7.88 g, 0.035 mol) was added to the previously degassed solution of KOH (6.05 g, 0.108 mol) in EtOH (50 mL). The mixture was stirred at 20 °C for 15 min, followed by addition of acetone (3.8 mL, 0.052 moles) and refluxing with stirring for 1 h. After the end-point of the reaction the mixture was poured into an 85% solution of H_3PO_4 (8 mL) in 150 mL of H_2O. The yellow precipitate formed was filtered off, washed with water (3×20 mL) and EtOH (15 mL), and then dried *in vacuo* to give compound **2** (7.31 g, 88%) (m.p. 114–116 °C). Found: C, 89.99; H, 10.01. $C_{18}H_{24}$. M = 240.39. Calculated (%): C, 89.94; H, 10.06. ^1H NMR spectrum (benzene-d_6, 30 °C), δ: 6.69 (dd, 1 H, J_1 = 5.38 Hz, J_2 = 1.57 Hz), 6.60 (dd, 1 H, J_1 = 5.37 Hz, J_2 = 2.2 Hz), 6.24 (t, 1 H, 1.95) (—CH=); 1.97 (br.s, 3 H), 1.88 (br.s, 6 H), 1.70 (br.s, 6 H) (adamantane); 1.87, 1.81 (both s, 3 H in each, $-CH_3$). The ^{13}C NMR spectrum ($CDCl_3$, 30 °C), δ: 156.9, 147.0, 141.8 (=C<); 129.6, 121.1, 111.5 (=CH—); 42.0, 36.9 ($-CH_2$); 34.1 (>C<); 28.5 ($-CH_3$); 22.7 (—CH<).

[3-(Adamant-1-yl)cyclopenta-2,4-dien-1-ylidene]-*N,N,N',N'*-tetramethylmethylenediamine (3). To a solution of compound **1** (5.8 g, 0.029 mol) in 45 mL of THF under argon at −70 °C a 1.6 *M* solution of butyllithium (18.1 mL, 0.029 mol) was added dropwise with stirring. The reaction mixture was stirred for 20 min at about 20 °C and then cooled to −70 °C and $[(Me_2N)_2C(Cl)]^+Cl^-$ (4.96 g, 0.029 mol) was added. The mixture formed was stirred for 2 h at 20 °C and 1 h with refluxing. Then NEt_3 (4.8 mL, 0.035 mol) was added and the mixture was refluxed with stirring for 22 h. The resulting mixture was diluted with 30 mL of H_2O and extracted with Et_2O (4×40 mL). The organic portions were combined, washed with water, dried over $MgSO_4$, and evaporated under reduced pressure. The dark-brown oil formed was purified using column chromatography: the unreacted 1-(cyclopentadienyl)adamantane (2.74 g) was separated by elution with hexane; then acetone was used as eluent. After solvent removal 3.81 g (44.1%) of compound **3** was isolated as dark-red crystals, m.p. 86 °C. Found (%): C, 10.13; H, 10.08. $C_{20}H_{30}N$. M = 298.48. Calculated (%): C, 80.48; H, 10.13. The ^1H NMR spectrum ($CDCl_3$, 30 °C), δ: 6.32 (dd, 1 H, J_1 = 4.56 Hz, J_2 = 2.4 Hz), 6.25 (dd, 1 H, J_1 = 4.8 Hz, J_2 = 2.0 Hz), 6.04 (t, 1 H, J = 2.2 Hz) (ABC, =CH— of the Cp-ring); 3.40 (s, 3 H, CH_3); 2.00 (br.s, 3 H), 1.88 (m, 6 H), 1.72 (m, 6 H) (adamantane).

1-(3-Isopropylcyclopentadien-1-yl)adamantane (4) (three isomers differing in the position of the double bond, in the ratio ~1 : 3 : 9). A suspension of compound **2** (4.34 g, 0.018 mol) in 30 mL of Et_2O was added dropwise at 0 °C under argon to a suspension of $LiAlH_4$ (0.69 g, 0.018 mol) in 100 mL of Et_2O, then the cooling was stopped, and the reaction mixture was refluxed with stirring for 20 min. After cooling the reaction mixture to 0 °C water was added dropwise until gas ceased to be released. After neutralization of the mixture formed with 30 mL of diluted hydrochloric acid, the organic layer was separated, washed with H_2O (2×50 mL), dried over $MgSO_4$, and evaporated to give 4.09 g (94%) of compound **4** as a light-brown oil. Found (%): C, 84.44; H, 9.35. $C_{18}H_{26}$. M = 242.41. Calculated (%): C, 89.19; H, 10.81. The ^1H NMR spectrum ($CDCl_3$, 30 °C), δ: 1.08–1.16 (signals from three isomers, all d, 6 H, $-CH(C\underline{H}_3)_2$, J = 7.0 Hz); 1.70 (br.s, 6 H), 1.76 (br.s, 6 H), 2.02 (br.s, 3 H) (adamantane); 2.54–2.72 (m, 1 H, $-C\underline{H}(CH_3)_2$); 2.46, 2.86, 2.90 (signals from three isomers, all s, 2 H, $-CH_2-$); 1) 5.75, 6.22, 2) 5.79, 6.09, 3) 5.99, 6.02 (signals from three isomers, all m, 2 H, —CH=).

1-(3-Methylcyclopentadien-1-yl)adamantane (5) (three isomers differing in the position of the double bond, in the ratio ~1 : 1 : 1.4). To a suspension of $LiAlH_4$ (0.93 g, 0.025 mol) in 50 mL of THF under argon at −40 °C compound **3** (3.81 g, 12.3 mmol) was quickly added, then the cooling was stopped, and the reaction mixture was refluxed with stirring for 3 h. After cooling the reaction mixture to 0 °C water was added dropwise until gas ceased to be released. Then the mixture formed was neutralized with 30 mL of diluted hydrochloric acid; the organic layer was separated, washed with H_2O (2×50 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The brown oil obtained was purified by column chromatography with hexane as eluent. After solvent removal

1.43 g (54.4%) of compound **5** were isolated as a light-brown oil. Found (%): C, 89.60; H, 10.39. $C_{16}H_{22}$. M = 214.35. Calculated (%): C, 89.65; H, 10.35. ^{1}H NMR spectrum ($CDCl_3$, 30 °C), δ: 1) 6.22, 5.71, 2) 6.00, 5.82, 3) 5.99, 5.96 (signals from three isomers, all m, 2 H, =CH—); 2.90, 2.85, 2.81 (signals from three isomers, all br.s, 2 H, $-CH_2-$); 2.05, 2.02 (both d, J = 1.4 Hz), 1.97 (dd, J_1 = 4.15 Hz, J_2 = 1.9 Hz) (signals from three isomers, 3 H, $-CH_3$); 1.99, 1.77—1.68 (all m, 15 H, adamantane).

Bis[3-(adamant-1-yl)cyclopenta-2,4-dien-1-yl]-dimethylsilane (6). To a solution of 4.4 g of compound **1** (0.022 mol) in 35 mL THF cooled to 0 °C under argon a 2.0 *M* solution of butyllithium (10.5 mL, 0.021 mol) was added dropwise under stirring. The reaction mixture was stirred at 20 °C for 1 h, then $SiMe_2Cl_2$ (1.26 mL, 0.011 mol) was added, and the resulting mixture was stirred for 2 h. After the end-point of the reaction the mixture was neutralized with 20 mL of diluted HCl solution and extracted with hexane (4×30 mL). The combined organic extracts were separated, washed with H_2O, dried over $MgSO_4$, and evaporated under reduced pressure to give a light-yellow oil with some precipitate. The raw product was recrystallized from 7 mL of hexane to give 1.47 g (32.8%) of compound **6** as colorless crystals, m.p. 115—117 °C. Found (%): C, 84.08; H, 9.70. $C_{32}H_{44}Si$. M = 456.79. Calculated (%): C, 84.14; H, 9.71. ^{1}H NMR spectrum (C_6D_6, 20 °C), δ: 6.70 (br.s, 2 H), 6.45 (br.s, 2 H), 6.04 (br.s, 2 H) (ABC, =CH— of Cp-ring); 3.24 (br.s, 2 H, $-CH<$); 2.02 (br.s, 6 H), 1.80 (br.s, 12 H), 1.74 (br.s, 12 H) (adamantane); −0.22 (s, 6 H, $>Si(CH_3)_2$).

1-{3-[1-Methyl-1-(9*H*-fluoren-9-yl)ethyl]cyclopentadien-1-yl}adamantane (7) (three isomers differing in the position of the double bond, in the ratio ~1 : 2.5 : 5). The procedure is similar to that described earlier.[19] To a solution of 9*H*-fluorene (2.79 g, 0.017 mol) in THF (30 mL) at −20 °C under argon a 1.08 *M* solution of methyllithium in Et_2O (16.8 mL) was added dropwise with stirring, after that the mixture was stirred at −20 °C for 3 h (until gas completely ceased to be released), and then compound **2** (4.03 g, 0.017 mol) was added. The resulting dark-red solution was stirred at −20 °C for 2 days. After that 50 mL of water was added dropwise to the reaction mixture, which was then neutralized by a diluted solution of HCl (20 mL). The mixture was extracted with hexane (4×30 mL). The combined organic portions were separated, washed with H_2O, dried over $MgSO_4$, and evaporated under reduced pressure. Compound **7** (6.56 g, 96.2%) was obtained as a yellow crystalline substance, m.p. 108 °C. Found (%): C, 91.50; H, 8.50. $C_{31}H_{34}$. M = 406.62. Calculated (%): C, 91.57; H, 8.43. ^{1}H NMR spectrum ($CDCl_3$, 30 °C), δ: 7.70 (m, 2 H), 7.35—7.00 (m, 6 H) (fluorene); 1) 6.50, 5.68, 2) 6.14, 5.92, 3) 6.09, 6.00 (signals from three isomers, all m, 2 H, =CH—); 4.14, 4.10, 4.06 (signals from three isomers, all s, 1 H, $-CH<$ of fluorene); 3.12, 3.10, 2.99 (signals from three isomers, all br.s, 2 H, $-CH_2-$); 1.03, 1.02, 1.01 (all br.s, 15 H) (adamantane); 1.86, 1.83, 1.80 (signals from three isomers, all s, 6 H, —Me).

Bis[η^5-3-(adamant-1-yl)cyclopentadienyl]dichlorozirconium (8). To a solution of 5.56 g of compound **1** (27.6 mmol) in 40 mL of Et_2O cooled to −40 °C a 1.6 *M* solution of butyllithium (20 mL, 32 mmol, an excess) was carefully added. The reaction mixture was stirred at −20 °C for 1 h, then the precipitate formed was washed with Et_2O (3×40 mL) and dried *in vacuo*, giving 4.9 g (86%) of dilithium derivative **1a**. The resulting salt was added to a suspension of $ZrCl_4$ (5.53 g, 23.4 mmol) in CH_2Cl_2 (100 mL) cooled to −80 °C. The mixture was stirred at −80 °C for 1 h, then warmed to −20 °C, and the solution was decanted from the lithium chloride precipitate. After removing the solvent the residue was recrystallized from Et_2O. After another recrystallization from hexane 0.13 g (2%) of zirconocene **8** were obtained. Found (%): C, 64.42; H, 6.72. $C_{30}H_{38}Cl_2Zr$. M = 560.75. Calculated (%): C, 64.26; H, 6.83. The ^{1}H NMR spectrum (CD_2Cl_2, 30 °C), δ: 6.43, 6.32 (both t, 4 H in each, Cp-ring, J = 2.8 Hz); 2.02 (br.s, 6 H), 1.95 (br.s, 12 H), 1.72 (br.s, 12 H) (adamantane).

{μ-Dimethylsilylidenebis[η^5-3-(adamant-1-yl)cyclopentadienyl]}dichlorozirconium (9). To a solution of 0.6 g of compound **6** (1.31 mmol) in Et_2O (15 mL) cooled to −40 °C a 1.6 *M* solution of butyllithium in hexane (2 mL, 3.2 mmol, an excess) was carefully added. The resulting white suspension was cooled to −60 °C and Et_3SnCl (0.8 mL, 4.74 mmol, an excess) was added. After that the solution was decanted from the precipitate and evaporated. The yellow oil obtained was dissolved in toluene (20 mL) and $ZrCl_4$ (0.31 g, 1.31 mmol) was added. The reaction mixture was stirred at 60°C for 2 h, then cooled to −20 °C. The solution was decanted and evaporated to give 0.5 g (62%) of complex **9** as a light-yellow crystalline residue. The *rac*- and *meso*-forms of zirconocene **9** were separated by recrystallization from an ether-hexane mixture (1 : 1). Found (%): C, 61.19; H, 6.82. $C_{32}H_{42}Cl_2SiZr$. M = 616.90. Calculated (%): C, 62.30; H 6.86. ^{1}H NMR spectrum (CD_2Cl_2, 30 °C), δ: *rac*-**9**: 6.73, 5.98, 5.84 (all t, 2 H in each, Cp-ring, J = 2.9 Hz); 2.11 (br.s, 3 H), 2.08 (br.s, 6 H), 1.92 (br.s, 6 H) (adamantane); 0.68 (s, 6 H, $-SiMe_2-$); *meso*-**9**: 6.87, 6.07, 5.93 (all t, 2 H in each, Cp-ring, J = 2.9 Hz); 2.00 (br.s, 9 H), 1.70 (br.s, 6 H) (adamantane); 0.74 (s, 3 H), 0.58 (s, 3 H, $-SiMe_2-$).

{μ-(1-Methylethylidene)[η^5-3-(adamant-1-yl)cyclopentadien-1-yl][η^5-(9*H*-fluoren-9-yl)]}dichlorozirconium (10). To a solution of compound **7** (4.07 g, 10 mmol) in Et_2O (50 mL) cooled to −40 °C a 1.6 *M* solution of butyllithium in hexane (12.5 mL, 10 mmol) was carefully added. The dark-red solution obtained was warmed to −20 °C; in an hour a red-brown liquid phase was formed, which crystallized in 2 days. The precipitate formed was washed with Et_2O (3×20 mL) and dried to give 3.27 g (78%) of dilithium derivative **7a**. A portion of dilithium salt **7a** (2.05 g, 4.9 mmol) was added to the cooled to −80 °C and vigorously agitated suspension of $ZrCl_4$ (1.14 g, 4.9 mmol) in CH_2Cl_2 (100 mL) and stirred at this temperature for 1 h. The reaction mixture was heated to −20 °C, the solution was decanted, and CH_2Cl_2 was substituted for ether. The precipitated bright-red crystalline powder was washed with ether and dried to give 1.86 g (67%) of complex **10**. Found (%): C, 65.58; H, 5.62. $C_{31}H_{32}Cl_2Zr$. M = 566.73. Calculated (%): C, 65.70; H 5.69. The ^{1}H NMR spectrum (CD_2Cl_2, 30 °C), δ: 8.10, 7.85, 7.54, 7.24 (all m, 2 H in each, fluorenyl); 6.15, 5.77, 5.61 (all t, 2 H in each, Cp-ring, J = 3.0 Hz); 2.37, 2.36 (both s, 3 H in each, $-CH_3$); 1.87 (br.s, 3 H), 1.78 (br.s, 6 H), 1.62 (br.s, 6 H) (adamantane).

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