Preparation of the *ansa*-Zirconocenes with an *N*-Methylpiperidine Bridge

Ilya E. Nifant'ev,*,† Pavel V. Ivchenko,† Vladimir V. Bagrov,† and
Lyudmila G. Kuz'mina‡

*Department of Chemistry, Moscow University, 119899 Moscow, Russia, and N. S. Kurnakov
Institute of General and Inorganic Chemistry, Russian Academy of Science,
31 Leninskii Prospect, V-71 Moscow 117907, Russia*

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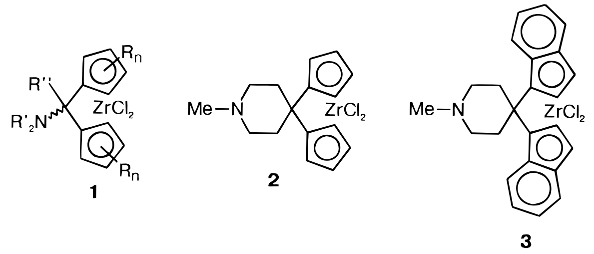
Bridged ligands 4,4-di(cyclopentadienyl)-*N*-methylpiperidine (**4**) and 4,4-di(indenyl)-*N*-methylpiperidine (**5**) were prepared by condensation of cyclopentadiene or indene with *N*-methylpiperidone. Dilithium salts **4a** and **5a** were subsequently transformed into the corresponding *ansa*-zirconocenes **2** and **3**. No direct contact Zr···N was found in the crystal structure of **2**. The attempt to prepare zirconocene **3** from distannyl derivative **5b** gave an unexpected monoindenyl complex **6** comprising one unreacted stannylated indenyl group and having direct coordination of Zr by nitrogen.

Several zirconocenes, including the complexes of the *ansa*-type, are under active investigation as a new generation of catalysts for the (co)polymerization of α-olefins.[1,2] The main work nowadays is directed toward the elucidation of the relationship between the ligand structure of the zirconocenes and their catalytic activity. Hence the preparation of the new complexes comprising various functional groups that would introduce new internal interactions into the metallocene structure is without doubt of interest.

Some studies have been devoted to the synthesis and investigation of the zirconocenes with nitrogen-containing functional groups. Possessing a lone pair of electrons, the nitrogen atom can interact with the acidic zirconium center, greatly effecting its chemical and catalytic activity.[3] Such interaction very often is undesirable because it usually leads to deactivation of the zirconocene catalyst. Admittedly, sometimes a need arises to prepare a zirconocene comprising nitrogen *without* any direct Zr···N interactions. To avoid such interaction, it is reasonable to arrange Zr and N atoms sufficiently far from each other. One quite reliable model of such derivatives would be the structural type **1** comprising nitrogen incorporated into the bridging group of *ansa*-type zirconocenes.

Chart 1



The goal of the present paper was to prepare the complexes **2** and **3**, representing particular examples of **1** (Chart 1). We also aimed to understand if the preparation of such compounds has any kinetic limitations.

Recently we elaborated a new synthetic approach to several bis-cyclopentadienyl(indenyl)methanes. These substances can be easily prepared with satisfactory yields from the corresponding cyclopentadienes (indenes) and ketone in a two-phase system KOH/DME.[4] We applied this reaction for the preparation of ligands **4** and **5**, using *N*-methylpiperidone as a ketone (Scheme 1).

We found the reaction of *N*-methylpiperidone with cyclopentadiene and indene to be similar to that of simple ketones. The relatively low isolated yield of **4** was due to product decomposition during distillation. Dilithium salts **4a** and **5a** were converted into the corresponding *ansa*-metallocenes **2** and **3** (Scheme 2).

Complex **2** was found to behave similarly to other zirconocenes. We have found no chemical evidence of

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* To whom correspondence should be addressed. E-mail: inif@org.chem.msu.su.

† Moscow University.

‡ Russian Academy of Science.

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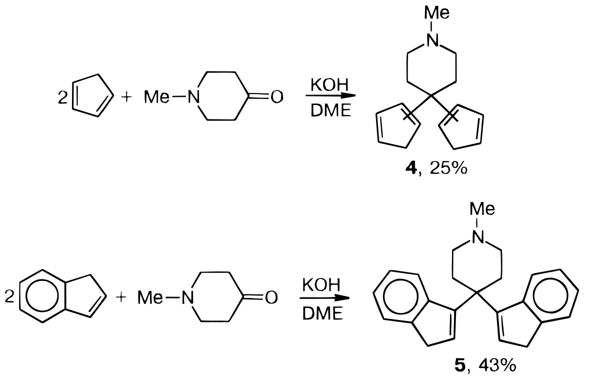
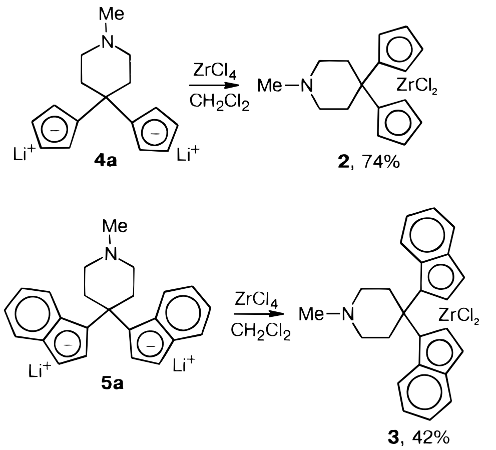
Scheme 1



Scheme 2



an interaction between zirconium and the nitrogen atoms inside **2**. The molecular structure of **2**, determined by X-ray analysis (Figure 1), proves this conclusion.

Complex **3** was isolated as a 1/1 *rac*/*meso* mixture of isomers. Since the yield of **3** was moderate, we tried to increase it. It was taken into consideration that the best results in the synthesis of *ansa*-zirconocenes may be reached using dielement-substituted (usually stannylated or silylated) ligands as the cyclopentadienylating agents.[5] In our case we used bis(triethylstannyl) derivative **5b** in situ as described in ref 5c. Obviously, **5b** represents a 1/1 *rac*/*meso* mixture, and its ^{1}H NMR spectrum comprises of two equimolecular sets of the corresponding signals.

Surprisingly, we were unable to isolate any of **3** starting from **5b**. The main product of the reaction was a white solid that recrystallized as large white crystals **6** (Scheme 3). By means of both ^{1}H NMR and X-ray analysis we revealed that its structure contained two unequal indenyl fragments (Figure 2). We failed to isolate the isomer of **6** differing by the configuration at the chiral allylic carbon bearing the triethyltin fragment. Presumably its relatively high solubility precluded isolating the pure crystalline form.

It is important that stannylindenyl and indenyldichlorozirconium fragments of **6** coexist in one molecule without interaction. This very unusual effect can only be attributed to coordination of the zirconium center with the nitrogen-containing group. This result demonstrates firmly the considerable difference in reactivity of zirconium derivatives with and without coordinated ligands. Obviously, the same effects could play a very significant role in the synthesis of other complexes from nitrogen-containing indenyl, fluorenyl, and cyclopentadienyl ligands.

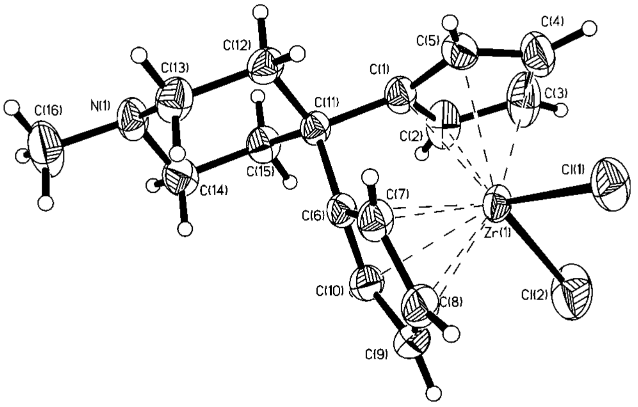


Figure 1. Molecular structure of **2**.

Molecular Structure of 2. Figure 1 shows the molecular structure of the **2**. The zirconium atom is coordinated by the η^5-cyclopentadienyl fragments of two *ansa*-type ligands and two chlorine atoms.

The molecule has noticeable distortions due to short *N*-Me piperidine bridge between two cyclopentadienyl fragments. The dihedral angle between the planes of the Cp rings is 116.39°, whereas in ordinary zirconocenes it is commonly more than 125°. The C(1)C(11)C(6) angle (99.7°) is significantly reduced compared to the tetrahedral value (109.5°). The angle between the normal to the Cp plane and the line from the zirconium atom to the centroid of the Cp ring is 3.4° and 3.5° for the C(1)···C(5) and C(6)···C(10) rings, respectively. The C(11) atom is displaced from the planes of two Cp ligands toward Zr(1) by −0.37 and 0.37 Å; the angles between the C(1)−C(14) and C(1′)−C(14) bonds and the planes of the corresponding Cp ring are equal to 14.7° and 14.5°, respectively.

The Zr−C(Cp) distances are not equal for both Cp rings. The Zr−C(1) and Zr−C(6) bonds (2.451(3) and 2.447(3) Å) are the shortest, whereas similar bonds with C(3), C(4), C(8), and C(9) atoms (2.549(4), 2.547(3), 2.550(3), and 2.545(3) Å, respectively) are the longest in the molecule.

The Zr(1)−Cl(1) and Zr(1)−Cl(2) bond lengths (2.431(2) and 2.432(2) Å) and Cl(1)Zr(1)Cl(2) (100.6(3)°) have usual values.

The *N*-Me piperidine fragment has a chair conformation with an equatorial orientation of the Me group. All of the ligand bond lengths and bond angles are close to standard values.

Molecular Structure of 6. Figure 2 shows the molecular structure of **6**. The molecule represents a binuclear heterometallic complex. The Zr atom is η^5-coordinated by the Cp fragment of one indenyl moiety of the *ansa*-type ligand, and the Sn atom is connected by a σ bond with another indenyl moiety of the ligand. The Sn atom has tetrahedral coordination. The Sn-

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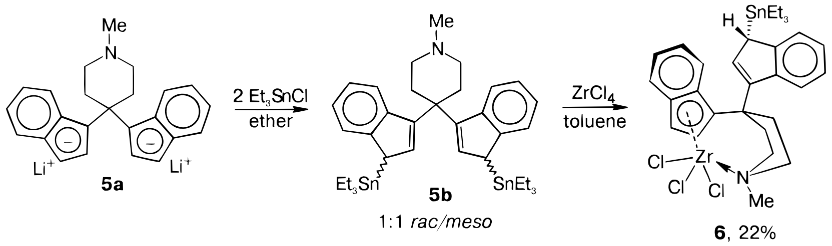
Scheme 3



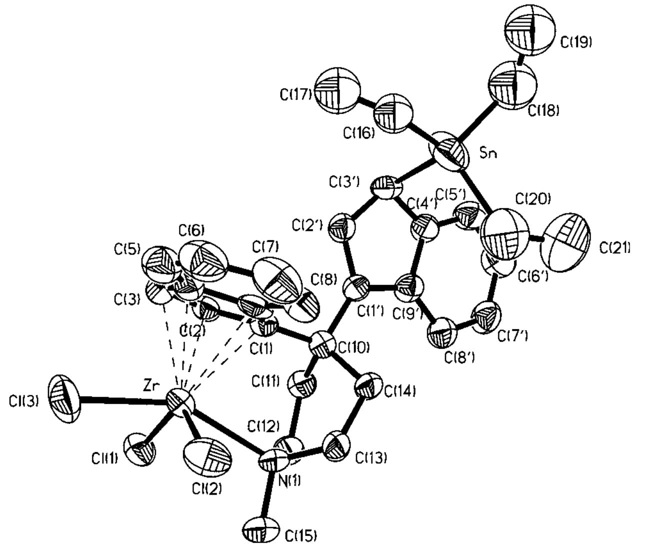


Figure 2. Molecular structure of **6**.

containing indenyl fragment of the molecule adopts the conformation (around the C(1′)−C(10) bond) that maximizes the space between the two metal atoms. The conformation of the other indenyl group is fixed by the very specific coordination of the ligand to Zr. The Zr atom has a distorted piano stool coordination. Except for the Cp fragment, Zr is coordinated by three chlorine ligands and a nitrogen atom of the *N*-methylpiperidine bridge between two indenyls. As a result, the piperidine cycle adopts a screw boat conformation rather than the chair conformation, which is energetically more preferable for saturated six-membered cycles. Because the size of this cycle is restricted, the nitrogen atom occupies an irregular position in the coordination sphere of Zr. Actually, the bond angles between the adjacent Zr−Cl bonds are 86.9(1)° and 86.2(1)°, whereas the area between the opposite Zr−Cl bonds (the Cl(1)ZrCl(2) angle) is equal to 128.5(1)°. The bond angles N(1)ZrCl(1) and N(1)ZrCl(2) (79.3(2)° and 86.4(2)°) are significantly different. The N(1) atom appeared to be in the trans position to the Cl(3) atom; the N(1)ZrCl(3) angle equals 151.7(2)°. Probably because of this fact, the Zr−Cl(3) bond length is elongated to 2.449(3) Å compared to the two other ones (Zr−Cl(1) 2.419(3) and Zr−Cl(2) 2.416(3) Å). The Zr−N(1) bond distance is equal to 2.438(8) Å. The Zr−C bond distances vary within the range 2.43(1)−2.57(1) Å, the bond lengths with the C(4), C(9), and C(1) being the longest (2.553(9), 2.566(9), and 2.493(8) Å, respectively).

Both cycles of the first indenyl radical (C(1)···C(9)) are planar and form a dihedral angle of 3.8°. In the second indenyl radical (C(1′)···C(9′), the dihedral angle between the cycle least-squares planes is also equal to 3.8°. However, in this fragment, the five-membered cycle is bent along the C(2′)···C(4′) line by 8.2°. The C(3′) atom is displaced from the plane through the other atoms of the cycle toward the Sn atom.

All the other bond distances and angles are normal within experimental error.

Experimental Part

General Methods. The etheral solvents (DME, diethyl ether) used in this work were purchased from Merck and distilled under argon from Na/benzophenone. CH_2Cl_2 was distilled from CaH_2. Other solvents were used without special purification. KOH powder was purchased from Merck. Synthetic procedures were performed under an atmosphere of argon. The *dilithio* derivatives and complexes were prepared and characterized using Schlenk techniques.[6] ^1H and ^{13}C NMR spectra were measured on a Varian XR-300 spectrometer. Chemical shifts were referenced against internal H-impurities in deuterated solvents.

4,4-Di(1,3-cyclopentadienyl)-1-methylpiperidine (4). Cyclopentadiene (22.6 mL, 0.9 mol) was added within 0.5 h at 0 °C and under vigorous stirring to a suspension of KOH powder (56 g) in DME (400 mL). Then the mixture was allowed to warm to room temperature, then cooled to 0 °C. *N*-Methylpiperidone-4 (22.6 mL, 0.2 mol) was added. The mixture was heated until reflux. After 1 h the resulting mixture was cooled, treated with water (200 mL), and neutralized with 85% H_3PO_4 (48 mL). Then Et_2O (500 mL) was added, and the organic layer was separated, washed with water (2 × 100 mL), and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was distilled (105−130 °C, 0.1−0.3 Torr), yielding 11.5 g (25%) of product as a viscous oil. ^1H NMR (benzene-d_6; 30 °C): δ 6.62−5.94 (group of m, 6H, =CH−), 2.66, 2.64, 2.59, 2.40 (s, 3H, >NCH_3), 2.40 (bm, 4H), 2.10−2.30 (group of m, 4H), 2.19, 2.20 (group of bs, 4H) {−CH_2−}. ^{13}C NMR (benzene-d_6, 30 °C): δ 133.6, 133.5, 133.4, 132.33, 132.26, 131.3, 131.2 (=CH−), 127.1, 126.7, 126.0, 125.2 (=C<), 52.9, 52.8, 52.7, 46.7, 46.66, 46.62, 41.4 (double), 40.7 {-CH_2}, 40.58 (>C<), 40.28 (>C<), 39.4 (>C<), 36.4, 35.82, 35.12 (−CH_3). Anal. Calcd for $C_{16}H_{21}N$, 227.34: C, 84.53; H, 9.31. Found: C, 84.44; H, 9.35.

4,4-Di(1*H*-3-indenyl)-1-methylpiperidine (5). Indene (46.4 mL, 0.4 mol) was added within 0.5 h under vigorous stirring to a suspension of KOH powder (40 g) in DME (250 mL). The mixture was heated to reflux. After 0.5 h *N*-methylpiperidone-4 (11.3 mL, 0.1 mol) was added. After 2 h the resulting mixture was cooled, treated with water (100 mL), and neutralized with 85% H_3PO_4 (24 mL). Then Et_2O (300 mL) was added, and the organic layer was separated, washed by water (2 × 50 mL), and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was recrystallized from heptane, yielding 14.2 g (43%) of product as beige crystals. Mp: ∼ 130 °C.^1H NMR (benzene-d_6; 30 °C): δ 7.58 ("d", 2H), 7.20 ("d", 2H), 7.04 ("t", 2H), 6.97 ("t", 2H), 6.28 (bs, 2H) {=CH−}, 3.07 (bs, 4H, −CH_2− in indene); 2.57 (m, 4H); 2.43 (m, 4H) {−CH_2− in piperidine}; 2.16 (s, 3H, >NCH_3). ^{13}C NMR

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Table 1. Crystallographic Data and Measurements for 2 and 6

	2	6
empirical formula	$C_{16}H_{19}Cl_2NZr$	$C_{29}H_{28}Cl_3NSnZr$
fw	387.44	706.78
temperature	293(2) K	293(2) K
wavelength	0.71073 Å	0.71069 Å
cryst syst	triclinic	monoclinic
space group	*P-1*	$P2_1/c$
unit cell dimens	$a = 8.393(8)$ Å	$a = 10.121(2)$ Å
	$b = 8.665(5)$ Å	$b = 15.191(3)$ Å
	$c = 11.603(6)$ Å	$c = 20.323(4)$ Å
	$\alpha = 97.64(4)°$	$\alpha = 90°$
	$\beta = 103.80(6)°$	$\beta = 102.78(3)°$
	$\gamma = 98.56(6)°$	$\gamma = 90°$
volume	797.8(10) Å^3	3047.2(10) Å^3
Z	2	4
density (calcd)	1.613 g/cm^3	1.541 g/cm^3
abs coeff	1.013 mm^{-1}	1.442 mm^{-1}
F(000)	392	1400
cryst size	0.76 × 0.68 × 0.72 mm	0.36 × 0.46 × 0.08 mm
τηετα range	2.41−27.97°	2.05−27.96°
index ranges	$-10 < h < 11, -11 < k < 11, -15 < l < 0$	$-11 < h < 13, 0 < k < 18, -25 < l < 0$
reflns collected	3913	4992
independent reflns	3733 [R(int) = 0.0125]	4862 [R(int) = 0.0452]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	3727/0/181	4852/0/306
goodness-of-fit on F^2	1.081	1.345
final R indices [$I > 2\sigma(I)$]	R1 = 0.0387, wR2 = 0.1068	R1 = 0.0677, wR2 = 0.2030
R indices (all data)	R1 = 0.0434, wR2 = 0.1109	R1 = 0.1205, wR2 = 0.2242
largest diff peak and hole	1.039 and −1.679 e Å^{-3}	1.480 and −1.240 e Å^{-3}

($CDCl_3$; 30 °C): δ 147.2, 145.1, 143.7 (=C<), 129.8, 125.2, 123.9, 123.5, 121.7 (=CH−), 52.2, 37.2, 34.1 ($-CH_2-$), 46.4 ($-CH_3$), 39.7 (>C<). Anal. Calcd for $C_{24}H_{25}N$, 327.46: C, 88.03; H, 7.70. Found: C, 87.96; H, 7.77.

***μ*-1-Methyl-4,4-piperidinylenebis(*η*⁵-cyclopentadienyl)dichlorozirconium (2).** 4,4-Di(1,3-cyclopentadienyl)-1-methylpiperidine (**4**) (11.5 g, 50.6 mmol) was dissolved in Et_2O (200 mL), cooled to −40 °C, and then treated with 2.0 M *n*-BuLi in hexane (55 mL, 110 mmol). The white precipitate of **4a** was isolated, washed with ether (3 × 50 mL), and dried. Yield: 10.3 g (85%).

The suspension of $ZrCl_4$ (3.44 g, 14.8 mmol) in CH_2Cl_2 (50 mL) was cooled to −60 °C and mixed with dilithium derivative **4a** (3.53 g, 14.8 mmol). The resulting mixture was stirred for 2 h and allowed to warm to room temperature. The solution was separated by decantation and evaporated. The product was recrystallized from CH_2Cl_2. Yield: 4.3 g (74%). ^{1}H NMR (CD_2Cl_2, 30 °C): δ 6.69 (t, 4H), 5.81 (t, 4H) {AA′BB′ of cyclopentadienyl}, 2.65 (broad, 4H, $-CH_2$), 2.46 (broad, 4H, $-CH_2-$), 2.32 (bs, 3H, $-CH_3$). Anal. Calcd for $C_{16}H_{19}Cl_2NZr$: C, 49.60; H, 4.94. Found: C,49.49; H, 4.95.

***μ*-1-Methyl-4,4-piperidinylenebis(*η*⁵-inden-1-yl)dichlorozirconium (3).** 4,4-Di(1*H*-3-indenyl)-1-methylpiperidine (14.9 g, 43.4 mmol) was dissolved in Et_2O (200 mL), cooled to −40 °C, and then treated with 2.0 M *n*-BuLi in hexane (50 mL, 100 mmol). The resuulting yellow precipitate of **5a** was isolated, washed with ether (3 × 50 mL), and dried. Yield: 13.5 g (92%).

The suspension of $ZrCl_4$ (2.6 g, 11.2 mmol) in CH_2Cl_2 (50 mL) was cooled up to −60 °C and mixed with the dilithium derivative of **5** (3.79 g, 11.2 mmol). The resulting mixture was stirred for 1 h and allowed to warm to room temperature. The solution was separated by decantation and evaporated. Yield: 1.13 g (42%) for the mixture of *rac*- and *meso*-forms (1/1). ^{1}H NMR (CD_2Cl_2, 30 °C): δ 7.70 ("d"), 7.65 ("d"), 7.50 ("d"), 7.45 ("d"), 7.29 ("t"), 7.1 ("t"), 7.5 ("t"), 6.9 ("t"H) {Σ=8H, ABCD of indene}, 6.70 (d), 6.65 (d), 6.18 (d), 6.10 (d) {Σ=4H, AB of five-membered ring}, 3.40 (bs, 3H, $-CH_3$), 3.2−2.7 (broad, 8H, $-CH_2$). Anal. Calcd for $C_{24}H_{23}Cl_2NZr$: C, 59.12; H, 4.75. Found: C, 59.05; H, 4.79.

1-Methyl-4-((trichlioizirconium)-*η*⁵-inden-1-yl)-4-((triethylstannyl)*η*⁵-inden-1-yl)piperidine (6). A well-stirred suspension of dilithium derivative **5a** (7.46 g, 22 mmol) in ether (150 mL) was cooled to −40 °C and mixed with chlorotriethylstannane (7.4 mL, 44 mmol). The resulting mixture was allowed to warm to room temperature. The solution was separated by decantation and evaporated. The resulting yellow oil represents a 1/1 **5b*rac*-/5b*meso*** mixture. ^{1}H NMR (cyclohexane-d_8, 30 °C): δ 7.50−7.00 (gr. of m, 8H); 6.53 (s, 1H) and 6.44 (s, 1H) {−CH=}; 3.98 (bs, 1H) and 3.91 (bs, 1H) {−CH<}; 2.7−2.3 (gr. of br m, Σ=11H, piperidine); 1.1 (m, Σ=18H; $-Sn(CH_2CH_3)$); 0.7 (m, Σ=12H, − $Sn(CH_2CH_3)$). **5b** so obtained was dissolved in toluene (100 mL), and $ZrCl_4$ (5.12 g, 22 mmol) was added. The reaction mixture was heated for 1 h (80 °C). Toluene and Et_3SnCl were removed, and the residue was recrystallized from toluene to give 3.4 g (22%) of **6**. ^{1}H NMR (CD_2Cl_2, 30 °C): δ 7.90−7.10 (group of m, Σ=10H, aromatic H), 7.05 (s, 1H, =CH−), 4.00 (s, 1H, >CH−), 2.90−2.70 (broad, 8H, $-CH_2-$), 2.72 (bs, 3H, $-CH_3$), 0.90 (t, 9H, $-CH_2CH_3$), 0.60 (q, 6H, $-CH_2CH_3$). Anal. Calcd for $C_{30}H_{38}Cl_3NSnZr$: C, 49.39; H, 5.25. Found: C, 49.33; H, 5.20.

Crystal Structure Determination of 2 and 6. Diffraction-quality single crystals of **2** and **6** were obtained by slow crystallization from CH_2Cl_2 and toluene, respectively. The experimental reflections were collected on an Enraf Nonius CAD4 diffractometer (Mo Kα radiation, graphite monochromator, ω scan mode, θ(max) = 28°). No absorption correction was applied.

The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 in the anisotropic approximation. In the difference Fourier synthesis, in the case of **2**, all of the hydrogen atoms were found. These atoms were included in the further structure refinement as ridden at the corresponding carbon atoms with isotropic thermal parameters *U*(iso), which is 1.5 times as much as the *U*(eq) parameters of the corresponding carbon atom. The final least-squares in the anisotropic approximation for the atoms of the main molecule converged to $R_1 = 0.0387$, $wR_2 = 0.1068$ for 3733 reflections with $I > 2\sigma(I)$. Electron density residuals are 1.039 and −1.679 e/A^3.

In the case of **6** the refinement resulted in bad geometry of two ethylene groups at Sn and high thermal parameters of these group atoms. In addition, several electron density peaks in the vicinity of ethylene group atoms were found in the difference Fourier synthesis. These facts pointed out some disorder of these groups. We failed to rationally describe this disorder. Most likely it reduces to many orientations of the terminal methyl groups due to rotation around the corresponding Sn−C bonds. Further, atoms of $-CH_3$ were only refined in the isotropic approximation. The hydrogen atoms except for those at disordered Et groups were calculated in idealized positions and included in the anisotropic full-matrix refinement on F^2 using the riding scheme. The isotropic thermal parameters of these atoms were taken to be 1.5 times as much as U(eq) parameters of the corresponding carbon atom. The final least-squares converged to $R1 = 0.0677$, $wR2 = 0.2030$ for 4862 reflections with $I > 2\sigma(I)$. Electron density residuals were 1.480 and −1.240 e/A^3, the highest peaks being situated in the vicinity of the heavy atoms (Zr and Sn) and the disordered ethylene groups. Rather high R indices and errors in geometrical parameters are mainly due to the above disorder in the crystal.

All the calculations were performed using SHELX-76[7] and SHELXL-93[8] software. The relevant crystal data along with the refinement details are given in Table 1.

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