Tetramethyl(2-methoxyethyl)cyclopentadienyl complexes of zirconium(IV). Crystal structure of $[\eta^5:\eta^1\text{-}C_5(CH_3)_4(CH_2CH_2OCH_3)]ZrCl_3$

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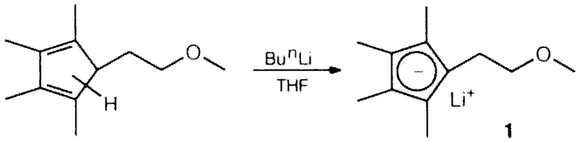
Several novel zirconium(IV) complexes with the chelating oxygen-containing cyclopentadienyl ligand, tetramethyl(2-methoxyethyl)cyclopentadiene, have been synthesized. $[\eta^5:\eta^1$-Tetramethyl(2-methoxyethyl)cyclopentadienyl]trichlorozirconium (**2**), bis[η^5-tetramethyl(2-methoxyethyl)cyclopentadienyl]dichlorozirconium (**3**), [η^5-pentamethylcyclopentadienyl][η^5-tetramethyl(2-methoxyethyl)cyclopentadienyl]dichlorozirconium (**4**), and [η^5-tetramethyl(2-methylthioethyl)cyclopentadienyl][η^5-tetramethyl(2-methoxyethyl)-cyclopentadienyl]dichlorozirconium (**5**) have been prepared from the corresponding lithium cyclopentadienide (**1**). The crystal structure of cyclopentadienyl complex **2** has been established by X-ray analysis. The coordination O→Zr bond in compound **2** exists both in the crystalline state and in solutions. No coordination of this type was observed in complexes **3**—**5**. Synthesized complexes **2**—**5** are discussed in comparison with their sulfur-containing analogs.

Key words: cyclopentadienes with oxygen-containing substituents, cyclopentadienyl zirconium complexes, crystal structure.

We reported previously[1] on the synthesis of zirconium complexes based on the chelating tetramethyl(2-methylthioethyl)cyclopentadienyl ligand. In this work, continuing studies in this area, we synthesized several novel zirconium(IV) tetramethyl(2-methoxyethyl)cyclopentadienyl complexes, studied their structures, and compared them with their sulfur-containing analogs.

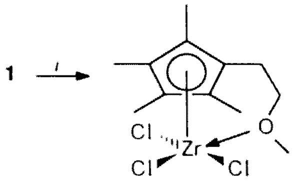
Synthesis and structure of zirconium(IV) cyclopentadienyl complexes

The initial tetramethyl(2-methoxyethyl)cyclopentadiene (as a mixture of three isomers) was synthesized according to the procedure described in Ref. 2. Lithium cyclopentadienide (**1**) obtained from this diene was then used as the initial reagent in syntheses of zirconium cyclopentadienyl complexes.



1

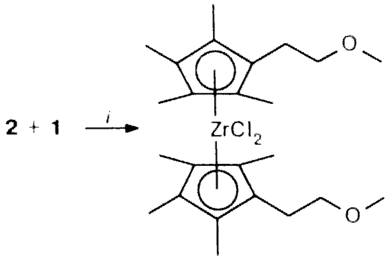
The reaction of lithium salt **1** with $ZrCl_4$ in ether results in the formation of the monocyclopentadienyl complex (**2**), which, like its sulfur-containing analog, can be purified by high-vacuum sublimation.



2

i. $ZrCl_4$, Et_2O, 60 °C, 4 h

The treatment of complex **2** with lithium salt **1** in THF gives the dicyclopentadienyl derivative (**3**).



3

i. THF, 80 °C, 4 h

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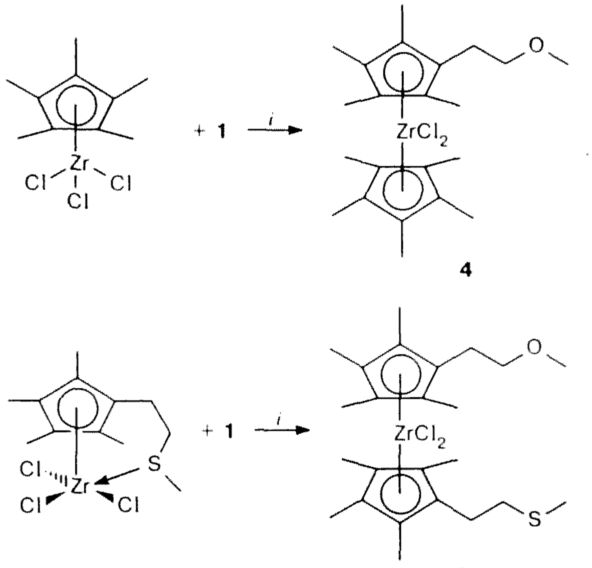
An attempt to obtain compound **3** in one stage by the reaction of $ZrCl_4$ with 2 eq. of salt **1** was unsuccessful due to the formation of an almost inseparable mixture of compounds **2**, **3**, and nonidentified products.

Similarly, dicyclopentadienyl complexes **4** and **5** were obtained in high yields from $(\eta^5\text{-}C_5Me_5)ZrCl_3$ and $[\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2CH_2SCH_3)]ZrCl_3$.[1]



4

5

i. THF, 80 °C, 4 h

It should be mentioned that monocyclopentadienyl derivative **2**, as $[\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2CH_2SCH_3)]ZrCl_3$, is a convenient intermediate product for further cyclopentadienylation with the purpose of preparing various homo- and heteroligand zirconium cyclopentadienyl complexes.

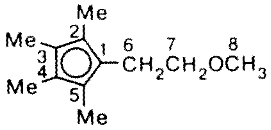
The parameters of the ^1H and ^{13}C NMR spectra of compounds **1**—**5** are presented in Table 1. The signals in the spectra were assigned on the basis of experiments using the homonuclear Overhauser effect and selective heteronuclear decoupling.

As can be seen from Table 1, the chemical shifts of protons and carbon atoms in the CH_2OCH_3 fragments in all dicyclopentadienyl complexes **3**—**5** almost coincide and slightly differ from the corresponding values for the anion of compound **1**. This fact testifies that the coordination of the cyclopentadienyl ring has a weak effect on the considered fragment. The same was previously observed for sulfur-containing complexes. It also can be mentioned that the NMR parameters of the $\eta^5\text{-}C_5Me_4(CH_2CH_2SCH_3)$ ligand in compound **5** are very close to those of sulfur-containing dicyclopentadienyl derivatives.[1] This indicates that the O→Zr coordination in compounds **3**—**5** (like the S→Zr coordination in compound **5**) is absent in solution.

A different situation is observed for monocyclopentadienyl complex **2**. The chemical shifts of the protons and carbon atoms in the CH_2OCH_3 fragment move considerably downfield (both in THF-d_8 and CD_2Cl_2)

Table 1. Parameters of the ^1H and ^{13}C NMR spectra of compounds **1**—**5**

Compound	Solvent	T/°C	δ ^{13}C ($^1J_{C-H}$/Hz)^a							δ ^1H ($^3J_{H-H}$/Hz)^a			
			Me(2—5)	C(1)	C(2,5)	C(3,4)	C(6)	C(7)	C(8)	Me(2—5)	H(6)	H(7)	H(8)
1	THF-d_8	30	10.86 (123) 11.02 (123)	106.29	104.49	107.39	26.82 (123)	75.00 (140)	58.28 (139)	1.81 (s) 1.82 (s)	2.55 (t, 7.8)	3.21 (t, 7.8)	3.23 (s)
3	THF-d_8	30	12.19 (127) 12.32 (127)	124.87	124.30	124.49	28.46 (128)	72.94 (140)	58.59 (140)	1.98 (s) 2.00 (s)	2.71 (t, 7.0)	3.27 (t, 7.0)	3.22 (s)
4	THF-d_8	30	12.14 (127) 12.27 (127) 12.21 (127)^b	124.85	124.19 124.15^c	124.32	28.43 (128)	72.96 (140)	58.61 (140)	1.98 (s) 2.00 (s) 1.97 (s)^b	2.71 (t, 7.0)	3.28 (t, 7.0)	3.22 (s)
5	THF-d_8	30	12.15 (127)^d 12.21 (127)^d 12.30 (127)^e 12.34 (127)^e	125.00^d 126.47^e	124.41^d 123.68^e	124.52^d 124.55^e	28.47^d (127) 28.20^e (129)	72.93^d (140) 34.54^e (137)	58.60^d (139) 15.58^e (137)	1.979 (s)^d 1.983 (s)^d 2.002 (s)^e 2.015 (s)^e	2.71^d (t, 7.0) 2.74^e (t, 7.9)	3.28^d (t, 7.0) 2.43^e (t, 7.9)	3.22^d (s) 2.07^e (s)
2			Me(2,5) Me(3,4)							Me(2,5) Me(3,4)			
	THF-d_8	30	14.17 12.79 (127) (127)	127.55	129.56	125.81	23.52 (128)	82.17 (148)	65.00 (146)	2.20 (s) 2.06 (s)	2.68 (t, 6.4)	4.23 (t, 6.4)	3.69 (s)
		−85	14.50 12.96	127.79	129.62	124.61	23.12	82.59	65.89	2.17 (s) 2.01 (s)	2.67 (t)	4.25 (t)	3.74 (s)
	CD_2Cl_2	30	13.29 12.94	133.09	128.05 128.71		23.97	82.90	63.95	2.19 (s) 2.26 (s)	2.87 (t, 6.6)	4.33 (t, 6.6)	3.70 (s)
		−85								2.05 (br. s) 2.16 (br. s)	2.73 (br)	4.25 (br)	3.64 (br. s)

[a] The numeration of atoms in all compounds **1**—**5** corresponds to the presented numeration 

[b] C_5Me_5. [c] C_5Me_5. [d] Oxygen-containing ligand. [e] Sulfur-containing ligand.

from the shifts for compounds **3**—**5**, the $^1J_{C-H}$ values for the C(7) and C(8) atoms increase simultaneously, and the value of the vicinal coupling constant $^3J_{H(6)-H(7)}$ decreases (the same tendencies were observed for $[\eta^5:\eta^1\text{-}C_5Me_4(CH_2CH_2SCH_3)]ZrCl_3$). These data unambiguously indicate the existence of a coordination O→Zr bond in half-sandwich **2**, and the very weak temperature dependence of the chemical shifts in both solvating and nonsolvating solvents (see Table 1) favors the retention of the coordination of oxygen to the metal atom in the whole temperature range studied. The decrease in the value of $^3J_{H(6)-H(7)}$ when the ether function is coordinated to the metal is explained by the fact that it is the average of the values of four vicinal coupling constants between two pairs of H(6) and H(7) protons in the metallacycle, while in the absence of coordination its measurable value is averaged over all possible rotamers in the noncoordinated substituent. Unfortunately, unlike the sulfur-containing half-sandwich for which the barrier of the degenerate inversion of the metallacycle was estimated, an attempt to obtain the total dynamic picture in solution was unsuccessful. The triplet structure of the signals of the H(6) and H(7) protons is retained in THF-d_8 up to −85 °C; in CD_2Cl_2 at −85 °C the signals of these protons strongly broaden, and the coalescence point for H(7) is likely close to the freezing point of the solvent. This difference in the behaviors of compound **2** and its sulfur-containing analog has two possible causes: there is either a substantial decrease in the inversion barrier for compound **2**, which is rather improbable because of the similarity of the structural parameters of both metallacycles (see below), or there is a small difference in the chemical shifts of the corresponding pairs of nonequivalent protons in the $C(6)H_2-C(7)H_2$ fragment during the hindered inversion of the metallacycle. Most likely, these factors act in combination.

The IR spectroscopy data confirm the absence of coordination of the oxygen atom to the metal in dicyclopentadienyl compounds **3**—**5** and its existence in half-sandwich **2**, in which the frequency of stretching vibrations of the C—O bond shifts 35 cm^{-1} lower than that of the free ligand (ν(C—O) = 1107 cm^{-1}), while for compounds **3**—**5** this frequency almost coincides with the value for the initial cyclopentadiene (see Experimental). A similar shift in the frequencies of the stretching vibrations of the C—O bond when the ether function is coordinated to the metal was observed for titanium $Cp'TiCl_3$ ($Cp' = C_5H_4(CH_2CH_2OCH_3)$;[3] $Cp' = C_5H_4CH_2$-(2-tetrahydrofuryl)[4]) and yttrium Cp'_2YAlH_4, $Cp'_2Y(m\text{-}H_2)BH_2$, $[Cp'_2Y(m\text{-}H_2)]_2$ ($Cp' = C_5H_4(CH_2CH_2OCH_3)$) complexes.[5]

Crystal structure of complex 2

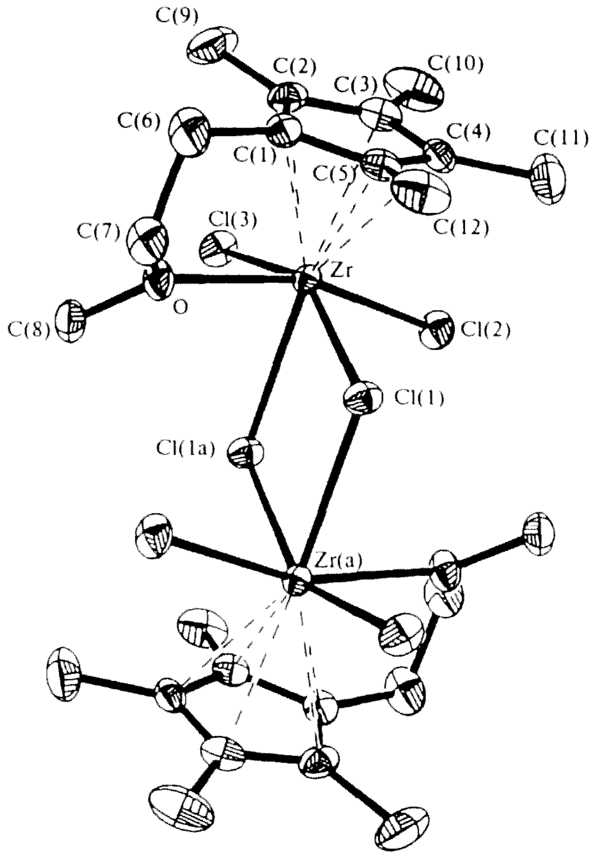


Fig. 1. Molecular structure of complex **2**.

Compound **2** crystallizes in the monoclinic space group $P2_1/c$. Its molecular structure (Fig. 1) is very close to that previously determined for $[\eta^5:\eta^1\text{-}C_5Me_4(CH_2CH_2SCH_3)]ZrCl_3$.[1] The molecule of compound **2** is a centered-symmetric dimer, in which the zirconium atoms are linked by two bridge Cl(1) and Cl(1a) atoms. The oxygen atom of the ligand is coordinated to the Zr atom. The coordination O→Zr bond length is 2.279(2) Å, which slightly differs from the values determined for the $(C_5H_5)ZrCl_3(DME)$ complex in which the O→Zr distances are 2.26(1) and 2.37(1) Å in the equatorial and apical positions of the oxygen atoms, respectively.[6] A substantial difference of complex **2** from its sulfur-containing analog is that in the latter the sulfur atom is tetrahedral, while in compound **2** the oxygen atom lies in fact in the plane of the Zr, C(7), and C(8) atoms linked to the O atom (the deviation of the O atom from the plane is 0.056 Å) and exists in the sp^2-hybrid state. It is likely that this effect is related to the interaction of the d-orbital of zirconium with the unshared pair of oxygen in the pπ-orbital. The bond lengths and some bond angles for complex **2** are presented in Tables 2 and 3.

Experimental

NMR spectra were recorded on a VXR-400 spectrometer (400 MHz) in THF-d_8 or CD_2Cl_2 (Table 1). IR spectra were recorded on an IKS-29 spectrometer as suspensions in Nujol mulls.

Table 2. Bond lenghts (*d*) in complex **2**

Bond	*d*/Å	Bond	*d*/Å
Zr—Cl(1)	2.560(1)	Zr—Cl(3)	2.463(1)
Zr—Cl(2)	2.461(1)	Zr—O	2.279(2)
Zr—C(1)	2.507(3)	Zr—C(2)	2.515(3)
Zr—C(3)	2.529(3)	Zr—C(4)	2.559(3)
Zr—C(5)	2.563(3)	Zr—Cl(1a)	2.718(1)
Cl(1)—Zr(a)	2.718(1)	O—C(7)	1.458(4)
O—C(8)	1.449(4)	C(1)—C(2)	1.422(4)
C(1)—C(5)	1.412(4)	C(1)—C(6)	1.505(4)
C(2)—C(3)	1.405(4)	C(2)—C(9)	1.504(5)
C(3)—C(4)	1.407(4)	C(3)—C(10)	1.505(5)
C(4)—C(5)	1.411(4)	C(4)—C(11)	1.503(5)
C(5)—C(12)	1.503(5)	C(6)—C(7)	1.508(5)
Zr—Zr(a)	4.258	Cl(1)—Cl(1a)	3.121
Zr—Cp_{cent}*	2.232		

* Cp_{cent} is the center of the cyclopentadienyl ring C(1),C(2),C(3),C(4),C(5).

Таблица 3. Main bond angles (ω) in complex **2**

Angle	ω/deg	Angle	ω/deg
Cl(1)—Zr—Cl(1a)	72.45(2)	Cl(1)—Zr—Cl(3)	150.17(2)
Cl(1)—Zr—Cl(2)	91.06(2)	Cl(1)—Zr—O	85.82(5)
Cl(1a)—Zr—Cl(3)	78.17(2)	Cl(1a)—Zr—O	78.68(5)
Cl(3)—Zr—Cl(2)	89.33(2)	Cl(3)—Zr—O	83.45(5)
Cl(2)—Zr—O	159.35(5)	Zr—Cl(1)—Zr(a)	107.55(2)
Zr—O—C(7)	117.0(2)	Zr—O—C(8)	128.9(2)
C(7)—O—C(8)	113.8(2)	C(2)—C(1)—C(5)	108.1(2)
C(2)—C(1)—C(6)	125.5(3)	C(5)—C(1)—C(6)	126.4(3)
C(1)—C(2)—C(3)	107.4(3)	C(1)—C(2)—C(9)	126.9(3)
C(3)—C(2)—C(9)	125.3(3)	C(2)—C(3)—C(4)	108.7(3)
C(2)—C(3)—C(10)	125.9(3)	C(4)—C(3)—C(10)	125.2(3)
C(3)—C(4)—C(5)	108.0(2)	C(3)—C(4)—C(11)	126.5(3)
C(5)—C(4)—C(11)	125.3(3)	C(1)—C(5)—C(4)	107.8(2)
C(1)—C(5)—C(12)	125.4(3)	C(4)—C(5)—C(12)	126.0(3)
C(1)—C(6)—C(7)	110.9(3)	Cp_{cent}—Zr—Cl(1a)[a]	172.5
Cp_{cent}—Zr—Cl(1)	102.1	Cp_{cent}—Zr—Cl(2)	104.6
Cp_{cent}—Zr—Cl(3)	106.7	Cp_{cent}—Zr—O	96.0
PL—C(1)—C(6)[b]	93.6		

[a] Cp_{cent} is the center of the cyclopentadienyl ring C(1),C(2),C(3),C(4),C(5). [b] PL is the plane of the cyclopentadienyl ring C(1),C(2),C(3),C(4),C(5).

Table 4. Crystallographic data, parameters of X-ray experiment, and refinements for compound **2**

Empirical formula	$Zr_2Cl_6C_{24}H_{38}O_2$
Molecular weight	753.8
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	12.271(8)
b (Å)	8.253(6)
c (Å)	14.991(4)
β (deg)	103.57(4)
V (Å^3)	1475.8(2.7)
Z	2
Calculated density (g cm^{-3})	1.696
F(000)	760.0
Absorption coefficient (cm^{-1})	12.64
Radiation	Mo-Kα, graphite monochromator
λ/Å	0.71069
2θ-Range (deg)	$2 < 2\theta < 50$
Scan type	ω
Total number of reflections	2688
Number of independent reflections	2477
Number of reflections with $I > 2\sigma(I)$	2204
R_{int}	0.027
Number of parameters refined	230
$R = \Sigma\|\|F_o\| - \|F_c\|\| / \Sigma\|F_o\|$	0.024
$R_w = [\Sigma_w(\|F_o\| - \|F_c\|)^2/\Sigma_w(F_o)^2]^{1/2}$	0.025
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000348F^2$
Quality factor	1.36
Residual electron density, min/max (e · Å^{-3})	−0.533/0.612

Initial cyclopentadienes were synthesized in a dry argon atmosphere in standard glassware. The rest of the work, including preparation of samples for NMR spectroscopy, was carried out using all-sealed evacuated systems of the Shlenk flask type (residual gas pressure was not higher than 3×10^{-3} Torr). Solvents were purified and dehydrated by standard procedures. Commercial zirconium(IV) chloride (Merck) was used.

Pentamethylcyclopentadiene was obtained by the procedure presented in Ref. 7. Tetramethyl(2-methoxyethyl)cyclopentadiene was synthesized by the previously described method.[2] Pentamethylcyclopentadienylzirconium(IV) trichloride was obtained from C_5Me_5Li and $ZrCl_4$ in diethyl ether[8] and purified by high-vacuum sublimation.

Lithium tetramethyl(2-methoxyethyl)cyclopentadienide (1). A solution of tetramethyl(2-methoxyethyl)cyclopentadiene (10.83 g, 55.7 mmol) in 100 mL of dehydrated THF was treated with a 1.50 *M* solution (37.2 mL) of *n*-butyllithium in hexane (55.8 mmol) at −30 °C. The mixture was allowed to warm up to -20 °C and left for 12 h. The obtained dark-red solution was concentrated to 30 mL, and diethyl ether (150 mL) was added. The white precipitate that formed was filtered off and triply washed on a filter with the same mixture of solvents. After recrystallization of the obtained salt from a minimum volume of THF, washing with ether, and drying *in vacuo*, a white finely crystalline product (6.03 g, 32.4 mmol, 58.1 %) was isolated.

[η^5:η^1-Tetramethyl(2-methoxyethyl)cyclopentadienyl]trichlorozirconium(IV) (2). A suspension of lithium salt **1** (1.31 g, 7.03 mmol) in 50 mL of ether was added to a suspension of $ZrCl_4$ (1.55 g, 6.65 mmol) in 10 mL of pentane. The reaction mixture was heated for 4 h at 60—70 °C and stirred vigorously. The precipitate was filtered off, twice washed with small portions of ether, dried, and sublimed in a high vacuum (10^{-3} Torr, 220 °C). The sublimate was recrystallized from THF, washed with ether, and dried *in vacuo*. A white crystalline, moisture sensitive product (1.35 g, 3.58 mmol, 53.9 %) was isolated. IR, ν/cm^{-1}: 1072 (C—O).

Crystals of compound **2** for X-ray analysis were obtained by high-vacuum sublimation.

Bis[η^5-tetramethyl(2-methoxyethyl)cyclopentadienyl]dichlorozirconium(IV) (3). Solutions of complex **2** (0.73 g, 1.94 mmol) and lithium salt **1** (0.36 g, 1.94 mmol) in THF (total volume 50 mL) were mixed, heated for 4 h at 80 °C, and allowed to stand for 12 h. The solvent was removed at elevated temperature, the residue was dried in a high vacuum, and toluene (40 mL) was added. The precipitated LiCl was filtered off, and the solvent was removed. Recrystallization from pentane (20 mL) gave a pure product (0.53 g, 1.02 mmol, 52.5 %) as concretions of thin plates. Found (%): C, 54.97; H, 7.50. $C_{24}H_{38}Cl_2O_2Zr$. Calculated (%): C, 55.36; H, 7.36. IR, ν/cm^{-1}: 1114 (C—O).

[η^5-Pentamethylcyclopentadienyl][η^5-tetramethyl(2-methoxyethyl)cyclopentadienyl]dichlorozirconium(IV) (4) was synthesized similarly from $C_5Me_5ZrCl_3$ (0.93 g, 2.79 mmol) and lithium salt **1** (0.52 g, 2.79 mmol). Recrystallization from ether gave the target product (0.99 g, 2.08 mmol, 74.5 %) as thin yellowish plates. Found (%): C, 54.52; H, 7.28. $C_{22}H_{34}Cl_2OZr$. Calculated (%): C, 55.44; H, 7.19. IR, ν/cm^{-1}: 1111 (C—O).

[η^5-Tetramethyl(2-methylthioethyl)cyclopentadienyl][η^5-tetramethyl(2-methoxyethyl)cyclopentadienyl]dichlorozirconium(IV) (5) was obtained by a similar procedure from [η^5:η^1-$C_5Me_4(CH_2CH_2SCH_3)$]$ZrCl_3$[1] (0.58 g, 1.48 mmol) and salt **1** (0.27 g, 1.48 mmol). Recrystallization from ether gave the product (0.59 g, 1.10 mmol, 74.3 %) as thin yellowish plates. Found (%): C, 53.47; H, 7.26. $C_{24}H_{38}Cl_2OSZr$. Calculated (%): C, 53.70; H, 7.14. IR, ν/cm^{-1}: 1110 (C—O).

X-ray study of compound 2. All measurements were performed on an automated four-circle Enraf-Nonius CAD 4 diffractometer at –20 °C. The structure was solved by the direct method (SHELX-86). The final refinement was accomplished by the full-matrix least squares method with anisotropic thermal parameters for all nonhydrogen atoms. All hydrogen atoms were localized from the differential series and refined isotropically. The details of the X-ray diffraction study are presented in Table 4.

References

1. D. P. Krut'ko, M. V. Borzov, V. S. Petrosyan, L. G. Kuz'mina, and A. V. Churakov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 984 [*Russ. Chem. Bull.*, 1996, **45**, 940 (Engl. Transl.)].
2. P. Jutzi and J. Dahlhaus, *Synthesis*, 1993, 684.
3. Q. Huang, Y. Qian, and Y. Tang, *Trans. Met. Chem.*, 1990, **15**, 483.
4. Y. Qian, G. Li, W. Chen, B. Li, and X. Jin, *J. Organometal. Chem.*, 1989, **373**, 185.
5. D. A. Laske, R. Duchateau, and J. H. Teuben, *J. Organometal. Chem.*, 1993, **462**, 149.
6. N. J. Wells, J. C. Huffman, and K. G. Caulton, *J. Organometal. Chem.*, 1981, **213**, C17.
7. R. S. Trelkel and J. E. Bercaw, *J. Organometal. Chem.*, 1977, **136**, 1.
8. J. H. Wengrovices and R. R. Schrock, *J. Organometal. Chem.*, 1981, **205**, 319.

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