Tetramethyl(2-methylthioethyl)cyclopentadienyl complexes of zirconium(IV): synthesis, crystal structure, and dynamic behavior in solutions

D. P. Krut'ko,[a] M. V. Borzov,[a] V. S. Petrosyan,[a] L. G. Kuz'mina,[b] and A. V. Churakov[b]*

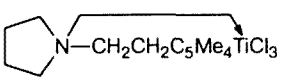
[a]*Department of Chemistry, M. V. Lomonosov Moscow State University, Vorob'evy Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 939 5546*

[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 117907 Moscow, Russian Federation. Fax: +7 (095) 954 1279*

Chelating sulfur-containing cyclopentadienyl ligand tetramethyl(2-methylthioethyl)cyclopentadiene (**1**), was synthesized for the first time. Its sodium (**2a**) and lithium (**2b**) derivatives were isolated in the crystalline state. Starting from compound **1** some novel Zr^{IV} complexes were prepared: [tetramethyl(2-methylthioethyl)cyclopentadienyl]trichlorozirconium (**3**), bis[tetramethyl(2-methylthioethyl)cyclopentadienyl]dichlorozirconium (**4**), and [pentamethylcyclopentadienyl][tetramethyl(2-methylthioethyl)cyclopentadienyl]dichlorozirconium (**5**). The crystal structures of **3** and **5** were determined by X-ray diffraction analysis. The dynamic behavior of complex **3** in various solvents was investigated by ^1H and ^{13}C NMR spectroscopy. The S→Zr coordination bond was shown to exist in complex **3** both in the crystalline state and in solution. No coordination of this type was found in compounds **4** and **5**.

Key words: substituted sulfur-containing cyclopentadienes, cyclopentadienyl zirconium complexes, dynamic behavior, crystal structure.

In recent years, complexes of Group IVB metals with cyclopentadienyl ligands became an object of extensive studies. A number of Ti and Zr complexes with monosubstituted cyclopentadienes containing a donor heteroatom (N, O) in the side chain have been synthesized.[1—7] Recently, a monocyclopentadienyl complex of titanium has been synthesized, and its crystal structure has been established by X-ray diffraction analysis.[8]



To date, tetramethylcyclopentadienes with various potentially chelating functional groups in the side chain have been prepared: $C_5Me_4(H)(CH_2)_nX$ (n = 1, 2; X = NMe_2, OMe)[9]; $C_5Me_4(H)(CH_2)_2PPh_2$ [10]; and $C_5Me_4(H)CH_2X$ (X = NHBu^t; NHPh; PHBu^t).[11]

In the present work, we synthesized a new chelating sulfur-containing cyclopentadienyl ligand $C_5Me_4(H)(CH_2)_2SMe$ and zirconium complexes based on it. The crystal structures of two complexes were studied by X-ray diffraction analysis.

Results and Discussion

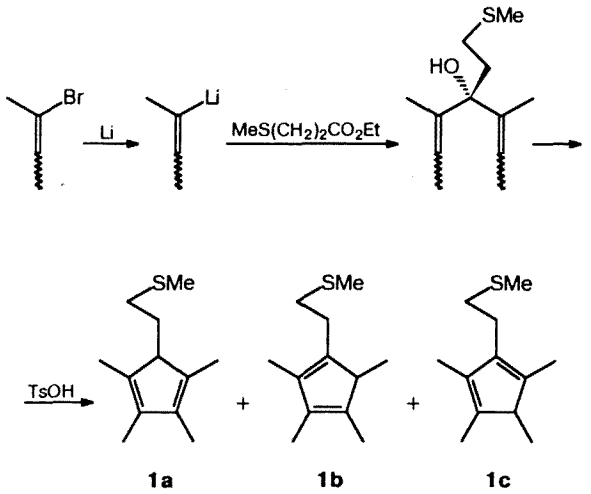
Synthesis of tetramethyl(2-methylthioethyl)cyclopentadiene (1) and its sodium (2a) and lithium (2b) derivatives. Tetramethyl(2-methylthioethyl)cyclopentadiene (**1**) was synthesized as a mixture of three isomers (**1a—c**) by the scheme used previously for preparative-scale synthesis of pentamethylcyclopentadiene[12] and for the preparation of a series of tetramethyl(methoxyalkyl)cyclopentadienes,[9] including the oxygen analog of compound **1** (Scheme 1).

In our case, dehydration of the tertiary alcohol with simultaneous cyclization is much more difficult. In fact, with *p*-toluenesulfonic acid monohydrate, which is normally used as the catalyst in this reaction, the reaction is much more prolonged (compared to the synthesis of pentamethylcyclopentadiene) and yields numerous side products. We found that appreciably better results are achieved when anhydrous TsOH, readily obtainable from the commercial monohydrate, is used as the catalyst.[13] However, in this case, too, the target product **1** isolated by fractionation under high vacuum still contained con-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 984—992, April, 1996.

1066-5285/96/4504-0940 $15.00

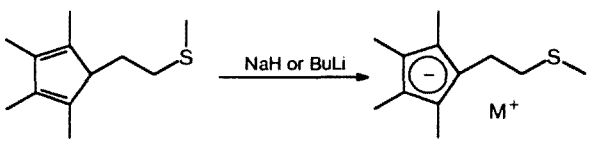
Scheme 1



siderable amounts of impurities. Compound **1** was completely purified by converting it into the sodium or lithium derivative followed by hydrolysis.

The treatment of compound **1** with sodium hydride or *n*-butyllithium leads smoothly to formation of the corresponding salts **2a** and **2b** in high yields (Scheme 2).

Scheme 2



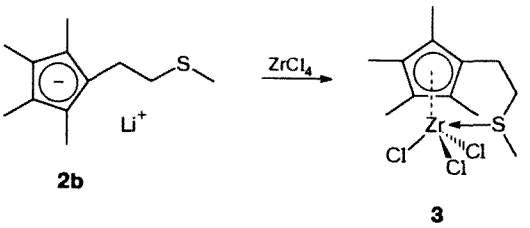
M = Na (**2a**), Li (**2b**)

Both salts **2a** and **2b**, unlike the corresponding pentamethylcyclopentadiene salts, are readily soluble in THF; recrystallization affords high-purity compounds. Crystalline salts **2a** and **2b** do not incorporate solvating molecules and can serve as convenient reagents in organometallic synthesis.

To carry out NMR identification of **1a—c**, a small amount of the Na derivative **2a** was treated with acetic acid. The ratio of isomers in the mixture at 30 °C was **1a** : **1b** : **1c** ≈ 3 : 4 : 5. The assignment of the ^1H and ^{13}C NMR signals (see Experimental) was based on two-dimensional homo- and heteronuclear correlation spectra and on the ^{13}C NMR spectrum.

Synthesis of cyclopentadienyl complexes of zirconium. The interaction of lithium derivative **2b** with $ZrCl_4$ in ether under mild conditions gives monocyclopentadienyl complex (**3**), which can be purified by sublimation under high vacuum (Scheme 3). The crystal structure of compound **3** and its dynamic behavior in solution will be discussed in detail below.

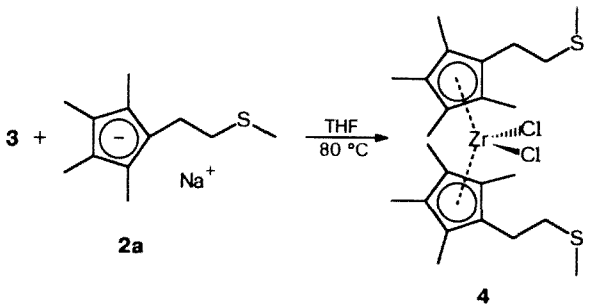
Scheme 3



2b **3**

The reaction of **3** with a slight excess of cyclopentadienide **2a** at an elevated temperature affords dicyclopentadienyl derivative (**4**) (Scheme 4).

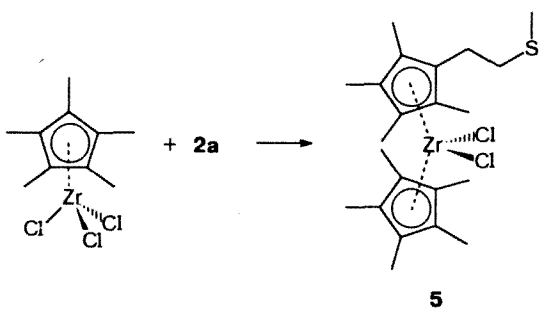
Scheme 4



2a **4**

A similar reaction of $(\eta^5\text{-}C_5Me_5)ZrCl_3$ with salt **2a** yields the heteroligand dicyclopentadienyl complex (**5**) (Scheme 5).

Scheme 5



5

We have found that the two-step synthetic scheme involving the preparative isolation and purification of the intermediate monocyclopentadienyl complex **3** is optimal for the preparation of the symmetrical complex **4** as well. Our attempt to prepare **4** in one step by the treatment of $ZrCl_4$ in THF with two equivalents of sodium derivative **2a** led to a mixture of products **3** and **4**; only complex **3** could be isolated from this mixture in a pure state.

The use of the sodium derivative **2a** in the step of the preparation of compound **5** is preferred over the use of

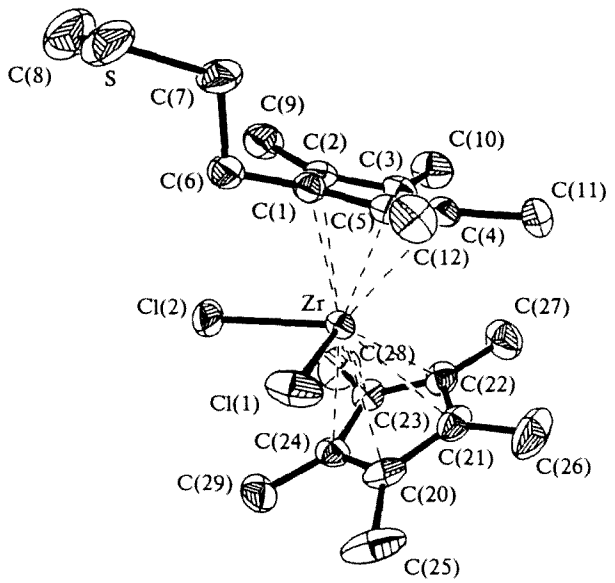


Fig. 1. Structure of molecule **5A** (hydrogen atoms are not shown).

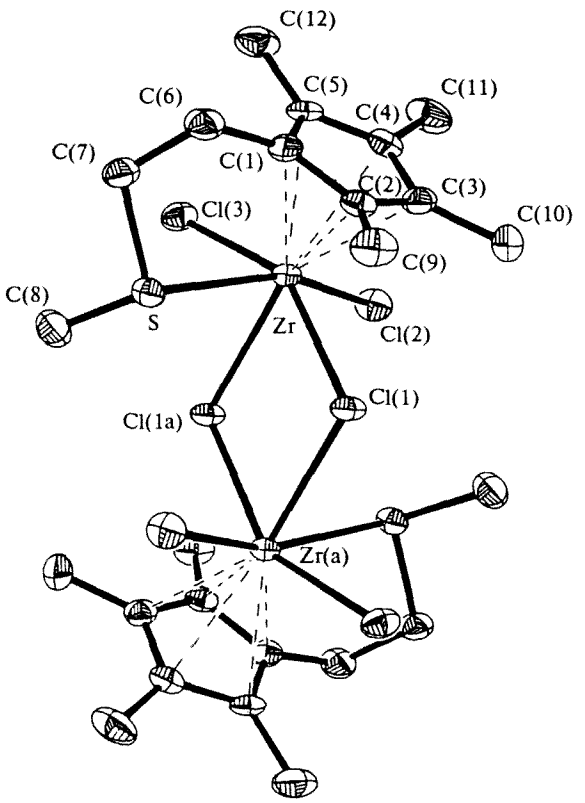


Fig. 2. Structure of molecule **3** (hydrogen atoms are not shown).

lithium derivative **2b**, because the NaCl formed (unlike LiCl) is insoluble in THF, which facilitates the isolation of the product.

Structures of dicyclopentadienyl complexes of zirconium 4 and 5. The crystal structure of complex **5** was established by X-ray diffraction analysis (Fig. 1, Tables 1 and 2). The mixed sandwich **5** crystallizes in the triclinic group $P\bar{1}$; the unit cell incorporates two crystallographically independent molecules, whose parameters are, in general, close to each other. As in the case of nonmethylated oxygen-containing

Table 1. Bond lengths (d) in the molecule of complex **5**

Molecule **A**		Molecule **B**	
Bond	d/Å	Bond	d/Å
Zr—Cl(1)	2.429(2)	Zr′—Cl(1′)	2.426(2)
Zr—Cl(2)	2.439(2)	Zr′—Cl(2′)	2.445(2)
Zr—C(1)	2.526(5)	Zr′—C(1′)	2.521(5)
Zr—C(2)	2.555(4)	Zr′—C(2′)	2.552(5)
Zr—C(3)	2.547(5)	Zr′—C(3′)	2.541(5)
Zr—C(4)	2.542(5)	Zr′—C(4′)	2.554(5)
Zr—C(5)	2.551(5)	Zr′—C(5′)	2.545(5)
Zr—C(20)	2.569(5)	Zr′—C(20′)	2.550(5)
Zr—C(21)	2.547(5)	Zr′—C(21′)	2.570(5)
Zr—C(22)	2.534(5)	Zr′—C(22′)	2.539(6)
Zr—C(23)	2.517(5)	Zr′—C(23′)	2.538(6)
Zr—C(24)	2.541(5)	Zr′—C(24′)	2.500(5)
S—C(7)	1.801(7)	S′—C(7′)	1.802(7)
S—C(8)	1.73(1)	S′—C(8′)	1.77(1)
C(1)—C(2)	1.435(7)	C(1′)—C(2′)	1.412(7)
C(1)—C(5)	1.408(7)	C(1′)—C(5′)	1.424(7)
C(1)—C(6)	1.503(7)	C(1′)—C(6′)	1.490(7)
C(2)—C(3)	1.402(7)	C(2′)—C(3′)	1.413(7)
C(2)—C(9)	1.486(7)	C(2′)—C(9′)	1.494(8)
C(3)—C(4)	1.421(7)	C(3′)—C(4′)	1.427(7)
C(3)—C(10)	1.501(7)	C(3′)—C(10′)	1.495(7)
C(4)—C(5)	1.405(7)	C(4′)—C(5′)	1.406(7)
C(4)—C(11)	1.502(7)	C(4′)—C(11′)	1.465(8)
C(5)—C(12)	1.485(8)	C(5′)—C(12′)	1.499(7)
C(6)—C(7)	1.530(8)	C(6′)—C(7′)	1.535(7)
C(20)—C(21)	1.420(8)	C(20′)—C(21′)	1.392(8)
C(20)—C(24)	1.412(8)	C(20′)—C(24′)	1.403(7)
C(20)—C(25)	1.498(9)	C(20′)—C(25′)	1.493(8)
C(21)—C(22)	1.406(7)	C(21′)—C(22′)	1.439(8)
C(21)—C(26)	1.466(8)	C(21′)—C(26′)	1.498(9)
C(22)—C(23)	1.399(7)	C(22′)—C(23′)	1.432(8)
C(22)—C(27)	1.511(9)	C(22′)—C(27′)	1.485(9)
C(23)—C(24)	1.412(7)	C(23′)—C(24′)	1.397(7)
C(23)—C(28)	1.498(8)	C(23′)—C(28′)	1.497(9)
C(24)—C(29)	1.500(8)	C(24′)—C(29′)	1.501(8)
$Cp_{cent}(1)$—ZR [a]	2.242	$Cp_{cent}(1')$—ZR′ [b]	2.239
$Cp_{cent}(2)$—ZR [c]	2.32	$Cp_{cent}(2')$—ZR′ [d]	2.312

[a] $Cp_{cent}(1)$ is the center of the cyclopentadienyl ring C(1)C(2)C(3)C(4)C(5). [b] $Cp_{cent}(1')$ is the center of the cyclopentadienyl ring C(1′)C(2′)C(3′)C(4′)C(5′). [c] $Cp_{cent}(2)$ is the center of the cyclopentadienyl ring C(20)C(21)C(22)C(23)C(24). [d] $Cp_{cent}(2')$ is the center of the cyclopentadienyl ring C(20′)C(21′)C(22′)C(23′)C(24′).

Table 2. Main bond angles (ω) in complex **5**

Molecule **A**		Molecule **B**	
Angle	ω/deg	Angle	ω/deg
Cl(1)—Zr—Cl(2)	94.3(1)	Cl(1′)—Zr′—Cl(2′)	94.4(1)
C(7)—S—C(8)	98.9(4)	C(7′)—S′—C(8′)	99.4(4)
C(2)—C(1)—C(5)	108.3(4)	C(2′)—C(1′)—C(5′)	107.6(4)
C(2)—C(1)—C(6)	123.5(4)	C(2′)—C(1′)—C(6′)	124.9(5)
C(5)—C(1)—C(6)	128.0(4)	C(5′)—C(1′)—C(6′)	127.2(4)
C(1)—C(2)—C(3)	107.2(4)	C(1′)—C(2′)—C(3′)	108.1(4)
C(1)—C(2)—C(9)	127.2(5)	C(1′)—C(2′)—C(9′)	126.3(5)
C(3)—C(2)—C(9)	125.1(5)	C(3′)—C(2′)—C(9′)	125.2(5)
C(2)—C(3)—C(4)	108.3(4)	C(2′)—C(3′)—C(4′)	108.3(4)
C(2)—C(3)—C(10)	122.6(4)	C(2′)—C(3′)—C(10′)	122.5(5)
C(4)—C(3)—C(10)	127.7(5)	C(4′)—C(3′)—C(10′)	127.3(5)
C(3)—C(4)—C(5)	108.4(4)	C(3′)—C(4′)—C(5′)	107.2(4)
C(3)—C(4)—C(11)	126.3(4)	C(3′)—C(4′)—C(11′)	126.3(4)
C(5)—C(4)—C(11)	123.8(5)	C(5′)—C(4′)—C(11′)	125.2(5)
C(1)—C(5)—C(4)	107.8(4)	C(1′)—C(5′)—C(4′)	108.7(4)
C(1)—C(5)—C(12)	125.9(4)	C(1′)—C(5′)—C(12′)	126.4(4)
C(4)—C(5)—C(12)	125.9(4)	C(4′)—C(5′)—C(12′)	124.5(5)
C(1)—C(6)—C(7)	110.4(5)	C(1′)—C(6′)—C(7′)	111.4(4)
S—C(7)—C(6)	112.9(4)	S′—C(7′)—C(6′)	113.3(4)
C(21)—C(20)—C(24)	107.9(5)	C(21′)—C(20′)—C(24′)	108.4(4)
C(21)—C(20)—C(25)	126.3(5)	C(21′)—C(20′)—C(25′)	124.9(5)
C(24)—C(20)—C(25)	125.2(5)	C(24′)—C(20′)—C(25′)	126.4(5)
C(20)—C(21)—C(22)	107.4(5)	C(20′)—C(21′)—C(22′)	107.7(5)
C(20)—C(21)—C(26)	123.8(6)	C(20′)—C(21′)—C(26′)	128.3(5)
C(22)—C(21)—C(26)	128.0(6)	C(22′)—C(21′)—C(26′)	123.4(6)
C(21)—C(22)—C(23)	108.8(4)	C(21′)—C(22′)—C(23′)	107.3(5)
C(21)—C(22)—C(27)	124.2(5)	C(21′)—C(22′)—C(27′)	124.6(6)
C(23)—C(22)—C(27)	124.8(5)	C(23′)—C(22′)—C(27′)	127.4(6)
C(22)—C(23)—C(24)	108.0(4)	C(22′)—C(23′)—C(24′)	106.8(4)
C(22)—C(23)—C(28)	126.8(5)	C(22′)—C(23′)—C(28′)	124.4(6)
C(24)—C(23)—C(28)	124.8(5)	C(24′)—C(23′)—C(28′)	126.4(5)
C(20)—C(24)—C(23)	107.8(5)	C(20′)—C(24′)—C(23′)	109.7(5)
C(20)—C(24)—C(29)	125.7(5)	C(20′)—C(24′)—C(29′)	124.9(5)
C(23)—C(24)—C(29)	126.1(5)	C(23′)—C(24′)—C(29′)	125.1(5)
$Cp_{cent}(1)$—ZR—$Cp_{cent}(2)$	143.3	$Cp_{cent}(1')$—ZR′—$Cp_{cent}(2')$	146.2
PL(1)—PL(2) [a]	45.4	PL(1′)—PL(2′) [b]	45.8

[a] PL(1) — the plane of the cyclopentadienyl ring C(1)C(2)C(3)C(4)C(5). PL(2) — the plane of the cyclopentadienyl ring C(20)C(21)C(22)C(23)C(24). [b] PL(1′) — the plane of the cyclopentadienyl ring C(1′)C(2′)C(3′)C(4′)C(5′). PL(2′) — the plane of the cyclopentadienyl ring C(20′)C(21′)C(22′)C(23′)C(24′).

analogs of the Cp'_2MCl_2 type (M = Ti, Zr; Cp′ = $C_5H_4(CH_2)_2OMe$, $C_5H_4CH_2$ (tetrahydrofuran-2-yl), $C_5H_4CH(Me)CH_2OMe$),[2–4] no coordination of the donor heteroatom to the zirconium atom was found in **5**. The length of the Zr—Cl bonds (on average, 2.46 Å) practically does not differ from that measured previously[14] for decamethylzirconocene hydroxide chloride (2.48 Å). The distances from the zirconium atoms to the centers of the cyclopentadienyl rings, in general, differ only slightly from the data reported in the literature for a number of decamethylzirconocene derivatives, whereas the $Cp_{cent}(1)$—Zr—$Cp_{cent}(2)$ angles, equal to 143.3° and 146.2°, are much greater than their normal values.[15,16] A comparable value for this angle, equal to 147.4°, has been observed previously[17] only for $(C_5Me_5)_2Zr(CO)_2$.

The parameters of the ^1H and ^{13}C NMR spectra of complexes **4** and **5** are listed in Table 3. The signals for the C(2, 5) and C(3, 4) carbon atoms in the ^{13}C NMR spectra were assigned using selective decoupling from the protons of the Me(2—5) methyl groups; the signal of C(3, 4) was registered as a singlet, while that of C(2, 5) was a triplet due to coupling with the H(6) protons.

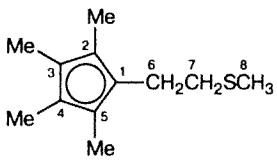
The fact that the parameters of the ^1H and ^{13}C NMR spectra of compounds **4** and **5** are almost identical makes it possible to state that the symmetrical complex **4** also contains no S→Zr coordination bond.

Crystal structure of complex 3. Compound **3** crystallizes in the monoclinic group $P2_1/c$. The molecule is dimeric and has a symmetry center; the zirconium atoms are connected *via* two bridge chlorine atoms Cl(1) and Cl(1a) (Fig. 2, Tables 4 and 5). The sulfur atom of

Table 3. Parameters of the ^1H and ^{13}C NMR spectra of compounds **2—5**

Compound	Solvent	T/°C	$\delta(^{13}C)$ ($^1J_{C,H}$/Hz)[a]							$\delta(^1H)$ ($^3J_{H,H}$/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)
2a	THF-d_8	30	11.85 (122)	109.55	105.91	105.29	27.69 (123)	38.33 (137)	15.25 (138)	1.97 (s); 1.99 (s)	2.69 (t, 7.6)	2.45 (t, 7.6)	2.04 (s)
4	THF-d_8	30	12.15 (127); 12.31 (127)	126.59	123.79	124.67	28.24 (130)	34.55 (139)	15.55 (137)	1.98 (s); 2.02 (s)	2.74 (t, 8.0)	2.43 (t, 8.0)	2.07 (s)
5	THF-d_8	30	12.08 (127); 12.23 (127); 12.20 (127) ($C_5\underline{Me}_5$)	126.42	123.55; 124.25 ($\underline{C}_5Me_5$)	124.39	28.17 (130)	34.55 (139)	15.56 (137)	1.98 (s); 2.01 (s); 1.97 (s) ($C_5\underline{Me}_5$)	2.74 (t, 8.0)	2.43 (t, 8.0)	2.07 (s)
3	THF-d_8	30	Me(2, 5) 14.17 (127)	Me(3, 4) 13.08 (127)	129.9	130.42	125.51	23.85 (130)	42.72 (142)	18.59 (142)	Me(2, 5) 2.21 (s)	Me(3, 4) 2.06 (s)	2.84 (t, 6.5)	3.16 (t, 6.5)	2.22 (s)
		−72	14.45; 14.28	13.31; 13.23	130.32	130.70; 130.30	125.44; 124.02	23.46	42.73	18.46	2.21 (s); 2.18 (s)	2.01 (s)	2.85 (m) 2.90 (m)	3.29 (m) 3.11 (m)	2.24 (s)
	CD_2Cl_2	30	13.50	13.01	*b*	*b*	*b*	22.93	42.68	19.39	2.22 (s)	2.12 (s)	2.87 (t, 6.4)	3.14 (t, 6.4)	2.29 (s)
		−95									2.13 (s); 2.09 (s)	1.99 (s); 1.98 (s)	2.84 (m); 2.71 (m)	3.11 (m); 2.93 (m)	2.20 (s)

[a] The numbering of atoms in compounds **2—5** is as follows:



. [b] The signal could not be accumulated due to the low solubility of the complex.

Table 4. Bond lengths (d) in the molecule of complex **3**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
Zr—Cl(1)	2.565(2)	C(1)—C(5)	1.437(9)	Zr—S	2.767(2)	C(2)—C(9)	1.50(1)
Zr—Cl(3)	2.452(2)	C(2)—C(3)	1.405(8)	Zr—C(2)	2.527(8)	C(3)—C(10)	1.49(1)
Zr—C(1)	2.531(6)	C(3)—C(4)	1.42(1)	Zr—C(4)	2.552(6)	C(4)—C(11)	1.48(1)
Zr—C(3)	2.511(8)	C(4)—C(5)	1.412(9)	Zr—Cl(1a)	2.735(2)	C(6)—C(7)	1.51(1)
Zr—C(5)	2.565(6)	C(5)—C(12)	1.47(1)	S—C(7)	1.809(6)	Zr—Zr(a)	4.291
Cl(1)—Zr(a)	2.735(2)	Cp_{cent}—Zr [a]	2.232	C(1)—C(2)	1.42(1)		
S—C(8)	1.78(1)	Zr—Cl(2)	2.441(2)	C(1)—C(6)	1.493(8)		

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

Table 5. Main bond angles (ω) in the molecule of complex **3**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Cl(1)—Zr—Cl(2)	90.6(1)	C(3)—C(4)—C(11)	126.9(7)	C(7)—S—C(8)	99.6(4)
Cl(2)—Zr—Cl(3)	92.6(1)	C(1)—C(5)—C(4)	107.3(6)	C(2)—C(1)—C(6)	126.7(6)
Cl(2)—Zr—S	159.6(1)	C(4)—C(5)—C(12)	126.0(6)	C(1)—C(2)—C(3)	107.9(6)
Cl(1)—Zr—Cl(1a)	71.9(1)	S—C(7)—C(6)	107.3(5)	C(3)—C(2)—C(9)	127.1(7)
Cl(3)—Zr—Cl(1a)	77.7(1)	Cp_{cent}—Zr—Cl(2)	105.0	C(2)—C(3)—C(10)	127.3(8)
Zr—Cl(1)—Zr(a)	108.1(1)	Cp_{cent}—Zr—S	95.3	C(3)—C(4)—C(5)	108.1(5)
Zr—S—C(8)	112.9(3)	Cl(1)—Zr—Cl(3)	148.6(1)	C(5)—C(4)—C(11)	124.6(7)
C(2)—C(1)—C(5)	108.1(5)	Cl(1)—Zr—S	82.9(1)	C(1)—C(5)—C(12)	125.9(6)
C(5)—C(1)—C(6)	124.9(6)	Cl(3)—Zr—S	83.3(1)	C(1)—C(6)—C(7)	112.4(6)
C(1)—C(2)—C(9)	124.5(6)	Cl(2)—Zr—Cl(1a)	81.3(1)	Cp_{cent}—Zr—Cl(1)[a]	102.8
C(2)—C(3)—C(4)	108.7(6)	S—Zr—Cl(1a)	78.3	Cp_{cent}—Zr—Cl(3)	106.5
C(4)—C(3)—C(10)	123.8(7)	Zr—S—C(7)	98.9(2)	Cp_{cent}—Zr—Cl(1)	172.0

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

the ligand is coordinated to the Zr atom, which is in agreement with the data reported for analogous complexes of Ti and Zr with $C_5H_4CH_2$ (tetrahydrofuran-2-yl),[1] $C_5H_4(CH_2)_2OMe$,[4] $C_5H_4(CH_2)_2NMe_2$,[7] and $C_5H_4(CH_2)_2$(pyrrolidino)[8] as ligands. An unusual feature is the octahedral coordination of zirconium atom with the bulky Period 3 atoms (Cl(1), Cl(2), Cl(3), Cl(1a), and S), which has been observed previously only in a few cases.[18,19]

It is noteworthy that Cl(1a) is *trans*-arranged with respect to the cyclopentadienyl ring (the Cp_{cent}—Zr—Cl(1a) angle is 172.0°) and "supplements" the square-pyramidal configuration usual for these systems to an octahedral configuration, the distortion of the initial square pyramid being relatively small. For example, the average value of the Cl(1)—Zr—Cl(2), Cl(2)—Zr—Cl(3), Cl(3)—Zr—S, and S—Zr—Cl(1) angles is 87.3°, which is only slightly greater than that for the dimer of pentamethylcyclopentadienyltrichlorozirconium, which is 83.0°. The Zr—Cl(1a) bond length is 2.735 Å; it is probably the longest among the known bonds in the $Zr(\mu\text{-}Cl)_2Zr$ bridged systems.[20,21]

The $Zr(\mu\text{-}Cl)_2Zr$ central fragment is a planar parallelogram with Zr—Cl(1) and Zr—Cl(1a) bond lengths of 2.565 and 2.735 Å, respectively. The Cl(1)—Zr—Cl(1a) angle is 71.9°, which is somewhat less than that in the related complex $(C_5Me_5ZrCl_3)_2$ (74.54°),[20] and in the indenylhafnium trichloride (75.66°)[21]. The geometry of the central fragment forces the bridge chlorine atoms to come closer to within a distance of 3.12 Å, while the sum of their van der Waals radii is 3.6 Å.

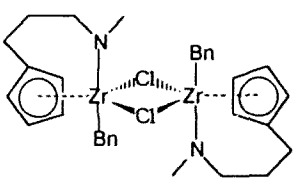
To the best of our knowledge, no structural data for cyclopentadienyl compounds of zirconium containing a donor-acceptor S→Zr bond have been reported. As should be expected, the bond length of 2.767 Å found by us proved to be much greater than that in the complexes incorporating the covalent S—Zr bond: for example, the sulfur—zirconium distance in $Cp_2Zr(SH)_2$ is 2.52 Å.[22]

NMR study of the dynamic behavior of complex 3 in solution. The parameters of the ^1H and ^{13}C NMR spectra of complex **3** are listed in Table 3. The signals of the protons of the Me(2, 5) and Me(3, 4) methyl groups were assigned using the homonuclear Overhauser effect with saturation of the H(6) protons. The signals of the C(2, 5) and C(3, 4) carbon atoms and also the signals of the corresponding methyl groups in the ^{13}C NMR spectrum were assigned using selective decoupling from the protons of the Me(2, 5) and Me(3, 4) groups. Since the simultaneous decoupling of both types of methyl protons is hampered due to the substantial difference between the chemical shifts in the ^1H NMR spectrum (see Table 3), the assignment of the signals of C(2, 5) and C(3, 4) was confirmed by recording the differential ^{13}C NMR spectra using the heteronuclear Overhauser effect with saturation of the signals of the protons of the Me(2, 5) and Me(3, 4) groups and with off-resonance irradiation of the sample.

We studied the dynamic behavior of compound **3** in solvating (THF-d_8) and nonsolvating (CD_2Cl_2) solvents over a broad temperature range by ^1H and ^{13}C NMR spectroscopy in order to find out whether or not the S→Zr bond and the dimeric structure of the complex are retained in solution, whether or not THF becomes coordinated, and whether conformational transformations in the Cp′—CH_2—CH_2—S(Me)—Zr moiety occur.

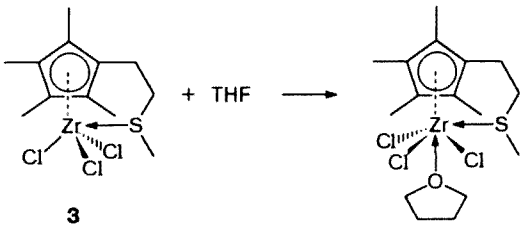
The $\delta(^1H)$ and $\delta(^{13}C)$ values for the SMe and, especially, for the SCH_2 fragment of complex **3** are markedly shifted downfield with respect to those for the dicyclopentadienyl derivatives **4** and **5**, which is consistent with coordination of sulfur with the metal.

It can be seen from Fig. 3 and Table 3 that when the temperature of solutions of compound **3** in THF-d_8 and CD_2Cl_2 decreases to −72 and −95 °C, respectively, the ^1H and ^{13}C NMR spectra exhibit signals corresponding to the four nonequivalent methyl groups in the Cp-ring and to the C(2—5) atoms, and a spin system of the ABXY type corresponding to the protons of the bridge methylene groups, which unambiguously points to the S→Zr coordination. The different characters of the multplicity (and, hence, different $^3J_{H,H}$ values) of the signals associated with the H(6a), H(6b), H(7a), and H(7b) protons in THF-d_8 and CD_2Cl_2 (see Fig. 3) indicate that the conformations of the five-membered metallocycles in these two solvents are dissimilar. The angles estimated from the vicinal spin-spin coupling constants in THF-d_8 ($^3J_{H(6a),H(7a)}$ = 4.2; $^3J_{H(6a),H(7b)}$ = 5.6; $^3J_{H(6b),H(7a)}$ = 4.8; $^3J_{H(6b),H(7b)}$ = 11.2 Hz) using the Karplus equation are in good agreement with the experimental values for the angles in the CH_2—CH_2 fragment found by X-ray diffraction analysis (Fig. 4). The geminal spin-spin coupling constants, in their turn, have normal values: $^2J_{H(6a),H(6b)}$ = 14.8; $^2J_{H(7a),H(7b)}$ = 12.6 Hz. The possibility of the formation of a dimeric structure of complex **3**, similar to that occurring in the crystal, should be ruled out in both solvents, because if this structure existed, the spectra recorded at any temperature would exhibit signals for four nonequivalent diastereotopic bridging protons and also for four nonequivalent methyl groups and for the C(2—5) carbon atoms of the ring, due to the presence of an asymmetric center at the Zr atom (the C_i symmetry), as has been observed[6] for the dimeric complex.



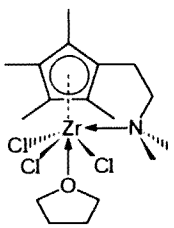
It is natural to suggest that the solvation of complex **3** in THF occurs according to Scheme 6.

Scheme 6



3 **3a**

This leads to complex **3a**, which is similar to the complex obtained recently.[7]



The weak temperature dependence of ^1H and ^{13}C NMR chemical shifts (in particular, those for the SCH_2 and SMe groups) in both solvents (see Table 3) implies that the donor—acceptor S→Zr bond in **3** is retained over the whole temperature range studied. Thus, the dynamic behavior of compound **3** in solution is probably governed by two processes: the inversion of the five-membered metallacycle shown in Fig. 4, and also, in the case of THF, by the additional coordination of the solvent.

The barriers to the ring inversion determined from the temperatures of coalescence of the signals of the protons in $C\underline{H}_2$—S (T_c = 234 K (THF-d_8) and 220 K (CD_2Cl_2)) are $\Delta G^{\#}$ = 11.2±0.2 and 10.5±0.2 kcal mol^{-1} in THF and dichloromethane, respectively. The increase in $\Delta G^{\#}$ by 0.7 kcal mol^{-1} on going from the nonsolvating solvent to THF is consistent with the fact that complex **3a** is sterically more hindered than **3**.

The degenerate inversion of the five-membered ring in complex **3** probably occurs as a rotation of the Cp-ring around the Cp_{cent}—Zr axis resulting in the mirror reflection of the whole structure with respect to the Zr—C(1)—C(6) plane and thus, in the case of the rapid exchange process, in an increase in the observed symmetry to C_s (a mirror plane that passes through Cp_{cent}, Zr, and S).

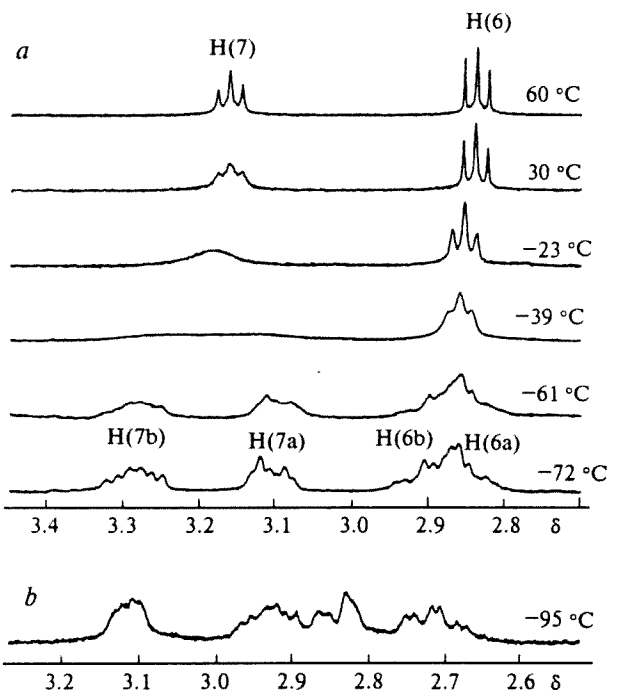


Fig. 3. Temperature dependence of the ^1H NMR spectrum of the Cp'CH_2CH_2S moiety in complex **3** in THF-d_8 (*a*) and CD_2Cl_2 (*b*).

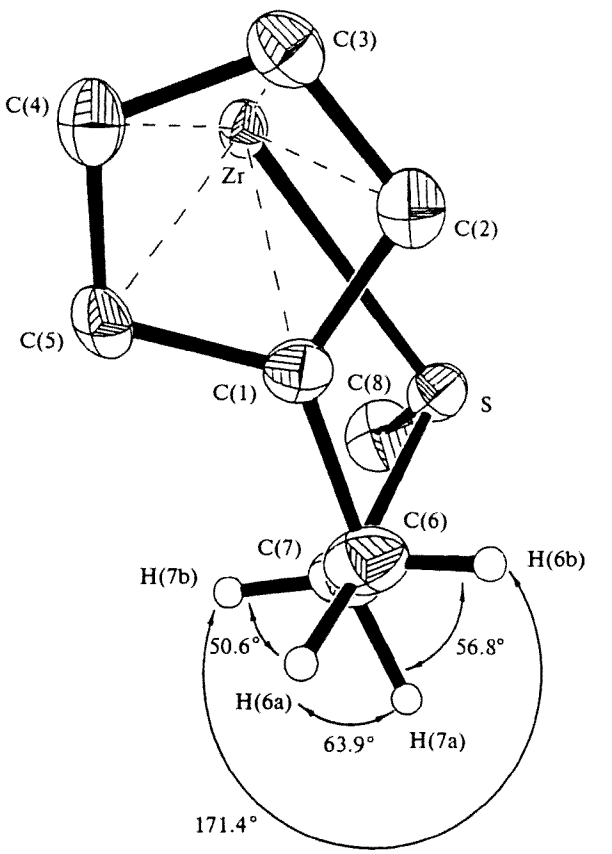


Fig. 4. Conformation of the Zr—C(1)—C(6)—C(7)—S five-membered metallacycle in molecule **3** and H—C—C—H dihedral angles in the $(CH_2)_2$ fragment (the chlorine atoms and the methyl groups in the Cp ring are not shown).

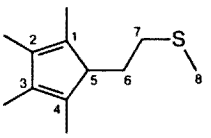
Experimental

The NMR spectra were recorded on a VXR-400 (400 MHz) instrument.

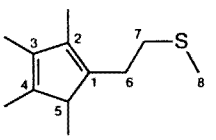
The starting cyclopentadiene **1** was synthesized in an atmosphere of dry argon using ordinary glassware. All other operations including the preparation of samples for NMR spectroscopy were carried out in seamless evacuated glass Schlenk type systems (the residual pressure was no more than $3 \cdot 10^{-3}$ Torr). The solvents were purified and dried according to the standard procedures. Commercial zirconium(IV) chloride (Merck) was used.

Z,E-2-Bromo-2-butene was synthesized by the standard three-step procedure involving dehydration of *sec*-butanol, bromination of *Z,E*-2-butenes, and dehydrobromination with KOH in ethylene glycol.[23] Ethyl 3-methylthiopropionate was prepared by the reaction of CH_2=CHCN with MeSH followed by hydrolysis of 3-methylthiopropionitrile to the corresponding acid, conversion of the acid into the corresponding chloride by treatment with PCl_3 in pyridine, and esterification by a standard procedure. 1,2,3,4,5-Pentamethylcyclopentadiene was obtained by a known procedure.[12] $(\eta^5\text{-}C_5Me_5)ZrCl_3$ was synthesized from lithium pentamethylcyclopentadienide and $ZrCl_4$ in diethyl ether[24] and was purified by sublimation under a high vacuum.[25]

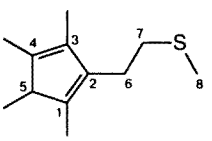
Tetramethyl(2-methylthioethyl)cyclopentadienes (a mixture of isomers 1a—c). Ethyl 3-methylthiopropionate (14.82 g, 0.1 mol) in 20 mL of diethyl ether was slowly added with vigorous stirring to a solution of 2-buten-2-yllithium prepared from lithium (3.0 g, 0.43 g-at.) and 2-bromobut-2-ene (27.0 g, 0.2 mol) in 200 mL of anhydrous diethyl ether by a standard procedure. The reaction mixture was stirred for 3 h at ~20 °C and left for 16 h. Then the mixture was poured into 500 mL of a saturated aqueous solution of NH_4Cl, the organic layer was separated, the aqueous layer was extracted three times with ether, and the combined extracts were dried with Na_2SO_4. The solution was concentrated to a volume of 30 mL and was slowly (over a period of 1 h) added to an intensely stirred mixture of *p*-toluenesulfonic acid hydrate (3.8 g, 20 mmol) and 100 mL of diethyl ether. The reaction mixture was stirred for an additional 3 h at ~20 °C and neutralized with a saturated solution of $NaHCO_3$. The organic phase and the combined ethereal extracts (three extractions) were dried with Na_2SO_4, the solvent was removed, and the residue was distilled *in vacuo*, the fraction at 115—124 °C (5 Torr) being collected. Repeated distillation gave 5.29 g (26.9 mmol, 26.9 %) of the target product. Further purification was carried out *via* the corresponding sodium (**2a**) or lithium (**2b**) derivative. The use of anhydrous *p*-TsOH (0.69 g, 10 mmol) in 50 mL of anhydrous ether makes it possible to obtain 2.42 g (12.3 mmol, 61 %) of cyclopentadiene **1** as a yellow oil, slowly oxidizable in air, from 4.26 g (20 mmol) of crude tertiary alcohol. The sample for the NMR identification of isomers **1a—c** was prepared by treating 60 mg of sodium derivative **2a** in 1 mL of anhydrous THF with glacial acetic acid with subsequent evaporation of excess acetic acid and of the solvent and molecular distillation of the product (10^{-3} Torr) repeated twice. The numbering of the atoms in the ^1H and ^{13}C NMR spectra of **1a—c** corresponds to that presented below.



1a



1b



1c

^1H NMR ($CDCl_3$), δ: 0.99 (d, $Me(5)_{b,c}$, $^3J_{H,H}$ = 7.6 Hz); 1.75—1.83 (all s, $Me(1—4)_{a,b,c}$); 1.93 (m, $H(6,7)_a$); 2.04 (s, $H(8)_a$); 2.11 (s, $H(8)_c$); 2.12 (s, $H(8)_b$); 2.48 (s, $H(6,7)_b$); 2.49 (m, $H(5)_b$); 2.52 (m, $H(7)_c$); 2.57 (m, $H(6)_c$); 2.62 (m, $H(5)_c$); 2.64 (m, $H(5)_a$). ^{13}C NMR ($CDCl_3$), δ: 10.99, 11.04, 11.20, 11.61, 11.67, 11.74 ($Me(1—4)_{a—c}$, *J* = 125 Hz); 11.00, 11.01 ($Me(5)_{b,c}$, *J* = 126 Hz); 15.58, 15.69 ($C(8)_{a,b,c}$, *J* = 138 Hz); 26.11 ($C(6)_b$, *J* = 128 Hz); 26.32 ($C(6)_c$, *J* = 128 Hz); 27.69 ($C(6)_a$, *J* = 130 Hz); 28.59 ($C(7)_a$, *J* = 139 Hz); 34.14 ($C(7)_b$, *J* = 138 Hz); 34.79 ($C(7)_c$, *J* = 138 Hz); 49.43 ($C(5)_c$, *J* = 123 Hz); 51.56 ($C(5)_b$, *J* = 121 Hz); 55.63 ($C(5)_a$, *J* = 121 Hz); 133.00, 134.05, 134.32, 135.94, 136.17, 136.93, 138.56, 138.78, 139.75, 140.24 ($C(1—4)_{a,b,c}$).

Sodium tetramethyl(2-methylthioethyl)cyclopentadienide (2a). A solution of cyclopentadiene **1** (5.29 g, 26.9 mmol) in 30 mL of THF was added to a heated suspension of sodium hydride (1.32 g, 55 mmol), from which nujol had been preliminarily washed out, in 10 mL of THF in an atmosphere of dry argon. The mixture was heated at reflux for 3 h. When the evolution of hydrogen ceased, the reaction vessel was evacuated and sealed off; all further operations were carried out in seamless glass apparatus. The solution was separated from excess NaH, and most of the solvent was removed. The precipitated large colorless crystals were separated from the mother liquor, recrystallized from THF, washed with anhydrous diethyl ether, and dried under high vacuum to give 2.73 g (12.5 mmol) of the pure product. A similar workup of the mother liquor afforded an additional 1.07 g (4.9 mmol) of the sodium derivative. The overall yield was 3.80 g (17.4 mmol, 64.6 %). The ^1H and ^{13}C NMR spectral data are presented in Table 3.

Lithium tetramethyl(2-methylthioethyl)cyclopentadienide (2b). A 1.47 *M* solution (8.4 mL, 12.4 mmol) of *n*-butyllithium in hexane was added with vigorous stirring to a solution of cyclopentadiene **1** (2.42 g, 12.32 mmol) in 50 mL of diethyl ether cooled to −30 °C. The mixture was allowed to warm to ~20 °C and left for ~16 h. The white clotted precipitate was filtered off and washed three times on the filter with the solvent mixture used. Then the solvent was evaporated, and the residue was recrystallized from THF, washed with pentane, and dried under a high vacuum. Yield 2.06 g (10.2 mmol, 82.7 %). The ^1H and ^{13}C NMR spectra of the product were similar to those of **2a**.

[η^5-Tetramethyl(2-methylthioethyl)cyclopentadienyl]trichlorozirconium(IV) (3). A suspension of lithium derivative **2b** (0.65 g, 3.21 mmol) in 50 mL of ether was added to a suspension of $ZrCl_4$ (0.75 g, 3.21 mmol) in 5 mL of pentane. The reaction mixture was boiled with vigorous stirring for 30 min and kept for ~16 h. The heavy thick precipitate was filtered off, washed twice with small portions of ether, dried, and sublimed five times *in vacuo* (10^{-3} Torr, 220 °C). The sublimate was recrystallized from 30 mL of THF, washed with ether, and dried *in vacuo* to give 0.81 g (2.06 mmol, 64.2 %)

Table 6. Crystallographic data, parameters of the X-ray diffraction experiments and refinement for compounds **3** and **5**

Parameter	**3**	**5**
Molecular formula	$Zr_2Cl_6S_2C_{24}H_{38}$	$ZrCl_2SC_{22}H_{34}$
Molecular weight	785.9	492.7
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P\bar{1}$
a/Å	8.709(5)	8.430(10)
b/Å	22.324(24)	14.337(9)
c/Å	8.535(7)	19.267(9)
α/deg		93.53(4)
β/deg	113.65(5)	96.83(5)
γ/deg		90.08(6)
V/Å^3	1520.0(4.3)	2307.6(4.0)
Z	2	4
ρ_{calc}/g cm^{-3}	1.717	1.418
$F(000)$	792.0	1024.0
Absorption coefficient/cm^{-1}	13.55	7.94
Radiation	Mo-Kα, graphite monochromator	Mo-Kα, graphite monochromator
λ	0.71069	0.71069
2θ-region/deg	$2 < 2\theta < 50$	$2 < 2\theta < 60$
Type of scanning	ω	θ/2θ
Total number of reflections	2447	6741
Number of independent reflections	2293	6557
Number of reflections with $I > 2\sigma(I)$	1671	6491
R_{int}	0.037	0.061
Number of refinement variables	230	743
$R = \Sigma\|\|F_0\| - \|F_c\|\|/\Sigma\|F_0\|$	0.037	0.052
$R_w = [\Sigma_w(\|F_0\| - \|F_c\|)^2/\Sigma_w(F_0)^2]^{1/2}$	0.040	0.054
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.003780F^2$	$w^{-1} = \sigma^2(F) + 0.003476F^2$
Quality factor	0.76	1.07
Residual electron density*	−0.79	−1.67
/$e \cdot$ Å^{-3}	0.88	2.10

* The minimum value is given in the numerator, and the maximum value is in the denominator.

of the product as light-yellow crystals moderately stable in air. Found (%): C, 35.57; H, 4.83. $C_{12}H_{19}Cl_3SZr$. Calculated (%): C, 36.68; H, 4.87. The crystals of **3** for X-ray structural study were obtained by sublimation *in vacuo*.

Bis[η^5-tetramethyl(2-methylthioethyl)cyclopentadienyl]dichlorozirconium(IV) (4). A solution of monocyclopentadienyl complex **3** (0.48 g, 1.22 mmol) in THF was mixed with a solution of sodium derivative **2a** (1.65 g, 1.60 mmol) in THF (total volume 50 mL), and the mixture was heated for 4 h at 70—80 °C. The solution was decanted from the precipitate, the precipitate was washed with THF, and the solvent was removed. The orange-yellow oil readily crystallizing even at room temperature was separated from the insoluble residue by extraction with ether and crystallized from pentane to give 0.45 g (0.81 mmol, 66.6 %) of colorless crystals. Found (%): C, 50.87; H, 6.78. $C_{24}H_{38}Cl_2S_2Zr$. Calculated (%): C, 52.14; H, 6.93.

[η^5-Pentamethylcyclopentadienyl][η^5-tetramethyl(2-methylthioethyl)cyclopentadienyl]dichlorozirconium(IV) (5). Complex **5** was prepared from $(\eta^5\text{-}C_5Me_5)ZrCl_3$ (0.66 g, 1.98 mmol) and sodium derivative **2a** (0.43 g, 1.98 mmol) similarly to **4**. Crystallization from ether gave 0.69 g (1.40 mmol, 70.7 %) of colorless crystals moderately stable in air. Found (%): C, 53.70; H, 6.92. $C_{22}H_{34}Cl_2S_2Zr$. Calculated (%): C, 53.63; H, 6.96. The crystals for X-ray diffraction analysis were prepared by crystallization from ether.

X-ray structural study of compounds 3 and 5. The data were collected and the unit cell parameters were determined on an Enraf-Nonius CAD-4 four-circle automatic diffractometer at room temperature. The data were corrected taking into account the Lorentz factor and polarization. The structures of **3** and **5** were solved by the direct method (SHELX-76) and refined in the full-matrix anisotropic approximation for nonhydrogen atoms; the hydrogen atoms were placed in the calculated positions and then refined isotropically. The characteristics and the results of the X-ray structural study are presented in Table 6. Bond lengths and angles are listed in Tables 1, 2, 4, and 5.

References

1. Y. Qian, G. Li, W. Chen, B. Li, and X. Jin, *J. Organomet. Chem.*, 1989, **373**, 185.
2. Q. Huang, Y. Qian, and Y. Tang, *J. Organomet. Chem.*, 1989, **368**, 277.
3. Q. Huang, Y. Qian, and Y. Tang, *Trans. Met. Chem.*, 1989, **14**, 315.
4. Q. Huang, Y. Qian, and Y. Tang, *Trans. Met. Chem.*, 1990, **15**, 483.
5. Y. Qian and G. Li, *Polyhedron*, 1993, **12**, 967.

6. A. K. Hughes, A. Meetsma, and J. H. Teuben, *Organometallics*, 1993, **12**, 1936.
7. P. Jutzi and J. Kleimeier, *J. Organomet. Chem.*, 1995, **486**, 287.
8. W. A. Herrmann, M. J. A. Morawietz, T. Priermeier, and K. Mashima, *J. Organomet. Chem.*, 1995, **486**, 291.
9. P. Jutzi and J. Dahlhaus, *Synthesis*, 1993, 684.
10. J. Szymoniak, J. Besancon, A. Dormond, and C. Moise, *J. Org. Chem.*, 1990, **55**, 1429.
11. T. Heidemann and P. Jutzi, *Synthesis*, 1994, 777.
12. R. S. Trelkel and J. E. Bercaw, *J. Organomet. Chem.*, 1977, **136**, 1.
13. K. H. Slotta and W. Franke, *Chem. Ber.*, 1930, **63**, 678.
14. R. Botolin, V. Patel, I. Munday, N. J. Taylor, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1985, 456.
15. R. D. Sanner, J. M. Manriques, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1976, **98**, 8351.
16. M. A. Busch and G. A. Sim, *J. Chem. Soc., A*, 1971, 2225.
17. D. J. Sikora, M. D. Rausch, R. D. Rogers, and J. L. Atwood, *J. Am. Chem. Soc.*, 1981, **103**, 1265.
18. D. L. Hughes, G. J. Leigh, and D. G. Walker, *J. Organomet. Chem.*, 1988, **355**, 113.
19. K. A. Butakoff, D. A. Lemenovskii, P. Mountford, L. G. Kuz'mina, and A. V. Churakov, *J. Chem. Soc., Dalton Trans.*, in press.
20. A. Martin, M. Mena, and F. Palacious, *J. Organomet. Chem.*, 1994, **480**, C10.
21. S. L. Shaw, R. J. Morris, and J. C. Huffman, *J. Organomet. Chem.*, 1995, **489**, C4.
22. W. A. Howard and G. Parkin, *Organometallics*, 1993, **12**, 2363.
23. A. S. Dreiding and R. J. Pratt, *J. Am. Chem. Soc.*, 1954, **76**, 1902.
24. J. H. Wengrovices and R. R. Schrock, *J. Organomet. Chem.*, 1981, **205**, 319.
25. J. Blenkers, H. J. De Liefde Meijer, and J. H. Teuben, *J. Organomet. Chem.*, 1981, **218**, 383.

Received October 4, 1995