Regioselectivity of reactions of vinyl- and isopropenylcyclopentadienide anions with electrophilic agents. Synthesis and crystal structures of complexes $[C_5H_4C(Me)=CH_2]ZrCl_3 \cdot 2THF$ and $[C_5Me_4CH=CH_2]ZrCl_3 \cdot 2THF$

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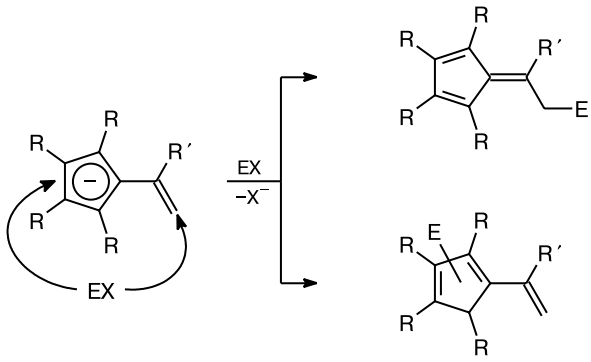
Regioselectivity of the reactions of lithium vinyl- and isopropenylcyclopentadienides $C_5H_4C(R)=CH_2^-Li^+$ (R = H, Me) and lithium tetramethylvinylcyclopentadienide $C_5Me_4CH=CH_2^-Li^+$ with various electrophilic agents (Me_3SiCl, Me_3SnCl, Et_2PCl, 2-chloro-1,3-dioxaphospholane, and MeI) was studied. Two new monocyclopentadienyl zirconium complexes, $[C_5H_4C(Me)=CH_2]ZrCl_3 \cdot 2THF$ and $[C_5Me_4CH=CH_2]ZrCl_3 \cdot 2THF$, were synthesized. Their crystal structures were established by X-ray diffraction. The results of quantum-chemical calculations for the $C_5H_4C(R)=CH_2^-$ (R = H, Me) and $C_5Me_4CH=CH_2^-$ anions by the DFT method (RMPW1PW91) with the 6-311+G(d,p) split-valence basis set are in good agreement with experimental data on the regioselectivity of their reactions with electrophilic agents.

Key words: vinylcyclopentadienide anion, isopropenylcyclopentadienide anion, electrophilic agents, regioselectivity, zirconium, X-ray diffraction analysis, NMR spectroscopy, quantum-chemical calculations.

Functionalized Cp ligands are widely used in organometallic chemistry. Of these compounds, various ethenylcyclopentadienes containing a double bond directly conjugated with the cyclopentadienyl ring are of great importance. In particular, this class of compounds includes the vinyl- and isopropenylcyclopentadienyl ligands, which were used in the synthesis of various sandwich and half-sandwich compounds with a wide range of transition and main-group metals.[1—10] Investigations of reactions of the vinyl- and isopropenylcyclopentadienide anions with electrophilic agents are of interest by themselves because these compounds contain two centers accessible to electrophilic attack, *viz.*, the Cp ring and the C_β atom of the ethenyl substituent (Scheme 1). The attack of an electrophilic organyl agent on the ethenyl group affords 7-substituted fulvene, which can be used to synthesize side-chain functionalized ligands. The attack on the ring gives rise to the corresponding heterosubstituted ethenylcyclopentadiene. Silylated, stannylated, and (with certain limitations) thalylated cyclopentadienes proved to be convenient reagents for the preparation of transition metal complexes.

Scheme 1



EX is an heteroorganic electrophilic agent

The aim of the present study was to investigate the regioselectivity of reactions of lithium vinyl- and isopropenylcyclopentadienides $C_5H_4C(R)=CH_2^-Li^+$ (R = H (**1**), Me (**2**)) and lithium tetramethylvinylcyclopentadienide $C_5Me_4CH=CH_2^-Li^+$ (**3**) with heteroorganic electrophilic agents (Me_3SiCl, Me_3SnCl, Et_2PCl,

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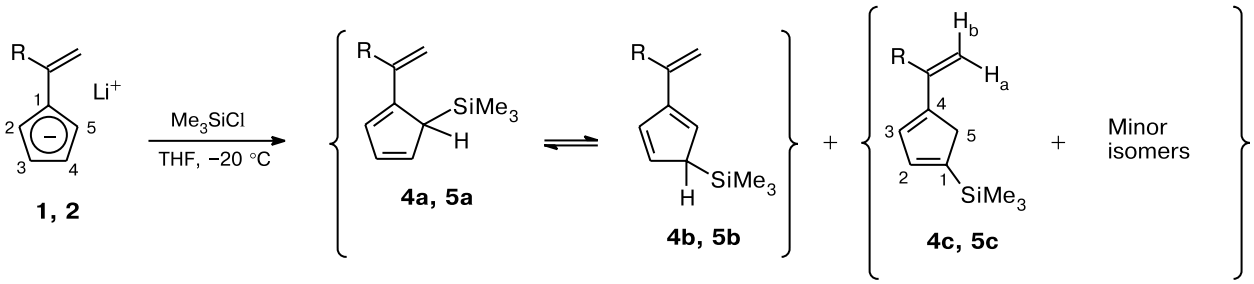
Scheme 2



R = H (**1**, **4a—c**), Me (**2**, **5a—c**)

2-chloro-1,3-dioxaphospholane) and, for comparison, with iodomethane as the simplest C-electrophilic agent. These reagents were used to synthesize two new monocyclopentadienyl zirconium complexes. The crystal structures of these complexes were established.

In addition, to reveal the electronic effect on the direction of electrophilic attack, it was of interest to carry out quantum-chemical calculations for the $C_5H_4C(R)=CH_2^-$ (R = H, Me) and $C_5Me_4CH=CH_2^-$ anions and analyze the electron density distribution in these anions.

Results and Discussion

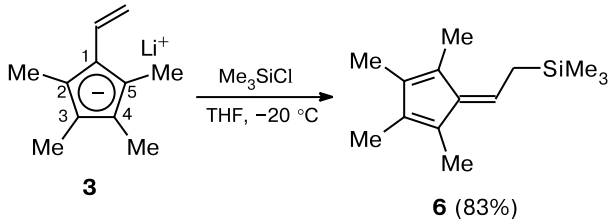
The starting vinylcyclopentadienyl salts **1—3** were synthesized according to known procedures[2,6,11] by deprotonation of the corresponding fulvenes. Salts **1—3** were isolated in the individual crystalline state. To obtain comparable results, the reactions of lithium vinylcyclopentadienides with heteroorganic electrophilic agents and iodomethane were carried out in the same fashion: a solution of the corresponding lithium salt was added with cooling to solutions of electrophilic agents (10—20% excess) in THF. After removal of the solvent and extraction with hexane, the products were distilled *in vacuo*. The structures of the products were established by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, including 2D COSY experiments and NOE difference spectra.

The reactions under study (unless they were accompanied by polymerization) proceeded smoothly and gave products in high total yields. However, in the case of salt **1**, only products of the reaction with Me_3SiCl were isolated. This is, apparently, attributable to the fact that the unsubstituted vinylcyclopentadienyl ring is highly prone to polymerization. Products isolated in the reactions of salt **2** with chlorodiethylphosphine and 2-chloro-1,3-dioxaphospholane, were also poly- or oligomers of unidentified structures.

Reactions of salts 1—3 with Me_3SiCl. We found that silylation of lithium vinylcyclopentadienide **1** and lithium isopropenylcyclopentadienide **2** occurs regioselectively at the Cp ring (Scheme 2) to give equilibrium mixtures of the corresponding isomeric cyclopentadienylsilanes **4a—c** and **5a—c** in total yields of 65 and 73%, respectively. These compounds undergo interconversions through elementotropic and prototropic rearrangements. For both silylated cyclopentadienes, the isomer ratio (**a** + **b**) : (**c** + minor vinyl isomers) was ~3 : 1, the isomer **c** prevailing (~80%) among isomers containing the Me_3Si group in the vinyl position. The structure analogous to cyclopentadienylsilane **5c** was assigned to isomer **4c**, whereas the structure of compound **5c** was unambiguously established by NMR spectroscopy. It should be noted that a mixture of silanes **4a—c** is unstable to heating and/or atmospheric oxygen. For example, product **4** was coated with a polymer film upon storage in air for a few hours. An attempt to distill compound **4** at high temperature (~80 °C, 7 Torr) leads to its polymerization. In this respect, silanes **5a—c** are much more stable.

Unlike monosubstituted cyclopentadienides **1** and **2**, silylation of tetramethylvinylcyclopentadienide **3** under the same conditions occurs regioselectively at the terminal C atom of the double bond to give one product, *viz.*, the corresponding fulvene **6** (Scheme 3).

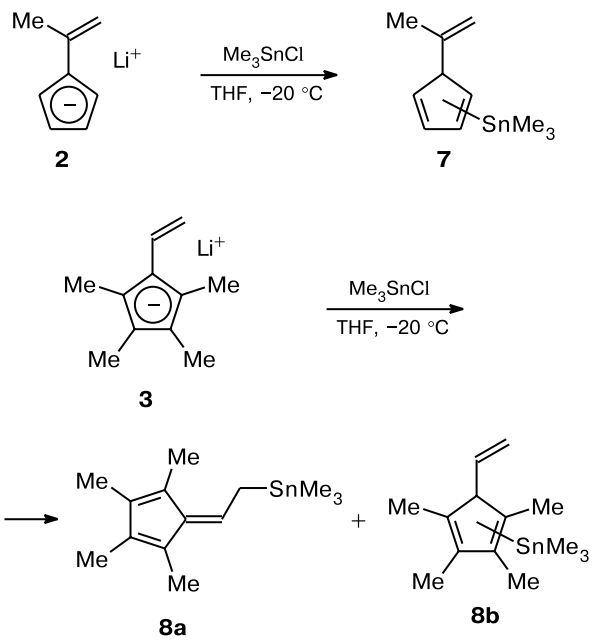
Scheme 3



Reactions of salts 2 and 3 with Me_3SnCl. Isopropenylcyclopentadienide **2** reacts with Me_3SnCl regioselectively at the Cp ring to form stannylated isopropenylcyclopentadiene **7** in 70% yield (Scheme 4). The reaction of tetramethylvinylcyclopentadienide **3** affords both possible

products, *viz.*, **8a** and **8b** (in a total yield of 86%), with fulvene-type product **8a** predominating (90%). Study of stannylated cyclopentadienes **7** and **8b** by NMR spectroscopy at room temperature demonstrated that these compounds exhibit dynamic behavior due to fast [1,2]-elementotropic shifts of the Me_3Sn group over the positions of the Cp ring.

Scheme 4



Reactions of salt 3 with phosphorus-containing electrophilic agents. The reaction of tetramethylvinylcyclopentadienide **3** with 2-chloro-1,3-dioxaphospholane occurs regioselectively to give vinylcyclopentadiene **9** in 68% yield (Scheme 5). The reaction product, like compound **8b**, exists as an equilibrium mixture of isomers at the dioxaphospholane substituent, which undergo rapid interconversion through [1,2]-elementotropic shifts.

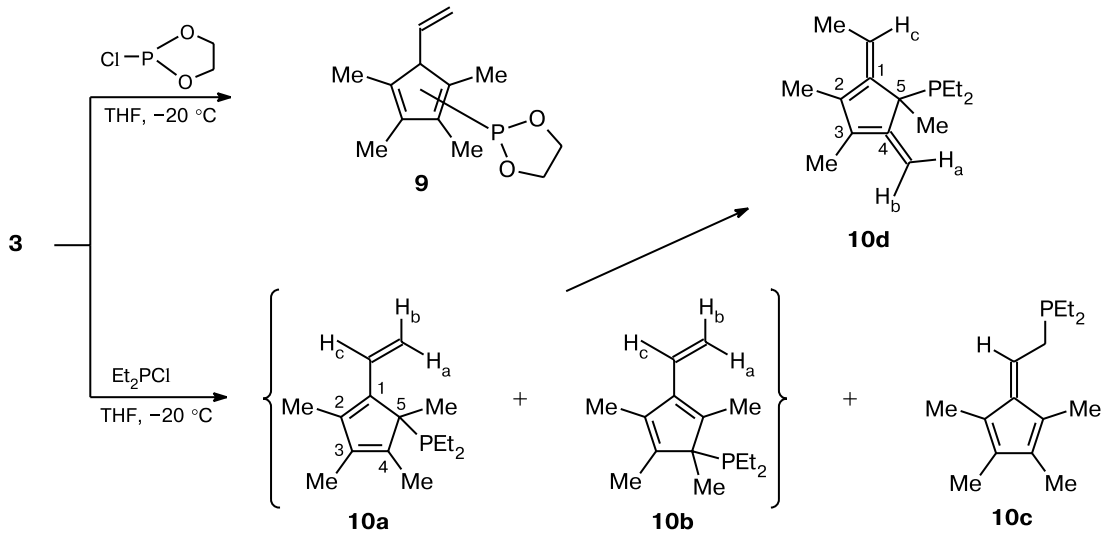
A more complex situation is observed in the reaction of salt **3** with chlorodiethylphosphine (see Scheme 5). The reaction affords a mixture of products of the electrophilic attack on both the Cp ring (**10a,b**) and the terminal C atom of the double bond (**10c**), with the attack on the Cp ring predominating (~5 : 1 ratio). At room temperature, the rate of the [1,2]-elementotropic shift in products **10a**,**b** is low, and the NMR spectra show narrow signals of both isomers.

In a solution at room temperature, compounds **10a**,**b** are slowly transformed into compound **10d** containing two exocyclic double bonds. We believe that this rearrangement is catalyzed by acidic admixtures, because the electrophilic reagent was used in excess.

It should be noted that the high-field part of the aliphatic region in the ^1H and ^{13}C NMR spectra of reaction products **10a—d** is difficult to interpret due to strong overlap of the signals. However, the signals in the most informative allyl and vinyl regions of the spectra were assigned unambiguously, which made it possible to reliably establish both the structures of the products and their ratios in the mixtures.

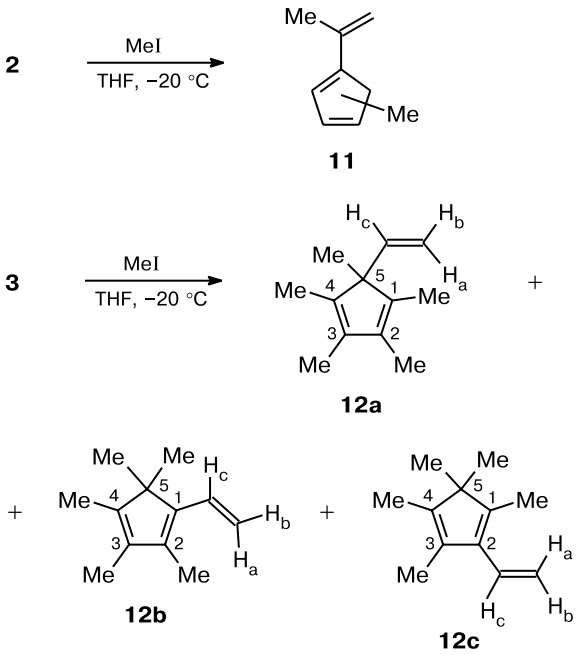
Reactions of salts 2 and 3 with MeI. Study of the reactions of salts **2** and **3** with iodomethane unambiguously demonstrated that both reactions involved exclusively the attack on the Cp ring (NMR spectra show no signals of the ethyl group) (Scheme 6). The reactions

Scheme 5



afford mixtures of isomeric (isopropenyl)methylcyclopentadienes **11** ($\leq$11 isomers at the Me group and the system of double bonds in a total yield of 72%) and pentamethyl(vinyl)cyclopentadienes **12a—c** (in a total yield of 84%), respectively. For the latter reaction, we made the complete assignment of the signals in the ^1H and ^{13}C NMR spectra and determined the isomeric composition of the mixture.

Scheme 6



12a : **12b** : **12c** = 1 : 1.6 : 1.3

Quantum-chemical calculations of anions 1—3 and analysis of regioselectivity of their reactions with electrophilic agents. Quantum-chemical calculations for the ground state of the $C_5H_4CH=CH_2^-$, $C_5H_4C(Me)=CH_2^-$, and $C_5(Me)_4CH=CH_2^-$ anions were carried out by the DFT method (RMPW1PW91)[12] with the 6-311+G(d,p) split-valence basis set with the inclusion of diffusion and polarization functions using the GAUSSIAN 98W program package.[13] To decrease the calculation time, the geometry of the anion was optimized in the conformation with the maximum possible symmetry (C_s). The wavefunctions for this conformation were tested for stability and then used to determine the Bader charges[14] by integrating over atomic basins with the use of the AIMPAC program package.[15]* The results of calculations are given in Table 1.

Analysis of the results of calculations revealed the following facts. First, if only the electronic factors are considered, the product of the attack on the C_β atom would not, under any circumstances, be the major product, and the attack on the ring is always the main process. Second, the expected percentage of the product of the attack on the C(7) atom can be predicted to increase with increasing rigidity of the electrophilic agent (sum of the squares of the orbital coefficients of two or three highest occupied molecular orbitals is taken into account), and this percentage is maximum in the limiting case of charge control. Third, the percentage of the product of the attack on the C(7) atom would be expected to increase in the case of the permethylated cyclopentadienide anion. Fourth, the introduction of the Me substituent at position 6 has virtually no effect on the expected product ratio.

In actuality, the attack on the C(7) atom was observed only in the reactions of sterically hindered lithium tetramethylvinylcyclopentadienide (**3**) with Me_3SiCl, Me_3SnCl, and Et_2PCl (percentage of the product of the attack on this atom was 100, 90, and 17%, respectively). It should be noted that the relative rigidity of the heteroorganic electrophilic agent decreases in the same order. However, even in the limiting case of charge control, the predicted percentage of the reaction product at the C(7) atom was at most 36%. Hence, in our opinion, the regioselectivity of the electrophilic attack on salt **3** is determined primarily by steric hindrance of the reagent, which decreases in the series Me_3SiCl > Me_3SnCl > > Et_2PCl ≫ 1,3-dioxaphospholane ≈ MeI.

Synthesis of zirconium half-sandwich complexes. We synthesized two new monocyclopentadienyl zirconium complexes, *viz.*, $[C_5H_4C(Me)=CH_2]ZrCl_3 \cdot 2THF$ (**13**) and $[C_5Me_4CH=CH_2]ZrCl_3 \cdot 2THF$ (**14**) (Scheme 7). Complex **13** was prepared by the reaction of the $ZrCl_4 \cdot 2THT$ adduct (THT is tetrahydrothiophene) with silylated cyclopentadiene **5**. Since the reaction of lithium tetramethylvinylcyclopentadienide with Me_3SiCl did not afford an analogous silane (see Scheme 3), half-sandwich complex **14** was synthesized starting from salt **3** and $ZrCl_4 \cdot 2THT$. Both complexes were isolated as solvates containing two THF molecules. The latter reaction produced a small amount of the sandwich complex $[C_5Me_4CH=CH_2]_2ZrCl_2$ (**15**) as an impurity, and the target product was purified by recrystallization from THF. Sandwich **15** was not isolated in the pure form. Complexes **13** and **14** do not form stable solvates with tetrahydrothiophene (integrated intensity of its signals in the ^1H NMR spectra corresponds to the composition $Cp'ZrCl_3 \cdot \sim 0.6THT$). Therefore, these complexes were isolated as stable adducts containing two THF molecules. These complexes are very sensitive to atmospheric oxygen. Even short exposure of solid compounds **13** and **14** to atmospheric oxygen leads (during dissolution under high vacuum) to their irreversible polymerization. The same process occurs during melting accompanied by the loss of the solvation solvent. In this case, autocatalysis

* The AIMPAC program package can be downloaded free of charge from Internet at http//www.chemistry.mcmaster.ca/aimpac/download/aimpac.zip.

Table 1. Total Bader atomic charges (q) and the sums of the squares of the HOMO orbital coefficients (wavefunctions RMPW1PW91 6-311+G(d,p)) in the competitive positions of the ring in anions **1—3** (the atomic numbering is given in Schemes 2 and 3)

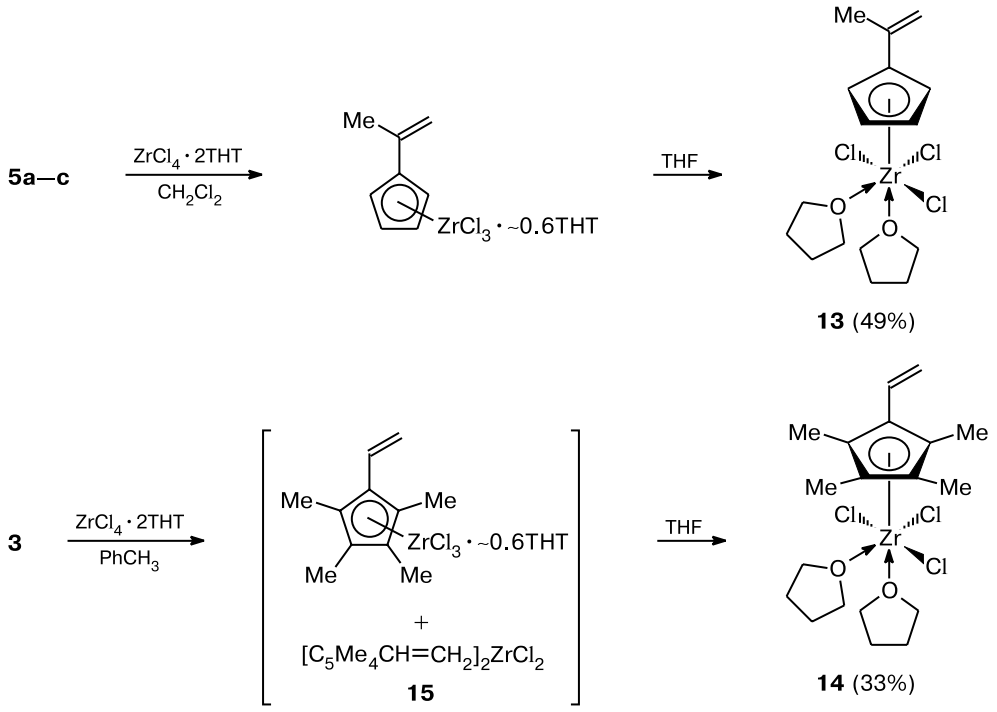
Atom	$-q$/e	Sum of squares of HOMO orbital coefficients[a]	Estimated ratio of alkylation products	
			charge control	orbital control[a]
		Anion **1**		
C(1)	0.0451	0.1863/0.1520	1.00 (6.7%)	1.00 (16.0%)/1.00 (16.4%)
C(2) + C(5)	0.2283[b]	0.3603/0.3435[c]	5.06 (33.8%)	1.93 (30.9%)/2.26 (37.1%)
C(3) + C(4)	0.2413[b]	0.3840/0.3035[c]	5.35 (35.7%)	2.06 (32.9%)/2.00 (32.8%)
C(6)	0.0362	0.1239/0.0028	—	—
C(7)	0.1611	0.2356/0.1270	3.57 (23.8%)	1.26 (20.2%)/0.84 (13.7%)
		Anion **2**		
C(1)	0.0571	0.1577/0.1486	1.00 (8.3%)	1.00 (13.9%)/1.00 (16.1%)
C(2) + C(5)	0.2301[b]	0.3597/0.3483[c]	4.03 (33.5%)	2.28 (31.8%)/2.34 (37.6%)
C(3) + C(4)	0.2426[b]	0.3712/0.3066[c]	4.23 (35.2%)	2.35 (32.8%)/2.06 (33.1%)
C(6)	0.0062	0.1246/0.0043	—	—
C(7)	0.1575	0.2443/0.1216	2.76 (23.0%)	1.55 (21.6%)/0.82 (13.1%)
		Anion **3**		
C(1)	0.0537	0.1515/0.1477	1.00 (11.3%)	1.00 (12.1%)/1.00 (14.4%)
C(2) + C(5)	0.1161[b]	0.4088/0.3775[c]	2.16 (24.4%)	2.70 (32.7%)/2.56 (36.9%)
C(3) + C(4)	0.1352[b]	0.4586/0.3695[c]	2.52 (28.4%)	3.03 (36.7%)/2.50 (36.1%)
C(6)	0.0455	0.1069/0.0014	—	—
C(7)	0.1710	0.2315/0.1296	3.18 (35.9%)	1.53 (18.5%)/0.88 (12.7%)

[a] The coefficients at AOs of three (E < 0.1 eV)/two (E < 0.015 eV) HOMOs with similar energies were taken into account.

[b] The total charges were summed for pairs of the equivalent atoms (C(2), C(5) and C(3), C(4)).

[c] The squares of the orbital coefficients at AOs were summed for pairs of the equivalent atoms (C(2), C(5) and C(3), C(4)).

Scheme 7



THT is tetrahydrothiophene

Table 2. Selected bond lengths (d) and bond angles (ω) in complexes **13** and **14**

Bond	d/Å	Angle	ω/deg
	Complex **13**		
Zr—O(1)	2.322(3)	O(1)—Zr—O(2)	75.2(1)
Zr—O(2)	2.369(3)	O(1)—Zr—Cl(3)	155.69(9)
Zr—Cl(3)	2.441(2)	O(2)—Zr—Cl(3)	80.46(9)
Zr—Cl(1)	2.474(1)	O(1)—Zr—Cl(1)	82.58(9)
Zr—Cl(2)	2.495(2)	O(2)—Zr—Cl(1)	77.36(9)
Cp_{cent}*—Zr	2.242	Cl(3)—Zr—Cl(1)	92.19(6)
C(6)—C(7)	1.372(8)	O(1)—Zr—Cl(2)	83.62(9)
C(6)—C(8)	1.446(8)	O(2)—Zr—Cl(2)	76.84(9)
C(1)—C(6)	1.464(7)	Cl(3)—Zr—Cl(2)	90.95(6)
		Cl(1)—Zr—Cl(2)	153.10(5)
		C(7)—C(6)—C(8)	121.4(6)
		C(7)—C(6)—C(1)	120.4(6)
		C(8)—C(6)—C(1)	118.1(6)
	Complex **14**		
Zr—O(1)	2.3033(13)	O(1)—Zr—O(2)	73.64(5)
Zr—O(2)	2.4168(13)	O(1)—Zr—Cl(2)	153.18(4)
Zr—Cl(2)	2.4695(5)	O(2)—Zr—Cl(2)	79.76(4)
Zr—Cl(3)	2.4841(5)	O(1)—Zr—Cl(3)	86.60(4)
Zr—Cl(1)	2.4963(5)	O(2)—Zr—Cl(3)	76.27(4)
Cp_{cent}*—Zr	2.268	Cl(2)—Zr—Cl(3)	90.422(18)
C(6)—C(7)	1.331(3)	O(1)—Zr—Cl(1)	83.78(4)
		O(2)—Zr—Cl(1)	77.71(3)
		Cl(2)—Zr—Cl(1)	87.371(17)
		Cl(3)—Zr—Cl(1)	153.864(17)

* Cp_{cent} is the center of the cyclopentadienyl ring.

apparently occurs (complex acts simultaneously as the catalyst and the substrate), because the metal center is a strong Lewis acid.

Crystal structures of complexes 13 and 14. Selected bond lengths and bond angles in complexes **13** and **14** are given in Table 2. In these complexes, the central Zr atom (Figs 1 and 2) is in a pseudooctahedral environment (assuming that the Cp ligand occupies one coordination site). The Cp fragment and one THF molecule occupy the apical positions, whereas three Cl atoms and the second THF molecule lie in the equatorial plane.

This coordination polyhedron is most favorable for monocyclopentadienyl derivatives of Zr^{IV}.[16—20] Exceptions are compounds, in which steric hindrance caused by the functionalized Cp ligand is too high to form such a structure.[21] Analysis of the structures retrieved from the Cambridge Structural Database[22] demonstrated that the Zr—Cl distances in complexes **13** and **14** (2.441(2)—2.4963(5) Å) fall in a range typical of the terminal Zr^{IV}—Cl bonds in monocyclopentadienyl derivatives of zirconium (2.357—2.542 Å). On the whole, the coordination environment of the Zr atom in compounds **13** and **14** is similar to that observed earlier in the related complexes $(CpR)ZrCl_3 \cdot 2THF$ (R = H, Me).[23]

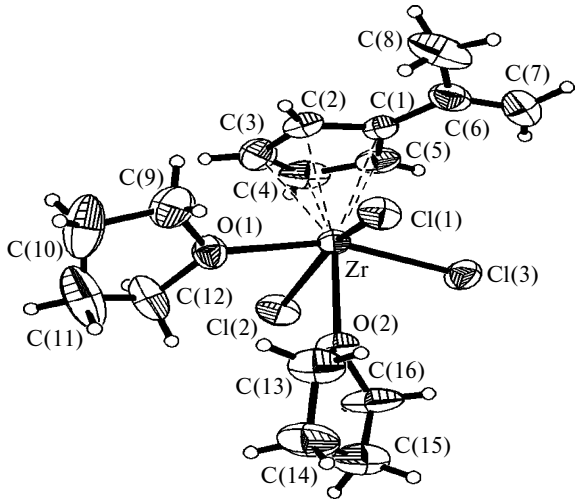


Fig. 1. Molecular structure of complex **13**.

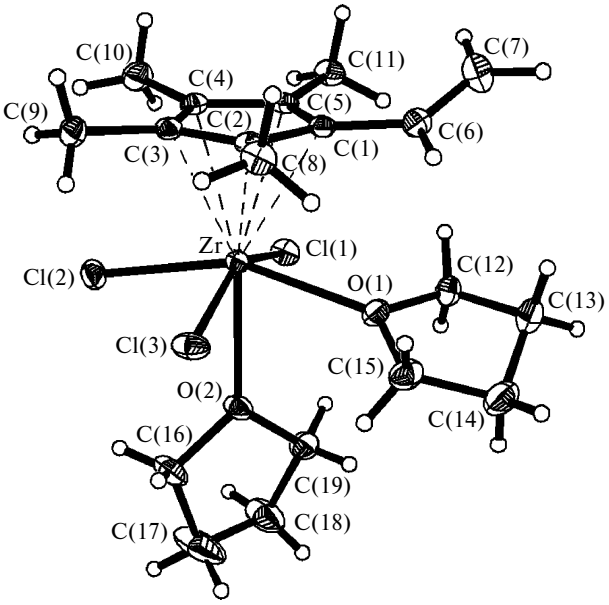


Fig. 2. Molecular structure of complex **14**.

The cyclopentadienyl ligands in complexes **13** and **14** are planar within 0.011 Å. The atoms of the double bonds conjugated with the Cp ligands lie virtually in the plane of the cyclopentadienyl rings. The C(7)—C(6)—C(1)—C(5) torsion angle is 8.7 and 21.7° in compounds **13** and **14**, respectively.

Experimental

All operations associated with the synthesis, reactions with electrophilic agents, and preparation of samples for NMR spectroscopy were carried out in an inert atmosphere or in all-sealed evacuated Schlenk type vessels. The solvents (including deuterated solvents), iodomethane, and chlorotrimethylsilane were

purified according to standard procedures.[24] Commercial Me_3SnCl, Et_2PCl, and $ZrCl_4$ were used. Chlorodiethylphosphine was additionally purified by vacuum distillation. Lithium vinylcyclopentadienide (**1**),[2,11] lithium isopropenylcyclopentadienide (**2**),[11] and 2-chloro-1,3-dioxaphospholane[25] were synthesized according to known procedures. The $ZrCl_4 \cdot 2THT$ adduct[26,27] was prepared by the reaction of $ZrCl_4$ with tetrahydrothiophene (2.5 equiv.) in CH_2Cl_2.

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian VXR-400 spectrometer (400, 100, and 162 MHz, respectively) at 25 °C. For the ^1H and ^{13}C NMR spectra, the chemical shifts of the signals of the corresponding deuterated solvents (δ 5.32 and 53.8 for CD_2Cl_2, δ 1.73 and 25.3 for THF-d_8, δ 7.15 and 128.0 for C_6D_6) were used as the internal standards. The mass spectra were measured on Kratos-MS-890 and Varian MAT CH7a Fa spectrometers. Elemental analysis was carried out on an automated Carlo-Erba analyzer.

Lithium tetramethylvinylcyclopentadienide (3) was prepared according to a known procedure[6] by deprotonation of 1,2,3,4,6-pentamethylfulvene with lithium diispropylamide in THF. The yield was 86% (white crystalline powder). ^1H NMR (THF-d_8), δ: 1.78 and 1.92 (both s, 6 H, Me); 4.27 (dd, 1 H, H_b, $^2J_{H,H}$ = 2.8 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz); 4.67 (dd, 1 H, H_a, $^2J_{H,H}$ = 2.8 Hz, *trans*-$^3J_{H,H}$ = 17.6 Hz); 6.56 (dd, 1 H, H_c, *trans*-$^3J_{H,H}$ = 17.6 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz). ^{13}C NMR, δ: 10.66 and 11.99 (both q, Me, $^1J_{C,H}$ = 124 Hz); 99.80 (br.t, $=CH_2$, $^1J_{C,H}$ = 160 Hz); 109.02 and 110.07 (both s, C(2)—C(5)); 111.33 (s, C(1)); 134.12 (d, =CH, $^1J_{C,H}$ = 143 Hz). The ^1H NMR spectrum agrees well with the published data.[6]

Reactions of salts 1—3 with electrophilic agents (general procedure). A solution of the corresponding lithium salt in THF was added with vigorous stirring to a solution of the electrophilic reagent (10—20% excess) in THF at −20 °C. The reaction mixture was heated to ~20 °C and allowed to stand for ~12 h. Then the solvent was removed *in vacuo*, hexane was added in an amount corresponding to one-half of the volume of the THF distilled, the inorganic salt was separated by filtration, and the residue was concentrated. The product was isolated by high vacuum distillation (molecular distillation; the residual pressure of noncondensable gases $\leq 4 \cdot 10^{-3}$ Torr) unless otherwise indicated.

(Trimethylsilyl)vinylcyclopentadiene (4) (mixture of isomers). The starting reagents: salt **1** (2.28 g, 23.2 mmol) in THF (10 mL), Me_3SiCl (2.77 g, 25.5 mmol) in THF (10 mL). After high vacuum distillation, a yellow oily product was obtained in a yield of 2.48 g (65%). ^1H NMR (C_6D_6), δ: −0.12 and −0.08 (both br, $SiMe_3$ (**4a**, **4b**)); 0.11 (s, $SiMe_3$ (**4c**)); 3.04 (t, $>CH_2$ (**4c**), $^4J_{H,H}$ = 1.2 Hz); 3.19 and 3.38 (both br, >CH (**4a**, **4b**)); 4.95—5.53 ($=CH_2$); 6.20—6.90 (=CH).

(Trimethylsilyl)isopropenylcyclopentadiene (5) (mixture of isomers). The starting reagents: salt **2** (2.70 g, 24.1 mmol) in THF (10 mL), Me_3SiCl (3.01 g, 27.7 mmol) in THF (10 mL). After high vacuum distillation, a yellow oily product was obtained in a yield of 3.14 g (73%), b.p. 92—93 °C (7 Torr). Found (%): C, 74.03; H, 10.07. $C_{11}H_{18}Si$. Calculated (%): C, 74.08; H, 10.17. ^1H NMR (C_6D_6), δ: −0.11 (br.s, $SiMe_3$ (**5a**, **5b**)); 0.13 (s, $SiMe_3$ (**5c**)); 1.91 (m, Me (**5c**)); 1.98 (br, Me (**5a**, **5b**)); 3.13 (t, $>CH_2$ (**5c**), $^4J_{H,H}$ = 1.3 Hz); 3.23 and 3.53 (both br, >CH (**5a**, **5b**)); 4.85 (m, H_b (**5c**)); 4.97 and 5.36 (both br, $=CH_2$ (**5a**, **5b**)); 5.14 (m, H_a (**5c**)); 6.33, 6.40, and 6.91 (all br, =CH (**5a**, **5b**)); 6.37 (m, H(3) (**5c**)); 6.70 (m, H(2) (**5c**)). NOE effects for isomer **5c** (%): η_{SiMe_3}(H(5)) = 0.9; η_{H_a}(H(5)) = 6.9; $\eta_{H(2)}$($SiMe_3$) = 5.0; $\eta_{H(5)}$($SiMe_3$) = 2.0. ^{13}C—{^1H} NMR, δ: −2.11 ($SiMe_3$ (**5a**, **5b**)); −0.78 ($SiMe_3$ (**5c**)); 20.87 (Me (**5c**)); 21.27 (br.s, Me (**5a**, **5b**)); 43.97 ($>CH_2$ (**5c**)); 52.06 (br.s, >CH (**5a**, **5b**)); 110.94 (br.s, $=CH_2$ (**5a**, **5b**)); 111.25 (s, $=CH_2$ (**5c**)); 129.02 and 133.96 (both br, =CH (**5a**, **5b**)); 129.68, 142.48 (=CH (**5c**)); 139.11 (br, Me<u>C</u>= (**5a**, **5b**)); 139.37 (Me<u>C</u>= (**5c**)); 146.0 (br, =C— (**5a**, **5b**)); 147.11, 153.38 (=C— (**5c**)). MS (GC/MS, EI, 70 eV, 280 °C), *m/z* (I_{rel} (%)): 178 $[M]^+$ (6.1), 163 $[M - Me]^+$ (3.4), 73 $[Me_3Si]^+$ (100).

1,2,3,4-Tetramethyl-6-(trimethylsilylmethyl)fulvene (6). The starting reagents: salt **3** (1.28 g, 8.3 mmol) in THF (15 mL), Me_3SiCl (1.00 g, 9.2 mmol) in THF (10 mL). After high vacuum distillation, an orange oily product was obtained in a yield of 1.51 g (83%). Found (%): C, 76.28; H, 11.04. $C_{14}H_{24}Si$. Calculated (%): C, 76.28; H, 10.97. ^1H NMR (C_6D_6), δ: −0.01 (s, 9 H, $SiMe_3$); 1.81 (s, 6 H, CMe); 2.04 (s, 3 H, CMe); 2.10 (d, 2 H, CH_2, $^3J_{H,H}$ = 10.0 Hz); 2.23 (s, 3 H, CMe); 6.24 (t, 1 H, =CH, $^3J_{H,H}$ = 10.0 Hz). ^{13}C NMR, δ: −1.63 (q, $SiMe_3$, $^1J_{C,H}$ = 119 Hz); 9.91, 11.03, 11.41, and 14.39 (all q, C<u>C</u>H_3, $^1J_{C,H}$ = 125 Hz); 21.84 (t, CH_2, $^1J_{C,H}$ = 123 Hz); 122.49, 124.98, 133.97, 139.01, and 144.73 (all s, =C); 130.07 (d, =CH, $^1J_{C,H}$ = 148 Hz). MS (GC/MS, EI, 70 eV, 280 °C), *m/z* (I_{rel} (%)): 220 $[M]^+$ (7.9), 205 $[M - Me]^+$ (1.1), 147 $[M - Me_3Si]^+$ (4.5), 146 $[M - Me_3SiH]^+$ (21.9), 131 $[M - Me - Me_3SiH]^+$ (16.0), 73 $[Me_3Si]^+$ (100).

(Trimethylstannyl)isopropenylcyclopentadiene (7). The starting reagents: salt **2** (0.25 g, 2.23 mmol) in THF (5 mL), Me_3SnCl (0.53 g, 2.68 mmol) in THF (5 mL). After high vacuum distillation, a yellow oily product was obtained in a yield of 0.42 g (70%). Found (%): C, 49.01; H, 6.64. $C_{11}H_{18}Sn$. Calculated (%): C, 49.12; H, 6.75. ^1H NMR (C_6D_6), δ: −0.06 (s, 9 H, $SnMe_3$, $^2J_{H,Sn}$ = 53.7 Hz); 1.99 (m, 3 H, Me); 4.87 (m, 1 H, =C<u>H</u>H); 5.13 (m, 1 H, =CH<u>H</u>); 5.85 and 5.93 (both t, 2 H each, H(2)—H(5), $^{3+4}J_{H,H}$ = 3.6 Hz). ^{13}C—{^1H} NMR, δ: −8.73 ($SnMe_3$, $^1J_{C,Sn}$ = 341 Hz); 21.47 (Me); 102.34, 114.04 (CH(2), CH(5)); 109.28 ($=CH_2$); 139.29, 144.76 (C(1), =<u>C</u>Me). MS (GC/MS, EI, 70 eV, 280 °C), *m/z* (I_{rel} (%)): 270 $[M]^+$ (11.2), 255 $[M - Me]^+$ (5.7), 225 $[M - 3\ Me]^+$ (18.7), 165 $[Me_3Sn]^+$ (100), 105 $[M - Me_3Sn]^+$ (15.1), 79 $[M - Me - Me_3SnH]^+$ (26.5).

Reaction of salt 3 with chlorotrimethylstannane (mixture of isomers 8a and 8b). The starting reagents: salt **3** (0.34 g, 2.21 mmol) in THF (10 mL), Me_3SnCl (0.48 g, 2.41 mmol) in 5 mL THF. After high vacuum distillation, an orange oily mixture of products was obtained in a yield of 0.59 g (86%). Found (%): C, 54.37; H, 7.89. $C_{14}H_{24}Sn$. Calculated (%): C, 54.06; H, 7.78. MS (GC/MS, EI, 70 eV, 280 °C), *m/z* (I_{rel} (%)): 312 $[M]^+$ (74.8), 297 $[M - Me]^+$ (19.8), 267 $[M - 3\ Me]^+$ (38.1), 165 $[Me_3Sn]^+$ (100), 147 $[M - Me_3Sn]^+$ (29.4), 146 $[M - Me_3SnH]^+$ (12.3), 131 $[M - Me - Me_3SnH]^+$ (13.6).

<u>Isomer **8a**</u> (90%). ^1H NMR (C_6D_6), δ: 0.05 (s, 9 H, $SnMe_3$, $^2J_{H,Sn}$ = 53.2 Hz); 1.84 (s, 6 H, CMe); 1.97 and 2.15 (both s, 3 H each, CMe); 2.26 (d, 2 H, CH_2, $^3J_{H,H}$ = 10.4 Hz, $^2J_{H,Sn}$ = 74.7 Hz); 6.30 (t, 1 H, =CH, $^3J_{H,H}$ = 10.4 Hz, $^3J_{H,Sn}$ = 11.7 Hz). ^{13}C NMR, δ: −9.52 (q, $SnMe_3$, $^1J_{C,H}$ = 128 Hz, $^1J_{C,Sn}$ = 323 Hz); 9.95, 11.04, 11.46, and 14.59 (all q, C<u>C</u>H_3, $^1J_{C,H}$ = 124 Hz); 17.26 (t, CH_2, $^1J_{C,H}$ = 132 Hz, $^1J_{C,Sn}$ = 252 Hz); 122.14, 124.55, 133.27, 137.92, and 141.98 (all s, =C); 133.13 (d, =CH, $^1J_{C,H}$ = 147 Hz, $^2J_{C,Sn}$ = 56 Hz).

Isomer **8b** (10%). ^{1}H NMR (C_6D_6), δ: –0.05 (s, 9 H, $SnMe_3$, $^2J_{H,Sn}$ = 50.8 Hz); 1.79 and 1.83 (both s, 6 H, CMe); 5.07 (dd, 1 H, H_b, $^2J_{H,H}$ = 2.0 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz); 5.25 (dd, 1 H, H_a, $^2J_{H,H}$ = 2.0 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz); 6.67 (dd, 1 H, H_c, *cis*-$^3J_{H,H}$ = 11.6 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz).

(1,3-Dioxaphospholan-2-yl)tetramethylvinylcyclopentadiene (9). The starting reagents: salt **3** (1.42 g, 9.21 mmol) in THF (20 mL), 2-chloro-1,3-dioxaphospholane (1.40 g, 11.05 mmol) in THF (10 mL). After high vacuum distillation, a yellow-orange oily product was obtained in a yield of 1.49 g (68%). ^{1}H NMR (C_6D_6), δ: 1.67 (br.s, 6 H, Me); 1.83 (s, 6 H, Me); 3.36 and 3.69 (both m, 2 H, CH_2O); 5.24 (dd, 1 H, H_b, $^2J_{H,H}$ = 2.0 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz); 5.47 (dd, 1 H, H_a, $^2J_{H,H}$ = 2.0 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz); 6.78 (dd, 1 H, H_c, *cis*-$^3J_{H,H}$ = 11.6 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz). ^{13}C NMR, δ: 11.40 and 12.25 (both q, Me, $^1J_{C,H}$ = 127 Hz); 65.44 (td, CH_2O, $^1J_{C,H}$ = 150 Hz, $^2J_{C,P}$ = 8.9 Hz); 113.71 (t, $=CH_2$, $^1J_{C,H}$ = 157 Hz); 131.01 (d, =CH, $^1J_{C,H}$ = 151 Hz); 134.1 (v.br, =C); 136.6 (br, =C). ^{31}P—{^{1}H} NMR, δ: 164.3 (s). MS (GC/MS, EI, 70 eV, 280 °C), *m/z* (I_{rel} (%)): 238 $[M]^+$ (15.7), 223 $[M - Me]^+$ (17.8), 147 $[M - (OCH_2CH_2O)P]^+$ (19.1), 146 $[M - (OCH_2CH_2O)PH]^+$ (21.6), 131 $[M - Me - (OCH_2CH_2O)PH]^+$ (18.7), 91 $[(OCH_2CH_2O)P]^+$ (100).

Reaction of salt 3 with chlorodiethylphosphine (mixture of isomers 10a—d). The starting reagents: salt **3** (2.25 g, 14.6 mmol) in THF (20 mL), chlorodiethylphosphine (2.22 g, 17.8 mmol) in THF (10 mL). After high vacuum distillation, an orange oily mixture of products was obtained in a yield of 2.41 g (70%).

Isomer **10a**. ^{1}H NMR (C_6D_6), δ: 0.90—1.35 ($P(CH_2Me)_2$); 1.31 (d, >CMe, $^3J_{H,P}$ = 13.2 Hz); 1.69 and 1.85 (both br.s, =CMe); 1.77 (br.s, 4-Me); 5.21 (dd, H_b, $^2J_{H,H}$ = 1.8 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz); 5.52 (dd, H_a, $^2J_{H,H}$ = 1.8 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz); 6.59 (dd, H_c, *trans*-$^3J_{H,H}$ = 18.0 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz). NOE effects (%): $\eta_{4\text{-Me}}$(5-Me) = 0.7; η_{H_c}(5-Me) = 1.5; η_{H_a}(5-Me) = 1.5. ^{13}C—{^{1}H} NMR, δ: 10.88—12.88 (=C<u>C</u>H_3, $P(CH_2\underline{C}H_3)_2$); 16.91 (d, $P(\underline{C}H_2Me)$, $^1J_{C,P}$ = 20.1 Hz); 16.94 (d, $P(\underline{C}H_2Me)$, $^1J_{C,P}$ = 19.7 Hz); 18.82 (d, >C<u>C</u>H_3, $^2J_{C,P}$ = 17.9 Hz); 56.30 (d, >C<u>C</u>Me, $^1J_{C,P}$ = 25.1 Hz); 113.28 (d, $=CH_2$, $^4J_{C,P}$ = 8.8 Hz); 130.30 (=CH); 135.18, 139.25, 142.12, 144.06 (=C). ^{31}P—{^{1}H} NMR, δ: 15.3 (s).

Isomer **10b**. In the ^{1}H NMR spectrum, only signals of the vinyl group are given. ^{1}H NMR (C_6D_6), δ: 5.20 (dd, H_b, $^2J_{H,H}$ = 2.0 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz); 5.40 (dd, H_a, $^2J_{H,H}$ = 2.0 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz); 6.54 (dd, H_c, *trans*-$^3J_{H,H}$ = 18.0 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz). ^{31}P—{^{1}H} NMR, δ: 14.6 (s).

Isomer **10c**. ^{1}H NMR (C_6D_6), δ: 0.90—1.35 ($P(CH_2Me)_2$); 1.75 (2 Me); 1.90 and 2.16 (both br.s, =CMe); 2.63 (d, $C\underline{H}_2P(CH_2Me)_2$, $^3J_{H,H}$ = 9.2 Hz); 6.13 (dt, =CH, $^3J_{H,H}$ = 9.2 Hz, $^4J_{H,P}$ = 5.6 Hz). ^{13}C—{^{1}H} NMR, δ: 9.80—11.40 (=C<u>C</u>H_3, $P(CH_2\underline{C}H_3)_2$); 14.40 (=C<u>C</u>$H_3$); 19.40 (d, $P(\underline{C}H_2Me)_2$, $^1J_{C,P}$ = 14.8 Hz); 27.69 (d, $\underline{C}H_2P(CH_2Me)_2$, $^1J_{C,P}$ = 17.8 Hz); 122.98, 125.21, 135.24, 140.08 (=<u>C</u>Me); 147.17 (d, <u>C</u>=CH, $^3J_{C,P}$ = 6.4 Hz) (signal of =CH is overlapped with a triplet of C_6D_6). ^{31}P—{^{1}H} NMR, δ: –14.1 (s).

Isomer **10d**. ^{1}H NMR (C_6D_6), δ: 0.90—1.35 ($P(CH_2Me)_2$); 1.59 and 1.65 (both br.s, =CMe); 1.61 (d, >CMe, $^3J_{H,P}$ = 12.3 Hz); 2.13 (d, =C(H)C<u>H</u>$_3$, $^3J_{H,H}$ = 7.6 Hz); 4.45 (s, H_a); 4.82 (s, H_b); 5.30 (qd, H_c, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,P}$ = 2.8 Hz). NOE effects (%): η_{H_c}(5-Me) = 2.7; η_{H_a}(5-Me) = 1.2. ^{13}C—{^{1}H} NMR, δ: 10.37—15.31 (=C<u>C</u>H_3, $P(CH_2\underline{C}H_3)_2$); 16.07 (d, $P(\underline{C}H_2Me)$, $^1J_{C,P}$ = 21.4 Hz); 17.60 (d, $P(\underline{C}H_2Me)$, $^1J_{C,P}$ = 16.8 Hz); 23.57 (d, >C<u>C</u>H_3, $^2J_{C,P}$ = 22.2 Hz); 45.91 (d, >C<u>C</u>Me, $^1J_{C,P}$ = 22.9 Hz); 97.59 ($=CH_2$); 114.05 (d, =<u>C</u>H(Me), $^3J_{C,P}$ = 5.7 Hz); 137.10, 140.62 (=<u>C</u>Me); 151.37 (d, >C=, $^2J_{C,P}$ = 7.2 Hz); 158.36 (d, >C=, $^2J_{C,P}$ = 5.6 Hz). ^{31}P—{^{1}H} NMR, δ: 2.6 (s).

Reaction of salt 2 with iodomethane (mixture of isomers 11). The starting reagents: salt **2** (0.139 g, 1.24 mmol) in THF (5 mL), iodomethane (0.20 g, 1.41 mmol) in THF (5 mL). After high vacuum distillation, a yellow oily product was obtained in a yield of 0.106 g (72%). ^{1}H NMR (C_6D_6), δ: 1.11 and 1.12 (both d, CHC<u>H</u>$_3$, $^3J_{H,H}$ = 7.0 Hz); 1.66—2.10 (=CMe); 2.58—2.98 (>CH, $>CH_2$); 4.70—5.24 ($=CH_2$); 5.44—6.48 (=CH).

Reaction of salt 3 with iodomethane (mixture of isomers 12a—c). The starting reagents: salt **3** (0.091 g, 0.59 mmol) in THF (5 mL), iodomethane (0.10 g, 0.71 mmol) in THF (5 mL). After high vacuum distillation, a yellow oily product was obtained in a yield of 0.081 g (84%). ^{1}H NMR (C_6D_6), δ: 0.85 (s, 5-Me (**12c**)); 1.01 (s, 5-Me (**12a**)); 1.09 (s, 5-Me (**12b**)); 1.64 (s, =CMe); 1.65 and 1.79 (both s, 1-Me, 4-Me (**12c**)); 1.67 (s, 4-Me (**12b**)); 1.68 (s, 1-Me, 4-Me (**12a**)); 1.69, 1.76, and 1.86 (all s, =CMe); 5.00—5.20 (m, H_b (**12a—c**)); 5.06 (dd, H_a (**12a**), $^2J_{H,H}$ = 1.6 Hz, *trans*-$^3J_{H,H}$ = 17.6 Hz); 5.18 (dd, H_a (**12b**), $^2J_{H,H}$ = 1.2 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz); 5.21 (dd, H_c (**12a**), *cis*-$^3J_{H,H}$ = 10.0 Hz, *trans*-$^3J_{H,H}$ = 17.6 Hz); 5.41 (dd, H_a (**12c**), $^2J_{H,H}$ = 2.0 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz); 6.54 (dd, H_c (**12c**), *cis*-$^3J_{H,H}$ = 11.6 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz); 6.66 (dd, H_c (**12b**), *cis*-$^3J_{H,H}$ = 11.6 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz). NOE effects (%): $\eta_{1\text{-Me},4\text{-Me}}$(5-Me) = 4.3 (per Me group); η_{H_c}(5-Me) = 4.0; η_{H_a}(5-Me) = 6.5 (isomer **12a**); $\eta_{4\text{-Me}}$(5-Me) = 6.6; η_{H_c}(5-Me) = 4.7; η_{H_a}(5-Me) = 16.3 (isomer **12b**); $\eta_{4\text{-Me}}$(5-Me) = 3.7; $\eta_{1\text{-Me}}$(5-Me) = 3.7 (isomer **12c**). ^{13}C—{^{1}H} NMR, δ: 9.45, 9.52, 10.00, 10.56, 10.92, 11.27, 11.46, 12.59 (=C<u>C</u>H_3); 15.95, 21.67, 23.08 (>C<u>C</u>H_3); 52.06, 52.79, 60.01 (>C<u>C</u>Me); 109.81, 112.69, 115.15 ($=CH_2$); 129.28, 131.59, 142.35 (=CH); 131.02, 132.82, 134.75, 135.50, 139.53, 140.49, 143.28, 144.63, 147.57, 148.38 (=C).

Trichloro(η^5-isopropenylcyclopentadienyl)zirconium (13). A solution of silane **5** (1.22 g, 6.84 mmol) in CH_2Cl_2 (10 mL) was added with stirring and cooling to 0 °C to a solution of $ZrCl_4 \cdot 2THT$ (2.14 g, 5.23 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was heated to ~20 °C and stirred for one day. The solvent was distilled off until precipitation started and then the solution was cooled to 0 °C. A finely crystalline product was separated by filtration, washed with hexane (3×20 mL), and dried under high vacuum. The intermediate product corresponding to the $Cp'ZrCl_3 \cdot$ ~0.6THT formula (^{1}H NMR spectroscopic data) was recrystallized from THF (10 mL), twice washed with cold THF, and dried under high vacuum. The yield of complex **13** (as an adduct with two THF molecules) was 1.14 g (49%) (white crystalline powder). Found (%): C, 42.91; H, 5.60. $C_{16}H_{25}Cl_3O_2Zr$. Calculated (%): C, 43.00; H, 5.64. ^{1}H NMR (CD_2Cl_2), δ: 1.92 (br.m, 8 H, C<u>H</u>$_2$CH$_2$O in THF); 2.12 (s, 3 H, Me); 4.11 (br.m, 8 H, CH_2O in THF); 5.14 and 5.41 (both m, 1 H, $=CH_2$); 6.52 and 6.60 (both t, 2 H, C_5H_4, $^{3+4}J_{H,H}$ = 5.6 Hz). ^{13}C—{^{1}H} NMR, δ: 21.52 (Me); 25.62 (<u>C</u>H$_2$CH$_2$O in THF); 73.37 (CH_2O in THF); 114.32 ($=CH_2$); 116.29, 118.97 (CH in C_5H_4); 134.47, 137.39 (C in C_5H_4, =<u>C</u>Me). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 265 $[M - 2\ THF - Cl]^+$ (0.3), 251 $[C_7H_7ZrCl_2]^+$ (1.8), 249 $[M - 2\ THF - HCl - Me]^+$ (1.2), 230 $[M - 2\ THF - 2\ Cl]^+$ (0.7), 105 $[C_7H_6(Me)]^+$ (4.5), 91 $[C_7H_7]^+$ (7.8), 71 $[C_3H_7CO]^+$ (100).

[η^5-Tetramethyl(vinyl)cyclopentadienyl]trichlorozirconium (14). Salt **3** (1.14 g, 7.38 mmol) was added to a suspension of $ZrCl_4 \cdot 2THT$ (3.02 g, 7.38 mmol) in toluene (50 mL). The reaction mixture was stirred at 100 °C for 2 days. The precipitate was filtered off and the mother liquor was concentrated. The crystalline precipitate was washed with diethyl ether (3×20 mL) and dried *in vacuo*. The intermediate corresponds to the formula $[C_5Me_4CH{=}CH_2]ZrCl_3 \cdot {\sim}0.6THT$ (^{1}H NMR spectroscopic data) and contains impurities of zirconocene dichloride **15**. The product was recrystallized from THF (2×10 mL), washed with diethyl ether (3×15 mL), and dried under high vacuum. The yield of complex **14** (as an adduct with two THF molecules) was 1.19 g (33%) (white crystalline powder). Found (%): C, 46.59; H, 6.35. $C_{19}H_{31}Cl_3O_2Zr$. Calculated (%): C, 46.67; H, 6.39. ^{1}H NMR (THF-d_8), δ: 1.72 (m, 8 H, C$\underline{H}_2$CH$_2$O in THF); 2.02 and 2.13 (both s, 6 H, Me); 3.59 (m, 8 H, CH$_2$O in THF); 5.17 (dd, 1 H, H$_b$, $^2J_{H,H}$ = 2.0 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz); 5.22 (dd, 1 H, H$_a$, $^2J_{H,H}$ = 2.0 Hz, *trans*-$^3J_{H,H}$ = 18.0 Hz); 6.59 (dd, 1 H, H$_c$, *trans*-$^3J_{H,H}$ = 18.0 Hz, *cis*-$^3J_{H,H}$ = 11.6 Hz). ^{13}C—{^{1}H} NMR, δ: 13.56, 14.49 (Me); 26.36 (C$\underline{H}_2$CH$_2$O in THF); 68.59 (CH$_2$O in THF); 116.32 (=CH$_2$); 126.19 (C$\underline{C}$H=CH$_2$); 126.98, 128.99 (C$\underline{C}$Me); 132.26 (=CH). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 342 [M − 2 THF]$^+$ (0.6), 307 [M − 2 THF − Cl]$^+$ (5.6), 292 [M − 2 THF − Cl − Me]$^+$ (12.0), 147 [$C_7H_3(Me)_4$]$^+$ (52.4), 133 [$C_7H_4(Me)_3$]$^+$ (52.7), 119 [$C_7H_5(Me)_2$]$^+$ (44.1), 105 [$C_7H_6(Me)$]$^+$ (44.9), 91 [C_7H_7]$^+$ (56.2), 36 [HCl]$^+$ (100).

X-ray diffraction study of complexes 13 and 14. X-ray diffraction data sets were collected on Enraf-Nonius CAD4 (complex **13**) and Bruker SMART (complex **14**) diffractometers (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). Crystallographic data, details of X-ray diffraction study, and characteristics of structure refinement for complexes **13** and **14** are given in Table 3. The absorption corrections were applied based on the measured intensities of equivalent reflections. The structures were solved by direct methods (SHELXS-86).[28] All nonhydrogen atoms were refined by the full-matrix least-squares method with anisotropic displacement parameters against F^2 (SHELXL-97).[29] The H atoms in the structure of **14** were revealed from a difference electron density series and refined isotropically. The hydrogen atoms in the structure of **13** were placed in calculated positions and refined using a riding model.

Table 3. Crystallographic data, details of X-ray diffraction study, and characteristics of structure refinement for complexes **13** and **14**

Parameter	**13**	**14**
Molecular formula	$C_{16}H_{25}Cl_3O_2Zr$	$C_{19}H_{31}Cl_3O_2Zr$
Molecular weight	446.93	489.01
T/K	293	105(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a/Å	14.371(8)	8.3488(2)
b/Å	15.482(5)	28.1232(7)
c/Å	17.003(7)	9.1784(3)
β/deg	—	99.655(1)
V/Å^3	3783(3)	2124.5(1)
Z	8	4
d_{calc}/g cm^{-3}	1.569	1.529
μ/mm^{-1}	1.008	0.905
F(000)	1824	1008
θ Scan range/deg	2.27—24.96	1.45—27.00
Ranges of indices of measured reflections	$-2 \le h \le 17$, $-2 \le k \le 18$, $-2 \le l \le 20$	$-10 \le h \le 9$, $-35 \le k \le 35$, $-11 \le l \le 11$
Number of measured reflections	5161	14919
Number of independent reflections (R_{int})	3321 (0.0430)	4639 (0.0250)
Number of parameters in refinement	201	342
R_1 ($I \ge 2\sigma(I)$)	0.0349	0.0260
wR_2 (all reflections)	0.1000	0.0573
Goodness-of-fit on F^2	0.977	1.118
Residual electron density (max/min)/e Å^{-3}	0.453/−0.355	0.572/−0.442

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References

1. J. Muller, R. Stock, and J. Pickard, *Z. Naturforsch.*, *Teil B*, 1981, **36**, 1219.
2. D. W. Macomber, W. C. Spink, and M. D. Rausch, *J. Organomet. Chem.*, 1983, **250**, 311.
3. Y.-P. Wang, T.-S. Lin, R.-S. Shyu, J.-M. Hwu, Y. Wang, and M.-C. Cheng, *J. Organomet. Chem.*, 1989, **371**, 57.
4. T.-Y. Dong, M.-Y. Hwang, T.-L. Hsu, C.-C. Schei, and S.-K. Yeh, *Inorg. Chem.*, 1990, **29**, 80.
5. Y. Qian, G. Li, Y. He, W. Chen, B. Li, and S. Chen, *J. Mol. Catal.*, 1990, **60**, 19.
6. M. Ogasa, D. T. Mallin, D. W. Macomber, and M. D. Rausch, *J. Organomet. Chem.*, 1991, **405**, 41.
7. C. P. Gibson, D. S. Bern, S. B. Falloon, T. K. Hitchens, and J. E. Cortopassi, *Organometallics*, 1992, **11**, 1742.
8. L. Gelmini, R. J. Puddephatt, and J. J. Vittal, *Acta Crystallogr., Sect. C (Cryst. Struct. Commun.)*, 1993, **49**, 30.
9. T. E. Bitterwolf, S. Gallagher, J. T. Bays, B. Scallorn, A. L. Rheingold, I. A. Guzei, L. Liable-Sands, and J. C. Linehan, *J. Organomet. Chem.*, 1998, **557**, 77.
10. H. Schumann, A. Heim, J. Demtschuk, and S. H. Muhle, *Organometallics*, 2003, **22**, 118.
11. D. P. Krut´ko, M. V. Borzov, D. A. Lemenovskii, G. I. Dzhardimalieva, and A. D. Pomogailo, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 242 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 247].
12. C. Adamo and V. Barone, *J. Chem. Phys.*, 1998, **108**, 664.
13. M. J. Frisch G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck,

K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98 (Revision A.1)*, Gaussian, Inc., Pittsburgh (PA), 1998.

14. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1990, 438 pp.
15. F. W. Biegler-Konig, R. F. W. Bader, and T.-H. Tang, *J. Comput. Chem.*, 1982, **3**, 317.
16. M. D. Fryzuk, S. S. H. Mao, P. B. Duval, and S. J. Rettig, *Polyhedron*, 1995, **14**, 11.
17. P. Jutzi and U. Siemeling, *J. Organomet. Chem.,* 1995, **500**, 175.
18. P. Jutzi and J. Kleimeier, *J. Organomet. Chem.*, 1995, **486**, 287.
19. 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.)].
20. D. P. Krut´ko, M. V. Borzov, V. S. Petrosyan, L. G. Kuz´mina, and A. V. Churakov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1828 [*Russ. Chem. Bull.*, 1996, **45**, 1740 (Engl. Transl.)].
21. G. Erker, J. Chamberger, A. A. H. Zeijden, S. Dehnicke, C. Kruger, R. Goddard, and M. Nolte, *J. Organomet. Chem.*, 1993, **459**, 107.
22. F. H. Allen, *Acta Crystallogr.*, *Sect. B*, 2002, **58**, 380.
23. G. Erker, C. Sarter, M. Albrecht, S. Dehnike, C. Kruger, E. Raabe, R. Schlund, R. Benn, A. Rufinska, and R. Mynott, *J. Organomet. Chem.*, 1990, **382**, 89.
24. D. D. Perrin, W. L. F. Armarego, and D. N. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966, 362 pp.
25. H. J. Lukas, F. W. Mitchell, Jr., and C. N. Scully, *J. Am. Chem. Soc.*, 1950, **72**, 5491.
26. F. M. Chung and A. D. Westland, *Can. J. Chem.*, 1969, **47**, 195.
27. H. Brand and J. Arnold, *J. Am. Chem. Soc.*, 1992, **114**, 2266.
28. G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.
29. G. M. Sheldrick, *SHELXL-97. Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.

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