

СИНТЕЗ И СТРОЕНИЕ ГЕКСАХЛОРОЦИРКОНАТОВ ТРИФЕНИЛБУТ-2-ЕНИЛ- И ТРИФЕНИЛМЕТОКСИМЕТИЛФОСФОНИЯ

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Взаимодействием тетрахлорида циркония с хлоридами трифенилорганилфосфония в ацетонитриле впервые синтезированы и охарактеризованы методами ИК-, ЯМР-спектроскопии и рентгеноструктурного анализа гексахлорцирконаты трифенил(бут-2-енил)фосфония (1a) и трифенилметоксиметилфосфония (1b). В ИК спектрах синтезированных соединений наиболее интенсивными являются полосы, относящиеся к валентным колебаниям CAr-H и CAr-CAr связей ароматических колец трифенилорганилфосфониевых катионов. В спектрах ^{13}C ЯМР исследуемых комплексов наблюдается характерное для фосфорсодержащих органических соединений расщепление сигналов атомов углерода ароматических колец и алкильных групп за счет взаимодействий с атомом ^{31}P , КССВ атомов углерода, непосредственно связанных с фосфором составляют 48–85 Гц. По данным РСА соединение 1a кристаллизуется в моноклинной кристаллической решетке (пространственная группа симметрии P21/c), для гексахлорцирконата 1b характерна триклинная кристаллическая решетка и пространственная группа симметрии – P-1. Кристалл соединения 1a характеризуется менее плотной упаковкой молекул в кристаллической решетке по сравнению с соединением 1b, вычисленная плотность для данных структур составляет 1,355 г/см³ 1,466 г/см³ соответственно. Структурная организация комплексов в кристаллах обусловлена образованием водородных связей между атомами хлора аниона и водорода фенильных и алкильных групп катионов. Атомы фосфора в катионах трифенилорганилфосфония имеют искаженную тетраэдрическую координацию (углы CPC составляют 107,01(4)°-114,10(6)° для 1a, 107,38(9)°-112,06(7)° Å для 1b, длины связей P-C равны 1,790(14)-1,865(14) Å для 1a, 1,7838(12)-1,8293(18) Å для 1b). В центросимметричных октаэдрических гексахлорцирконатных анионах (транс ClZrCl 180°) расстояния Zr-Cl составляют 2,4654(15)-2,4952(17) Å для 1a и 2,4641(14)-2,4711(12) Å для 1b.

Ключевые слова: гексахлорцирконаты трифенилорганилфосфония, кристаллическая структура, РСА

SYNTHESIS AND STRUCTURE OF TRIPHENYLBUT-2-ENYL- AND TRIPHENYLMETOXYMETHYLPHOSPHONIUM HEXACHLOROZIRCONATES

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Triphenylbut-2-enyl- (1a) and triphenylmetoxymethylphosphonium (1b) hexachlorozirconates have been synthesized by the reactions of zirconium tetrachloride with the triphenylalkylphosphonium chlorides in acetonitrile for the first time and characterized by the IR, NMR spectroscopy and X-ray analysis. The most intensive bands in IR spectra correspond to the valence vibrations of the CAr-H and the CAr-CAr bonds in the triphenylalkylphosphonium cations. The splitting of carbon atoms signals is observed due to the presence of $^{13}\text{C} - ^{31}\text{P}$ coupling. SSCC for carbon atoms directly connected with phosphorus are about 48–85 Hz. According to the X-Ray data, compound 1a crystallizes in the monoclinic crystal lattice (the P21/c space symmetry group). Hexachlorozirconate 1b forms the triclinic crystals belong to the P-1 space symmetry group. Crystals of compound 1a is characterized by the less dense molecular packing in the crystal lattice in comparison with compound 1b. Calculated densities for the structures 1a,b are 1.355 g/cm³ and 1.466 g/cm³, respectively. Structural organization of the complexes in crystals is caused by the formation of hydrogen bonds between chlorine atoms of the anion and hydrogens of phenyl and alkyl groups of the cations. The phosphorus atoms in the triphenylalkylphosphonium cations have distorted tetrahedral coordination (CPC 107.01(4)°-114.10(6)° for 1a, 107.38(9)°-112.06(7)° for 1b, the P-C bonds are 1.790(14)-1.865(14) Å for 1a, 1.7838(12)-1.8293(18) Å for 1b). In centrosymmetric octahedral anions [ZrCl₆]²⁻ (trans-ClZrCl 180°) the Zr-Cl distances are 2.4654(15)-2.4952(17) Å for 1a and 2.4641(14)-2.4711(12) Å for 1b.

Key words: tetraalkylphosphonium hexachlorozirconates, crystal structure, X-Ray analysis

Для цитирования:

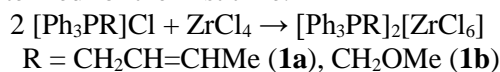
Шарутин В.В., Шарутина О.К., Тарасова Н.М., Лобанова Е.В., Андреев П.В. Синтез и строение гексахлорцирконатов трифенилбут-2-енил- и трифенилметоксиметилфосфония. *Изв. вузов. Химия и хим. технология*. 2019. Т. 62. Вып. 6. С. 36–40

For citation:

Sharutin V.V., Sharutina O.K., Tarasova N.M., Lobanova E.V., Andreev P.V. Synthesis and structure of triphenylbut-2-enyl- and triphenylmetoxymethylphosphonium hexachlorozirconates. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2019. V. 62. N 6. P. 36–40

INTRODUCTION

Many achievements in the field of organic chemistry are associated with the use of transition metal complexes. Among them, zirconium compounds have been described as effective catalysts for transformation of unsaturated hydrocarbons and organometallic compounds [1]. Zirconium (IV) complexes exhibit high catalytic activity in the polymerization reactions of ethylene [2-9], hydrogenation of olefins [10] and enantioselective alkylation of aromatic compounds [11, 12]. Furthermore, the reactions of stereoselective carbalumination of alkenes and alkynes with participation of zirconium complexes (ZACA-reactions) are widely applied [13-21]. It is also worth noting that ZrCl₄ itself is widely used in catalysis [22]. On the other hand, moisture-resistant hexachlorozirconate complexes, for example tetraalkylphosphonium hexachlorozirconates, can be used to prepare multicomponent catalysts. Among them only *bis*(tetraphenylphosphonium) hexachlorozirconate has been structurally characterized [22-25]. In the present study the zirconium complexes [Ph₃PR]₂[ZrCl₆]²⁻, R = CH₂CH=CHCH₂ (**1a**), CH₂OMe (**1b**) have been synthesized and structurally characterized for the first time.



EXPERIMENTAL

IR-spectra of complexes **1a** and **1b** were obtained with the use of a IR-Fourier spectrometer Shimadzu IR Affinity-1S in the KBr pellets.

The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance-500 500 and 126 MHz apparatus (TMS as an internal standard).

X-ray diffraction study. Diffraction data of **1a** and **1b** were collected on a Bruker D8 QUEST diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Collection, data editing and refinement of element cell parameters, as well as absorption record were carried up on programs SMART and SAINT-Plus [26]. All calculations on determination and definition of structures were performed using the SHELXTL/PC [27], OLEX2 programs [28]. The structure was solved by direct methods and refined by least-squares method in anisotropic approximation for non-hydrogen atoms. The main crystallographic data and results of structure refinement are presented in Table 1, and main bond distances and valent angles are presented in Table 2. Full tables of atomic coordinates, bond lengths, and valence angles are deposited in the Cambridge Crystallographic Data Centre (CCDC 1587676 (for **1a**) and CCDC 1587677 (for **1b**) www.ccdc.cam.ac.uk/data_request/cif).

General procedure of synthesis

To the solution of 0.86 mmol triphenylbut-2-enylphosphonium chloride (or (methoxymethyl)triphenylphosphonium chloride) in 15 mL acetonitrile (MeCN) 100 mg (0.43 mmol) $ZrCl_4$ was added under stirring. Colorless crystals were observed during slowly concentrating the clear solution to 3 mL. They were filtered and dried.

[Ph₃PCH₂CH=CHCH₃]⁺[ZrCl₆]⁻ (1a). 351 mg (87%) (colorless transparent crystals, mp (decomp.) 244.8–245.7 °C). IR-spectra (ν , cm⁻¹): 509 (s), 690 (s), 719 (s), 1111 (s), 1437 (Ph), 1483 (m), 1587 (m), 2897 (m), 2937 (m) 3026 (C_{Ar}-H), 3057 (C_{Ar}-H). ¹H NMR (DMSO-*d*₆): 1.59 (6H, t, ³J = 5.99 Hz, CH₃); 4.61 (4H, dd, ³J = 16.02 Hz, ³J = 7.17 Hz, PCH₂); 5.34 (2H, m, =CH-); 5.74 (2H, m, =CH-); 7.74–7.84 (24 H, m, CH_{Ar}); 7.88–7.94 (6H, m, CH_{Ar}). ¹³C NMR (DMSO-*d*₆): 17.92 (2C, d, ⁴J = 2.68 Hz, CH₃); 25.52 (2C, d, ¹J = 48.80 Hz, PCH₂); 116.3 (2C, d, ³J = 9.91 Hz, -CH=) 118.40 (d, ¹J = 85.30 Hz, 6C_{Ar}); 130.20 (d, ²J = 12.44 Hz, 12C_{Ar}); 133.80 (d, ³J = 9.88 Hz, 12C_{Ar}); 134.90 (d, ⁴J = 2.65 Hz, 6C_{Ar}); 135.9 (2C, d, ²J = 13.72 Hz, -CH=). Found, %: C 56.21, H 4.73. C₄₄H₄₄Cl₆P₂Zr. Calculated, %: C 56.29, H 4.69.

[Ph₃PCH₂OMe]⁺[ZrCl₆]⁻ (1b) 359 mg (91%) (colorless transparent crystals, mp (decomp.) 232.6–233.4 °C). IR-spectra (ν , cm⁻¹): 501 (s), 530 (s), 688 (s), 1112 (s), 1437 (Ph), 2827 (w), 2929 (w), 3055 (C_{Ar}-H), 3080 (C_{Ar}-H). ¹H NMR (DMSO-*d*₆): 3.49 (3H, d, ⁴J = 0.6 Hz, OCH₃); 5.72 (2H, d, ²J = 4.9 Hz, PCH₂); 7.70–7.87 (12H, m, CH_{Ar}); 7.89–7.98 (3H, m, CH_{Ar}). ¹³C NMR (DMSO-*d*₆): 61.82 (d, ³J = 13.0 Hz, OCH₃); 64.50 (d, ¹J = 66.9 Hz, PCH₂); 116.78 (d, ¹J = 85.6 Hz, 3C_{Ar}); 130.31 (d, ²J = 12.6 Hz, 6C_{Ar}); 133.95 (d, ³J = 10.2 Hz, 6C_{Ar}); 135.32 (d, ⁴J = 2.8 Hz, 3C_{Ar}). Found, %: C 52.16, H 4.41. C₄₀H₄₀Cl₆O₂P₂Zr. Calculated, %: C 52.29, H 4.36.

Table 1

Crystal data, experimental parameters and structure refinement parameters for 1a and 1b

Таблица 1. Кристаллические данные, экспериментальные параметры и параметры уточнения структуры для 1a и 1b

	1a	1b
<i>M</i>	938.65	918.58
<i>T</i> , K	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	P2 ₁ /c	P-1
<i>a</i> , Å	11.233(10)	10.240(5)
<i>b</i> , Å	16.284(12)	10.493(6)
<i>c</i> , Å	12.691(10)	10.805(6)
α , deg	90	80.19(3)
β , deg	97.60(4)	69.35(2)
γ , deg	90	73.96(2)
<i>V</i> , Å ³	2301(3)	1040.6(10)

<i>Z</i>	2	1
ρ (calc.), g/sm ³	1.355	1.466
μ , mm ⁻¹	0.686	0.760
<i>F</i> (000)	960	468
Crystal size, mm	0.78×0.41×0.40	0.35×0.24×0.13
2 θ Range of data collection, deg	5.96–72.64	5.96–94.04
Range of refraction indices	-18 ≤ <i>h</i> ≤ 18, -27 ≤ <i>k</i> ≤ 27, -21 ≤ <i>l</i> ≤ 21	-21 ≤ <i>h</i> ≤ 20, -21 ≤ <i>k</i> ≤ 21, -22 ≤ <i>l</i> ≤ 22
Measured reflections	86799	163988
Independent reflections	11147 (R _{int} = 0.0386)	18779 (R _{int} = 0.0392)
Refinement variables	358	254
<i>GOOF</i>	1.042	1.050
R factors for <i>F</i> ² > 2 σ (<i>F</i> ²)	R ₁ = 0.0411, wR ₁ = 0.0815	R ₁ = 0.0477, wR ₁ = 0.1113
R factors for all reflections	R ₁ = 0.0666, wR ₁ = 0.0925	R ₁ = 0.0891, wR ₁ = 0.1367
Residual electron density (min/max), e/Å ³	-0.679/0.679	-0.998 / 0.824

Table 2

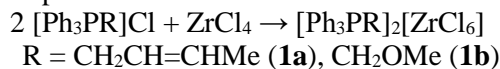
Selected bond lengths and valent angles in 1a and 1b

Таблица 2. Выбранные длины связей и валентных углов в 1a и 1b

Bond <i>d</i> , Å		Angle ω , grad	
1a			
Zr(1)–Cl(3)	2.4654(15)	Cl(3)Zr(1)Cl(3)*	180.0
Zr(1)–Cl(3)*	2.4654(15)	Cl(3)Zr(1)Cl(1)*	90.13(6)
Zr(1)–Cl(1)*	2.4785(15)	Cl(3)*Zr(1)Cl(1)*	89.87(6)
Zr(1)–Cl(1)	2.4785(15)	Cl(3)Zr(1)Cl(1)	89.87(6)
Zr(1)–Cl(2)*	2.4951(17)	Cl(3)*Zr(1)Cl(1)	90.13(6)
Zr(1)–Cl(2)	2.4952(17)	Cl(2)*Zr(1)Cl(2)	180.0
P(1)–C(27B)	1.790(14)	Cl(3)Zr(1)Cl(1)	89.87(6)
P(1)–C(11)	1.7973(19)	Cl(3)*Zr(1)Cl(1)	90.13(6)
P(1)–C(1)	1.806(2)	Cl(3)Zr(1)Cl(2)	90.53(5)
P(1)–C(21)	1.808(2)	Cl(3)*Zr(1)Cl(2)	89.47(5)
P(1)–C(27A)	1.865(14)	Cl(1)Zr(1)Cl(2)	90.25(4)
Symmetry codes: *) -x+1, -y+1, -z+2			
1b			
Zr(1)–Cl(3)	2.4641(14)	Cl(3)Zr(1)Cl(3)*	180.00(2)
Zr(1)–Cl(3)*	2.4642(14)	Cl(3)Zr(1)Cl(2)*	90.59(4)
Zr(1)–Cl(2)*	2.4673(10)	Cl(3)*Zr(1)Cl(2)*	89.41(4)
Zr(1)–Cl(2)	2.4673(10)	Cl(3)Zr(1)Cl(2)	89.41(4)
Zr(1)–Cl(1)	2.4711(12)	Cl(3)*Zr(1)Cl(2)	90.59(4)
Zr(1)–Cl(1)*	2.4711(12)	Cl(2)*Zr(1)Cl(2)	180.0
P(1)–C(1)	1.7838(15)	Cl(3)Zr(1)Cl(1)	90.01(4)
P(1)–C(21)	1.7872(15)	Cl(3)*Zr(1)Cl(1)	89.99(4)
P(1)–C(11)	1.7927(16)	Cl(2)*Zr(1)Cl(1)	90.12(4)
P(1)–C(7B)	1.8293(18)	Cl(2)Zr(1)Cl(1)	89.88(4)
P(1)–C(7A)	1.8293(18)	Cl(3)Zr(1)Cl(1)*	89.99(4)
Symmetry codes: *) -x+1, -y, -z+2			

RESULTS AND DISCUSSION

Complexes **1a**, **1b** have been synthesized from zirconium tetrachloride and triphenylalkylphosphonium chlorides in MeCN, wherein zirconium chloride was added to an acetonitrile solution of triphenylalkylphosphonium chloride:



The formation of large colorless crystals of the desired product was observed during the slow evaporation of the solution.

According to the X-ray data, the crystals consist of tetrahedral cations of triphenylalkylphosphonium (the CPC angles 107.01(4)°–114.10(6)° for **1a**, 107.38(9)°–112.06(7)° for **1b**, the P–C bonds are 1.790(14)–1.865(14) Å for **1a**, 1.7838(12)–1.8293(18) Å for **1b**) and the centrosymmetric hexachlorozirconate anion, with ideal octahedral shape (*trans*-ClZrCl angles are 180°), in which the Zr–Cl distances are 2.4654(15)–2.4952(17) Å for **1a** and 2.4641(14)–2.4711(12) Å for **1b** (Figs. 1 and 2). It is slightly larger than the sum of the covalent zirconium and chlorine semidiameters (2.44 Å [34]).

The crystals of compounds **1a**, **1b** are characterized by the presence of statistical disorder. In the crystal the cation of compound **1a** contains the disordered butenylic fragment, in which the probability of occupancy of positions A and B is 47% and 53%, respectively. The cation in the crystal of compound **1b** contains disordered methoxymethylic fragment, in which the probability of occupancy of positions A and B is 62% and 48%, respectively.

The structural organization of the crystals **1a** and **1b** is caused by intermolecular hydrogen bonds Cl⋯H (2.73–2.89 Å and 2.80–2.92 Å, respectively) (Figs. 3 and 4).

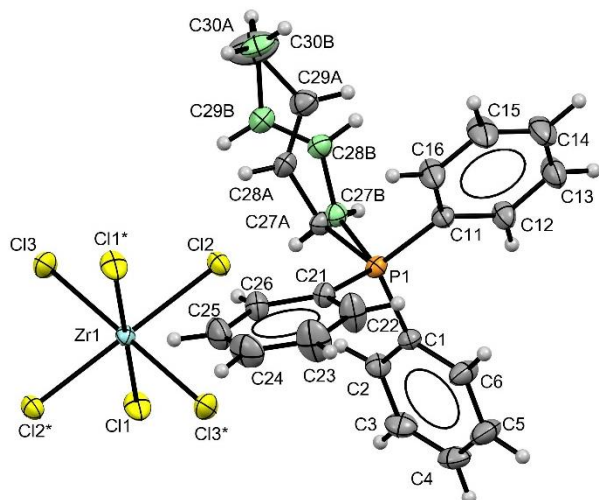


Fig. 1. The structure of complex **1a**
Рис. 1. Структура комплекса **1a**

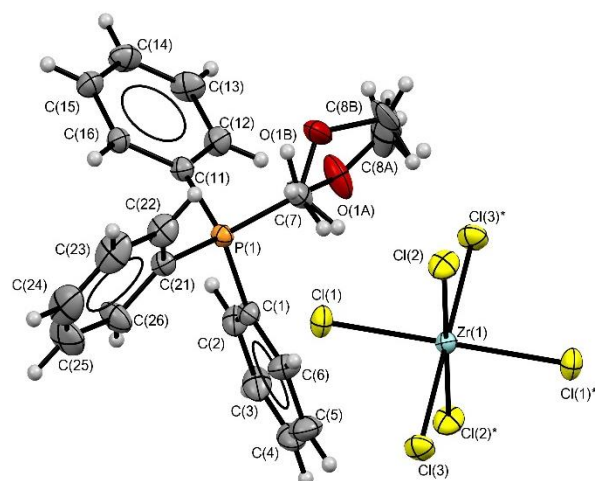


Fig. 2. The structure of complex **1b**
Рис. 2. Структура комплекса **1b**

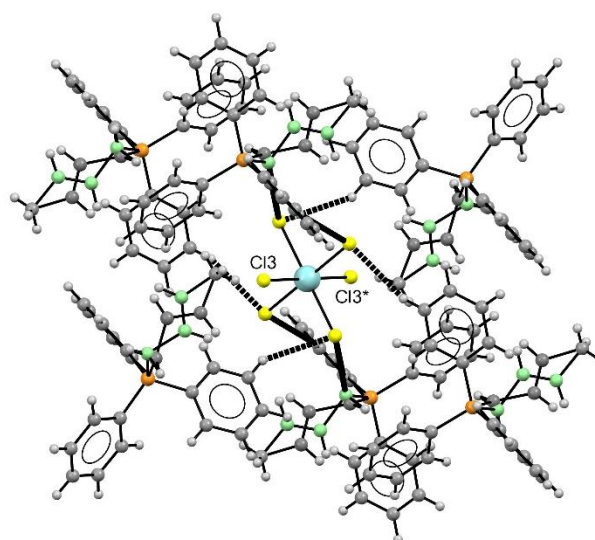


Fig. 3. The intramolecular hydrogen bonds of compound **1a**
Рис. 3. Внутримолекулярные водородные связи соединения **1a**

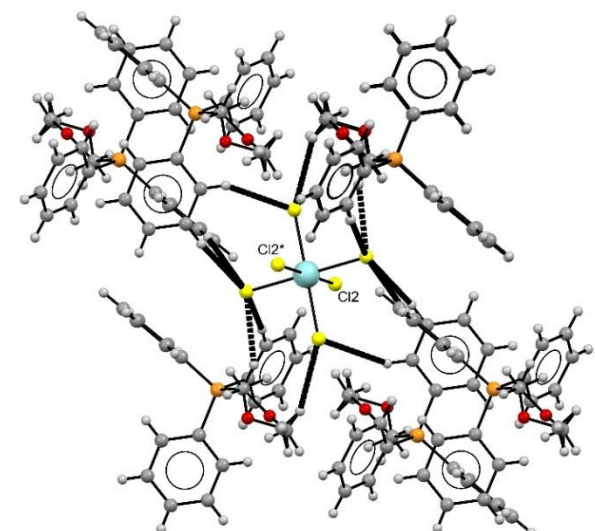


Fig. 4. The intramolecular hydrogen bonds of compound **1b**
Рис. 4. Внутримолекулярные водородные связи соединения **1b**

CONCLUSION

Thereby, the $[\text{Ph}_3\text{PR}]^+_2[\text{ZrCl}_6]^{2-}$ complexes have been synthesized by the reaction of triphenyl(methoxymethyl)phosphonium and triphenyl(but-2-enyl)phosphonium chlorides with ZrCl_4 . The structures of the obtained compounds are fully characterized by spectral methods and the X-ray analysis. According to the obtained results, the crystals consist of tetrahedral triphenylalkylphosphonium cations and centrosymmetric octahedral ZrCl_6^- anions. Alkylphosphonium cations are characterized by the presence of statistical disorder in the butenylic and methoxymethyl fragments.

This work was supported by the Ministry of Education and Science of the Russian Federation [grant number 4.6151.2017/8.9].

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Поступила в редакцию (Received) 07.08.2018

Принята к опубликованию (Accepted) 12.03.2019