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(4-Fluorobenzyl)triphenylphosphonium Hexachlorozirconate $[Ph_3PCH_2C_6H_4F\text{-}4][ZrCl_6]$: Synthesis and Structure

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Abstract—(4-Fluorobenzyl)triphenylphosphonium hexachlorozirconate $[Ph_3PCH_2C_6H_4F\text{-}4][ZrCl_6]$ (**I**) is synthesized by the reaction of (4-fluorobenzyl)triphenylphosphonium chloride with zirconium tetrachloride in an acetonitrile solution. The structure of the compound is characterized by IR spectroscopy, ^{1}H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction (XRD). According to the XRD data, the crystals of complex **I** (CIF file CCDC no. 2063132) consist of tetrahedral (4-fluorobenzyl)triphenylphosphonium cations (CPC 99.44(13)°–114.94(12)°, P–C 1.706(2)–1.935(3) Å) of two types and octahedral anions $[ZrCl_6]^{2-}$ (*trans*-ClZrCl angles 177.35(3)°–178.62(3)°, distances Zr–Cl 2.4308(9)–2.5350(11) Å). The structure of complex **I** is formed due to weak hydrogen bonds between the cations and anions. The IR spectrum of complex **I** exhibits an intense band of stretching vibrations of the $F-C_{Ar}$ bond at 997 cm^{-1}, a band of vibrations of the $P-C_{Ar}$ bonds at 1439 cm^{-1}, and bending and stretching C–H vibration bands at 743 and 3059, 2912 cm^{-1}. The doublet due to the long-range interaction on the fluorine atom ($J = 8.8$ Hz) is the characteristic signal in the ^{31}P NMR spectrum of complex **I**. All signals of the carbon atoms in the ^{13}C NMR spectrum are observed as doublets and doublet-doublets due to the direct and long-range interactions with the fluorine and phosphorus atoms.

Keywords: zirconium tetrachloride, (4-fluorobenzyl)triphenylphosphonium chloride, (4-fluorobenzyl)triphenylphosphonium hexachlorozirconate, addition reaction

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INTRODUCTION

Many significant achievements in the area of organic chemistry are associated with the use of transition metal complexes. Among them, the zirconium complexes can be emphasized as efficient catalysts of transformations of unsaturated hydrocarbons and organometallic compounds [1–4]. A high catalytic activity of the zirconium complexes in ethylene polymerization [5–10], olefin hydrogenation [11, 12], and enantioselective alkylation of aromatic compounds [13, 14] is known. Zirconium tetrachloride itself is also used in catalysis [15]. The synthesis of multicomponent catalytic systems containing zirconium complexes has not been reported previously, although hexachlorozirconate complexes resistant to moisture can be used for the preparation of multicomponent catalysts, for example, tetraorganylphosphonium hexachlorozirconates [16–24]. Zirconium complex $[Ph_3PCH_2C_6H_4F\text{-}4]_2[ZrCl_6]^{2-}$ was synthesized and structurally characterized for the first time in this work.

EXPERIMENTAL

IR spectra were recorded on a Shimadzu IR Affinity-1S FT-IR spectrometer in KBr pellets in a range of 4000–400 cm^{-1}.

^{1}H (600 MHz), ^{13}C (151 MHz), ^{31}P (243 MHz), and ^{19}F (565 MHz) NMR spectra were recorded for CD_3CN solutions of the compounds on a Bruker AVANCE NEO 600 MHz NMR spectrometer equipped with a Prodigy cryoprobe using signals of the solvent as the standard.

Elemental analysis to C and H was carried out on a Carlo Erba CHNS-O EA 1108 elemental analyzer.

The melting point was measured on a Netzsch 449C Jupiter instrument.

Synthesis of (4-fluorobenzyl)triphenylphosphonium hexachlorozirconate (I). Zirconium tetrachloride (0.200 g, 0.860 mmol) was added to a solution of (4-fluorobenzyl)triphenylphosphonium chloride (0.698 g, 1.720 mmol) in acetonitrile (30 mL), and the mixture was stirred for 1 h. After 24 h, the solvent was removed and the precipitate was recrystallized from a mixture of acetonitrile (30 mL) and isopropyl alcohol (10 mL). Colorless transparent crystals of compound **I** were filtered off and dried in air. The yield was 0.736 g (82%), $T_m = 280$°C.

IR (KBr; ν, cm^{-1}): 3059 (C–H), 2912 (C–H), 1601, 1585, 1508, 1483, 1439 ($P-C_{Ar}$), 1398, 1314, 1244, 1111, 997 (F–C_{Ar}), 843, 833, 768, 743 (C–H), 718, 689, 554, 515, 503, 478, 442.

^{1}H NMR (600 MHz; acetonitrile-d_3; δ, ppm): 7.93–7.85 (m, 3H); 7.69 (td, *J* = 8.0 Hz; 3.6, 6H); 7.60 (dd, *J* = 8.4 Hz; 1.1, 3H); 7.58 (dd, *J* = 8.4 Hz; 1.1, 3H); 7.08–6.91 (m, 4H); 4.71 (d, *J* = 14.4 Hz; 2H).

^{13}C NMR (151 MHz; acetonitrile-d_3; δ, ppm): 163.77 (dd, *J* = 246.6 Hz; 4.1); 136.28 (d, *J* = 3.3 Hz); 135.23 (d, *J* = 9.8 Hz); 134.00 (d, *J* = 5.3 Hz); 133.95 (d, *J* = 5.4 Hz); 131.17 (d, *J* = 12.0 Hz); 124.36 (dd, *J* = 8.4 Hz; 3.2); 116.83 (d, *J* = 25.1 Hz); 29.98 (d, *J* = 49.0 Hz).

^{19}F NMR (565 MHz; acetonitrile-d_3, δ, ppm): 114.32 (m).

^{31}P NMR (243 MHz; acetonitrile-d_3, δ, ppm): 22.56 (d, *J* = 8.8 Hz).

For $C_{50}H_{42}F_2P_2Cl_6Zr$

Anal. calcd., %	C, 57.31	H, 4.01
Found, %	C, 57.25	H, 4.12

XRD of single crystals of compound **I** was carried out on a Bruker D8 QUEST diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Data were collected and processed, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [25]. All calculations were performed using the SHELXTL/PC [26] and OLEX2 [27] software. The structure was solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and structure refinement results for compound **I** are given in Table 1.

The full tables of atomic coordinates, bond lengths, and bond angles for compound **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2063132; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Complex **I** was formed by the addition of zirconium tetrachloride to a solution of (4-fluorobenzyl)triphenylphosphonium chloride in acetonitrile

$$2[Ph_3PCH_2C_6H_4F\text{-}4]Cl + ZrCl_4 \rightarrow \underset{(\mathbf{I})}{[Ph_3PCH_2C_6H_4F\text{-}4]_2[ZrCl_6]^{2-}}.$$

Colorless transparent crystals of compound **I** were obtained after the crystallization of the substance from a mixture of MeCN and EtOH (3 : 1). The isolated crystals are stable in air, highly soluble in acetonitrile and methanol, and insoluble in water at room temperature.

It is known that the absorption bands of F–C_{Ar} lie in a sufficiently narrow range (1110–1000 cm^{-1}) [28] because of the absence of a significant effect of the environment on these bond vibrations and are easily detected in the IR spectra. For instance, the IR spectrum of complex **I** exhibits an intense band at 997 cm^{-1} that can be attributed to the F–C_{Ar} stretching vibrations. The P–C_{Ar} bond vibrations in the IR spectrum of compound **I** correspond to the band at 1439 cm^{-1} in a range of 1450–1435 cm^{-1} characterized earlier for similar derivatives [28]. In addition, the bands at 743 and 3059, 2912 cm^{-1} assigned to the C–H bending and stretching vibrations, respectively, are observed.

The ^{1}H NMR spectrum of the complex exhibits the signals of protons, whose chemical shifts, integral intensity, and multiplicity correspond to the structure of 4-fluorobenzyltriphenylphosphonium hexachlorozirconate. The doublet with a spin-spin coupling constant of 8.8 Hz due to the long-range interaction on the fluorine atom observed in the ^{31}P NMR spectrum is characteristic. All signals of carbons in the ^{13}C NMR spectrum due to direct and long-range interactions with the fluorine and phosphorus atoms are observed as doublets and doublet-doublets.

According to the XRD data, the crystal of compound **I** contains crystallographically independent tetrahedral 4-fluorobenzyltriphenylphosphonium cations of two types and octahedral hexachlorozirconate anions $[ZrCl_6]^{2-}$ (see Fig. 1).

The tetrahedral coordination of the phosphorus atoms in the cations is somewhat distorted: the CPC angles undergo deviations from the theoretical value and are equal to 99.44(13)°–114.94(12)°, and the P–C_{Ph} bond lengths (1.706(2)–1.935(3) Å) are close to each other, as well as the P–C_{Alk} distances (1.710(3), 1.868(3) Å). The zirconium–carbon bonds in the $[ZrCl_6]^{2-}$ anions deviate from a linear configuration (*trans*-ClZrCl angles are 177.35(3)°–178.62(3)°). The Zr–Cl distances in the anions somewhat differ from each other (2.4308(9)–2.5350(11) Å) and are close to the sum of covalent radii of the atoms (2.44 Å [29]). The structural organization of the crystal of complex **I** is predominantly caused by intermolecular hydrogen bonds Cl···H. The cations localized at the center of the crystal cell form hydrogen bonds with the peripheral anions via the Cl···H contacts (2.74–2.79 Å). There is

Table 1. Crystallographic data and experimental and structure refinement parameters for compound **I**

Parameter	Value
Empirical formula	$C_{50}H_{42}F_2P_2Cl_6Zr$
FW	1046.69
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	19.871(6)
b, Å	12.900(4)
c, Å	21.463(9)
α, deg	90
β, deg	116.959(13)
γ, deg	90
V, Å^3	4904(3)
Z	4
ρ_{calc}, g/cm^3	1.418
μ, mm^{-1}	0.658
F(000)	2128.0
Crystal size, mm^3	0.39 × 0.27 × 0.24
Range of data collection over 2θ, deg	5.684–57
Range of reflection indices	$-26 \le h \le 26$, $-17 \le k \le 17$, $-27 \le l \le 27$
Measured reflections	141 773
Independent reflections (R_{int})	12 275 (0.0439)
Refinement variables	551
GOOF	1.059
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0424$, $wR_2 = 0.1071$
R factors for all reflections	$R_1 = 0.0610$, $wR_2 = 0.1221$
Residual electron density (min/max), e/Å^3	0.80/–0.70

no association of ions due to the Zr···Cl···Zr contacts in the crystals, which is explained by a large volume of organophosphorus cations excluding a possibility of approaching together the anions and the formation of polymer chains from them. Nevertheless, the crystal of complex **I** contains F···H contacts (2.33, 2.56 Å), which is possibly related to specific features of its crystal packing.

Thus, the hexachlorozirconate anions are monomeric in the crystal of 4-fluorobenzyltriphenylphosphonium hexachlorozirconate synthesized from 4-fluorobenzyltriphenylphosphonium chloride and zirco-

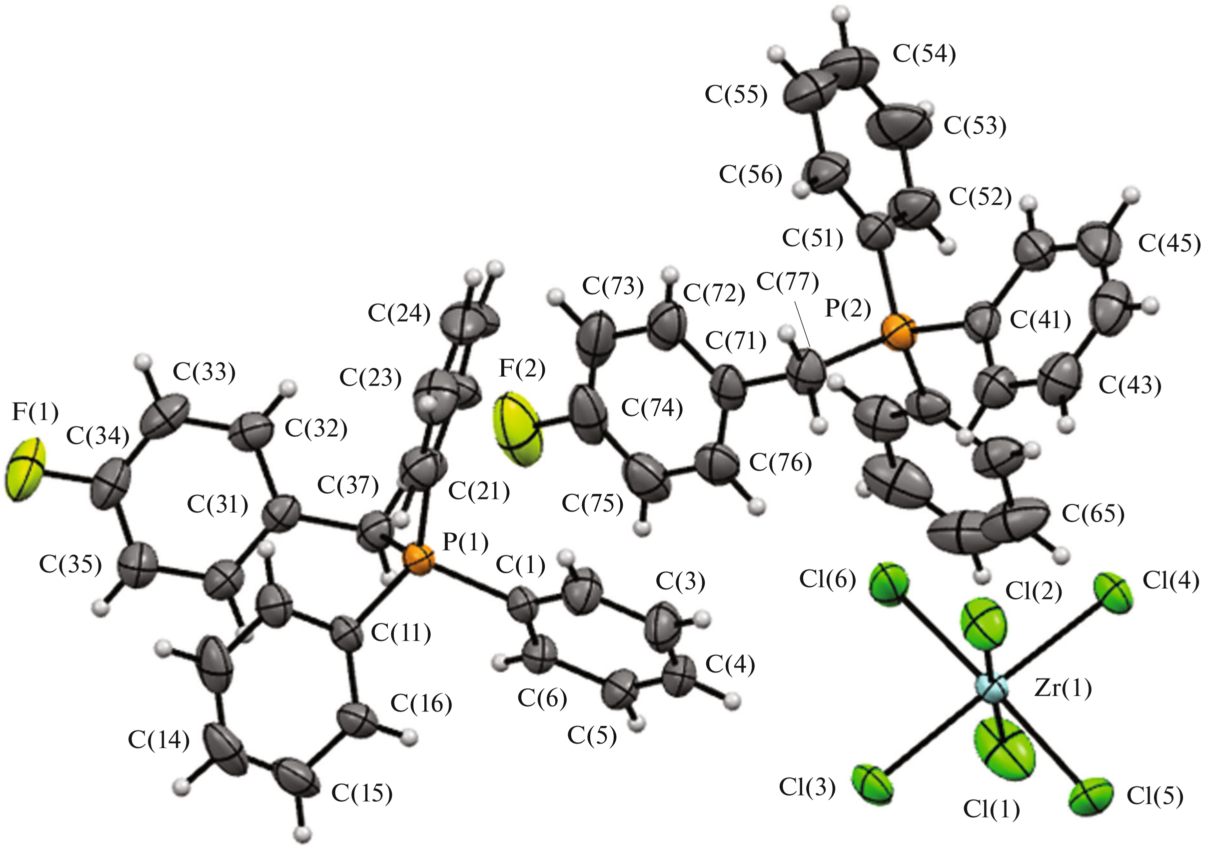

Fig. 1. Structure of (4-fluorobenzyl)triphenylphosphonium hexachlorozirconate **I**.

nium tetrachloride in acetonitrile. The structure of the complex is formed due to weak hydrogen bonds between the cations and anions.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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