CYCLOPENTADIENYL COMPOUNDS OF ZIRCONIUM CONTAINING A Zr–O–Zr GROUP

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Abstract

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CYCLOPENTADIENYL COMPOUNDS OF ZIRCONIUM CONTAINING A Zr—O—Zr GROUP

Organic compounds with zirconoxane bonds ⩾ Zr—O—Zr ⩽ have been little studied. Hexaacyloxydizirconoxanes [(1)] have been described: $(ROCO)_3Zr—O—Zr(OCOR)_3$, R = $C_9H_{19}, C_{11}H_{23}, C_{15}H_{31}, C_{17}H_{35}$, and butoxyzirconoxanes [(2)]: $(C_4H_9O)_{2n+2}Zr_nO_{n-1}$ (n = 2—10). Zirconoxane compounds containing cyclopentadienyl groups are unknown.

We have obtained tetracyclopentadienyldizirconoxane dichloride by hydrolysis of ethoxydicyclopentadienylzirconium chloride. The starting compound was chosen on the assumption that in it the $Zr—OC_2H_5$ bond would be hydrolytically cleaved most readily, according to the scheme:

$$2(C_2H_5O)(C_5H_5)_2ZrCl + H_2O \rightarrow [(C_5H_5)_2ZrCl]_2O\ (I) + 2C_2H_5OH.$$

Subsequently it turned out that tetracyclopentadienyldizirconoxane dichloride (I) can be obtained in one stage by hydrolysis of dicyclopentadienylzirconium dichloride with water in the presence of alcohol and amine. Compound (I) is a crystalline substance, soluble in benzene and chloroform, insoluble in hexane and diethyl ether. Analysis and the molecular weight, determined by the cryoscopic method in benzene, confirmed the proposed formula (I). The zirconoxane bonds in compound (I) are readily destroyed, as was also the case for butoxyzirconoxanes [(2)]; thus, under the action of acetylacetone, zirconium cyclopentadienylacetylacetonate chloride is formed:

$$[(C_5H_5)_2ZrCl]_2O + 2C_5H_8O_2 \rightarrow 2(C_5H_5)Zr(C_5H_7O_2)_2Cl + 2C_5H_6 + H_2O.$$

Hydrogen chloride reacts with compound (I), forming dicyclopentadienylzirconium dichloride:

$$[(C_5H_5)_2ZrCl]_2O + 2HCl \rightarrow 2(C_5H_5)_2ZrCl_2 + H_2O.$$

The starting substances $(RO)(C_5H_5)_2ZrCl$ ($R = C_2H_5$, iso-C_3H_7) were obtained by the action of alcohols on dicyclopentadienylzirconium dichloride in the presence of triethylamine:

$$(C_5H_5)_2ZrCl_2 + ROH \xrightarrow{(C_2H_5)_3N} (C_5H_5)_2(RO)ZrCl\ (II) + (C_2H_5)_3NHCl.$$

The crystalline compounds (II) obtained are extremely hygroscopic; the action of acetylacetone leads to replacement of the alkoxy and cyclopentadienyl groups by acetylacetonate residues:

$$(C_5H_5)_2(RO)ZrCl \xrightarrow{C_5H_8O_2} (C_5H_5)(C_5H_7O_2)_2ZrCl.$$

In 1963 a paper [3] was published in which a crystalline compound of unknown structure, formed by the action of various amines on dicyclopentadienylzirconium dichloride, was described. The authors assign to this compound the formula: $C_{10}H_9ZrCl$ (III). In our opinion, the substance obtained in that work is apparently identical with the dizirconoxane $[(C_5H_5)_2ZrCl]_2O$ (I) described by us. This follows from a comparison of the chemical and physical properties of compounds (I) and (III)—the action of hydrogen chloride, solubility, and also the analytical data:

Found for (I), %: C 45.01; H 4.07; Zr 34.77; Cl 13.45
Found for (III), %: C 45.2; H 4.1; Cl 13.4
For $[(C_5H_5)_2ZrCl]_2O$. Calculated, %: C 45.33; H 3.80; Zr 34.45; Cl 13.40
For $C_{10}H_9ZrCl$. Calculated, %: C 46.8; H 3.5; Cl 13.8

According to our data, the action of dry triethylamine on dicyclopentadienylzirconium dichloride or dibromide in dry benzene does not lead to the formation of the amine hydrochloride, as occurred in the cited work ([3]), if the experiment is carried out with complete exclusion of the action of atmospheric moisture.

In the IR spectrum of the compound (I) obtained by us there are bands characteristic of vibrations of cyclopentadienyl rings (3100, 1450, 1022–1018, 850–840–835 and 812 cm^{-1}), shifted only insignificantly in comparison with the bands in the spectrum of dicyclopentadienylzirconium dichloride. Along with this, new bands appear in the region of 1406 cm^{-1} of medium intensity and very intense bands at 777 cm^{-1} and 748 cm^{-1}. The spectrum of compound (I) proved to be very close to the spectrum of compound (III); in particular, the most characteristic bands are present: 777 cm^{-1} and 748 cm^{-1} for (I), 775 cm^{-1} and 749 cm^{-1} for (III)*.

Experimental Part

Interaction of dicyclopentadienylzirconium dichloride with alcohols in the presence of triethylamine.

a) **Ethyl alcohol.** A solution of dicyclopentadienylzirconium dichloride (5 g, 0.017 mole) in 120 ml of benzene was combined with a solution of dry ethyl alcohol (1.6 g, 0.034 mole) and triethylamine (3.5 g, 0.034 mole) in benzene. The reaction was carried out at 60° with stirring for three hours. The precipitated triethylamine hydrochloride was separated, the solvent was distilled off from the filtrate, and the viscous residue was recrystallized from a mixture of hexane and benzene. A crystalline product was obtained (2.22 g, 43% of theory), which melts at about 70° (with decomposition).

Found, %: C 47.76, 47.13; H 5.17, 4.81; Zr 30.82, 30.57;
Cl 11.50, 11.59

$(C_5H_5)_2Zr(OC_2H_5)(Cl)$. Calculated, %: C 47.71; H 5.01; Zr 30.22;
Cl 11.85

Mol. wt.: found (cryoscopically in benzene) 270, 302.7; calculated 301.8. The presence of two cyclopentadienyl groups was demonstrated as thallium cyclopentadienide (88% of theory).

b) **Isopropyl alcohol.** The experiment was carried out analogously to the preceding one. From 3 g (0.01 mole) of dicyclopentadienylzirconium dichloride, 1.3 g (0.02 mole) of isopropyl alcohol and 2.1 g (0.02 mole) of triethylamine, 0.75 g (23% of theory) of dicyclopentadienylzirconium isopropoxy monochloride was obtained.

Found, %: C 49.72; H 5.29; Cl 11.62
$(C_5H_5)_2Zr(\text{iso-}OC_3H_7)Cl$. Calculated, %: C 49.40; H 5.42; Cl 11.23

Mol. wt.: found 328, 306; calculated 315.81.

The reaction between acetylacetone (10 ml) and ethoxydicyclopentadienylzirconium chloride (0.3 g) was carried out at 50° with stirring; after distillation of the volatile products, 0.2 g (52% of theory) of a crystalline compound with m.p. 185 –186.5° was isolated. This substance showed no depression of the melting point with cyclopentadienyldiacetylacetonatozirconium chloride, obtained earlier ([4]).

Hydrolysis of ethoxydicyclopentadienylzirconium chloride. A solution of water (0.066 ml, 0.0036 mole) in alcohol was gradually added to an alcoholic solution of ethoxydicyclopentadienylzirconium chloride (2.2 g, 0.0072 mole). The reaction was carried out at 45° with stirring for one hour. The reaction mixture was filtered from a small precipitate and concentrated to a volume of 15 ml. In this process, 1 g (52%

* The IR spectra were recorded in the spectroscopy laboratory of the Institute of Natural Compounds, Academy of Sciences of the USSR, by G. G. Dvoryantseva, for which we express our deep gratitude.

of theoretical) crystalline substance.

$$Cl(C_5H_5)_2Zr{-}O{-}Zr(C_5H_5)_2Cl.$$

Found, %: C 45.04; H 4.07; 34.77; Cl 13.45
Calculated, %: C 45.33; H 3.80; 34.45; Cl 13.40

The substance, recrystallized from benzene, melts over a wide temperature range (270-280°) with decomposition.

Found, %: C 45.90, 45.72; H 4.11, 3.98; Zr 33.97, 33.99; Cl 13.25, 13.36

Mol. wt. (cryoscopically in benzene): found 570.4, 520.3; calculated 529.5. The cyclopentadienyl groups were determined as thallium cyclopentadienide (85% of theoretical).

It should be noted that, when recrystallization of ethoxydicyclopentadienylzirconium chloride was carried out without careful protection from atmospheric moisture, as a result of uncontrolled absorption of moisture the starting compound was converted into a crystalline substance that melts over a broad range from 147 to 156° and is apparently ethoxytetracyclopentadienyldizirconoxane chloride.

$$(C_5H_5)_2(Cl)Zr{-}O{-}Zr(C_5H_5)_2(OC_2H_5).$$

Found, %: C 48.54, 48.95; H 4.95, 4.88;
Zr 34.01, 34.13; Cl 6.37, 6.29

Calculated, %: C 48.97; H 4.67;
Zr 33.83; Cl 6.87

In this compound the cyclopentadienyl groups were determined (76% of theoretical).

The corresponding bromide was obtained analogously (m.p. 184-192°).

$$(C_5H_5)_2(Br)Zr{-}O{-}Zr(C_5H_5)_2(OC_2H_5).$$

Found, %: C 45.80; H 4.24; Zr 31.27
Calculated, %: C 45.08; H 4.38; Zr 31.76

Hydrolysis of dicyclopentadienylzirconium dichloride. Dicyclopentadienylzirconium dichloride (1.17 g, 0.004 mole) was dissolved in 40 ml of benzene; to this was added, at 40° and with vigorous stirring, a benzene solution of triethylamine (0.40 g, 0.004 mole), ethyl alcohol (0.184 g, 0.004 mole), and water (0.036 g, 0.002 mole). The reaction was carried out for one hour. The precipitate of triethylamine hydrochloride was filtered off; the filtrate was concentrated to

~10 ml, and the precipitated solid (0.77 g, 77% of theoretical) was recrystallized from benzene (m.p. 280° with decomposition).

$$[(C_5H_5)_2ZrCl]_2O.$$

Found, %: C 45.94; H 3.85; Zr 34.35; Cl 12.73
Calculated, %: C 45.33; H 3.80; Zr 34.45; Cl 13.40

Reaction of tetracyclopentadienyldizirconoxane dichloride (I) with acetylacetone. Tetracyclopentadienyldizirconoxane dichloride (0.3 g) was dissolved in acetylacetone (20 ml), and the reaction was carried out at 40° for 20 min. There was obtained 0.43 g (97% of theoretical) of a substance (m.p. 186–188°); its mixed melting-point test with an authentic sample of acetylacetonatodicyclopentadienylzirconium chloride gives no depression.

Action of hydrogen chloride on (I). From 0.25 g of substance (I), dissolved in 5 ml of dry chloroform, upon saturation with hydrogen chloride for 7 hr, there was obtained 0.20 g (72% of theoretical) of dicyclopentadienylzirconium dichloride with m.p. 236–240°. The substance shows no depression of the melting point in a mixture with an authentic sample.

$$(C_5H_5)_2ZrCl_2.$$

Found, %: C 41.16; H 3.55; Zr 31.08; Cl 24.51
Calculated, %: C 41.07; H 3.69; Zr 31.22; Cl 24.05

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Note: Figure translations are in progress. See original paper for figures.