Reports of the Academy of Sciences of the USSR

Corresponding Member of the Academy of Sciences of the USSR R. Kh. FREIDLINA, E. M. BRAJNINA,

1961

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1961. Vol. 138, No. 6

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR R. Kh. FREIDLINA, E. M. BRAJNINA,
and Academician A. N. NESMEYANOV

SYNTHESIS OF MIXED CHELATE-LIKE CYCLOPENTADIENYL COMPOUNDS OF ZIRCONIUM

At the present time, among cyclopentadienyl compounds of zirconium, the dibromide (as well as the dichloride) of dicyclopentadienylzirconium ([1,2]) and dichlorobis-methylcyclopentadienylzirconium ([3]) are known. These compounds have been obtained from zirconium halides and the corresponding sodium cyclopentadienides. The infrared spectra of these compounds are analogous to the corresponding spectra of neutral bis-cyclopentadienyl compounds, and also to the spectra of ferricinium salts $(C_5H_5)_2Fe^+$. They are cited by the authors as evidence of their sandwich-like structure.

Cyclopentadienyl compounds of zirconium containing one cyclopentadienyl group have not been described. Of compounds containing simultaneously a chelate-like group and a cyclopentadienyl ring, only one is known—of composition ([4]): $(C_5H_7O_2)C_5H_5CrBr$. The following structure has been proposed for it:

[[structural formula shown: $(C_5H_7O_2)C_5H_5CrBr$, with CH_3, CH, O, Br, Cr labels]]

This compound was obtained in 3% yield from cyclopentadienylmagnesium bromide and chromium triacetylacetonate.

In continuation of our investigation devoted to exchange reactions of chelate-like compounds of transition metals ([5–7]), we have studied the interaction of sodium cyclopentadienide with zirconium acetylacetonate dichloride. In this process a mixed compound of composition $C_5H_5(C_5H_7O_2)_2ZrCl$ was obtained. The same compound is formed in nearly quantitative yield upon the interaction of dicyclopentadienylzirconium dichloride with an excess of acetylacetone. By the same routes the corresponding compound containing benzoylacetonate groups

was obtained. Apparently, these reactions may constitute a general route for the synthesis of analogous mixed zirconium compounds containing other chelate-like groups.

The compounds synthesized by us are colorless crystalline substances, soluble in chloroform at room temperature, in benzene and tetrahydrofuran upon heating, and insoluble in petroleum ether. In their properties they are close to dihalide dicyclopentadienyl compounds of zirconium.

It may be assumed that the chelate cyclopentadienyl compounds under study are built according to the type of octahedral zirconium compounds, and in that case one should expect the possibility of formation of cis- and trans-isomeric compounds of such a structure:

[Two structural diagrams of possible cis- and trans-isomeric chelate cyclopentadienyl zirconium compounds are shown.]

The IR absorption spectra* of zirconium triacetylacetonate monochloride, dicyclopentadienylzirconium dichloride, and the mixed diacetylacetonatocyclopentadienylzirconium monochloride were studied. Zirconium triacetylacetonate monochloride (NaCl prism) is characterized by frequencies of 819, 938, 1015-1029, 1192, 1281-1300, 1356-1378, 1419, 1454, 1533, 1564 cm^{-1}. Dicyclopentadienylzirconium dichloride is characterized in the same region by frequencies of 814-820, 842-854, 1016, 1438 cm^{-1}. The mixed compound in the indicated region is characterized by frequencies of 806, 934, 1020-1028, 1280, 1368-1378, 1458, 1530-1540, 1572-1584 cm^{-1}. The spectra obtained do not contradict the assumption made concerning the structure of the mixed compound.

We have developed a simple method for the synthesis of the previously difficultly accessible dichlorides of chelate zirconium compounds, which are starting substances for obtaining the mixed compounds described above. The method consists in the interaction of zirconium tetrachloride with complete chelate zirconium compounds. The reaction may be described by the scheme:

$$\left(\begin{array}{cc} & R \\ & \diagdown \\ HC & C{=}O \\ \| & \diagdown \\ C & -O \end{array}\right)_4 \mathrm{Zr} + \mathrm{ZrCl_4} \xrightarrow{\mathrm{THF}} 2\left(\begin{array}{cc} & R \\ & \diagdown \\ HC & C{=}O \\ \| & \diagdown \\ C & -O \end{array}\right)_2 \mathrm{ZrCl_2}.$$

Experimental Part

Dicyclopentadienylzirconium dichloride. The synthesis was carried out by the method described for obtaining dicyclopentadienylzirconium dibromide ([1,2]), with certain modifications that made it possible to simplify the isolation of the product and increase the yield. The reaction was carried out starting from 35 g (0.15 mole) of zirconium tetrachloride and cyclopenta-

* The IR spectra were recorded in the spectral laboratory of Moscow University by L. A. Kazitsyna, to whom we express our sincere gratitude.

sodium dienide (obtained from 7.0 g of sodium and 20.1 g (0.30 mole) of cyclopentadiene) in tetrahydrofuran (THF) at room temperature with stirring for 1.5 hr. After the solvent had been distilled off, the residue was extracted with chloroform in a stream of hydrogen chloride. The extract, containing dicyclopentadienylzirconium dichloride together with a large amount of a black resinous impurity, was heated with activated charcoal and filtered; most of the solvent was distilled off from the filtrate, and the colorless precipitate that separated was washed with petroleum ether and diethyl ether; weight of the dry product 4.1 g. Repeated extractions gave a further 25 g of substance. Total weight 29.1 g (66% of theory). The product melts at 243–244° with decomposition.

	Found, %:	C 41.53; 41.40;	H 3.54; 3.34;	Zr 31.08; 31.45	Cl 24.47; 24.57
$(C_5H_5)_2ZrCl_2$.	Calculated, %:	C 41.07;	H 3.69;	Zr 31.22;	Cl 24.03

The substance recrystallized from benzene melts at 244.5–245°. Literature data ([8]): m.p. 232°. Found, %: C 41.32; H 3.64; Zr 31.44; Cl 23.95. Mol. wt.: found 282.9 (cryoscopically in benzene), $(C_5H_5)_2ZrCl_2$ calculated 292.2.

Monochloro diacetylacetonatocyclopentadienylzirconium.

A. From dicyclopentadienylzirconium dichloride. A solution of dicyclopentadienylzirconium dichloride (4.9 g) in 50 ml of acetylacetone was heated for 2 hr at 70–80° and reduced pressure. During the reaction the volatile products were distilled off. The solution was evaporated in vacuo to half its initial volume. The precipitate obtained was filtered off, washed with petroleum ether, and dried in a stream of dry air. This gave 6.2 g of a colorless crystalline powder (95% of theory). The product recrystallized from benzene melts, as before recrystallization, at 188–190° with decomposition.

	Found, %:	C 46.22; 46.28;	H 5.09; 4.80;	Zr 23.72; 23.68;	Cl 9.15; 9.39
$(C_5H_7O_2)_2C_5H_5ZrCl$.	Calculated, %:	C 46.18;	H 4.91;	Zr 23.40;	Cl 9.09

Mol. wt.: found 387 (in benzene), $(C_5H_5)(C_5H_7O_2)_2ZrCl$, calculated 389.9. The molecular weight was determined by a procedure allowing the cryoscopic method to be applied to associated metal alkoxide compounds ([9]).

B. From diacetylacetonatozirconium dichloride. The synthesis of diacetylacetonatozirconium dichloride was carried out as described below, without isolation of the product from the reaction mixture. To a solution containing 7.2 g

(0.02 mole) of the dichloride in 80 ml of tetrahydrofuran was added an equimolecular amount of sodium cyclopentadienide in 10 ml of tetrahydrofuran. The reaction was carried out in a nitrogen atmosphere, at room temperature; stirring was continued for 2 hr. The precipitated NaCl was filtered off, the solvent was distilled off from the filtrate, and the residue was recrystallized from benzene; 2.2 g (28% of theory) of monochloro diacetylacetonatocyclopentadienylzirconium was obtained, m.p. 188–190° with decomposition. A mixed sample with the specimen obtained in the preceding experiment (A) showed no depression of the melting point. Found, %: C 46.28; H 5.14; Zr 23.22. The substance is stable in an atmosphere of dry air; on heating with excess water it slowly decomposes.

Monochloro dibenzoylacetonatocyclopentadienylzirconium.

A benzene solution of 1.0 g (0.003 mole) of dicyclopentadienylzirconium dichloride and 1.1 g (0.006 mole) of benzoylacetone was heated at 95–100° and reduced pressure for 15 hr, with repeated addition of benzene, until traces of chloride ions disappeared in the distillate. The solvent was distilled off, and the dry residue was recrystallized from a mixture of benzene and petroleum ether (3:2). The recrystallized product weighs 1.2 g (69% of theory). After a second recrystallization from benzene, m.p.

184–185.5°, with decomposition. The product was thoroughly dried at 1 mm and 80°.

$(C_{10}H_9O_2)_2C_5H_5ZrCl$. Found, %: C 58.47; 58.58; H 4.74; 4.42; Zr 17.92; 17.67; Cl 6.58; 6.59
Calculated, %: C 58.38; H 4.51; Zr 17.75; Cl 6.90

Diacetylacetonatozirconium dichloride. Solutions of tetraacetylacetonatozirconium (4.87 g; 0.01 mole) in 80 ml of tetrahydrofuran and of zirconium tetrachloride (2.33 g; 0.01 mole) in 14 ml of tetrahydrofuran were combined. The reaction mixture was stirred at 40° for 2 hours; then the solvent was distilled off, and the residue was recrystallized from a mixture of tetrahydrofuran and petroleum ether. An oil separated, which crystallized on cooling to −40°. The weight of crystals was 3 g (38% of theory), m.p. 68–70° with decomposition. The crystals rapidly become wet on drying. The product analyzed was dried at 1 mm for 1.5 hours at 40°.

$[(C_5H_7O_2)_2ZrCl_2]_2C_4H_8O$. Found, %: C 36.67; 36.49; H 5.17; 5.13; Zr 22.30; 22.57; Cl 17.11; 17.27
Calculated, %: C 36.35; H 4.58; Zr 23.02; Cl 17.90

The substance is highly hygroscopic and is readily hydrolyzed.

Dibenzoylacetonatozirconium dichloride. The experiment was carried out analogously to the preceding one. From 1.84 g (0.0025 mole) of tetrabenzoylacetonatozirconium there was obtained 1.80 g (68% of theory) of dibenzoylacetonatozirconium dichloride. The substance consists of colorless crystals, melting in a sealed capillary at 116–119°; the melt then solidifies and, on further heating, melts at 228–230° with decomposition. After recrystallization from tetrahydrofuran, the resulting compound behaves on heating in a sealed capillary similarly to the unrecrystallized product, m.p. 231–234° with decomposition. Literature data [10]: m.p. 232–234°.

$(C_{10}H_9O_2)_2ZrCl_2C_4H_8O$. Found, %: C 51.87; 51.21; H 4.91; 4.77; Zr 16.02; 16.78; Cl 12.43; 12.71
Calculated, %: C 51.82; H 4.70; Zr 16.40; Cl 12.75

Heating this substance at 80–115° and 1 mm for 2 hours led to almost complete liberation from tetrahydrofuran.

$(C_{10}H_9O_2)_2ZrCl_2$. Found, %: C 50.36; H 4.01; Zr 18.78
Calculated, %: C 49.57; H 3.74; Zr 18.84

Institute of Organoelement Compounds
Received
4 II 1961

REFERENCES CITED

1. G. Wilkinson, P. L. Pauson et al., *J. Am. Chem. Soc.*, **75**, 1011 (1953).

2. G. Wilkinson, J. M. Birmingham, *J. Am. Chem. Soc.*, **76**, 4281 (1954).

3. L. T. Reynolds, G. Wilkinson, *J. Inorg. and Nucl. Chem.*, **9**, 86 (1959).

4. J. C. Thomas, *Chem. and Ind.*, **1956**, 1388.

5. R. Kh. Freidlina, E. M. Brainina, A. N. Nesmeyanov, *Izv. AN SSSR, OKhN*, **1957**, 43.

6. R. Kh. Freidlina, E. M. Brainina, A. N. Nesmeyanov, *Izv. AN SSSR, OKhN*, **1960**, 59.

7. E. M. Brainina, R. Kh. Freidlina, A. N. Nesmeyanov, *Izv. AN SSSR, OKhN*, **1960**, 63.

8. G. Wilkinson, F. A. Cotton, *Progr. Inorg. Chem.*, **1959**, 14.

9. A. N. Nesmeyanov, O. V. Nogina, V. A. Dubovitskii, *Izv. AN SSSR, OKhN*, **1959**, 8.

10. W. Dilthey, *J. Pract. Chem.*, **111**, 147 (1925).

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