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Abstract

Full Text

Chemistry

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Cyclopentadienyl Dizirconoxane Compounds Containing Aryl or Chelate-like Groups

For most transition elements, organometallic compounds have by now been obtained that contain metal-aryl or metal-alkyl bonds together with π-cyclopentadienyl or carbonyl groups. For zirconium, such compounds have not been obtained.

In a previous paper (^{1}) we showed that cyclopentadienyl dizirconoxane compounds can be obtained by hydrolysis of dicyclopentadienylzirconium dichloride or chloride-alkoxide according to scheme 1:

$$(C_5H_5)_2Zr(Cl)X \xrightarrow{H_2O} Cl(C_5H_5)_2ZrOZr(C_5H_5)_2Cl \tag{1}$$

where $X = \text{Cl},\ \text{OC}_2\text{H}_5$.

In the present paper we report the preparation of new representatives of other types of cyclopentadienyl dizirconoxane compounds containing phenyl, n-tolyl, or acetylacetonate groups.

Diphenyltetracyclopentadienyldizirconoxane (I) was obtained by the action of phenyllithium on dicyclopentadienylzirconium dichloride, followed by treatment with water according to scheme 2:

$$(C_5H_5)_2ZrCl_2 + C_6H_5Li \xrightarrow{H_2O} (C_6H_5)(C_5H_5)_2ZrOZr(C_5H_5)_2(C_6H_5)\,H_2O. \tag{2}$$

I

The compound I obtained is relatively unstable at room temperature.

The following reactions proved the structure of substance I. Reaction with thallous sulfate showed the presence in compound I of two cyclopentadienyl groups for each zirconium atom. The presence of phenyl groups was proved by the action of sulema on compound I, with formation of phenylmercuric chloride. The reaction of hydrogen chloride with I leads to cleavage of the Zr—O—Zr and Zr—C_6H_5 bonds and to formation of dicyclopentadienylzirconium dichloride. By careful action of a calculated amount of chlorine on I, the already known (^{1}) dichloride of tetracyclopentadienyldizirconoxane (II) was obtained according to scheme 3:

$$(C_6H_5)(C_5H_5)_2ZrOZr(C_5H_5)_2(C_6H_5) + 2Cl_2 \rightarrow Cl(C_5H_5)_2ZrOZr(C_5H_5)_2Cl, \tag{3}$$

I II

whereas, conversely, by the action of phenyllithium on II, I was obtained, which may be regarded as a counter synthesis.

The structure of diphenyltetracyclopentadienyldizirconoxane I is also confirmed by its IR spectrum (Table 1).

From dicyclopentadienylzirconium dichloride and *n*-tolyllithium, di-*n*-tolyltetracyclopentadienyldizirconoxane was synthesized,

$$(n\text{-}CH_3C_6H_4)(C_5H_5)_2ZrOZr(C_5H_5)_2(C_6H_4CH_3\text{-}n)$$

III

On treatment of compound III with sulema, *n*-tolylmercuric chloride was obtained. The structure of III is also confirmed by its IR spectrum (Table 1).

Table 1

IR spectra of cyclopentadienyl compounds of zirconium (in cm^{-1})

$(C_5H_5)_2Cl(C_2Zr_5H_5)_2Br(C_2Zr_5H_5)_2Zr(Cl)HO)_2Zr(Br)HO)_2C(C_6H_5Zr_5)_2O\ldots C_5H_5Zr)_2O$

–606 w.–815 w., 840, 855– 1016– 1025 w., 112613681442 –1650 w., 1680 w.1765 w., 1875 w.3105	–606 w.721 w.–813 w., 839, 849– 1013– 1020 w., 112513681442 –1650 w., 1670 w.1765 w., 1875 w.3105	––611 w.–750 s775 s808 s, 833– 840 w. –1014 –1019 w., 1070 w., [1130]13651445 –1650 w., 1750 w.1845 w.3088 –3106	––606 w.739 w.804– 814 w., 839– 1019, 1070 w., [1125]13701440 –1640 w., 1445 w.1732 w.1830 w.3030 –3108	458– 610675 w.750 w.796– 809993 w., 1013 w.,1053 –1170 w., 1129 w.,1154 –1163 w.,1191 w., 1241 w.12921365 1440 w., 1480,1560 w.15921712 w.1871 w., 1882 w.1950 w.3040 –3055, 3400– 3410	485545593 w.644, 675728 –741 w.790– 806 w., 846 w.880 w., 945 w.,1016, 1043 w.,1070 w., 1126 w.,1167 w., 12851365 1450, 1508 w.16101720 w.,1810 w.,1905 w.,2870, 2920– 29303010, 3050, 3100– 3410	408, 433, 445 w.542, 560606665 –800 w., 809 –819 w.,835 w.9351019 –1028 w., 1072 w.,1130, 1189 w.,1205 w., 1279 w.1362 w.1455 w., 1548 w., 1570 w.1588 w.1601 w.3103 –3145	407, 423542610660727 w.775 w.788 w., 800 w., 8079321025 w., 1076, 1130 w.,1140 w., 1177 w.,1275 w.1362 w.1450 w., 1526 w., 1590 w.1610 –1620 w.3090 –3410

Notes. w. –weak band; s –strong band; without an index –a band of medium intensity; in parentheses –a band of very weak intensity.

By hydrolysis of monochloride diacetylacetonatocyclopentadienylzirconium (for preparation see (²)) according to scheme 4, a compound belonging to another type of dizirconoxanes was obtained–tetraacetyldiacetonatodicyclopentadienyldizirconoxane (IV).

$$(C_5H_5)(C_5H_7O_2)_2ZrCl + H_2O \rightarrow (C_5H_5)(C_5H_7O_2)\cdot ZrOZr(C_5H_5)(C_5H_7O_2)_2 \quad (4)$$

IV

The IR spectrum of this compound is given in Table 1.

By hydrolysis of dibromide dicyclopentadienylzirconium, dibromide tetraacetylcyclopentadienyldizirconoxane was obtained.

Table 1 gives the frequencies in the IR spectra of the compounds obtained by us. From the results of these measurements it is seen that the spectra of all the compounds obtained contain frequencies characteristic of vibrations of cyclopentadienyl rings in the regions 800—850, 1010—1030, 1130, 1365, 1440, and 3090—3120 cm^{-1}.

In the spectra of the aryl derivatives $((C_5H_5)_2C_6H_5 \cdot Zr)_2O$ and $((C_5H_5)_2CH_3C_6 \cdot H_4Zr)_2O$, absorption bands are observed that are characteristic of substituted aryl groups: 450—490, 1000—1100, 1570—1610, 3000—3050 cm^{-1}.

The spectra of all dizirconoxane compounds contain intense bands in the region 720—775 cm^{-1}, absent in $(C_5H_5)_2 \cdot ZrCl_2$, $(C_5H_5)_2ZrBr_2$, and $C_5H_5(C_5H_7O_2)_2ZrCl$, which makes it possible to assign these bands to vibrations of the Zr—O—Zr bond.

The IR spectra of the substances studied were measured on a double-beam IR spectrometer VR-10 in the region

from 400 to 4000 cm^{-1} with KBr, NaCl, and LiF prisms, in crystals with Vaseline oil and fluorinated hydrocarbons.

Diphenyltetracyclopentadienyldizirconoxane.

a) **From dicyclopentadienylzirconium dichloride.** To a suspension of $(\mathrm{C_5H_5})_2\mathrm{ZrCl_2}$ (3 g, 10 mmoles) in 40 ml of ether, phenyllithium was slowly added (prepared from 0.36 g (51 mmoles) Li and 2.4 ml (22 mmoles) $\mathrm{C_6H_5Br}$). The reaction was carried out in a stream of argon with stirring at room temperature for two hours. The precipitated inorganic solid was filtered off, washed with methylene chloride, the filtrates were poured into an equal volume of cold water, the organic layer was separated, hexane was added to it, and after cooling a small precipitate was filtered off; the filtrate was concentrated under reduced pressure. The precipitate obtained (1.7 g, 52.5% of theory) contains no halide and melts over the broad range 250-260°.

$((\mathrm{C_5H_5})_2\mathrm{C_6H_5Zr})_2\mathrm{O} \cdot \mathrm{H_2O})$ Found %: C 60.88, 61.00; H 5.21, 5.16; Zr 29.11, 29.39
Calculated %: C 60.99; H 5.11; Zr 28.92

Cyclopentadienyl groups were found as $\mathrm{C_5H_5Tl}$—about 100% of theory.

b) **From tetrcyclopentadienyldizirconoxane dichloride (II).** The reaction was carried out analogously to the preceding experiment. From 1.45 g (2 mmoles) of II and phenyllithium, prepared from 0.65 ml (4 mmoles)

C_6H_5Br and 0.14 g (20 mmoles) lithium, 0.85 g (49% of theory) of diphenyltetracyclopentadienyldizirconoxane was isolated.

Found %: C 60.78; H 4.95; Zr 29.43

The spectra of the compounds obtained by methods a and b are identical.

Action of chlorine on diphenyltetracyclopentadienyldizirconoxane (I). To a cooled solution of I (0.5 g, 0.79 mmoles) in 30 ml of benzene, a benzene solution of chlorine was added (0.11 g, 1.57 mmoles); the small precipitate formed was filtered off, and from the filtrate, concentrated to 7 ml, 0.23 g (57% of theory) of tetracyclopentadienyldizirconoxane dichloride (II) was isolated (m.p. 270–280°).

$((C_5H_5)_2ZrCl)_2O$. Found %: C 45.57; H 3.62; Zr 34.49; Cl 13.11
Calculated %: C 45.33; H 3.80; Zr 34.45; Cl 13.40

The spectra of this compound and of the compound obtained by us by another method ([1]) are identical.

Action of sublimate on diphenyltetracyclopentadienyldizirconoxane (I). A solution of (I) (0.2 g, 0.3 mmoles) in tetrahydrofuran (2.5 ml) was combined with a solution of sublimate (0.18 g, 0.6 mmoles) in 2 ml of tetrahydrofuran. The reaction was carried out at 60–65° with stirring for two hours. The insoluble precipitate (0.08 g) contains no mercury. The filtrate was concentrated; the precipitated solid (0.1 g) was filtered off, washed with hexane, dried, and recrystallized from benzene. 0.03 g (13% of theory) of phenylmercuric chloride was obtained, m.p. 257–258°; literature data ([3]): m.p. 258°. A mixed melting-point test with an authentic sample of phenylmercuric chloride gives no depression.

Action of hydrogen chloride on diphenyltetracyclopentadienyldizirconoxane (I). Dry hydrogen chloride was passed through a solution of I (0.3 g) in 15 ml of chloroform for 2.5 hours at room temperature. From the clear filtrate, the greater part of the solvent was distilled off; the precipitated solid was filtered off, weight 0.25 g (90% of theory), m.p. 242.5–243°. A mixed melting-point test with an authentic sample of $(C_5H_5)_2ZrCl_2$ gives no depression.

Di-*p*-tolyltetracyclopentadienyldizirconoxane (III). The reaction was carried out analogously to the preparation of I (experiment).

From 1.75 g (6 mmol) of dicyclopentadienylzirconium dichloride and *p*-tolyllithium from 2.57 g (15 mmol) of *p*-$CH_3C_6H_4Br$ and 0.27 g (40 mmol) of lithium, 0.85 g (44% of theory) of di-*p*-tolyltetracyclopentadienyldizirconoxane was obtained, mp 210–224°.

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Found, %:	C 63.27, 63.20;	H 5.50, 5.79;	Zr 28.45, 28.07
$((p\text{-}CH_3C_6H_4)(C_5H_5)_2Zr)_2O$. Calculated, %:	C 63.68;	H 5.34;	Zr 28.47

Cyclopentadienyl groups found: 85% of theory. Molecular weight (cryoscopically in benzene): found 612, 608; calculated 640.7*.

On treatment of substance III with sublimate in tetrahydrofuran, *p*-tolylmercury chloride was isolated; after recrystallization from chloroform (yield 14% of theory) it melts at 233-235°. A mixed melting-point test with an authentic sample of *p*-tolylmercury chloride gives no depression.

Tetraacetylacetonate dicyclopentadienyldizirconoxane (IV). A mixture in benzene consisting of 0.184 g (4 mmol) of absolute ethanol, 0.405 g (4 mmol) of triethylamine, and 0.036 g (2 mmol) of water was added to a benzene solution of 1.56 g (4 mmol) of $(C_5H_5)(C_5H_7O_2)_2ZrCl$. The reaction was carried out at 30-35° for one hour. The precipitated triethylamine hydrochloride was filtered off. The solvent was distilled off from the filtrate, giving 0.8 g (55% of theory) of substance, mp 164.5-165.5° (from a benzene-hexane mixture).

Found, %:	C 49.90, 49.79;	H 5.16, 5.24;	Zr 25.29, 25.29
$[(C_5H_5)(C_5H_7O_2)_2Zr]_2O$. Calculated, %:	C 49.68;	H 5.28;	Zr 25.27

Mol. wt. (cryoscopically in benzene): found 720; 757, calculated 725.

Cyclopentadienyl groups found: 84% of theory.

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* During determination of the molecular weight, decomposition of substance III was observed (gradual precipitation of a solid); therefore each determination was made from a weighed portion of freshly prepared substance, and the first two readings were used in the calculation.

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

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