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Synthesis and Properties of Methyl(phenyl)zirconium

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In our previous studies [1, 2] it has been established that interaction of titanium and zirconium biscyclopentadienyl derivatives with organolithium compounds proceeds by the general scheme with formation of unstable at-complexes. Decomposition of $[Cp_2MR_2R']Li^+$ was used as preparation method for titanium and zirconium covalent derivative synthesis of the lowest oxidation states.

The present study involves the preparation and investigation of properties of a bivalent non-symmetric compound of zirconium – methyl(phenyl)zirconium.

The interaction between organo-zirconium and -lithium compounds in systems: Cp_2ZrPh_2 + 2MeLi and Cp_2ZrMe_2 + 2PhLi in diethyl ether at 20 °C results in the formation of methane, benzene and cyclopentadienyllithium. The main zirconium-containing product is etherate of methyl(phenyl)zirconium, $MeZrPh{\cdot}3Et_2O$. Brown pyrophoric crystals are slightly soluble in most organic solvents; this points to a polymer structure of the compound.

The IR-spectrum of methyl(phenyl)zirconium shows bands characteristic of methyl (630 cm^{-1}), phenyl (680, 720 cm^{-1}) groups and coordinatively linked ether (1020, 1070, 1160, 1700 cm^{-1}).

In comparison with thermally unstable Me_4Zr and Ph_4Zr, bivalent zirconium complex $MeZrPh{\cdot}3Et_2O$ is stable. By the DTA method it has been found that $MeZrPh{\cdot}3Et_2O$ begins to decompose at 74 °C with maximum exothermic effect at 92 °C. Thermal decomposition of $MeZrPh{\cdot}3Et_2O$ at 120 °C for 1 hr yields methane (0.49 mol), benzene (0.51 mol), toluene (0.08 mol) and ether (0.49 mol)*. The further heating of the sample to higher temperatures is not accompanied by prominent thermal effects, though the yield of decomposition products increases. After heating up to 300 °C, methane (0.80 mol), benzene (0.72 mol), toluene (0.10 mol), ether (0.57 mol) were totally detected. Interaction of thermal decomposition products of $MeZrPh{\cdot}3Et_2O$ with DCL/D_2O leads to the formation of CD_4 (85%) and CD_3H (15%). It is supposed that upon the thermal decomposition of $MeZrPh{\cdot}3Et_2O$ the hydrogen source for methane and benzene elimination can be σ-bonded ligand and coordinative ether.

Investigation of the chemical properties of $MeZrPh{\cdot}3Et_2O$ has shown that two types of reaction are characterized in this compound: *1*) reactions accompanied by oxidation of the central atom from Zr^{II} to Zr^{IV}; *2*) reactions proceeding with conservation of the zirconium valence.

The reactions with water, acids and metal salts are of the first type. We have investigated the interaction of methyl(phenyl)zirconium with water, acetic acid and mercuric chloride.

The hydrolysis reaction confirmed the composition of the compound mentioned. It proceeded at 20 °C in the presence of 6N HCl with formation of methane (0.95 mol), benzene (1.00 mol), hydrogen (0.70 mol), ether and tetravalent zirconium salt.

The reaction with acetic acid proceeds rather quickly at room temperature and is accompanied by zirconium–carbon σ-bond cleavage with formation of methane (1.00 mol), benzene (0.90 mol), hydrogen (0.85 mol), diethyl ether (2.70 mol) and zirconium tetraacetate (0.82 mol).

The set of experimental data on reactions with compounds containing active hydrogen indicates that they proceed according to the general scheme:

$$MeZrPh{\cdot}3Et_2O + 4HX \xrightarrow[20\ ^{\circ}C]{toluene} MeH + PhH + 3Et_2O + H_2 + ZrX_4 \qquad (1)$$

$X = OH^-, CH_3COO^-, Cl^-$.

Contrary to the above-mentioned reactions methyl(phenyl)zirconium interacts with mercuric chloride only on heating. The transfer of all σ-bound groups to mercury occurred with formation of equimolar quantities of methylmercurichloride (0.90 mol) and phenylmercurichloride (0.90 mol) in the process of this reaction. Simultaneously, the reduction of mercuric chloride to mercurious chloride and oxidation of zirconium to the tetravalent state occurred.

$$MeZrPh{\cdot}3Et_2O + 4HgCl_2 \xrightarrow[80\ ^{\circ}C]{THF} MeHgCl + PhHgCl + Hg_2Cl_2 + ZrCl_4{\cdot}3Et_2O \qquad (2)$$

The second type of reactions was studied on the example of interaction with ketones, carbon dioxide and carbon monoxide.

MeZrPh reacts with CO under normal pressure and at room temperature, absorbing to moles of CO per 1 g-atom of zirconium irreversibly. Brown crystals sensitive to oxygen were isolated from the reaction mixture. The IR-spectrum of these crystals has absorption bands typical of carbonyl and alkoxyl groups.

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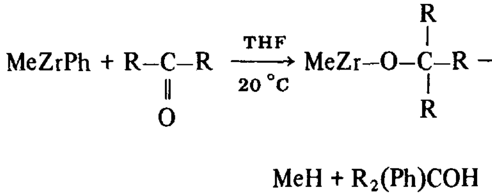
*Here and later on the yield is given in mol per mol of initial ZrOC.

Hydrolysis of the reaction product gives a complex non-identifiable mixture of products. It is known from the literature data that organozirconium compound carbonylation is a complex process involving several stages [3–5]. Initially coordination of CO molecule on-zirconium atom occurs with subsequent migration of R-groups to coordinated carbon monoxide. The acyl derivatives formed interact readily with non-reacted initial ZrOC, yielding alkoxyl fragments. Therefore, hydrolysis of reaction products in known systems $(PhCH_2)_4Zr$ + CO and Cp_2ZrAlk_2 + CO yield a large set of various compounds involving aldehydes, ketones and alcohols [3–5].

Methyl(phenyl)zirconium can react as a Grignard compound. Thus, MeZrPh interacts with benzophenone at 20 °C in the THF medium in the ratio of 1:1. After hydrolysis of the reaction product, methane (0.98 mol) and triphenylcarbinol (0.92 mol) are formed. Similarly MeZrPh with acetone yield methane (0.92 mol) and dimethylphenylcarbinol (0.87 mol). Experimental data allow to consider that introduction of ketones occurs through the zirconium–phenyl bond.



$$\mathrm{MeZrPh} + \underset{\underset{\displaystyle O}{\|}}{\mathrm{R{-}C{-}R}} \xrightarrow[20\,^{\circ}\mathrm{C}]{\mathrm{THF}} \mathrm{MeZr{-}O{-}}\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{\mathrm{C}}}\mathrm{{-}R} \xrightarrow{\mathrm{HOH}} \mathrm{MeH} + R_2(\mathrm{Ph})\mathrm{COH} \qquad (3)$$

I: R = Me;
II: R = Ph.

The covalent derivative of bivalent zirconium investigated by us reacts readily with carbon dioxide contrary to Cp_2ZrMe_2 which does not interact with CO_2, and to $(PhCH_2)_4Zr$, which absorbs only two mols of CO_2 per 1 g-atom of zirconium [6, 7]. When passing carbon dioxide through a toluene solution of MeZrPh for 10 hours under normal conditions CO_2 introduction occurs through zirconium–carbon σ-bonds. The insertion product is isolated as light-brown crystals which are sensitive to oxygen and moisture. The IR-spectrum shows a bond at 1620 cm^{-1}, characteristic of the carboxyl group. Elemental analysis of the product corresponds to (MeOCO)Zr(OCOPh)·$3Et_2O$ formula, containing Zr^{II}, and agrees with the data of the IR-spectra. Hydrolysis of the compound prepared gave the equivalent quantities of acetic and benzoic acids.

Experimental

Preparation of Methyl(phenyl)zirconium

The ether solution of phenyllithium (12.0 mmol) was added to a solution of Cp_2ZrMe_2 (1.52 g, 6.0 mmol) in diethyl ether (60 ml) at 20 °C with stirring. The reaction mixture turned black after standing for 24 hr. C_6H_6 (5.9 mmol) and CH_4 (6.0 mmol) were detected. The resulting solution was cooled to 0 °C and the precipitate was filtered off, washed with chilled petroleum and dried *in vacuo*. Brown crystals of MeZrPh·$3Et_2O$ (2.02 g, 5.0 mmol) were isolated. *Anal.* Calcd. for $C_{10}H_{38}O_3Zr$: Zr, 22.40%. Found: Zr, 22.38%.

Hydrolysis of Methyl(phenyl)zirconium

10 ml of diluted hydrochloric acid were added to a solution of MeZrPh·$3Et_2O$ (1.00 g, 2.1 mmol) in 30 ml of toluene. The reaction mixture was heated at *ca.* 90 °C for 4 hr to get a colourless solution. H_2 (1.4 mmol), CH_4 (2.0 mmol), C_6H_6 (2.1 mmol) and Et_2O (5.2 mmol) were found in the gaseous phase and in the reaction solution.

Reaction of Methyl(phenyl)zirconium with Acetic Acid

The mixture of MeZrPh·$3Et_2O$ (1.22 g, 2.6 mmol) and acetic acid (5 ml) in toluene (30 ml) was kept at 20 °C for 24 hr.

H_2 (4.9 mmol) and CH_4 (2.5 mmol) were determined in the gaseous phase. C_6H_6 (2.4 mmol) was found in the reaction mixture. White precipitate was washed with toluene and dried *in vacuo*. Yield 75%. *Anal.* Calcd. for $C_8H_{12}O_8Zr$: Zr, 27.50 %. Found: Zr, 27.50%.

Reaction of Methyl(phenyl)zirconium with Mercuric Chloride

MeZrPh·$3Et_2O$ (1.00 g, 2.1 mmol) and $HgCl_2$ (2.85 g, 10.5 mmol) in THF (40 ml) were heated for 4 hr at 80 °C. Then the solvent was removed *in vacuo*. The solid was distilled with water vapour into the water solution of KI. A white crystalline product separated, which was filtered, dried to yield the pure compound, methylmercuric iodide (0.61 g, 1.8 mmol). PhHgCl (0.65 g, 2.1 mmol) and Hg_2Cl_2 (0.39 g, 0.8 mmol) were detected in the resulting residue by titration.

Reaction of Methyl(phenyl)zirconium with Benzophenone

The mixture of benzophenone (0.23 g, 1.3 mmol) and MeZrPh·$3Et_2O$ (0.57 g, 1.3 mmol) in toluene (30 ml) was kept at 20 °C for 24 hr. Then water (20 ml) was added to the resulting solution with stirring. CH_4 (1.3 mmol) was determined. The toluene soluble material was recrystallised from methanol. The pure product, Ph_3COH (0.29 g, 1.1 mmol) melts at 121 °C.

Reaction of Methyl(phenyl)zirconium with Acetone

A mixture of acetone (3.8 mmol) and MeZrPh·$3Et_2O$ (1.54 g, 3.8 mmol) in toluene (30 ml) was kept at 20 °C for 24 hr. CH_4 (3.2 mmol) and Me_2PhCOH (3.0 mmol), m.p. 35 °C, were found in the products of this reaction.

Reaction of Methyl(phenyl)zirconium with Carbon Dioxide

CO_2 was passed through toluene solution of $MeZrPh \cdot 3Et_2O$ (0.0019 mol) for 10 hr. The colour of the reaction mixture changed from brown to light-brown and a brown precipitate appeared. It was recrystallised from toluene to give (MeOCO)Zr(OCOPh). *Anal.* Calcd. for $C_{21}H_{38}O_7Zr$: C, 51.11; H, 7.70; Zr, 18.46%. Found: C, 51.80; H, 7.45; Zr, 18.59%.

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