Journal of Organometallic Chemistry, 49 (1973) 441–444

PHENYLZIRCONIUM DERIVATIVES

G. A. RAZUVAEV, V. N. LATYAEVA, L. I. VISHINSKAYA and A. M. RABINOVITCH
Institute of Chemistry, Akad. Nauk, Gorky (U.S.S.R.)
(Received July 13th, 1972)

SUMMARY

Syntheses and reactions of phenylzirconium derivatives are reported.

INTRODUCTION

Compared with the extensive chemistry of covalent titanium compounds very little is known at present about similar derivatives of zirconium. First attempts to alkylate and arylate $ZrCl_4$ have been unsuccessful. Only recently have a few papers appeared on the preparation of organic compounds of zirconium containing a zirconium–carbon σ-bond. Thiele, using Alk_2Zn compounds, which have slight reductive properties, isolated derivatives of the type $AlkZrX_3$ and Alk_2ZrX_2, where $Alk = CH_3$, C_2H_5, C_3H_7 and $X = Cl$, Br[1]. Of tetracovalent zirconium compounds only $(CH_3)_4Zr$[2] and $(C_6H_5CH_2)_4Zr$[3] have been described. Treating the latter compound with gaseous HCl gives rise to a number of compounds with the general formula $(C_6H_5CH_2)_nZrCl_{4-n}$[4].

RESULTS AND DISCUSSION

Covalent phenylzirconium derivatives have not been obtained until now. Therefore, it was of interest to prepare tetraphenylzirconium and to compare its properties with those of previously studied compounds of titanium and vanadium.

With this purpose in mind the exchange reaction of the chlorine atoms in zirconium tetrachloride etherate for the phenyl groups was applied. It was found that the reaction of 1.44 g (0.0062 mol) of $ZrCl_4$ with 0.0248 mol of C_6H_5Li in diethyl ether solution at −40° and under argon is accompanied by quantitative isolation of LiCl (0.0245 mol) according to eqn. (1).

$$ZrCl_4 + 4\,C_6H_5Li \xrightarrow[-40°]{(C_2H_5)_2O} (C_6H_5)_4Zr + 4\,LiCl \qquad (1)$$

Tetraphenylzirconium was not isolated in the crystalline state because of its thermal instability but its presence in the reaction mixture was confirmed by reaction with mercuric chloride. When an excess of mercuric chloride in THF is added to an ether solution of 0.0027 mol of $(C_6H_5)_4Zr$ at −40° phenylmercuric chloride is precipitated (0.0103 mol, 95% yield), (eqn. 2).

$$(C_6H_5)_4Zr + 4\,HgCl_2 \xrightarrow[-40°]{(C_2H_5)_2O} 4\,C_6H_5HgCl + ZrCl_4 \qquad (2)$$

It has been shown earlier that phenyl-titanium and -vanadium derivatives decompose readily at low temperatures, being reduced to bivalent metal compounds[5,6]. In our experiments obvious decomposition of tetraphenylzirconium started at 0°. These observations agree with literature data on the thermal stability of tetrabenzyl compounds of titanium and zirconium[3,4].

In the process of decomposition an ether solution of $(C_6H_5)_4Zr$ changes colour from light brown to black owing to the formation of a low-valency zirconium derivative. In contrast to the decomposition of $(C_6H_5)_4Ti$ and $(C_6H_5)_4V$ the products of the decomposition of $(C_6H_5)_4Zr$ in ether contained not only biphenyl [0.5 mole per mole of $(C_6H_5)_4Zr$], but also benzene [1 mole per mole of $(C_6H_5)_4Zr$]. In order to isolate the final compound, ether was completely removed from the mixture under vacuum. The dry residue was recrystallized several times from a benzene/pentane mixture to give shining black crystals of $[(C_6H_5)_2Zr \cdot O(C_2H_5)_2]_2$ which were spontaneously inflammable in air. The compound was identified as a dimer from measurements of the molecular weight (cryoscopy in benzene). $[(C_6H_5)_2Zr \cdot O(C_2H_5)_2]_2$ is very soluble in ether. THF, dioxane and aromatic hydrocarbons, and is poorly soluble in saturated hydrocarbons (Fig. 1). The presence of a phenylzirconium σ-bond was determined by reaction with mercuric chloride.

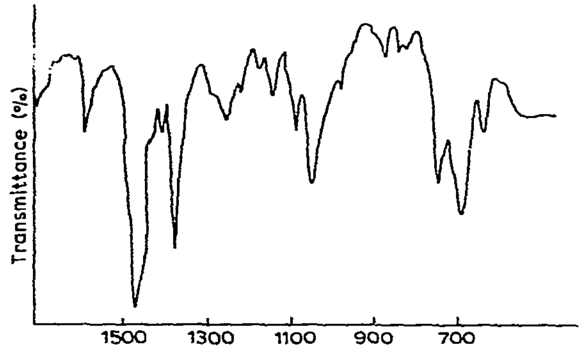

Fig. 1. IR Spectrum of $[(C_6H_5)_2Zr \cdot O(C_2H_5)_2]$

Diphenylzirconium gives 2 moles of phenylmercuric chloride per mole of the original compound according to eqn. (3).

$$(C_6H_5)_2Zr + 4\,HgCl_2 \xrightarrow{(C_2H_5)_2O/THF} 2\,C_6H_5HgCl + Hg_2Cl_2 + ZrCl_4 \tag{3}$$

The reaction of ethanol with a solution of diphenylzirconium etherate in toluene occurs readily with elimination of ether and the splitting of phenyl–zirconium bonds followed by the isolation of a mole of hydrogen, 2 moles of benzene and oxidation of zirconium (eqn. 4).

$$(C_6H_5)_2Zr \cdot O(C_2H_5)_2 + 4\,C_2H_5OH \xrightarrow{20^\circ} 2\,C_6H_6 + (C_2H_5)_2O + Zr(OC_2H_5)_4 + H_2 \tag{4}$$

Diphenylzirconium forms a thermally stable complex with ether. Whilst etherates of $(C_6H_5)_2Ti$ and $(C_6H_5)_2V$ lose coordinatively bonded ether during the drying of samples of the compounds at room temperature under vacuum ($p = 1$

mmHg), it is impossible to split ether from $[(C_6H_5)_2Zr \cdot O(C_2H_5)_2]_2$ even on standing the product, for a long time (20 h at 20°) under high vacuum ($p = 10^{-5}$ mmHg).

Diphenyltitanium and diphenylvanadium are known to decompose at 200–250° to form biphenyl and the corresponding metal[5,6] (eqn. 5).

$$(C_6H_5)_2M \xrightarrow{\Delta} (C_6H_5)_2 + M \qquad (M = Ti, V) \tag{5}$$

Thermal decomposition of diphenylzirconium etherate, prepared by us, is somewhat different. As the temperature was increased from 50 to 180°, a slow increase was observed in the amount of benzene in the reaction products, which was 1 mole per mole of the original diphenylzirconium after 30 h of heating. Apart from benzene, 0.5 mole of biphenyl was also determined; free-state ether was not detected in the reaction products. Considerable amounts of gas, containing mainly ethane (96%) and a small fraction of methane (4%), evolved during the decomposition. The ethylene which is expected to be formed is converted into oligomer, which was identified by IR-spectroscopy. It is noteworthy that metallic zirconium was not observed to form during the thermal decomposition. Thus, the thermal decay of diphenylzirconium etherate can be described by eqn. (6).

$$\begin{aligned}[(C_6H_5)_2Zr \cdot O(C_2H_5)_2]_2 \xrightarrow{\Delta} 2C_6H_5ZrOC_2H_5 + C_6H_6 &+ \\ + \tfrac{1}{2}(C_6H_5)_2 + \tfrac{1}{2}C_2H_6 + \tfrac{3}{2}C_2H_4 &\end{aligned} \tag{6}$$

Thiele observed such a decay resulting in the formation of similar products while studying the decomposition of intermediate unstable tribenzyltitanium etherate[7]. He believes that in the course of the reaction the C–O bond in diethyl ether splits; the ethoxy groups so formed combining with titanium and the ethyl radicals being responsible for the evolution of the gas, consisting mainly of ethane, which is observed[7]. The zirconium containing product of the thermal decomposition is a black crystalline substance, insoluble in organic solvents; it is easily oxidized in air but is stable to ethanol, water and dilute mineral acids at low temperature. Its IR-spectrum shows absorption bands at 760 and 1280 cm^{-1} characteristic of phenyl and ethoxy groups. (Fig. 2). We identified the compound as phenylzirconium ethoxide. The presence of the ethoxy group is confirmed by oxidation of the substance with chromic acid to acetic acid.

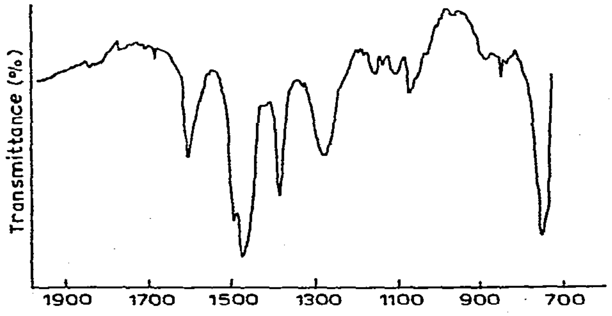

Fig. 2. IR spectrum of $C_6H_5ZrOC_2H_5$.

EXPERIMENTAL

Preparation of tetraphenylzirconium and its thermal decomposition

An ether solution of phenyllithium (0.0248 mol) was added to zirconium tetrachloride etherate prepared from 1.44 g (0.0062 mol) of $ZrCl_4$ and 100 ml of absolute diethyl ether in a current of argon at −30 to −40°. The reaction mixture turned light brown in colour. The mixture was stirred for 2 h at −30° with subsequent heating to room temperature. The reaction mixture turned black after standing for 18 h and 0.46 g (0.0060 mol) of C_6H_6 and 0.86 g (0.0056 mol) of $(C_6H_5)_2$ were detected in the solution.

Ether was removed from the reaction mixture under vacuum. The black residue was dissolved in benzene and filtered. By evaporating the filtrate and recrystallizing the residue from benzene/pentane we obtained a black crystalline product (3.8 g, 95% yield) of $[(C_6H_5)_2Zr \cdot O(C_2H_5)_2]_2$. (Found: C, 59.63; H, 6.38; Zr, 28.37; mol. wt. (cryoscopy in benzene), 658. $C_{16}H_{20}OZr$ calcd.: C, 60.10; H, 6.28; Zr, 28.50%; mol. wt., 638.)

The reaction of tetraphenylzirconium with mercuric chloride

$HgCl_2$ [5.6 g (0.0210 mol)] in 10 ml THF was added to a brown ether solution of $(C_6H_5)_4Zr$, obtained from 0.63 g (0.0027 mol) of $ZrCl_4$ and 0.0108 mol of C_6H_5Li at −40°. A white residue precipitated immediately. It was then filtered, dried, washed with ethanol and recrystallized from hot acetone. Yield 3.9 g (0.0103 mol) of C_6H_5-HgCl, m.p. 256°.

Alcoholysis of diphenylzirconium etherate with ethanol in inert medium

Absolute ethanol (10 ml) was added to a solution of 0.47 g (0.00075 mol) of $[(C_6H_5)_2Zr \cdot O(C_2H_5)_2]_2$ in 15 ml of THF. The solution turned pale yellow and a white, flaky precipitate was observed. Chromatography detected 0.12 g (0.00150 mol) of C_6H_6 in the reaction mixture.

Thermal decomposition of diphenylzirconium etherate

$[(C_6H_5Zr \cdot O(C_2H_5)_2]_2$ [0.91 g (0.0014 mol)] was heated for 30 h at 180° in an evacuated, sealed ampoule. 15 ml (0.0007 mol) of a gas (96% ethane, 4% methane) were isolated. The reaction mixture was washed with pentane which was afterwards found to contain 0.11 g (0.0014 mol) of C_6H_6 and 0.10 g (0.0007 mol) of $(C_6H_5)_2$. The remaining black residue was washed several times with benzene to remove ethylene oligomers. (Found: C, 45.33; H, 4.26; Zr, 42.00. $C_8H_{10}OZr$ calcd.: C, 45.60; H, 4.60; Zr, 42.70%.)

REFERENCES

1 K. H. Thiele and J. Krüger, *Z. Anorg. Allg. Chem.*, 383 (1971) 272.
2 H. J. Berthold and J. Groh, *Angew. Chem.*, 78 (1966) 495.
3 U. Lucchoni, V. Giannoni, E. Albizzati and R. D. Angelo, *Chem. Commun.*, (1969) 1174.
4 U. Lucchoni, E. Albizzati and U. Giannoni, *J. Organometal. Chem.*, 26 (1971) 357.
5 G. A. Razuvaev, V. N. Latyaeva, A. V. Malysheva and G. A. Kilyakova, *Dokl. Akad. Nauk SSSR*, 150 (1963) 566.
6 G. A. Razuvaev, V. N. Latyaeva, B. G. Zateev and G. A. Kilyakova, *Dokl. Akad. Nauk SSSR*, 172 (1967) 1337.
7 K. H. Thiele and W. Schäfer, *Z. Anorg. Allg. Chem.*, 379 (1970) 63.