The Chemistry of Polyhalozirconates.
Part 3. The Preparation of Phosphonium Hexachlorozirconates

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Abstract

The preparation of various phosphonium hexachlorozirconates from zirconium tetrachloride and zirconium oxide chloride octahydrate is described. In one case a product $[(C_6H_5)_3PH]_2ZrCl_6$ was found to be unusually resistant to hydrolysis.

Introduction

Metal salts and quaternary ammonium salts of the hexachlorozirconate anion have been prepared previously from both zirconium tetrachloride and zirconium oxide chloride octahydrate [1–3]. In recent years an interest has developed in the use of doped hexachlorozirconates for use as phosphors [4, 5]. We now report the synthesis and characterisation of a number of previously unknown phosphonium hexachlorozirconates.

Experimental

Most of the compounds handled in this work are sensitive to moisture, they were therefore manipulated in a nitrogen atmosphere using Schlenk tubes or a conventional dry-box. Zirconium tetrachloride and zirconium oxide chloride octahydrate were obtained commercially and in most cases were used without further purification. In some cases zirconium tetrachloride was purified by vacuum sublimation.

Zirconium was determined by precipitation as the mandelate followed by pyrolysis to zirconium dioxide [6]. Chloride was determined by Volhards method. Carbon, hydrogen and nitrogen analysis was carried out by Butterworth Microanalytical Consultancy Ltd.

Infrared spectra were measured using a Perkin-Elmer 1710 FTIR and a Pye Unicam SP3-300.

The Reaction of $ZrCl_4$ *with* $(C_6H_5)_3(C_6H_5CH_2)PCl$

A. In $SOCl_2$

Zirconium tetrachloride (3.0 g, 0.013 m) in thionyl chloride (20 ml) was added to an ice cold solution of triphenylbenzylphosphonium chloride (9.9 g, 0.025 m) and the mixture stirred at −2 °C for 30 min. The resultant precipitate was separated by filtration under nitrogen and dried *in vacuo* to yield a white solid (14.1 g, melting point (m.p.) 266–268 °C). Attempts to analyse this product gave inconsistent results. Thermal gravimetric analysis gave the following cumulative mass losses: ambient −120 °C, 17.2%; 259–422 °C, 85.2%; 422–580 °C, 87.0%; 580–852 °C, 87.5%. Infrared spectroscopic examination shows the following main absorption bands: 1456, 1438, 1396, 1233, 1100, 1110, 996, 750, 718, 700, 688, 568, 500 (sh), 490, 346, 332, 285, 215 cm^{-1}. A sample of the product (5.3 g) was heated to 60 °C *in vacuo* over NaOH to give a white product (4.3 g, 18.87% wt. loss, m.p. 269.2–269.8 °C. Found: Zr, 8.82; Cl, 20.97; C, 59.72; H, 4.42. Calc. for $[(C_6H_5)_3(C_6H_5CH_2)P)]_2ZrCl_6$: Zr, 9.00; Cl, 21.04; C, 59.41; H, 4.35%). TG analysis shows no mass loss below 259 °C but a gradual mass loss of 91.4% up to 961 °C. Infrared spectroscopic examination shows essentially the same absorption bands as above except that the bands at 1233 and 700 cm^{-1} are now absent.

B. In Acetonitrile

Zirconium tetrachloride (5.0 g, 0.022 m) was dissolved in acetonitrile (50 ml) and added slowly to an ice-cold suspension of triphenylbenzylphosphonium chloride (16.7 g, 0.043 m) in acetonitrile (50 ml). The phosphonium salt dissolved and within a few minutes a precipitate formed. The precipitate was separated by filtration under nitrogen to give a white product (16.2 g, m.p. 257.6–258.3 °C. Found: Zr, 8.81; Cl, 20.6; C, 58.96; H, 4.54. Calc. for $[(C_6H_5)_3(C_6H_5CH_2)P]_2ZrCl_6$: Zr, 9.00; Cl, 21.04; C, 59.41; H, 4.35%). TG analysis gave the following cumulative mass losses: ambient −254 °C, 0%; 254–448 °C, 88.8%; 448–637 °C, 90.8% and 637–961 °C, 91.9%. The infrared spectrum is similar to that obtained for the product prepared in thionyl chloride.

The Reaction of $ZrOCl_28H_2O$ *with* $(C_6H_5)_3(C_6H_5CH_2)PCl$ *in* $SOCl_2$

A solution of benzyltriphenylphosphonium chloride (11.6 g, 0.03 m) in thionyl chloride (50 ml)

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was added slowly to a solution of zirconium oxide chloride octahydrate (5.0 g, 0.015 m) in thionyl chloride (50 ml). The mixture was stirred for 12 h to ensure complete reaction and the solid product separated by filtration to yield a white solid (9.1 g, m.p. 265 °C. Found: Zr, 10.4; Cl, 20.8; C, 58.9; H, 4.3. Calc. for $[(C_6H_5)_3(C_6H_5CH_2)P]_2ZrCl_6$: Zr, 9.00; Cl, 21.04; C, 59.41; H, 4.35%). The infrared spectrum is similar to that of the product prepared from zirconium tetrachloride.

The Reaction of $ZrCl_4$ with $(C_6H_5)_3P$ in Ethanolic HCl

Zirconium tetrachloride (11.6 g, 0.05 m) was dissolved in ethanol (150 ml) and the solution saturated with HCl, a take up of ~15% *w/w* was obtained. The solution was cooled and triphenylphosphine (26.2 g, 0.113 m) in ethanol (150 ml) was added. A fine white precipitate formed which was separated by filtration (38.0 g, m.p. 285–295 °C. Found: Zr, 7.6; Cl, 19.8; C, 51.74; H, 3.75. Calc. for $[(C_6H_5)_3PH]_2ZrCl_6$: Zr, 8.4; Cl, 19.79; C, 52.05; H, 3.85%). The infrared spectrum showed the following principal absorption bands: 2426, 1586, 1485, 1441, 1129(sh), 1114, 892, 870, 756, 744, 690, 500, 481, 360, 348, 331, 290, 280, 225(sh), 212 cm^{-1}.

The product is not readily hydrolysed. On initial contact with water the compound shows some hydrophobic character and floats on the surface. In time the product becomes wetted but shows no obvious signs of reaction.

A sample of the compound was heated in water until it dissolved. The resultant solution was cooled to yield a crop of crystals which infrared spectroscopy showed to be triphenylphosphine. This procedure was followed and the triphenylphosphine removed before following the standard zirconium and chloride analytical procedures.

The Reaction of $ZrCl_4$ with $(C_6H_5)_3(CH_2OH{\cdot}CH_2)PCl$ in CH_3CN

This reaction was carried out under nitrogen. Zirconium tetrachloride (6.3 g, 0.027 m) in acetonitrile (50 ml) was added slowly to a suspension of $(C_6H_5)_3(CH_2OH{\cdot}CH_2)PCl$ (14.1 g, 0.041 m) in acetonitrile (50 ml) with constant stirring. The suspension dissolved and within a few minutes a precipitate formed. The mixture was stirred for 15 min to ensure complete precipitation and the solid product separated by filtration (9.2 g, m.p. 209–210 °C. Found: Zr, 9.95; Cl, 23.13; C, 51.77; H, 4.20. Calc. for $[(C_6H_5)_3(CH_2OH{\cdot}CH_2)P]_2ZrCl_6$: Zr, 9.93; Cl, 23.15; C, 52.96; H, 4.40%). The infrared spectrum showed the following principal absorption bands: 3479, 3063, 2937, 2905, 1484, 1440, 1412, 1386, 1338, 1320, 1293, 1228, 1112, 1070, 763, 749, 732, 721, 691, 534, 490, 476, 435, 348, 215 cm^{-1}.

The Reaction of $ZrCl_4$ with $(HOCH_2)_4PCl$ in $SOCl_2$

The compound $(HOCH_2)_4PCl$ was obtained commercially as an 80% aqueous solution from which the water was removed by freeze drying to leave the solid compound.

Tetrakishydroxymethylphosphonium chloride (17.0 g, 0.0898 m) was dissolved in thionyl chloride (100 ml). When gas evolution had ceased the solution was cooled in ice and zirconium tetrachloride (10.5 g, 0.045 m) in thionyl chloride (150 ml) added slowly. The mixture was stirred for 20 h and the white product separated by filtration and dried in a stream of dry nitrogen (4.0 g. Found: Zr, 11.72; C, 12.57; H, 2.1. Calc. for $[(ClCH_2)_4P]_2ZrCl_6$: Zr, 11.98; C, 12.61; H, 2.12%). The infrared spectrum showed the following principal absorption bands: 1380, 1237, 1217, 1208, 1143, 1103, 884, 875, 854, 787, 702, 368, 350, 320, 293, 280, 218 cm^{-1}.

The Preparation of $[(CH_3)_4N][(C_6H_5)_3(C_6H_5CH_2)P]ZrCl_6$

Zirconium oxide chloride (20 g, 0.062 m) was dissolved in thionyl chloride (300 ml) and to this solution was added tetramethylammonium chloride (6.8 g, 0.062 m) in thionyl chloride (50 ml). The mixture was stirred for 2 h during which time a white precipitate formed. To this suspension was added triphenylbenzylphosphonium chloride (24.1 g, 0.062 m) in thionyl chloride (50 ml) and the stirring continued for a further 24 h. The resultant precipitate was separated by filtration, dried *in vacuo* at 100 °C over sodium hydroxide, until no coordinated thionyl chloride could be detected by infrared spectroscopy, to yield a white product. (35.5 g. Found: Zr, 12.74; Cl, 30.63; C, 44.6; H, 4.9; N, 2.3. Calc. for $[(CH_3)_4N][(C_6H_5)_3(C_6H_5CH_2)P]ZrCl_6$: Zr, 12.47; Cl, 29.08; C, 47.61; H, 4.69; N, 1.92%.) The infrared spectrum showed the following principal absorption bands: 1600, 1585, 1485, 1456, 1438, 1111, 996, 951, 844, 785, 753, 718, 689, 580, 498, 478, 347, 330, 295, 277, 215 cm^{-1}.

Discussion

Phosphonium salts of the hexachlorozirconate anion have been prepared in thionyl chloride, acetonitrile and ethanolic hydrogen chloride. In the latter two solvents the products are obtained directly in a one step process. In the case of the preparation of triphenylbenzylphosphonium hexachlorozirconate carried out in thionyl chloride, an intermediate product containing coordinated thionyl chloride is produced. Thermal gravimetric analysis of this intermediate shows a mass loss of 17.2% up to

120 °C which compares well with the theoretical value of 19.5% for the loss of 2 mol of $SOCl_2$ from $[(C_6H_5)_3(C_6H_5CH_2)P]_2ZrCl_6(SOCl_2)_2$ (A). *In vacuo* at 60 °C over sodium hydroxide the compound **A** showed a mass loss of 18.9% to give the product $[(C_6H_5)_3(C_6H_5CH_2P]_2ZrCl_6$. The infrared spectrum of A shows, *inter alia*, bands at 1233 and 700 cm^{-1} which are no longer present after the vacuum treatment. The band at 1233 cm^{-1} is attributed to the S–O stretching frequency of the coordinated thionyl chloride. This compares with a frequency of 1229 cm^{-1} in the free molecule. The band at 700 cm^{-1} is assigned to the Zr–O stretching frequency. Thus the thionyl chloride is coordinating via oxygen. This increase in coordination number from six to eight is consistent with the known tendency for zirconium to readily take both coordination types, due to an absence of any ligand field stabilisation energy.

A mixed quaternary ammonium phosphonium hexachlorozirconate has also been made in thionyl chloride. In this case the thionyl chloride adduct was not isolated. The mixed salt is prepared via the formation of tetramethylammonium pentachlorozirconate from zirconium oxide chloride as described previously [1]. The thionyl chloride suspension of the pentachlorozirconate is then treated with $(C_6H_5)_3(C_6H_5CH_2)PCl$ to give the mixed product $[(CH_3)_4N][(C_6H_5)_3(C_6H_5CH_2)P]ZrCl_6$ in a 77% yield. Thionyl chloride is also a useful solvent for the preparation of the compound $[(ClCH_2)_4P]_2ZrCl_6$, albeit in low yield (12%), although no attempt has been made to optimise yields. In this case the starting phosphonium compound was tetrakishydroxymethylphosphonium chloride, the hydroxy groups of which were chlorinated on dissolution in thionyl chloride; addition of this solution to one of zirconium tetrachloride, also in thionyl chloride, precipitates the desired product.

In order to preserve a hydroxy group in the phosphonium ion dry acetonitrile was used as solvent. In this way a 37% yield of the compound $[(C_6H_5)_3(CH_2OH{\cdot}CH_2)P]_2ZrCl_6$ was obtained from zirconium tetrachloride. The OH group is evidenced by an infrared band at 3479 cm^{-1}, the sharp nature of which suggests that the possibility of any hydrogen bonding to the anion can be discounted.

Phosphonium hexachlorozirconates have also been prepared by adding a phosphine to a solution of zirconium tetrachloride in alcoholic hydrogen chloride. Thus triphenylphosphine readily precipitates the compound $[(C_6H_5)_3PH]_2ZrCl_6$ according to the following equations

$$ZrCl_4 + HCl \longrightarrow H_2ZrCl_6$$

$$(C_6H_5)_3P + HCl \longrightarrow [(C_6H_5)_3PH]Cl$$

$$2[(C_6H_5)_3PH]Cl + H_2ZrCl_6 \longrightarrow [(C_6H_5)_3PH]_2ZrCl_6 + 2HCl$$

An absorption in the infrared occurs at 2426 cm^{-1} due to the P–H bond. This is a sharp band which suggests that there is no interaction between this hydrogen and the associated anion.

The compound $[(C_6H_5)_3PH]_2ZrCl_6$ is surprisingly resistant to atmospheric hydrolysis, does not react with cold water and is only completely destroyed on heating in water. This contrasts markedly with $[(C_6H_5)_3(C_6H_5CH_2)P]_2ZrCl_6$ which hydrolyses readily, as do other chlorozirconates. The reason for this hydrolytic stability is obscure at the present time. One possibility is that the phenyl groups on the phosphonium ion sterically hinder access of the nucleophile to the zirconium centre. The presence of the hydrogen enabling the compound to take a much more compact structure than the corresponding triphenylbenzylphosphonium compound. Structure determinations are planned for the future in order to resolve this point.

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