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The chemistry of polyhalozirconates IV: The preparation of some diphosphonium hexachlorozirconates

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Abstract

The synthesis of the phosphonium salts $[(C_6H_5)_3P–CH_2–P(H)(C_6H_5)_2]_2ZrCl_6$ (**III**), $[(C_6H_5)_2P–CH_2–P(CH_3)(C_6H_5)_2]_2ZrCl_6$ (**IV**), $[(C_6H_5)_3P–CH_2–C_6H_4–CH_2–P(C_6H_5)_3]ZrCl_6$ (**V**) and $[(C_6H_5)_3P–C_6H_4–P(C_6H_4)_3]ZrCl_6$ (**VI**) is described. Compound **III** shows an unexpected hydrolytic stability which is explained in steric terms. The ^1H and ^{31}P nuclear magnetic resonance spectra of these and related phosphine and simple phosphonium salts are discussed.

1. Introduction

Metal salts and quaternary ammonium salts of the hexachlorozirconate anion have been prepared previously from both zirconium tetrachloride and zirconium oxide chloride octahydrate [1–5]. In recent years an interest has developed in the use of doped hexachlorozirconates for use as phosphors [6, 7]. We have previously synthesized a number of phosphonium hexachlorozirconates and note in particular the unusually high resistance to hydrolysis of the compound $[(C_6H_5)_3PH]_2ZrCl_6$ [8]. It was interesting therefore to study the synthesis of similar diphosphonium complexes.

2. Experimental details

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. IR spectra were measured with a Perkin–Elmer 1710 Fourier transform IR instrument. Nuclear magnetic resonance (NMR) spectra were measured using a u.c. 300 MHz Bruker instrument.

Elemental analysis was carried out as previously described [8].

2.1. *The preparation of diphenylphosphinomethyldiphenylphosphonium hexachlorozirconate* $[(C_6H_5)_2P–CH_2–P(H)(C_6H_5)_2]_2ZrCl_6$

Zirconium tetrachloride (2.33 g, 0.01 mol) was dissolved in ethanol (50 cm^3) and hydrogen chloride gas passed into the solution until a pick-up of

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15% w/w of HCl was obtained. To the cooled solution was added a suspension of bis(diphenylphosphino)methane in ethanol (50 cm^3). The suspension dissolved readily in the reaction medium, and after stirring for 10 h a white crystalline material formed, which was separated by filtration, washed with ether and dried *in vacuo* to yield a white crystalline product (7 g; melting point, 183 °C). Found: Zr, 7.6%; Cl, 19.8%; C, 55.55%; H, 4.29%. $[(C_6H_5)_2P{-}CH_2{-}PH(C_6H_5)_2]_2ZrCl_6$ **(III)** requires the following: Zr, 8.49%; Cl, 19.79%; C, 55.87%; H, 4.32%. IR spectroscopic analysis showed the following bands: 2385, 1483, 1438, 735 and 695 cm^{-1}. The NMR data are given in Table 1 (compound **III**).

TABLE 1

Nuclear magnetic resonance data

$Ph_2P{-}CH_2{-}PPh_2$ **(I)**				
	In d^6 acetone		In CF_3COOH	
$-CH_2-$	t, 2.8 ppm,	1.5 Hz	t, 4.8 ppm,	16 Hz
$[Ph_2P{-}CH_2{-}(Me)PPh_2]I$ **(II)**				
	In d^6 acetone		In CF_3COOH	
$-CH_2-$	d, 4.15 ppm,	16.5 Hz	t, 5.2 ppm,	16 Hz
$(Me)P_B$	d, 2.72 ppm,	16 Hz	d, 2.8 ppm,	16 Hz
P_A	d, −27.1 ppm,	62 Hz	d, 14.7 ppm,	29 Hz
P_B	d, 23.25 ppm,	62 Hz	d, 68.8 ppm,	29 Hz
	In $CF_3{-}COOH{-}d^6$ acetone			
P_A	d, 14.7 ppm,	29 Hz and		
	d, −27.1 ppm,	62 Hz		
P_B	d, 68.8 ppm,	29 Hz and		
	d, 23.25 ppm,	62 Hz		
$[Ph_2P{-}CH_2{-}(H)PPh_2]_2[ZrCl_6]$ **(III)**				
	In d^6 acetone			
$-CH_2-$	d, 4.2 ppm,	16 Hz		
P_A	d, −27.6 ppm,	60 Hz		
P_B	d, 37.3 ppm,	60 Hz		
$Ph_2P{-}CH_2{-}(Me)PPh_2]_2[ZrCl_6]$ **(IV)**				
	In d^6 acetone			
P_A	d, −27 ppm,	60 Hz		
P_B	d, 23.2 ppm,	60 Hz		
$[Ph_3P{-}CH_2{-}C_6H_4CH_2{-}PPh_3]ZrCl_6$ **(V)**				
	In CD_3OD			
P	s, 22.9 ppm			
$[Ph_3P{-}C_6H_4{-}PPh_3]ZrCl_6$ **(VI)**				
	In CD_3OH			
P	s, 22.1			

P_A, a tertiary P atom; P_B, a quaternary P atom; (Me) P_B, methyl group of a quaternary P atom; $Ph \equiv C_6H_5$; $Me \equiv CH_3$.

2.2. *The preparation of p-xylylenebis(triphenylphosphonium)-hexachlorozirconate* $[(C_6H_5)_3P\text{–}CH_2\text{–}C_6H_4\text{–}CH_2\text{–}P(C_6H_5)_3]ZrCl_6$

The same procedure was followed as described above, except that the phosphonium salt bis(triphenylphosphonium bromide)paraxylene (7.9 g, 0.01 mol) was used instead of bis(diphenylphosphino)methane and stirring was continued for 24 hs before isolation of the final product (8.4 g, melting point, darkens above 300 °C but does not melt). Found: Zr, 9.75%; Cl, 23.5%; C, 55.87%; H, 4.28% $[(C_6H_5)_3P\text{–}CH_2\text{–}C_6H_4\text{–}CH_2\text{–}P(C_6H_5)_3]ZrCl_6$ (**V**) requires the following: Zr, 9.76%; Cl, 22.81%; C, 55.66%; H, 4.07%. IR spectroscopic examination showed the following bands: 3054, 2946, 2898, 1483, 1442 and 1112 cm^{-1}. NMR data are given in Table 1 (compound **V**).

2.3. *The preparation of diphenylphosphinomethyldiphenylmethylphosphonium hexachlorozirconate* $[(C_6H_5)_2P\text{–}CH_2\text{–}P(CH_3)(C_6H_5)_2][ZrCl_6]$

2.3.1. *In a moderately acid medium*

Zirconium tetrachloride (0.58 g, 2.5 mmol) was dissolved in ethanol (50 ml) and hydrogen chloride gas passed into the solution until an uptake of 15% had been achieved. After cooling, a suspension of $[(C_6H_5)_2P\text{–}CH_2\text{–}P(CH_3)(C_6H_5)_2]I$ (5.3 g, 3.2 mmol) in ethanol (50 ml) was added. The suspension dissolved readily and on the addition of diethyl ether (1 l) a white precipitate was produced which was separated by filtration and dried *in vacuo* (0.8 g; melting point, decomposition above 140 °C. Found: Zr, 8.2%; Cl, 20.1%; C, 55.87%; H, 4.27%. $[(C_6H_5)_2P\text{–}CH_2\text{–}P(CH_3)(C_6H_5)_2]_2ZrCl_6$ (**IV**) requires the following: Zr, 8.22%; Cl, 19.53%; C, 56.63%; H, 4.58%.

The IR spectrum exhibits bands at 3058, 2982, 2912, 1483, 1438 and 1169 cm^{-1}.

The NMR data are summarized in Table 1 (compound **IV**).

2.3.2. *In a high acidity medium*

Zirconium tetrachloride (1.17 g, 5.15 mmol) was dissolved in ethanol (50 ml), and HCl gas passed into the solution until an uptake of 25% was observed. To the cooled solution was added a suspension of $[(C_6H_5)_2P\text{–}CH_2P(CH_3)(C_6H_5)_2]I$ (5.26 g, 10 mmol) in ethanol (50 ml) which readily dissolved in the reaction medium. The addition of dry ether (1 l) precipitated a white product which was dried *in vacuo* (1.9 g; melting point, decomposes above 140 °C). Found: Zr, 10.89%, Cl, 23.25%; C, 46.8%; H, 4.07%. $[(C_6H_5)_2P(CH_3)\text{–}CH_2\text{–}P(C_6H_5)_2]_2ZrCl_6$ requires the following: Zr, 8.22%; Cl, 19.53%; C, 56.63%; H, 4.58%.

The IR spectrum exhibits bands at 3058, 2982, 2912, 2404, 1483, 1438 and 1169 cm^{-1}. The NMR data are similar to those observed for the compound prepared by the method described in Section 2.3.1.

2.4. *The preparation of p-benzenebis(triphenylphosphonium)hexachlorozirconate-*$[(C_6H_5)_3P-C_6H_4-P(C_6H_5)_3]ZrCl_6$

A thionyl chloride solution (400 ml) of zirconium oxide chloride (21.0 g, 65.4 mmol) was prepared. To 23.5 ml of this solution was added a solution of bis(triphenylphosphonium bromide)parabenzene (3.0 g, 3.85 mmol) and the resultant mixture stirred for 1 h. The thionyl chloride was removed at room temperature and the resultant solid washed with a mixture of diethyl ether (20 ml) and dichloromethane (20 ml), filtered and dried *in vacuo* to yield a white solid (3.13 g). Found: Zr, 9.7%; Cl, 22.8%; C, 53.82%; H, 3.65%. $\{(C_6H_5)_3P-C_6H_4-P(C_6H_5)_3ZrCl_6$ requires the following: Zr, 10.06%; Cl, 23.56%; C, 55.75%; H, 3.76%.

3. Discussion

Three diphosphonium complexes of the hexachlorozirconate anion have been prepared using either an ethanolic hydrogen chloride medium or by carrying out the reaction in thionyl chloride. These are

$[(C_6H_5)_2P-CH_2-P(H)(C_6H_5)_2]_2ZrCl_6$ **(III)**
$[(C_6H_5)_2P-CH_2-P(CH_2)(C_6H_5)_2]_2ZrCl_6$ **(IV)**
$[(C_6H_5)_3P-CH_2-C_6H_4-CH_2-P(C_6H_4-P)(C_6H_5)_3]ZrCl_6$ **(V)**
$[(C_6H_5)_3P-C_6H_4-P(C_6H_5)_3]ZrCl_6$ **(VI)**

Compounds **III**, **IV** and **V** were prepared in the ethanolic medium and compound **VI** in thionyl chloride.

Compound **III** was synthesized by the addition of the diphosphine $(C_6H_5)_2P-CH_2P-(C_6H_5)_2$ to a hydrogen chloride acidic solution of $ZrCl_4$. Good evidence for a P–H bond is given by a sharp band at 2385 cm^{-1} typical of this group. In addition the ^{31}P NMR spectrum shows the presence of two different phosphorus nuclei with widely separated NMR signals, namely -27.6 and 37.3 ppm. It is interesting to note that a similar separation is observed between phosphorus (III) and phosphorus (V) nuclei where one of the lone pair of electrons is occupied by bonding to selenium [9]. Thus only one phosphorus atom has been protonated and to this is attributed the doublet at 37.3 ppm. Failure to protonate the second phosphorus atom may be attributed to delocalization of the lone pair by the positive charge on the quaternary phosphorus atom.

The synthesis of compound **IV** is not so straightforward, the nature of the product being dependent upon the acidity of the reaction medium. Thus in an ethanolic medium containing 15% HCl the product **IV** is obtained in good yield. The IR spectra does not exhibit a band corresponding to a P–H bond and the NMR spectrum clearly indicates the presence of two inequivalent phosphorus nuclei *i.e.* no further quaternization of a phosphorus atom has taken place. When the reaction is carried out in a much stronger acid medium (25% HCl) a product of imprecise composition is obtained. The elemental analysis lies between that of **IV** and $[(C_6H_5)_2P(H)-CH_2-PMe(C_6H_5)_2]ZrCl_6$. In addition this product shows a weak absorption at 2404 cm^{-1}, suggesting the presence of a P–H group. It appears therefore that, in the stronger acid medium, partial protonation of the tertiary phosphorus atom is taking place with the establishment of the equilibrium

$$(C_6H_5)_2P{-}CH_2{-}{}^+P(CH_3)(C_6H_5)_2 + H^+ \rightleftharpoons (C_6H_5)_2{}^+P(H){-}CH_2{-}{}^+P(CH_3)(C_6H_5)_2$$

and at high acidities the isolation of a pure product is not possible.

Diphosphonium salts of the hexachlorozirconate ion have been isolated by other methods, as shown by compounds **V** and **VI**, there is thus no inherent instability in this class of compound. The failure to isolate $[(C_6H_5)_2P(H){-}CH_2{-}P(CH_3)(C_6H_5)_2]ZrCl_6$ and $[(C_6H_5)_2P(H){-}CH_2{-}P(H){-}(C_6H_5)_2]ZrCl_6$ is therefore entirely due to the inability to protonate the tertiary phosphorus atom under the reaction conditions used.

3.1. Hydrolytic stability of hexachlorozirconates

It is widely recognized that hexachlorozirconates are very susceptible to hydrolysis and decompose readily in moist air. It was surprising therefore to find that the monophosphonium salt $[(C_6H_5)_3PH]_2ZrCl_6$ was resistant to hydrolysis and even showed some hydrophobic character, whereas similar compounds not having a P–H bond showed typical hydrolytic instability [8]. We have now shown that this phenomenon extends to the diphosphonium series of salts. Thus compound **III** is resistant to hydrolysis whereas compounds **IV**, **V** and **VI** are hydrolytically unstable. The presence of a P–H bond is therefore essential to confer hydrolytic stability on the $ZrCl_6^{2-}$ anion.

There is clearly a steric difference between the two types of phosphonium cation, namely R_4P^+ and R_3PH^+. Although both cations will have a tetrahedral geometry, that of R_3PH^+ is likely to be distorted. The small size of the hydrogen atom relative to that of an R group may allow a closer approach of the phosphonium cation to a $ZrCl_6^{2-}$ anion in the crystal lattice, thus giving steric protection to the $ZrCl_6^{2-}$ anion. Any electronic interaction between the hydrogen atom of the P–H group and the zirconium or chlorine atom would not be expected to manifest itself in the IR spectrum. Further discussion of this hydrolytic stability must await a full structure determination.

3.2. The ^1H and ^{31}P nuclear magnetic resonance spectra

The ^1H and ^{31}P NMR spectra of three hexachlorozirconates and the parent phosphine and phosphonium salt are given in Table 1.

The methylene bridge of **I** in d^6 acetone appears as a triplet with a small coupling constant due to interaction with the two neighbouring equivalent phosphorus nuclei. In trifluoroacetic a broader triplet is observed at a higher frequency. The increased coupling constant of the triplet is attributed to protonation of the two phosphorus atoms, as expected in a trifluoroacetic acid medium.

A methylene group flanked by two inequivalent phosphorus nuclei (one tertiary and one quaternized) displays a doublet at about 4.2 ppm for both **II** and **III**. Thus the mode of quaternization does not make a significant difference to the resonance position. Although in both cases a doublet of doublets is to be expected, this is not observed, probably because of the small coupling with the tertiary phosphorus atom. In trifluoroacetic acid compound **II** displays the expected triplet due to quaternization of the tertiary phosphorus atom and the formation of a quasi-symmetrical system.

The ^1H decoupled ^{31}P spectra of compounds **II** and **III** in d^6 acetone each exhibit a pair of doublets attributed to the two phosphorus nuclei coupled to each other. The spectrum of compound **II** in d^6 acetone–CF_3COOH shows the appearance of an additional pair of doublets with a different coupling constant. These are attributed to protonation of the tertiary phosphorus leading to the diphosphonium cation $(C_6H_5)_2{}^+P(H)–CH_2–{}^+P(CH_3)(C_6H_5)_2$. The ^{31}P spectrum of **IV** also shows the presence of two types of phosphorus nucleus with coupling constants similar to those observed for compounds **II** and **III**.

It is interesting to note that quaternization of a phosphorus atom by a CH_3 or C_6H_5 group has very little influence on the resonance position of ^{31}P (compounds **IV** and **V**). By contrast, quaternization by hydrogen shows a considerable shift upfield, 37.3 ppm for compound **III**. This is attributed to the more effective shielding of the ^{31}P by hydrogen than by carbon.

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