

PENTAFLUOROPHENYLARSENIC COMPOUNDS

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Summary

$(C_6F_5)_3As$ has a very low coordinating capacity, and this permits isolation of the neutral $O_3ClOAgAs(C_6F_5)_3$ and the cationic $\Delta g[(C_6F_5)_3As]_2ClO_4$ silver compounds. $(C_6F_5)_3As$ is easily oxidized by chlorine or thallic chloride to give $(C_6F_5)_3AsCl_2$. Metathetical reactions of $(C_6F_5)_3AsCl_2$ with silver salts give mono-substituted derivatives of the type $(C_6F_5)_3AsClX$ ($X = NO_3, ClO_4, OAc$). Alcoholysis of $(C_6F_5)_3AsCl_2$ leads to the isolation of compounds of the type $(C_6F_5)_3AsCl(OR)$ ($R = CH_3, CH_2CH_3, C_6H_5$). Structural information on the new organoarsenic(V) derivatives has been obtained by IR spectroscopy.

Introduction

Organometallic compounds of pentavalent arsenic having formulas of the type R_3AsX_2 where X is a halogen or other electron attracting group, are known [1]. However, pentafluorophenyl derivatives of this type have not been described, and only arsenic(III) derivatives have been previously isolated [2,3].

In continuation of our studies on pentafluorophenyl derivatives we describe the chemical behaviour of $(C_6F_5)_3As$ as a ligand, and the preparation, structure and properties of compounds of the type $(C_6F_5)_3AsClX$ ($X = Cl, NO_3, ClO_4, CH_3COO, OCH_3, OCH_2CH_3, OC_6H_5$).

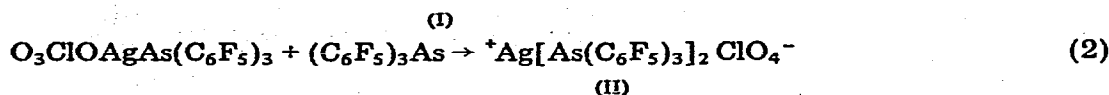
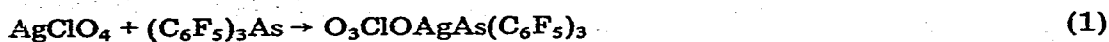
Results and discussion

(a) Preparative results

Treatment of ethanol solutions of $(C_6F_5)_3As$ prepared as described in ref. 3, with anhydrous halides such as $NiBr_2$ and $CoBr_2$ in various molar ratios and different temperatures always gives the unchanged starting material. It seems that the compound has a lower donating capacity than the solvent.

In order to reinforce the covalent bond by a higher back donation we tried to obtain complexes of $(C_6F_5)_3As$ with metals in a lower oxidation state. It has

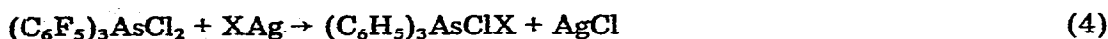
been reported [4] that $(C_6H_5)_3As$ stabilizes neutral nickel(I) complexes. Similar reduction of ethanol solutions of nickel(II) chloride with a stoichiometric amount of $NaBH_4$ in the presence of $(C_6F_5)_3As$ gives metallic nickel, indicating that the pentafluorophenylarsenic derivative is unable to stabilize nickel(I) under these conditions. Nevertheless it is possible to isolate $(C_6F_5)_3As$ complexes of metals in low oxidation state containing weakly donating anions and using non donor solvents. Thus the addition of $(C_6F_5)_3As$ to benzene solutions of $AgClO_4$ produces successively a neutral and a cationic complex, according to equations 1 and 2.



The oxidative addition of chlorine to $(C_6F_5)_3As$ gives $(C_6F_5)_3AsCl_2$ (III). This can also be obtained using $TlCl_3$ as the oxidant, thallos chloride being precipitated:



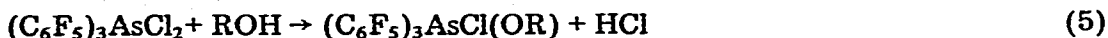
Treatment of compound III with various silver salts leads to the replacement of chlorine:



(X = NO_3 , ClO_4 , CH_3COO)

Only one of the chlorine atoms is replaced even when a molar ratio of As/Ag 1/2 is used. This behaviour is different from that of $(C_6H_5)_3AsCl_2$ [5], which undergoes replacement of both chlorine atoms in such reactions. Probably the higher electronegativity of the C_6F_5 groups increases the $p_\pi-d_\pi$ bond interaction and stabilizes the As—Cl bonds.

The As—Cl bond is also cleaved when compound III is stirred for several hours in methanol or ethanol, or with phenol in acetone:

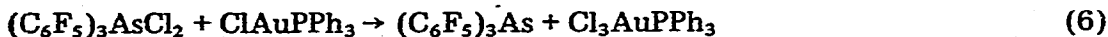


(R = CH_3 , CH_2CH_3 , C_6H_5)

This reaction also causes rupture of only one of the As—Cl bonds. The reaction presumably involves nucleophilic attack of the alcohol to give the hexacoordinate species, which then loses HCl.

Analytical data for the new compounds described are shown in Table 1.

Compound III oxidizes $ClAuPPh_3$ to Cl_3AuPPh_3 and is reduced to tris(pentafluorophenyl)arsenic(III):



When III is treated with a suspension of an excess of LiBr or NaI in acetone, reaction 7 (X = Br or I) takes place:



(X = Br, I)

TABLE 1
ANALYTICAL DATA FOR PENTAFLUOROPHENYLARSENIC COMPOUNDS

| Compound | Molecular formula | Analysis (found (calcd.) (%)) | | | | | |
|----------|---------------------------|-------------------------------|------------------|------------------|------------------|----------------|----------------|
| | | C | As | Ag | Cl | H | N |
| I | $C_{18}AsAgClF_{15}O_4$ | | | 13.26 (13.77) | | | |
| II | $C_{36}As_2AgClF_{30}O_4$ | 28.62 (28.06) | 11.08 (11.02) | 7.48 (7.93) | 2.65 (2.60) | | |
| III | $C_{18}AsCl_2F_{15}$ | 33.65 (33.39) | 11.62 (11.58) | | 10.85 (10.96) | | |
| IV | $C_{18}AsClF_{15}NO_3$ | 31.84 (32.07) | 11.18 (11.12) | | 5.31 (5.26) | | 2.18 (2.01) |
| V | $C_{18}AsCl_2F_{15}O_4$ | 29.58 (30.38) | 10.47 (10.53) | | 9.85 (9.97) | | |
| VI | $C_{20}AsClF_{15}H_3O_2$ | 35.61 (35.80) | 11.12 (11.17) | | 5.31 (5.28) | 0.58 (0.45) | |
| VII | $C_{19}AsClF_{15}H_3O$ | 35.40 (35.27) | 11.58 (11.66) | | 5.60 (5.51) | 0.60 (0.46) | |
| VIII | $C_{20}AsClF_{15}H_5O$ | 36.29 (36.56) | 11.38 (11.41) | | 5.42 (5.40) | 0.85 (0.71) | |
| IX | $C_{24}AsClF_{15}H_5O$ | 40.51 (40.85) | 10.68 (10.63) | | 5.08 (5.03) | 0.73 (0.69) | |

Reduction to the arsenic(III) derivative is accompanied by formation of bromine or iodine.

Complex I is very unstable in the presence of air in the solid and in benzene solution, but it is stable in a dry atmosphere in the dark. In the presence of light it blackens as metallic silver is slowly deposited. Complex II is stable in the dark even in the air, but decomposes in the light.

All the new arsenic(V) derivatives are indefinitely stable at room temperature in the solid state. They are soluble in chloroform, methanol, ethanol, acetone (with the exception of compound VI) and benzene (with the exception of com-

TABLE 2
MELTING POINTS AND CONDUCTIVITIES OF PENTAFLUOROPHENYLARSENIC DERIVATIVES

| Compound | M.p. (°C) | Λ (ohm ⁻¹ cm ² mol ⁻¹) ^a | |
|-------------------|-----------|---|---------|
| | | Acetone | Benzene |
| I | — | 175.59 | 0.14 |
| II | 213 | 187.04 | — |
| III | 190 | 1.64 | — |
| IV | 205 | 5.12 | — |
| V | 225 | 160.08 | — |
| VI | 210 | 5.74 | — |
| VII | 215 | 2.81 | — |
| V ₂ II | 210 | 2.52 | — |
| IX | 220 | 0.54 | — |

^a Measured for solution 5.10^{-4} M.

pound V) and insoluble in water and hexane. They are thermally stable and melt without decomposition between 170 and 220°C (see Table 2).

(b) Conductivity

Complex I is a non conductor in benzene. Its solutions in acetone have a conductivity which corresponds to a 1/1 electrolyte because of incorporation of the solvent in the coordination sphere of the metal in place of the ClO₄ group, which is displaced as the free anion. Complex II has the conductivity characteristic of a 1/1 electrolyte [6].

With the exception of compound V all the new arsenic(V) derivatives are non electrolytes in acetone. The perchlorate is completely dissociated in this solvent.



The conductivity indicates that this compound is a 1/1 electrolyte (See Table 2).

(c) IR spectra

All the compounds show IR absorption bands characteristic of the C₆F₅ group [7,8]. Complex II and compounds IV–IX show a band at 925 cm⁻¹ which is assigned to the stretching vibration ν(As–O). It indicates the covalent nature of the As–X bond, even in the case of the perchlorate derivative V in the solid state.

Compounds I and V show bands due to a monodentate C_{3v} ClO₄ group. Complex II show the characteristic IR absorptions of a T_d free ClO₄ anion. The anions in the remaining compounds are bound to the central arsenic atom as covalent monocoordinated ligands. Thus, compound III shows an absorption at 290 cm⁻¹ assigned to the ν(As–Cl). Similarly, compound IV contains the nitrate C_{2v} group, which gives the ν_{asym}(NO₂) absorption at 1450–1500 cm⁻¹, partly overlapped by an intense absorption due to the C₆F₅ group. The small difference between ν_{asym}(NO₂) and ν_{sym}(NO₂), less than 100 cm⁻¹, suggests the presence of a covalent As–O bond [9] (see Table 3).

TABLE 3

RELEVANT IR ABSORPTIONS DUE TO THE X ANION IN R₃AsClX^a COMPOUNDS (cm⁻¹)

| R ₃ AsCl(NO ₃) | R ₃ AsCl(ClO ₄) | R ₄ AsCl(OAc) | R ₃ AsClY ^b | R ₃ AsClOC ₆ H ₅ | Assignments |
|---------------------------------------|--|--------------------------|-----------------------------------|---|---|
| 300s | 300s | 300 | 300 | 300 | ν(As-Cl) |
| 1450–1500vs ^c | | | | | ν _{as} (NO ₂) ^d |
| 1260s | | | | | ν _s (NO ₂) |
| g. | | | | | ν _s (NO) |
| 800s | | | | | δ(NO ₃) |
| | | | 2920m | | ν(C-H) |
| | | 1635s ^c | | | ν _{as} (OCO) ^e |
| | | 1290s ^c | | | ν _s (OCO) |
| | 1150vs ^c | | | | ν ₁ ^f |
| | d | | | | ν ₂ |
| | 625m ^c | | | | ν ₃ |
| | d | | | | ν ₄ |
| | 635m ^c | | | | ν ₅ |

^a R=C₆F₅. ^b Y=OCH₃, OC₂H₅. ^c Overlapped by C₆F₅ absorptions. ^{d,e,f} Referred to the normal modes of the NO₃, ClO₄, AcO anions monodentates [13]. ^g Absent.

Experimental

IR spectra were recorded on a Perkin—Elmer 457 spectrophotometer (over the range 4000—250 cm^{-1}) using Nujol between CsI plates or KBr pellets. Conductivities were measured with a Phillips PW9501/01 conductometer, C, H, N analyses were carried out with a Perkin—Elmer 420 microanalyzer. Silver was determined according to ref. 10. Arsenic was determined according to ref. 11, and chlorine according to ref. 12.

$(\text{C}_6\text{F}_5)_3\text{AsAgOClO}_3$ (I)

$(\text{C}_6\text{F}_5)_3\text{As}$ (1 g, 1.736 mmol) is added to a benzene solution of AgClO_4 (0.360 g, 1.736 mmol) under dry nitrogen. After stirring for 2 h at room temperature the solvent is evaporated to give colorless crystals of complex I, which are filtered off in a dry atmosphere and washed with diethyl ether.

$\{\text{Ag}[(\text{C}_6\text{F}_5)_3\text{As}]_2\}\text{ClO}_4$ (II)

$(\text{C}_6\text{F}_5)_3\text{As}$ (1 g, 1.736 mmol) is added to a benzene solution of AgClO_4 (0.180 g, 0.868 mmol). After stirring for 2 h at room temperature the solution is evaporated to give white crystals of complex II which are filtered off and washed with diethyl ether. Yield 75%.

$(\text{C}_6\text{F}_5)_3\text{AsCl}_2$ (III)

(a) *Oxidation with chlorine.* 6.93 ml of a 0.5 N solution of Cl_2 (0.123 g, 1.736 mmol) in CCl_4 are added dropwise to a solution of $(\text{C}_6\text{F}_5)_3\text{As}$ (1 g, 1.736 mmol) in chloroform (50 ml). After stirring for 5 h at room temperature, the solution is concentrated by evaporation. White crystals of compound III are produced on cooling. The solid is filtered, washed with hexane, and dried under vacuum. Yield 92%.

(b) *Oxidation with thallic chloride.* Diethyl ether (35 ml) is added to a mixture of $(\text{C}_6\text{F}_5)_3\text{As}$ (1 g, 1.736 mmol) and TlCl_3 (0.539 g, 1.736 mmol) and the solution stirred under nitrogen at room temperature for 12 h. Insoluble TlCl is filtered off and the solution is evaporated to dryness under vacuum. The residue is recrystallized from chloroform and washed with hexane to give compound III. Yield 80%.

$(\text{C}_6\text{F}_5)_3\text{AsClX}$ (IV—VI)

Addition of solutions of silver salts XAg ($\text{X} = \text{NO}_3, \text{OAc}, \text{ClO}_4$) to solutions of compound III in an equimolar ratio causes precipitation of AgCl . Benzene is used as solvent for compounds IV and V, and AgCl is precipitated immediately at room temperature. For compound VI, it is necessary to use acetone containing a few drops of anhydrous acetic acid; the precipitation of AgCl is slow, so that the reaction must be carried on for 5 h under reflux. The AgCl is filtered off and solutions are concentrated by evaporation to give compounds IV—VI. The solids are washed with hexane and dried under vacuum. Yield ca. 50—60%.

$(\text{C}_6\text{F}_5)_3\text{AsCl(OR)}$ (VII—IX)

Compound III is soluble in ethanol but scarcely soluble in methanol. The suspension in methanol (150 ml) or solution in ethanol (150 ml) of III (1.500 g,

2.318 mmol) is stirred at room temperature for 12 h. After evaporation and cooling crystalline solids are obtained.

Compound IX is obtained using acetone as solvent and by adding an equimolar amount of phenol. Compound IX crystallizes after concentration by addition of a few drops of cyclohexane. The solids are filtered off washed with hexane, and dried under vacuum. Yield 75–90%

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