A Novel Arsenic Complex of Zirconium(III)

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Abstract

The prolonged reaction of zirconium tetrachloride with 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluoro-cyclobutene (tfars) in acetonitrile forms [ZrCl₃(tfars)] MeCN. This compound appears to be the first magnetically dilute complex of zirconium(III).

Introduction

The coordination chemistry of zirconium(III) is very uncertain. Attempts to prepare complexes by reaction of the polymeric trihalides with potential ligands results in oily mixtures, or products which have unusual stoichiometrics and/or magnetic properties.

Fowles *et al*,[1,2] found that the reaction between zirconium trichloride and aceto-nitrile for 3–5 days at room temperature yielded $ZrCl_3, 2\frac{1}{2}MeCN$ (μ_{eff} 0·46 B.M.), and it was deduced from infrared evidence and by the retention of the acetonitrile on heating under vacuum at 100°C, that all the acetonitrile was coordinated to the zirconium atom. Similarly these workers found that pyridine, 2,2′-bipyridyl and 1,10-phenan-throline in acetonitrile formed $ZrCl_3, 2py$ (μ_{eff} 1·29 B.M.), $ZrCl_3, 1\frac{1}{2}bpy$ (μ_{eff} 1·35 B.M.), and $ZrCl_3, 1\frac{1}{2}phen$ (μ_{eff} 1·27 B.M.) respectively. These compounds had electrical conductivities (1×10^{-3}M) in acetonitrile ranging from 28 to 122 cm² S mol⁻¹.

Larsen and Henzler[3] more recently described in detail the preparation of $ZrCl_3, 2$-(ligand) with 3,5-lutidine and $ZrCl_3, 1\cdot 2$–$1\cdot 3$(ligand) with 2,4-lutidine, from zirconium trichloride and the appropriate lutidine in benzene after 1–30 days at room temperature. These reactions were also complicated by the formation of soluble zirconium(IV) byproducts. The magnetic susceptibilities were approximately independent of tempera-ture, but were very dependent upon field strength. For example, the 3,5-lutidine adduct had the extraordinarily high corrected molar magnetic susceptibility of *c*. 230×10^{-9} at 2·93 kG, falling to *c*. 100×10^{-9} at 7·82 kG, whereas the value for the 2,4-lutidine adduct was less than one-tenth of these values. It was suggested that these lutidine adducts were intercalation compounds with lutidine inserted between the polymeric $ZrCl_3$ chains.

Whatever the exact nature of these compounds, it is clear that they are polymeric and their chemistry bears little resemblance to the relatively simple and extensively

[1] Fowles, G. W. A., Russ, B. J., and Willey, G. R., *Chem. Commun.*, 1967, 646.
[2] Fowles, G. W. A., and Willey, G. R., *J. Chem. Soc., A*, 1968, 1435.
[3] Larsen, E. M., and Henzler, T. E., *Inorg. Chem.*, 1974, **13**, 581.

studied chemistry of titanium(III) compounds,[4] for example, the paramagnetic mono-mer [TiCl$_3$(MeCN)$_3$] and [TiCl$_3$(py)$_3$].

We report here the first simple complex of zirconium(III) prepared by the adventitious reduction of zirconium tetrachloride with the unusual fluoroarsine ligand 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene, (CF$_2$)$_2$C$_2$(AsMe$_2$)$_2$ (tfars).[5]

Results and Discussion

The reaction of zirconium tetrachloride with tfars in acetonitrile yielded [ZrCl$_3$-(tfars)] MeCN. The brown solid, which slowly precipitated from a brown solution over a period of six months, resulted from a sealed tube reaction at 100°C for one week. Reduction was detected by a colour change from clear, through yellow, to a deep brown. The compound is a non-electrolyte in acetonitrile, and possesses a magnetic moment at room temperature of 1·73 B.M.

The acetonitrile in [ZrCl$_3$(tfars)] MeCN appears from the infrared spectrum to be uncoordinated. A weak signal at 2255 cm^{-1} is indicative of lattice,[6] rather than coordinated,[7] acetonitrile.

The diffuse reflectance spectrum shows only charge-transfer bands, the first being at 24000 cm^{-1}, which is in agreement with the results obtained by Fowles et al. (27600 cm^{-1}).[2] An intense band at 21100 cm^{-1}, and less intense bands at 11100 and 8000 cm^{-1} were observed for ZrCl$_3$(3,5-lutidine)$_2$.[3]

Niobium pentachloride is not reduced under these conditions used to reduce zirconium tetrachloride,[8] which is contrary to the conclusions of Larsen and Henzler.[3] o-Phenylenebisdimethylarsine on the other hand readily reduces niobium penta-chloride,[9] but not zirconium tetrachloride.[8] The reactions of tfars with niobium and hafnium tetrachlorides in acetonitrile also yield brown solutions, but brown oils resulted on removal of some of the solvent and no solid could be isolated. Reduction of zirconium tetrachloride with tfars also occurs in the solvents acetone and benzene.

Experimental

[1,2-Bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene]trichlorozirconium(III)–acetonitrile (1/1)

Zirconium tetrachloride (0·3 g), tfars (0·9 g) and acetonitrile (20 ml) were heated on a steam bath for 8 days to produce a deep brown solution. On standing for 6 months, a brown solid was deposited, and was filtered, washed and stored under vacuum. The *compound* is moderately air-sensitive, has a conductivity of 30 cm^2 S mol^{-1} in a 1·5 × 10^{-3}M acetonitrile solution, and a χ_M value of 13·2 × 10^{-9} m^3 mol^{-1} at 298 K (Found: C, 21·0; H, 2·9; Cl, 19·5; F, 13·8; N, 2·7. C$_{10}$H$_{15}$As$_2$Cl$_3$F$_4$NZr requires C, 21·0; H, 2·6; Cl, 18·6; F, 13·3; N, 2·4%).

Materials

Commercial zirconium tetrachloride was sublimed in evacuated sealed tubes at 350°C. The ligand preparation has been described elsewhere.[10] Acetonitrile was stored over molecular sieves, then dried with calcium hydride, and refluxed and distilled from sodium wire. Ethanol was finally removed by refluxing and distilling from niobium pentachloride.

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Spectra

Diffuse reflectance spectra were measured by means of the SP735 attachment to the Unicam SP700 spectrophotometer, which was calibrated against a solution of 4% holmium oxide in 1·4M perchloric acid.[11] Samples were prepared in a glove-box, with magnesium oxide as both a reference and a diluent. Infrared spectra were recorded as Nujol mulls prepared in a dry box, on a Perkin Elmer 337 grating Infracord spectrophotometer with polystyrene as standard.

Conductivity and Magnetic Susceptibility Measurements

Conductivity measurements were made on solutions prepared in a conventional vacuum line, shiny platinum electrodes being used. The conductance of a 1 : 1 electrolyte in acetonitrile is 140–160 cm^2 S mol^{-1}.[12] A Faraday balance equipped with a Stanton M10 microbalance and a 2·5-in. electromagnet were used to determine room temperature magnetic susceptibilities. Pascal's constants[13] were used to correct magnetic susceptibilities for the diamagnetism of the ligands. The air-tight sample holder, consisting of a glass bulb and rubber stopper, was calibrated with silver shot.[14]

Acknowledgment

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