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# SYNTHESIS AND STRUCTURE OF BIS(TRIFLUOROMETHYL)BIS(TRIMETHYLSILYL)AMINO DICHLOROARSORANE, $(CF_3)_2AsCl_2N(SiMe_3)_2$ *

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## SUMMARY

The synthesis of $(CF_3)_2AsCl_2N(SiMe_3)_2$ is reported. This compound has been characterized on the basis of an X-ray analysis. It has a trigonal bipyramidal geometry with axial chlorine atoms. Variable temperature $^1H$- and $^{19}F$-NMR data show no observable changes. In comparison to pentacoordinated phosphorus compounds the tendency to form tetracoordinated derivatives is strongly diminished in the case of arsenic compounds.

## INTRODUCTION

Diorganylarsoranes of the type $R_2AsX_3$ are rare as compared to triorganylarsoranes, $R_3AsX_2$ [1-3]. In addition to that no crystal structure data are available on compounds with the composition $R_2AsX_3$ and controversies exist (R = Me, Ph, X = F) regarding their solution stereochemistry [4-6]. We are interested in pentacoordinated arsenic compounds, containing an electron withdrawing group attached to the arsenic atom. In continuation of our earlier studies [7], we report here the synthesis and structure of a pentacoordinated organoarsorane, $(CF_3)_2AsCl_2N(SiMe_3)_2$.

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* Dedicated to Professor Ulrich Wannagat on the occasion of his 60th birthday.

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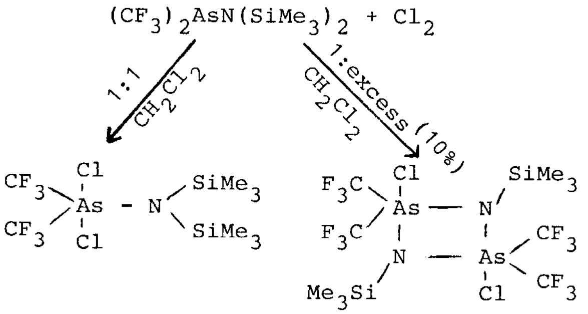
## EXPERIMENTAL

Chlorine (0.89 g, 12.5 mmol) is condensed into a solution of $(CF_3)_2AsN(SiMe_3)_2$ (4.7 g, 12.6 mmol) in 10 ml $CH_2Cl_2$, cooled to liquid air temperature and the mixture is allowed to warm up slowly to room temperature. 2-Methyl-1,3-butadien (10 ml) has to be added when any unreacted chlorine is present. The $^{19}F$-NMR spectra of this solution indicated a strong signal at $\delta_{CF_3}$ - 54.5 ppm. The volume of this solution is reduced to half by removing the solvent under reduced pressure. When this solution is kept at -30° C for about 24 h, crystals of $(CF_3)_2AsCl_2N(SiMe_3)_2$ separate out (3.7 g, 78 %). The compound can be recrystallized from n-hexane. Anal. Found : C, 21.7; H, 4.0 %. Calcd. for $(CF_3)_2AsCl_2N(SiMe_3)_2$ : C, 21.6; H, 4.0 %. M.P. 90° C (sealed capillary). IR (nujol) : 2960 vs, 2930 vs, 2860 s, 1462 m, 1376 w, 1260 m, 1208 s, 1190 m, 1168 m, 1105 m, 1060 s, 882 s, 852 s, 828 m, 740 m. $^{19}F$-NMR ($CH_2Cl_2$) ($\delta_{CF_3}$ - 54.7 ppm), $^{1}H$-NMR ($CH_2Cl_2$) ($\delta_{SiMe_3}$ - 0.508 ppm), Mass spectra ($M^+$, 444).

## RESULTS AND DISCUSSION

Reaction of $(CF_3)_2AsN(SiMe_3)_2$ with chlorine gives two products depending upon the molar ratios of the reactants :



$(CF_3)_2AsCl_2N(SiMe_3)_2$ is formed when chlorine is condensed into a solution of the aminoarsane in 1:1 molar ratio. If the above reaction is carried out in the presence of excess of chlorine, cyclodiars(V)-azene is formed [7]. We were not able to show that the monomeric species $(CF_3)_2ClAs{=}NSiMe_3$ with tetracoordinated arsenic is formed during the reaction. This compound immediately dimerizes to the four-membered ring. It seems that in the arsenic case in general compounds of arsenic with coordination number four are less stable than the corresponding phosphorus compounds.

$(CF_3)_2AsCl_2N(SiMe_3)_2$ is hygroscopic and monomeric in solution. It is soluble in common organic solvents. Thermal decomposition of it gives mainly six- and eight-membered arsazenes $[(CF_3)_2AsN]_3$ and $[(CF_3)_2AsN]_4$ [8].

Both $^1H$- and $^{19}F$-NMR spectra of $(CF_3)_2AsCl_2N(SiMe_3)_2$ in $CH_2Cl_2$ show one signal relatively unchanged from $-80^{\circ}$ C to room temperature at - 0.51 ppm ($\delta_{SiMe_3}$) and at - 54.7 ppm ($\delta_{CF_3}$) respectively. The corresponding signals of the starting material $(CF_3)_2AsN(SiMe_3)_2$ appear at 0.290 ppm ($\delta_{SiMe_3}$) and at - 51.5 ppm ($\delta_{CF_3}$) respectively, at room temperature. Under these conditions we do not observe any changes in the signals. Crystals of this compound are monoclinic, space group $P2_1/m$ with a = 9.298(4), b = 12.84(3), c = 15.090(2) Å, ß = 95.96(5) $^{\circ}$ and Z = 4. The molecular structure of $(CF_3)_2AsCl_2N$-$(SiMe_3)_2$ is shown in Fig. 1. the chlorine atoms are in axial positions while the $CF_3$ groups and the $N(SiMe_3)_2$ group occupy the equatorial sides. The crystals are very sensitive to moisture, grease and glue and therefore we were not able to fix the crystals in the capillary. During the measurements the crystal moved and the data obtained are not accurate.

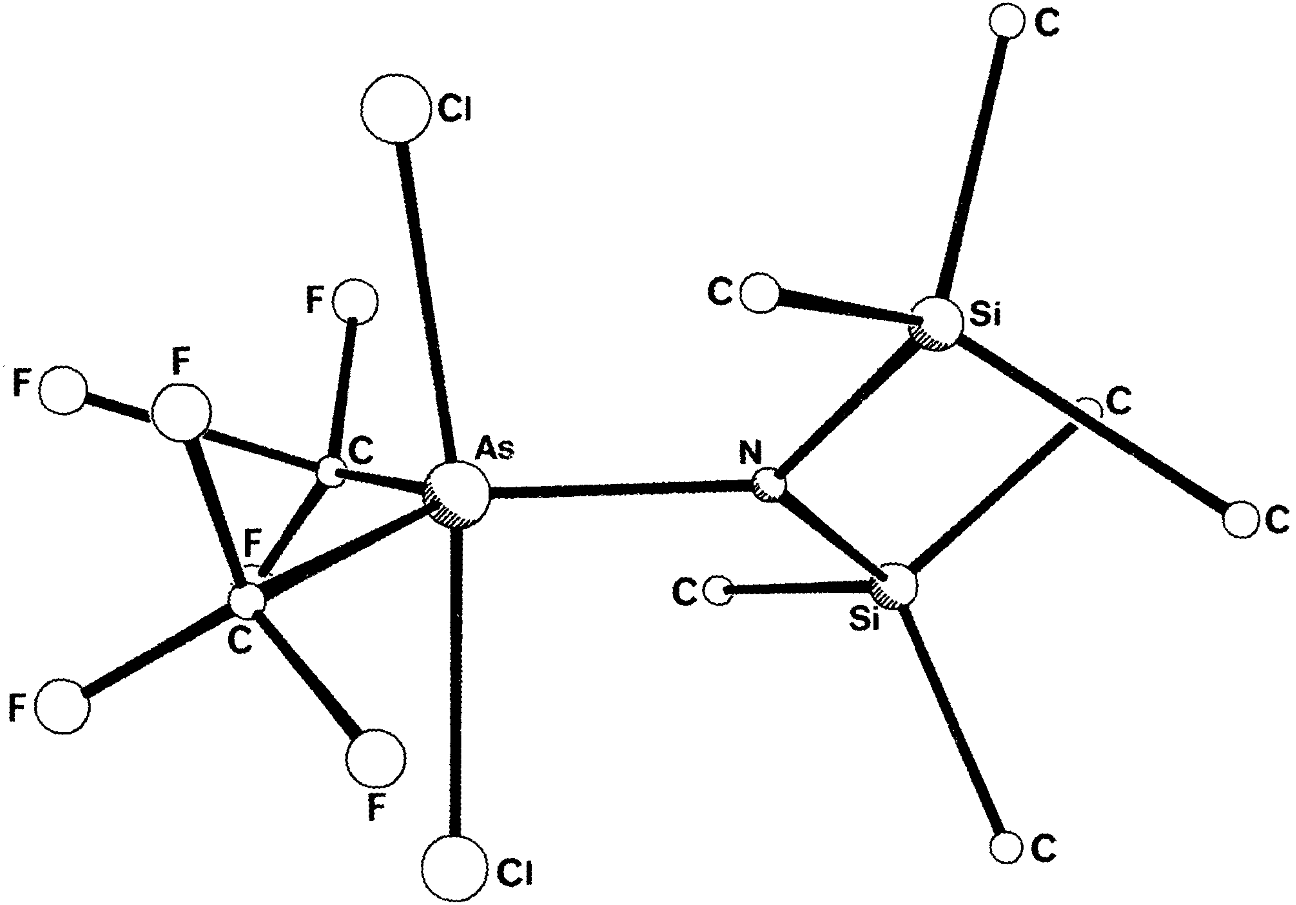


Fig. 1. Molecular structure of $(CF_3)_2AsCl_2N(SiMe_3)_2$.

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