

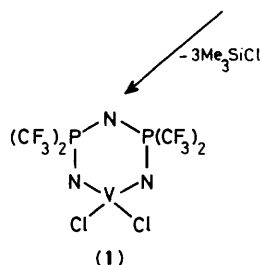
A Volatile Cyclic Metallaphosphazene; Preparation and X-Ray Structure of $[(CF_3)_2PN]_2NVCl_2$

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The reaction of $(CF_3)_2P(Cl)=NSiMe_3$ and $Me_3SiN=VCl_3$ in CH_2Cl_2 leads to volatile $[(CF_3)_2PN]_2NVCl_2$; the X-ray structure analysis shows a planar six-membered NVNPNP-ring with C_{2v} molecular symmetry.

Volatile compounds containing metals are, in general, interesting candidates for application in CVD (Chemical Vapour Deposition) or MOCVD techniques. Recently, we reported the first synthesis and structure of metal-containing cyclic phosphazenes.¹ These compounds are not volatile at room temperature and tend to form polymeric materials at elevated temperatures. However, the reaction of $(CF_3)_2P(Cl)=NSiMe_3$ † and $Me_3SiN=VCl_3$ ‡ in dichloromethane leads to the unexpected formation of the six-membered ring $[(CF_3)_2PN]_2NVCl_2$ (1).‡



† $(CF_3)_2P(Cl)=NSiMe_3$ was prepared from $(CF_3)_2PN(SiMe_3)_2$ and chlorine or sulphuryl dichloride under elimination of Me_3SiCl .⁴

‡ 2.4 g (10 mmol) $Me_3SiN=VCl_3$ were dissolved in CH_2Cl_2 (60 ml) and cooled to $-192^\circ C$; at this temperature $(CF_3)_2P(Cl)=NSiMe_3$ (5.8 g, 20 mmol) was added. This mixture was slowly warmed up and kept at room temperature and stirred for an additional 5 h. CH_2Cl_2 and Me_3SiCl were removed at room temperature *in vacuo* (2×10^3 Pa). The crude product was sublimed twice ($-10^\circ C/1$ Pa), giving crystals suitable for X-ray diffraction. Yield 1.4 g (28%)—satisfactory elemental analyses were obtained.

Compound (1) is a yellow volatile solid which melts at $22.5^\circ C$ and decomposes. In the mass spectrum [electron impact (e.i.)] it exhibits the parent ion at m/z 501 (4% relative intensity). $M^+ - CF_3$ is observed at m/z 432 (12%), and CF_3 (m/z 69, 100%) is the most abundant ion. The ^{19}F n.m.r. spectrum contains the typical doublet at $\delta -67.0$ with a coupling constant of 126.3 Hz indicating magnetically equivalent CF_3 groups. The ^{31}P - and the ^{51}V -n.m.r. spectra show a broad unresolved singlet (δ 22.0) and multiplet (δ 48.5)

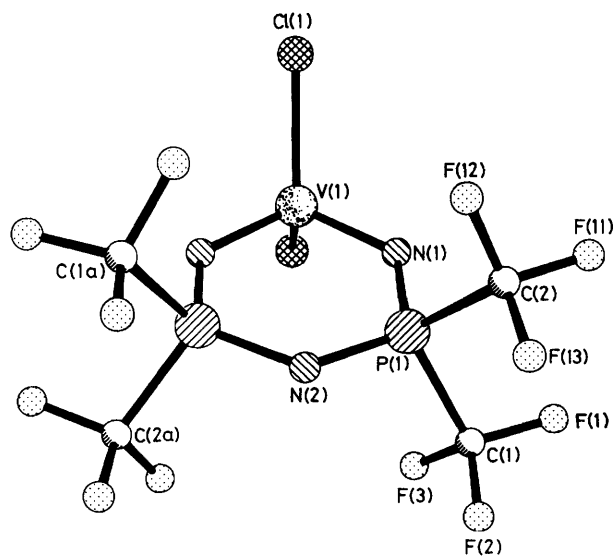


Figure 1. Molecular structure of $[(CF_3)_2PN]_2NVCl_2$ (1); important bond lengths (pm) and angles ($^\circ$): V-C(11) 215.9(2), N(1)-P(1) 161.2(4), N(2)-P(1) 159.5(3), N-V-N 104.1(3), P-N-P 121.3(4), V-N-P 129.0(3).

respectively. A crystal structure determination[§] confirms the six-membered ring (Figure 1). This ring is nearly planar (mean deviation 2.1 pm) and the molecule exhibits effective C_{2v} symmetry. It differs from the non-metallated analogues primarily in the considerably larger angles at the N atoms, [V–N–P 129.0(3)° *cf.* P–N–P 121.3(4)°]. The vanadium atom is co-ordinated tetrahedrally with short V–N bond lengths [172.1(5) pm]; the N–V–N angle [104.1(3)°] is smaller than Cl–V–Cl [119.1(1)°]. A similar effect is observed in CrO_2Cl_2 [O–Cr–O 108.5(4)°, Cl–Cr–Cl 113.2(3)°].³ The crystal structure resembles those of the molybdenum and tungsten compounds with composition $(\text{Ph}_2\text{PN})_2\text{NMCl}_3 \cdot 2\text{MeCN}$,¹ but

[§] *Crystal data* for (1); $\text{C}_4\text{Cl}_2\text{F}_{12}\text{N}_3\text{P}_2\text{V}$, $M = 501.8$, monoclinic, space group $C2/c$, $a = 1465.8(3)$, $b = 828.8(2)$, $c = 1531.6(3)$ pm, $\beta = 122.41(1)^\circ$, $D_c = 2.122 \text{ g cm}^{-3}$, $Z = 4$. The final R -value was 0.072 for 1248 unique data with $F > 4\sigma(F)$. Data were collected on a Stoe-Siemens AED diffractometer using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71069 \text{ \AA}$) at -80°C . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

crystals of the vanadium compound do not contain solvent molecules.

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