

## The Preparation and Structure of Trigermylphosphine

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WE have obtained the new compound trigermylphosphine,  $(\text{GeH}_3)_3\text{P}$ , by treating trisilylphosphine with a small excess of germyl bromide at room temperature, and have characterized it by hydrogen analysis, by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy, and by mass spectroscopy. The compound is a colourless liquid, m.p.  $-83.8^\circ$ , v.p. at  $0^\circ \sim 1$  mm., which decomposes slowly at room temperature and rapidly at  $55^\circ$ .

The vibrational spectra of the compound are of interest in relation to the possible shape of the heavy-atom skeleton. Considering the vibrations of the skeleton as separate from those involving the  $\text{GeH}_3$  groups (a procedure justified by studies of a number of methyl and silyl compounds), four skeletal modes are to be expected for either a planar or a pyramidal  $\text{Ge}_3\text{P}$  system. A molecule with a planar skeleton would be expected to give two Raman-active stretching modes (near  $350\text{--}400$   $\text{cm}^{-1}$ ), of which only one would be allowed in the infrared, and two infrared-active skeletal bending modes (near  $100$   $\text{cm}^{-1}$ ), only one of which would be allowed in the Raman.

For a pyramidal skeleton, all four modes would be allowed both in the Raman and the infrared; two of the Raman lines would be expected to be polarized.

We have obtained infrared spectra ( $4000\text{--}250$   $\text{cm}^{-1}$ ) of trigermylphosphine in the solid and vapour phases, and of thin liquid films; good-quality Raman spectra were obtained using Hg  $4358$  Å excitation and a sample of volume of about  $0.4$  ml. maintained at about  $-60^\circ$ . In the Raman spectrum, besides features near  $2100$   $\text{cm}^{-1}$  ( $\text{GeH}$  stretching),  $800$   $\text{cm}^{-1}$  ( $\text{GeH}_3$  bending), and  $550$   $\text{cm}^{-1}$  ( $\text{GeH}_3$  rocking), lines were observed at  $366$   $\text{cm}^{-1}$  (medium-strong),  $322$   $\text{cm}^{-1}$  (strong, polarized),  $112$   $\text{cm}^{-1}$  (weak, polarized), and  $88$   $\text{cm}^{-1}$  (medium). We assign these respectively to the antisymmetric stretching, the symmetric stretching, and the two bending modes of a pyramidal  $\text{Ge}_3\text{P}$  skeleton. The polarization data support these assignments, while the frequencies are in the ranges expected by analogy with the spectra of related molecules. The observation of the two skeletal bending modes in the Raman

spectrum affords very strong evidence that the skeleton is not planar. The infrared spectrum of the vapour shows only one of the two skeletal stretching modes; this would be consistent with a planar skeleton, but in view of the weakness of the symmetric  $C_3P$  stretching mode in the infrared spectrum of the pyramidal trimethylphosphine,<sup>1</sup> and the low pressure at which the spectrum of the vapour must be obtained, we regard the Raman evidence as decisive.

These results imply a structural difference between trigermylphosphine and trisilylphosphine

(whose vibrational spectra are consistent with a planar skeleton<sup>2</sup>), and suggest that ( $p \rightarrow d$ )  $\pi$ -bonding between phosphorus and germanium is not stereochemically significant; no evidence has been presented, so far as we are aware, to show that ( $p \rightarrow d$ )  $\pi$ -bonding has much influence on the molecular geometry of other germyl derivatives. At the same time, vibrational spectroscopy is at best an indirect method of structural analysis, and we hope to confirm our conclusions by  $X$ -ray investigation.

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<sup>1</sup> M. Halmann, *Spectrochim. Acta*, 1960, **16**, 407.

<sup>2</sup> G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick, and L. A. Woodward, *Chem. Comm.*, 1965, 122.