Vibrational Spectra of Trisilylphosphine: Evidence for Planar PSi_3 Structure

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RAMAN and infrared evidence has shown[1] that trisilylamine has a planar NSi_3 skeleton, as contrasted with the normal pyramidal NC_3 skeleton of trimethylamine, and this has been attributed to ($p \rightarrow d$) π-bond formation in the silyl compound. We have now obtained analogous evidence for a planar PSi_3 skeleton in trisilylphosphine.

The compound was prepared by the action of chlorosilane upon potassium phosphide (KPH_2) in dimethyl ether at approximately −100° C (*cf.* the original preparation by Amberger and Boeters[2]). The use of higher temperatures resulted in diminished yields. The corresponding completely deuterated species was obtained by using SiD_3Cl in

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[1] E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *Spectrochim. Acta*, 1958, **13**, 202.

[2] E. Amberger and H. Boeters, *Angew. Chem.*, 1962, **74**, 32.

place of SiH_3Cl. No isotopic exchange was detected.

Good-quality Raman spectra of liquid $P(SiH_3)_3$ were obtained, using Hg 4358 Å excitation and a sample of volume about 0·4 ml maintained at approximately $-60°$ c. The infrared spectra of $P(SiH_3)_3$ and $P(SiD_3)_3$ were recorded for the vapours at room temperature and at pressures up to about 17 mm. The bands observed for the former species agree well with those reported by Amberger and Boeters.[2]

Experience with trimethylboron[3] and trisilylamine[1] shows that the symmetry of the skeleton can be deduced from the skeletal features alone, without reference to those associated with the methyl or silyl groups. Of crucial importance are the two skeletal stretching frequencies (ν_1, symmetric and ν_3, asymmetric). If the skeleton is pyramidal (point group C_{3v}), both ν_1 and ν_3 are permitted in the infrared as well as in the Raman spectrum; whereas if the skeleton is planar (point group D_{3h}), both are still permitted in the Raman, but in the infrared only ν_3 is permitted, ν_1 being forbidden.

In the P–Si stretching region the Raman spectrum of $P(SiH_3)_3$ shows the expected two lines, at 414 and 455 cm.$^{-1}$ The former is very strong and polarized, and so is undoubtedly to be assigned to ν_1. The latter is less intense and depolarized, as expected for ν_3. The infrared spectrum shows a strong ν_3-band (456 and 463 cm.$^{-1}$, doublet), but no sign of a band near 414 cm.$^{-1}$. From this striking evidence, which is exactly analogous to that found for $N(SiH_3)_3$, we see that the PSi_3 skeleton obeys the *planar* selection rules.

Both the Raman and infrared spectra of $P(SiH_3)_3$ contain features in the expected regions for Si–H stretching, SiH_3 deformation, and SiH_3 rocking. That these assignments are correct is proved by the observation that all the frequencies in question show the expected large downward displacements in the infrared spectrum of $P(SiD_3)_3$. Thus there can be no doubt that the skeletal stretching frequencies have been correctly identified.

In the Raman spectrum of $P(SiH_3)_3$ there is a weak, ill-defined feature at approximately 134 cm.$^{-1}$ This is doubtless the in-plane skeletal deformation frequency. The out-of-plane skeletal deformation (permitted in the infrared only) is expected to lie below the experimental range, and so was not observed.

The observed obedience to the D_{3h}, and not to the C_{3v} selection rules strongly suggests that the PSi_3 skeleton is planar; but it leaves open the possibility that it may be "pseudo-planar", *i.e.* that the P atom may be only slightly out of the plane of the three Si atoms. Here it is relevant to recall the case of the "pseudo-linear" disilyl ether molecule, of which the Si–O–Si skeleton has been found[4] to obey the linear selection rules, and the Si–O–Si angle (though abnormally large) has been shown[5,6] to be less than 180°.

Whether the PSi_3 skeleton in trisilylphosphine be planar or "pseudo-planar", however, it remains necessary to invoke ($p \rightarrow d$) π-bond formation between phosphorus and silicon to account for the evident departure from the normally pronounced pyramidal shape. This appears to be the first case for which π-donation between two second-row elements has been shown to produce stereochemical consequences of this kind.

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[3] L. A. Woodward, J. R. Hall, R. N. Dixon, and N. Sheppard, *Spectrochim. Acta*, 1959, **15**, 249.

[4] R. C. Lord, D. W. Robinson, and W. C. Schumb, *J. Amer. Chem. Soc.*, 1956, **78**, 1327.

[5] D. C. McKean, R. Taylor, and L. A. Woodward, *Proc. Chem. Soc.*, 1959, 321.

[6] A. Almenningen, O. Bastiansen, V. Ewing, K. Hedburg, and M. Traetteberg, *Acta Chem. Scand.*, 1963, **17**, 2455.