

## NOTE

### COMMENT ON THE PAPER: MASSENSPEKTROMETRISCHE UNTERSUCHUNG VON PERPHENYLCYCLOSILANEN, PERPHENYLCYCLOGERMANEN UND EINEM PERPHENYLCYCLO- STANNAN<sup>1</sup>

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The mass spectrum of dodecaphenylcyclohexastannane  $(\text{Ph}_2\text{Sn})_6$ , reported by Kühlein and Neumann<sup>1</sup> (K&N), shows only peaks corresponding to ions containing one or two tin atoms. A comparison with the spectra of the silicon and germanium analogues demonstrates the specific simplicity of the spectrum of the tin compound. This simplicity has been attributed<sup>1</sup> to the labile Sn-Sn bonds. However, when such labile bonds are involved it is essential to establish whether the peaks present in the mass spectrum are the result of electron impact induced fragmentations or of thermochemical decomposition processes followed by ionization and subsequent fragmentation reactions. This is particularly true for compounds containing IVth Group metal-metal bonds, since it is known that the compounds  $(\text{Ph}_2\text{Pb})_n$  and  $\text{Ph}_3\text{SnPbPh}_3$ , for example, decompose even at room temperature into  $\text{Ph}_3\text{PbPbPh}_3$  and Pb and into  $\text{Ph}_4\text{Sn}$ ,  $\text{Ph}_3\text{PbPbPh}_3$  and Pb, respectively<sup>2</sup>.

We observed that quantitative thermal decomposition of  $(\text{SnPh}_2)_6$  occurs upon heating a sample in an evacuated sealed tube up to the ion source temperature used by K&N (220–250°). The decomposition products were metallic Sn and—as identified by thin-layer chromatography— $\text{SnPh}_4$ ,  $\text{Sn}_2\text{Ph}_6$  and minor quantities of  $\text{Sn}_3\text{Ph}_8$ . The latter products appear to be formed as a result of intermetallic phenyl 1,2-shifts in  $(\text{SnPh}_2)_6$ , analogous to those occurring under much milder conditions in  $(\text{PbPh}_2)_n$ <sup>2</sup>. The occurrence of thermochemical decomposition under the conditions used by K&N is supported by the observation<sup>1</sup> that the spectral intensities depend upon the method of introducing the sample probe into the ion source. Whereas the temperature of the sample rises only slowly when the ion source is vented by hand (this should be done at a temperature below 100°), it is heated instantaneously when using the vacuum lock system.

It follows that the mass spectrum of  $(\text{SnPh}_2)_6$  given by K&N is likely to be merely a combination of  $\text{Sn}_2\text{Ph}_6$  and  $\text{SnPh}_4$  spectra. Thus the ions  $\text{SnPh}_3^+$  may be formed by a simple bond cleavage in the ions  $\text{Sn}_2\text{Ph}_6^+$  or  $\text{SnPh}_4^+$ ; their formation by

means of a phenyl 1,2-shift\* in the  $(\text{SnPh}_2)_n^+$  ion<sup>1</sup> is questionable because no corresponding metastable ion transitions have been reported. Quantitative comparison of K&N's spectrum with the spectra of  $\text{Sn}_2\text{Ph}_6$  and  $\text{SnPh}_4$  reported in the literature<sup>5</sup> is handicapped by the lack of information about the thermal decomposition process and the relative amounts of the species being formed.

Although the analogous compounds  $(\text{SiPh}_2)_6$  and  $(\text{GePh}_2)_6$  are more stable, the possibility of similar thermal decompositions and subsequent formation of the ions  $\text{SiPh}_3^+$  and  $\text{GePh}_3^+$  by direct bond cleavages must be considered. Since the major number of the electron impact induced fragmentation reactions given for  $(\text{Ph}_2\text{Si})_4$ <sup>1</sup> are not metastable supported, there is no evidence for such reactions. Moreover, some of the apparent masses of metastable peaks which have been noted do not correspond with the transitions mentioned. Probably, the difficulties in interpreting the metastable peaks are caused by the spectral notation used, *viz.* the weighed mean mass numbers. The mass numbers assigned by K&N do not agree with those calculated on the basis of the weighed mean *atomic* mass numbers, *viz.*  $\text{Si} = 28.06$ ,  $\text{Ge} = 72.60$  and  $\text{Sn} = 118.70$ . This may be caused by the presence of hydrogen rearrangement ions. However, in contrast with alkyl-metal compounds<sup>6</sup>, there is no evidence for hydrogen rearrangements in the mass spectra of phenyl-metal compounds<sup>5</sup>. Consequently, the current calculation of mono-isotopic spectra, using the method described by Dibeler and Mohler<sup>7</sup> and mass and abundance tables like those of Carrick and Glockling<sup>8</sup>, and a tabulation of the spectra based on the mass numbers of the most abundant isotope is a more reliable method.

#### REFERENCES

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\* Contrary to the suggestion of K&N, rearrangements of this kind are not of the McLafferty type. The McLafferty rearrangement is a  $\beta$ -cleavage with concomitant specific transfer of a  $\gamma$ -hydrogen atom in a six-membered transition state in mono-unsaturated systems<sup>3,4</sup>.