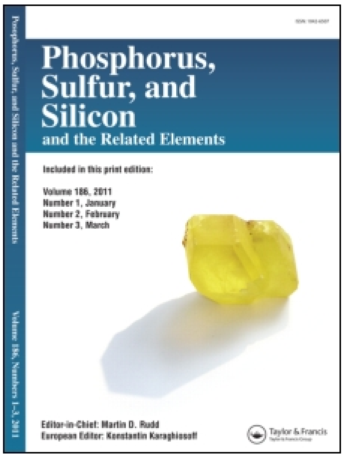

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DOES PHENYLPHOSPHINIDENE EXIST ? – MASS SPECTROMETRIC GENERATION AND CHARACTERIZATION OF Ph-P

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Dissociative electron impact ionization (70 eV) of $PhPBr_2$ yields $[C_6,H_5,P]^{\bullet+}$ ions with the PhP connectivity, as inferred from its collisional activation mass spectrum. Neutralization-Reionization experiments on this ion indicate that its neutral counterpart, phenylphosphinidene, Ph-P, is a stable species in the dilute gas phase.

Keywords: phenylphosphinidene; Mass spectra

INTRODUCTION

Whereas the simplest monovalent phosphorus compound having a sextet of electrons, phospinidene, H-P, is a well characterized species, the existence of organophosphinidenes R-P is still doubtful[1]. They are assumed to be short-lived intermediates in many reactions but, unlike carbenes, nitrenes or silylenes[2], their chemistry has not been widely explored except as ligands in metal complexes[3] where they can be stabilized in different bonding functions. Recently, however, ESR-spectroscopic evidence was presented for the generation of triplet mesityl-phosphinidene in matrix experiments involving photolysis of *trans*-2,3-dimethyl-1-mesityl-phosphirane[4]. We report here on the generation and characterization of Phenylphosphinidene, Ph-P, **1**, by mass spectrometric methods. As early

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as 1969 experiments were reported which point to the formation of this elusive neutral: the EI mass spectrum of the pyrolysis products of $[Ph\text{-}P]_5$ features m/z 108 $[C_6,H_5,P]^{\bullet +}$ ions, albeit that their connectivity remains unknown[5].

RESULTS AND DISCUSSION

The molecular ions of $PhPX_2$ (X = halogen) preferentially dissociate by loss of $X^{\bullet}$ and when X is Cl, the next step involves loss of HX yielding the abundant "even-electron" ion $[C_6,H_4,P]^+$ at m/z 107. However, when X = Br or I, the second step involves loss of $X^{\bullet}$ generating the desired m/z 108 $[C_6,H_5,P]^{\bullet +}$ ions of sufficient abundance for further structure analysis. Thus, the m/z 108 ions generated by dissociative ionization of $PhPBr_2$[6] were mass selected and subjected to a collisional activation (CA) process[7]. The most intense signal in the resulting CA mass spectrum, see Fig. 1, is found at m/z 107, $[C_6,H_4,P]^+$, indicating that loss of H• may well be the dissociation reaction of lowest energy requirement. In the lower mass region, signals are present at m/z 77, $[C_6,H_5]^+$, and m/z 31, P^+, which, as will be shown below, are of structure diagnostic value.

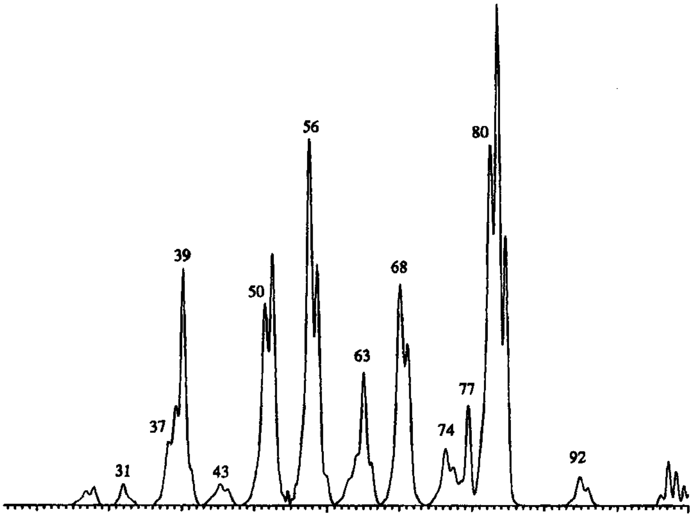
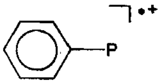


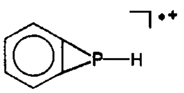
FIGURE 1 CA mass spectrum of $[C_6,H_5,P]^{\bullet +}$m/z 108. The signal m/z 107 was omitted

The Neutralization-Reionization (NR) mass spectrum[8] of the $[C_6,H_5,P]^{\bullet+}$ ions from $PhPBr_2$ is shown in Fig. 2. The spectrum displays a "survivor ion" signal at m/z 108 which testifies that in the rarefied gas phase stable neutral C_6,H_5,P species exist with a minimum lifetime of c. 1 µs. However, the intensity distribution of the peaks in the NR spectrum is not identical with that of the CA mass spectrum. In particular, in the lower mass region of the NR spectrum the intensity of the signals at m/z 26, $[C_2,H_2]^{\bullet+}$, m/z 31, P^+, and m/z 50, $[C_4,H_2]^{\bullet+}$ is clearly enhanced while the peaks at m/z 82, $[C_4,H_3,P]^{\bullet+}$, m/z 51, $[C_4,H_3]^+$, and m/z 39, $[C_3,H_3]^+$, are of lower abundance. Partial decomposition of the neutral C_6,H_5,P species prior to reionization is the most probable reason for these differences but an alternative explanation involving isomerization of the incipient neutrals cannot be dismissed. Therefore, the m/z 108 "survivor" ions from the NR experiment were mass selected and subjected to a collision experiment in the third field free region of the mass spectrometer. The resulting spectrum (not shown) appeared to be practically identical with the conventional CA mass spectrum shown in Fig. 1. This finding indicates (i) that the $[C_6,H_5,P]^{\bullet+}$ ions from $PhPBr_2$ are isomerically pure and (ii) that the reionized neutral counterpart has retained its structural integrity[9]. The presence of a mixture of isomeric $[C_6,H_5,P]^{\bullet+}$ ions and/or their neutral counterparts is **only** compatible with the experimental results if **both** the ions **and** their neutral counterparts would have very low interconversion barriers, which is clearly at odds with the computational results reported in ref. 10. Analogous experiments using PPh_3 and d_{15}-PPh_3 as precursor molecules for the generation of $[C_6,H_5,P]^{\bullet+}$gave essentially the same results.

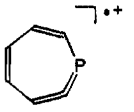
Thus, isomerically pure $[C_6,H_5,P]^{\bullet+}$ ions are generated by the consecutive loss of two Br atoms from $PhPBr_2$ in a reaction which may well involve direct bond cleavages leading to **1**$^{\bullet+}$. Nevertheless, two other reasonable isomers can be envisaged, viz. **2**$^{\bullet+}$and **3**$^{\bullet+}$. The latter ion is taken into account because there is mass spectrometric evidence that C_6H_6 and P^+ react with insertion of phosphorus into the phenyl ring[11].



1$^{\bullet+}$



2$^{\bullet+}$



3$^{\bullet+}$

That the $[C_6,H_5,P]^{\bullet+}$ ions most likely do have the connectivity of $1^{\bullet+}$ is inferred from the following:

i. The calculated (thermochemical) minimum energy requirement for the losses of P and PH leading to m/z 77 $[C_6,H_5]^+$ and m/z 76 $[C_6,H_4]^{\bullet+}$ ions respectively, is similar. Nevertheless, the CA mass spectrum shows a telltale peak at m/z 77, not at m/z 76. This observation is entirely compatible with the presence of $1^{\bullet+}$ (loss of P by direct bond cleavage) but makes the presence of $2^{\bullet+}$ highly unlikely.

ii. The preferred elimination of H• from ions m/z 108 is hardly compatible with the presence of $3^{\bullet+}$. Further, in the mass spectra of phosphacycles abundant signals are usually observed corresponding with the loss of H,C,P[11] but this process is of only marginal importance in the spectrum shown in Fig. 1 (peak at m/z 64). The same is true for the m/z 65 $[C_5,H_5]^+$ peak, which is an important fragment ion in the spectrum of the seven-membered phosphacyclus $[C_6,H_6,P]^{+}$[11].

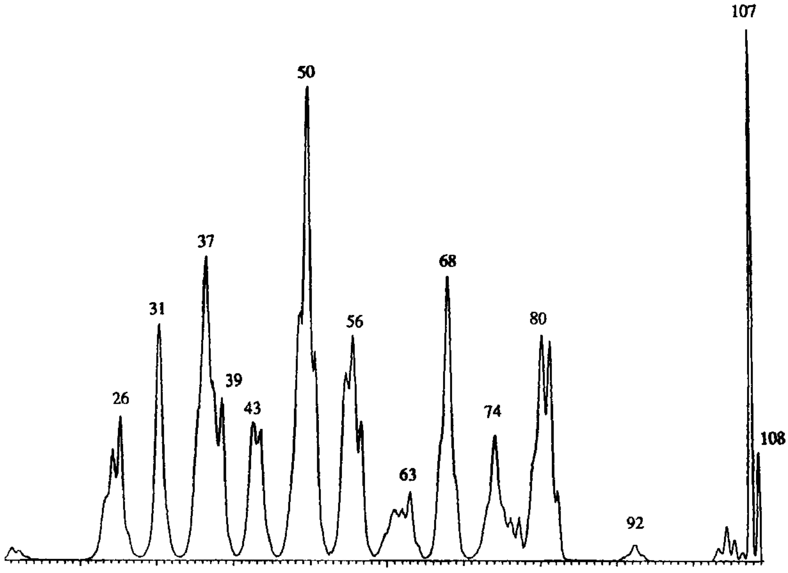


FIGURE 2 NR mass spectrum of $[C_6,H_5,P]^{\bullet+}$m/z 108

Considering these findings we feel confident that the $[C_6,H_5,P]^{\bullet+}$ ion m/z 108 has the connectivity $1^{\bullet+}$ and that its neutral counterpart, Ph-P, is a stable species in the rarefied gas phase of a mass spectrometer.

Recent high level *ab initio* calculations[12] predict that Ph-P has a triplet ground state with a singlet-triplet energy splitting of 21 kcal/mol. Preliminary *ab initio* calculations at a lower level of theory have been reported for $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$. their neutral counterparts as well as their interconversion barriers[10]. These indicate that $\mathbf{1}^{\bullet+}$ is more stable than $\mathbf{2}^{\bullet+}$ and that a sizable barrier separates the two isomers. The same holds true for the neutral counterparts. However, the $<S^2>$-values in this study were slightly out of range and a more elaborate computational study of this system is therefore in order.

EXPERIMENTAL

The CA and NR mass spectra were recorded using a VG Analytical ZAB-R mass spectrometer (McMaster University, Hamilton, Canada). For the CA mass spectra Helium was used as collision gas. Cyclopropane (80 % transmission) was used for the NR experiments.

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