Phosphonium ions of 2,4,6,8-tetra-*tert*-butyl-1,3,5,7-tetraphosphacubane and 1,2,5,6-tetraphosphatricyclo[4.2.0.0^{2,5}]-octa-3,7-diene in the gas phase: host–guest complexes, phosphonium ion decomposition pathways and interaction with onium ions (and carbocations). A field desorption (FD), fast atom bombardment (FAB) and tandem mass spectrometry (CAD–MS/MS) study †

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We report a mass spectrometric study (FDMS, FABMS) of a series of phosphonium triflate salts derived from 2,4,6,8-tetra-*tert*-butyl-1,3,5,7-tetraphosphacubane **1** and 1,2,5,6-tetraphosphatricyclo[4.2.0.0^{2,5}]octa-3,7-diene **2**, namely $\mathbf{3}^+(\mathrm{OTf})^-$, $\mathbf{4}^+(\mathrm{OTf})^-$, $\mathbf{5}^+(\mathrm{OTf})^-$, $\mathbf{6}^{2+}(\mathrm{OTf{\cdot}SbCl_6})^{2-}$, $\mathbf{7}^{2+}(\mathrm{OTf{\cdot}SbCl_6})^{2-}$ and $\mathbf{8}^+(\mathrm{OTf})^-$.

Except for the dications, the intact phosphonium ions were observed in all cases. The host–guest (H–G) chemistry of $\mathbf{3}^+$ and some of its fragment ions with dicyclohexano-24-crown-8 have been probed. Low energy collisional decomposition of $\mathbf{3}^+$ gives *m*/*z* 115 and 169 as prominent products for which structures $\mathbf{12}^+$ and $\mathbf{11}^+$ have been suggested in analogy with the recently discovered solution chemistries of phosphaalkynes and phosphirenes. The decomposition pathways of the studied phosphonium cations have been compared and discussed.

In the previous study[1] aimed at P-functionalization of 2,4,6,8-tetra-*tert*-butyl-1,3,5,7-tetraphosphacubane **1** (Fig. 1) by electrophilic chemistry, we reported on its mono- and diprotonation in superacid media, monoalkylation with potent alkylating agents [methyl triflate and Meerwein salts] and monoalkynylation with electron-deficient alkynes and discussed the multinuclear NMR characteristics of the resulting novel phosphonium ions.

We have since extended these studies to phosphonium ions from benzylation (with $\mathrm{PhCH_2OTf}$), ethylation (with EtOTf), acylation (with $\mathrm{MeCO^+SbCl_6^-}$) and adamantylation (with 1-AdCl/$\mathrm{SbCl_5}$) and also prepared mixed diphosphonium salts by the reaction with two different super electrophiles.[2] Several stable phosphonium cations of the novel 1,2,5,6-tetraphosphatricyclo[4.2.0.0^{2,5}]octa-3,7-diene **2** were also prepared.[3]

Our previous mass spectrometric studies[4–6] of fragile onium salts and delocalized dications and dication ether salts demonstrated the suitability of FDMS and FABMS techniques for detection of such singly (and doubly) charged cations. Our continuing interest in the gas phase H–G chemistry involving onium ions and crown ethers of calixarenes[6–9] has led to the mass spectrometric study of mono- and di-phosphonium salts derived from **1** and **2** reported here (Fig. 1). Facile MS detection of intact $\mathbf{3}^+$ not only allowed its cluster ions to be examined, but opened up the possibility of studying its fragmentation pathways by low energy FAB/CAD-MS/MS. Other phosphonium salts were studied by FABMS; high energy CAD mass spectra provided an insight into their common decomposition pathways. The structures of the phosphonium salts included in Fig. 1 have been established unequivocally by NMR experiments.[1–3]

Results and discussion

The FDMS of $\mathbf{3}^+(\mathrm{OTf})^-$ in the presence of dicyclohexano-24-crown-8 (Figs. 2–4) exhibits the intact phosphonium cation $\mathbf{3}^+$ (*m*/*z* 415) as the base peak. Apart from the protonated crown (*m*/*z* 461) and a less abundant crown/$\mathrm{Na^+}$ complex (*m*/*z* 483), a prominent cluster ion at *m*/*z* 875 is visible corresponding to the $\mathbf{3}^+$/crown complex. A two cation/one anion (triflate) cluster at *m*/*z* 979 is detected in low abundance (seen in Fig. 4). Four other minor cations at *m*/*z* 921, 677, 230 and 691 were also produced (see later discussion).

Consideration of the average P–C bond distance of 1.881 Å in **1**[10] and the cavity of dicyclohexano-24-crown-8 ‡ suggests that an insertion complex (cube inside the crown) would be feasible if the Bu^t groups in **1** were replaced by methyl groups. Molecular mechanics calculations (PCMODEL) are in accord, showing that a P-methylated tetramethyltetraphosphacubane fits in the crown cavity and remains snug in the energy minimized structure. With $\mathbf{3}^+$, the Bu^t groups create substantial steric crowding in an insertion model.

As a control experiment in solution, we found that addition of the crown to $\mathbf{3}^+(\mathrm{OTf})^-$ in $\mathrm{CDCl_3}$ caused only a slight change in the ^{31}P NMR shifts: the P$^+$ moved only 0.2 ppm upfield and the three equivalent cage P atoms moved *ca.* 1 ppm upfield, indicating that an insertion complex with sufficient lifetime for ^{31}P NMR observation is not formed.

In line with our previous studies with $\mathrm{ArN_2^+}$/crown clusters,[6] we propose that a 1 : 1 complex with little projection of the phosphonium cation inside the crown ring provides an adequate description for the $\mathbf{3}^+$/crown cluster ion. However,

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† Novel phosphonium cations. Part 4. For Part 3 see ref. 3.

‡ The diameter of 21-crown-7 is 3.4–4.2 Å (see: C.-C. Liou and J. S. Brodbelt, *J. Am. Chem. Soc. Mass Spectrom.*, 1992, **3**, 535); that of the larger 24-crown-8 is 3.6–4.8 Å (see H. Zollinger, in *Diazo Chemistry I*, VCH, Weinheim, 1994, ch. 11).

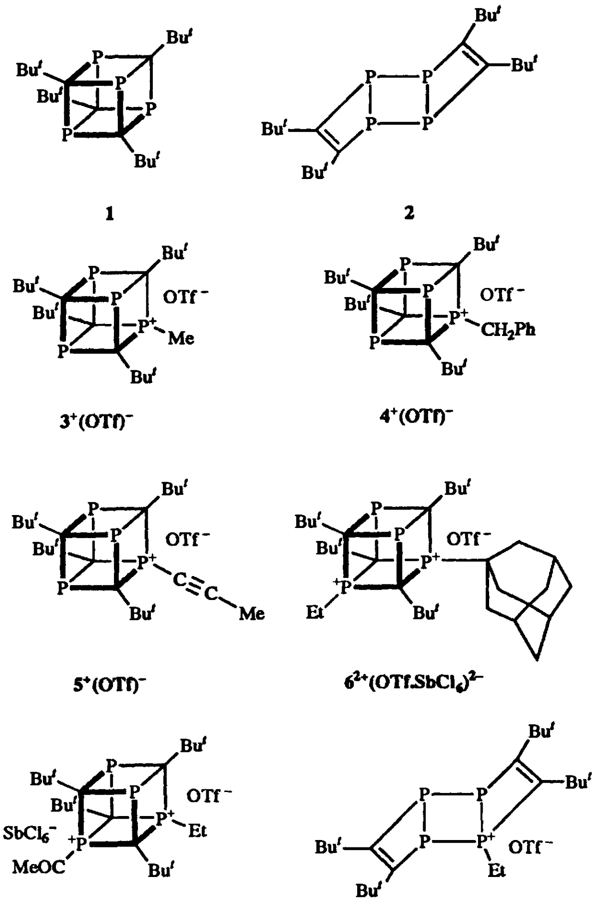

Fig. 1 Parent 2,4,6,8-tetra-*tert*-butyl-1,3,5,7-tetraphosphacubane **1**, 1,2,5,6-tetraphosphatricyclo[4.2.0.0^{2,5}]octa-3,7-diene **2** and their derived mono- and bis-phosphonium salts

since in a control FDMS experiment a phosphonium ion–crown cluster was not detected with the smaller 15-crown-5 (only the uncomplexed **3**$^+$ was seen), our model has to accommodate the importance of cavity size.

The FAB mass spectrum of **3**$^+$**(OTf)**$^-$ in the presence of dicyclohexano-24-crown-8 similarly showed an abundance of the phosphonium cation (*m*/*z* 415), but the minor cations observed in the FDMS were either absent or were too weak. However, in the presence of a thioglycerol matrix the *m*/*z* 979, 875 and 677 cations were clearly visible albeit in low abundance. In addition, a peak at *m*/*z* 629 was observable (Fig. 5).

Collisionally activated decomposition (low energy CAD) of **3**$^+$ (*m*/*z* 415) in the FAB mode (Fig. 6; see also Scheme 1) produced two prominent products at *m*/*z* 115 and 169 and minor ions at *m*/*z* 215 and 277.

The *m*/*z* 115 ion corresponds to methyl-cationised $Bu^tC\equiv P$. In line with our low temperature protonation studies on $Bu^tC\equiv P$ and 1-AdC≡P in superacid media[11] showing C-protonation to an incipient phosphavinyl cation followed by counter-ion trapping (FSO_3^- or $CF_3SO_3^-$) to form phosphaalkenes, and in accord with the suggested mechanism for cyclotrimerization of $Bu^tC\equiv P$ with $AlCl_3$[12] and 1-AdC≡P with $B(OTf)_3$[11] *via* initial Lewis acid complexation at the carbon atom of phosphaalkynes, our suggested structure for the *m*/*z* 115 ion is the phosphavinyl cation **12**$^+$ (rather than **12a**$^+$ $\longleftrightarrow$ **12b**$^+$). This ion can arise from **3**$^+$ by simple bond cleavages.

For the second product at *m*/*z* 169 the Hückel aromatic phosphirenylium cation **11**$^+$ is suggested. We have recently generated **11**$^+$ in solution by ionization of phosphirene triflate with $B(OTf)_3$ at low temperature.[13] It is conceivable that under CAD conditions ion **11**$^+$ is formed *via* the cyclic cation **15**$^+$ (*m*/*z* 215). The *m*/*z* 169 cation was previously observed as a prominent fragment ion in the EI mass spectrum (70 eV) of P-derivatised **1**.[14]

Possible assignments and/or structures for the minor cations observed in the normal FD mass spectra (Figs. 3 and 4) are shown in Fig. 7: the *m*/*z* 921 ion (not shown) corresponds to loss of Bu^{t}H from *m*/*z* 979 cluster or to (2 crown·H)$^+$. The *m*/*z* 677 ion corresponds to a cluster consisting of the cyclic cation **15**$^+$ and crown + 2H. It is likely that this is in fact an oxonium ion like **16**$^+$. Similarly for *m*/*z* 691 ion structure **17**$^+$ is suggested. The *m*/*z* 629 cation corresponds to an **11**$^+$/crown species, possibily an oxonium ion as depicted in **18**$^+$.

The FAB mass spectrum of the P-benzylated salt **4**$^+$**(OTf)**$^-$ with dicyclohexano-24-crown-8 as a matrix gave **4**$^+$ as the base peak (Fig. 2). The remaining ions were due to (crown + H)$^+$, crown/Na$^+$ and crown/Cs$^+$. The **4**$^+$/crown cluster ion (*m*/*z* 951) and the two cation/one anion cluster (*m*/*z* 1131) were present in low abundance. Cation **11**$^+$ is a major fragment ion (38%) in the normal FAB spectrum of **4**$^+$**(OTf)**$^-$. The use of sulfolane (tetrahydrothiophene 1,1-dioxide) instead of the crown as the matrix improved the FAB spectrum leading to a stronger *m*/*z* 491 (**4**$^+$) ion with little interference from the sulfolane-derived ions.

The FAB mass spectrum of the alkynylphosphonium salt **5**$^+$ **(OTf)**$^-$ using sulfolane as the matrix exhibited the **5**$^+$ ion as the base peak. Whereas the *m*/*z* 1027 cluster (Fig. 2) was very weak, **11**$^+$ (phosphirenylium cation) was observed as an important fragment ion (27%).

The diphosphonium salts **6**$^{2+}$**(OTf·SbCl$_6$)**$^{2-}$ and **7**$^{2+}$ **(OTf·SbCl$_6$)**$^{2-}$ were studied in the hope that doubly-charged phosphonium cations could be observed.§ In both cases the FAB mass spectra showed that intact cations did not survive (sulfolane matrix); instead deadamantylation of **6**$^+$ led to detection of **9**$^+$ (*m*/*z* 429) as the base peak, with **10**$^+$ (*m*/*z* 445; 77%) and **11**$^+$ (*m*/*z* 169; 55%) as prominent fragment ions.

Deacetylation of **7**$^+$ (and oxidation) led to detection of **10**$^+$ as the base peak with **11**$^+$ as a minor fragment ion (17%).

The FAB mass spectrum of **8**$^+$**(OTf)**$^-$ was also studied for comparison (sulfolane matrix). The intact phosphonium ion **8**$^+$ (*m*/*z* 429) was observed (85%) with **11**$^+$ (*m*/*z* 169) being the base peak, suggesting that decomposition of the cyclooctadiene cation **8**$^+$ to phosphirenylium cation is more efficient than those of tetraphosphacubane cations (consistent with the need to invoke more steps for **3**$^+$ $\longrightarrow$ **11**$^+$). The *m*/*z* 169 ion is also seen as a prominent fragment ion in the normal EI mass spectrum (70 eV) of **2** itself.[15] The second most prominent fragment ion in the FAB spectrum of **8**$^+$ is *m*/*z* 291 assigned to **22**$^+$ (corresponding to loss of di-*tert*-butylacetylene from **8**$^+$).

It is emphasized again at this point that Figs. 2 and 7 depict *possible* fragment ion structures. These structures arise from the respective precursors by minimum rearrangement. Since reference CAD spectra of isomeric phosphonium ions are not available, we cannot exclude the possibility that the ions shown have isomerized to other, more stable cations.

Collisional activation studies on selected phosphonium ions (Scheme 1 and Fig. 7)

In order to determine the decomposition pathways of phosphonium ions in the gas phase, we examined the high energy CAD spectra of the ions listed in Scheme 1. Product ions

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§ Intact doubly-charged phosphonium ions have been recently observed in FABMS of several diphosphonium salts in which the cation centres are far apart. See: J. Claerebaudt, W. Baetes, H. Geise and M. Claeys, *Org. Mass Spectrom.*, 1993, **28**, 71.

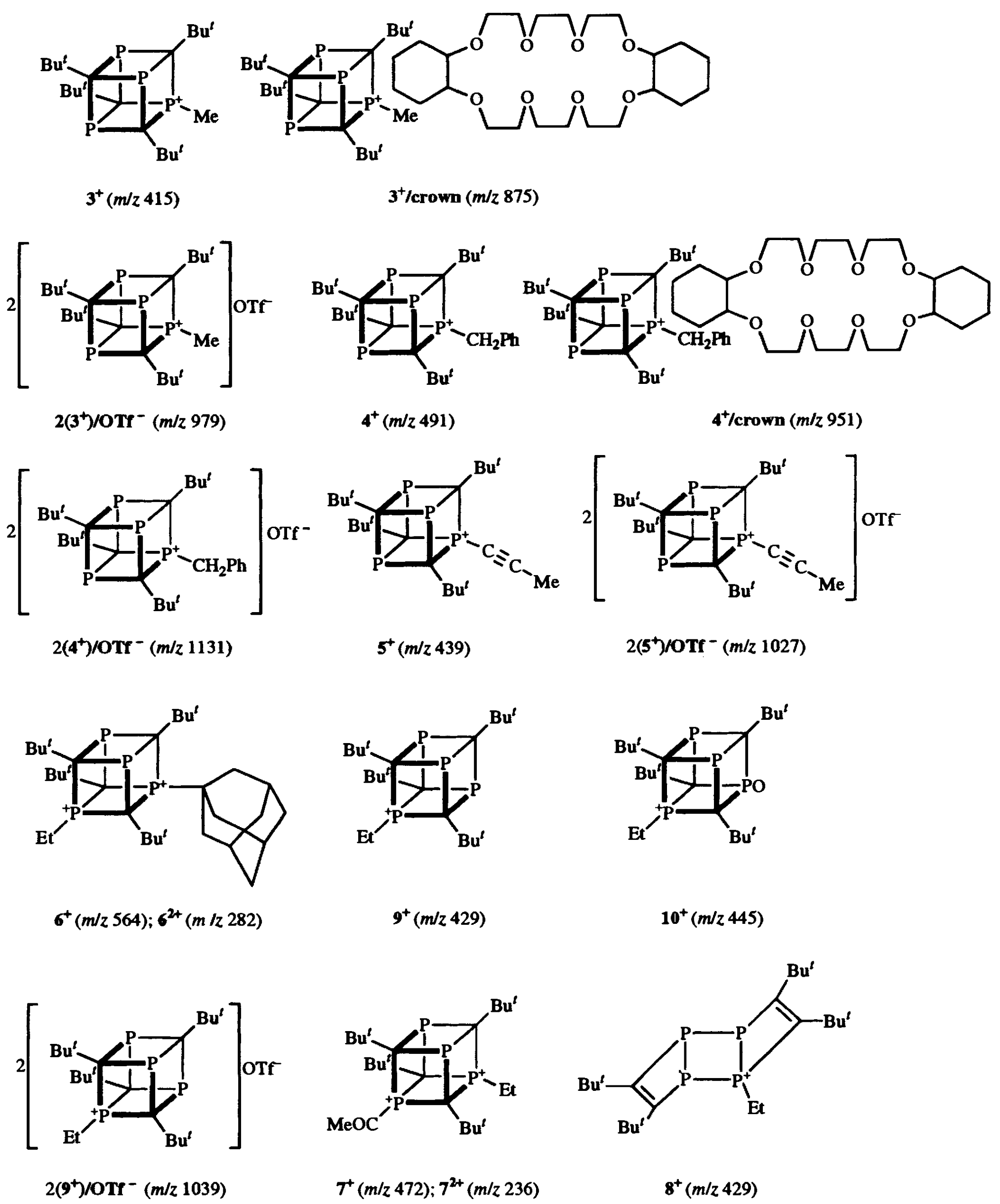

Fig. 2 Intact phosphonium cations derived from phosphonium salts in Fig. 1 and their cluster ions

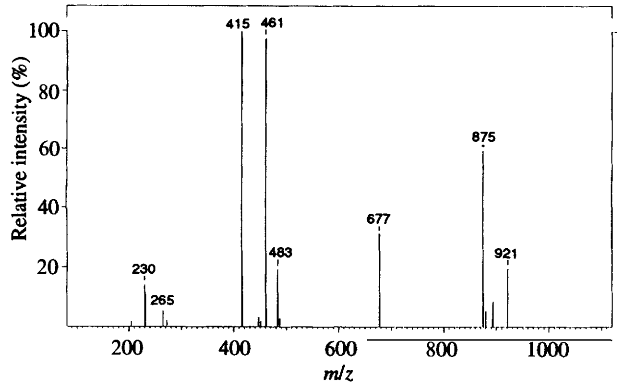

Fig. 3 Partial FD mass spectrum of $3^+(OTf)^-$ (early scan)

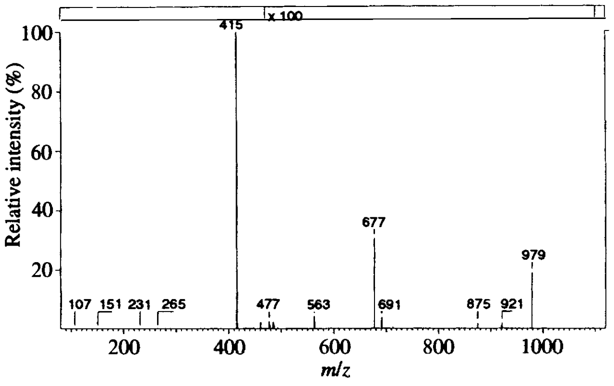

Fig. 4 Partial FD mass spectrum of $3^+(OTf)^-$ (later scan) showing the disappearance of *m/z* 461, dramatic reduction in *m/z* 921 and 875 and presence of *m/z* 979 and 691 ions

are listed in order of decreasing relative abundance and the suggested structures are indicated in parentheses and displayed in Fig. 7. The phosphirenylium cation **11**$^+$ is a common product ion for all the studied phosphonium ions. For cations **13**$^+$, **14**$^+$ and **20**$^+$ formed *via* decomposition of the alkynylated, benzylated and ethylated **1**, respectively, we propose the phosphavinyl structure, by analogy with the earlier suggestion

3$^+$ (m/z 415) $\longrightarrow$ m/z 115 (**12**$^+$), 169 (**11**$^+$), 215 (**15**$^+$)
4$^+$ (m/z 491) $\longrightarrow$ m/z 169 (**11**$^+$), 353, 399 (**1-H**)$^+$, 400 (**1**$^+$) 475 (loss of CH_4), 131, 262, 191 (**14**$^+$), 91 ($C_7H_7^+$)
5$^+$ (m/z 439) $\longrightarrow$ m/z 169 (**11**$^+$), 139 (**13**$^+$), 301 (**19**$^+$), 423 (loss of CH_4)
8$^+$ (m/z 429) $\longrightarrow$ m/z 169 (**11**$^+$), 153, 229 (**21**$^+$), 125, 291 (**22**$^+$)
9$^+$ (m/z 429) $\longrightarrow$ m/z 169 (**11**$^+$), 129 (**20**$^+$), 291 (**22**$^+$), 413 (loss of CH_4), 229 (**21**$^+$)
10$^+$ (m/z 445) $\longrightarrow$ m/z 196 (**11**$^+$), 229 (**21**$^+$), 129 (**20**$^+$), 415 (loss of CH_4)
11$^+$ (m/z 163 *via* m/z 564) $\longrightarrow$ m/z 127 (loss of C_3H_6), 113 (loss of C_4H_8), 57 [$C_4H_9^+$ or (c-C_2H_2P)$^+$], 121 (loss of CH_3PH_2), 139 (loss of C_2H_6), 153 (loss of CH_4), 154 (loss of Me)

Scheme 1 CAD mass spectra of selected intact phosphonium cations or their fragment ions (low energy for **3**$^+$ with air as a collision gas; high energy for others with oxygen as collision gas)

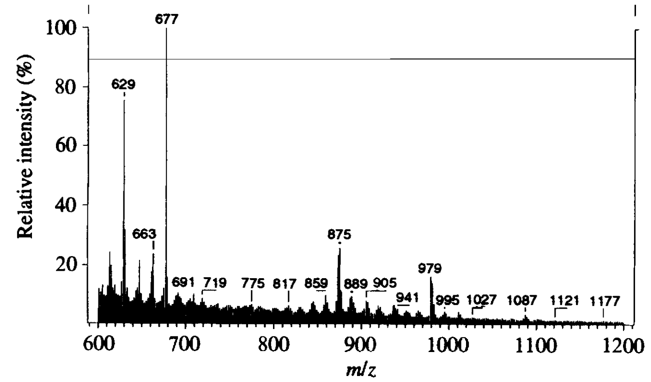

Fig. 5 Partial FAB mass spectrum of **3**$^+$**(OTf)**$^-$ using a thioglycerol matrix (only the high mass region is shown)

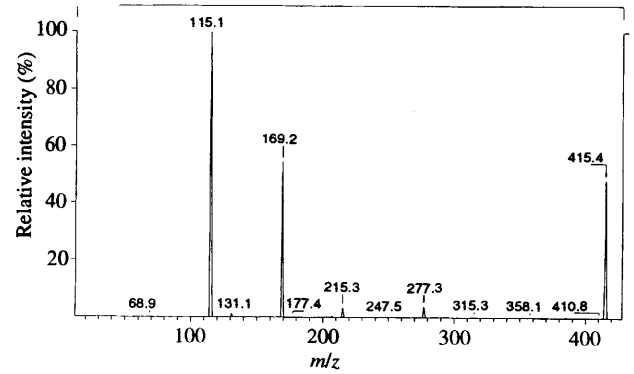

Fig. 6 CAD mass spectrum of m/z 415 cation

for **12**$^+$ The suggested structures for **21**$^+$ and **15**$^+$ appear logical. Cation **22**$^+$ (m/z 291) is formed by decomposition of both **8**$^+$ and **9**$^+$ (both at m/z 429). Note that the CAD mass spectra of **8**$^+$ and **9**$^+$ are different, pointing out that these cations indeed have different structures. Thus cation **20**$^+$ is a prominent decomposition product *via* **9**$^+$ (but not **8**$^+$), and **21**$^+$ is more favourably formed *via* **8**$^+$ rather than *via* **9**$^+$.

The decomposition of phosphirenylium cation **11**$^+$ (m/z 169) produced seven significant products, among them the m/z 57 ion, which may be ascribed to the parent phosphirenylium cation and/or to $C_4H_9^+$.

Interaction of 3$^+$ with Et_3O^+, Et_3S^+ and the trityl cation

The nP$\rightarrow\sigma$ P–C delocalization in tetraphosphacubane leads to a significant decrease in the nucleophilicity (basicity) at the phosphorus.[1] Although alkylation with powerful alkylating agents is not possible beyond the monoalkylation stage, we have shown that diphosphonium ion salts like **6** and **7** can be synthesized by the reaction with two different super electrophiles,[2] and diprotonation of **1** can be effected in superacids.[1,2] In the context of the present study it was of interest to examine the interaction between onium ion alkylating agents (and carbocations) with **3**$^+$**(OTf)**$^-$ to see if they would form detectable cluster ions or whether diphosphonium ion formation is feasible under FD- or FAB-MS conditions.

When the phosphonium triflate **3**$^+$**(OTf)**$^-$ was allowed to mix with $Et_3O^+SbCl_6^-$ in chloroform solvent at room temperature and a small aliquot was subsequently examined by FDMS, in addition to the ions expected from the $Et_3O^+SbCl_6^-$ system,[4] two prominent peaks at m/z 415 and 431 were displayed, corresponding to the intact phosphonium ion and its corresponding monoxide. Oxidation of the phosphonium ion at one of the three remaining cage P atoms is noteworthy. We have previously found monooxotetraphosphacubane formation on quenching of the 'magic acid' solutions of the diprotonated **1**.[1] Solution studies have shown already that monooxidation of tetraalkyltetraphosphacubane can be achieved by heating with Bu^{t}OCl or with Et_2O–H_2O–O_2.[14] In the present study, oxidation of **3**$^+$**(OTf)**$^-$ by reaction with the Meerwein salt must occur under FD conditions, since the monomethylated oxide was not observed in solution alkylation experiments with excess Meerwein salts (^{31}P NMR). Under FDMS conditions, a doubly-charged diphosphonium ion of ethylation (m/z 222) was not observed, nor was there any evidence for a cluster ion corresponding to **3**$^+$/$Et_3O^+X^-$ (X = OTf or $SbCl_6$). Interestingly, formation of monothioxophosphonium ion (m/z 431) was not observed when the $Et_3S^+BF_4^-$ salt was mixed with **3** in dichloroethane and examined by FDMS. The mass spectrum contained prominent ions for Et_3S^+ (m/z 119), $(Et_3S^+)_2BF_4^-$ (m/z 325) and **3**$^+$ (m/z 415).

Finally, the reaction of **3**$^+$**(OTf)**$^-$ with trityl tetrafluoroborate was examined. The FAB mass spectrum exhibited a prominent m/z 415 ion and two other ions at m/z 431 (the monooxophosphonium) and m/z 447 (the dioxophosphonium derivative), in addition to a small m/z 243 for the trityl cation. No evidence was found for a phenylated diphosphonium dication (m/z 246) and the cluster ion corresponding to **3**$^+$/$Ph_3C^+BF_4^-$ was barely visible at m/z 745.

In the FD mass spectrum, the m/z 415 cation was prominently displayed. The abundance of the monooxo- and the dioxo-phosphonium ions were much less and in addition the m/z 979 cluster ion was observed.

In summary, we have shown that fragile phosphonium salts derived from **1** and **2** are amenable to mass spectrometric studies. Once in the gas phase, the decomposition pathways can be examined by tandem mass spectrometry and their products compared with the known solution chemistry of phosphaalkynes and phosphirenes.

Formation of phosphonium cation/crown cluster ions between dicyclohexano-24-crown-8 and **3**$^+$ has been shown and the importance of cavity size for detection of such clusters has been noted. Sulfolane was found to be a suitable matrix for FAB studies with salts **4**–**8**. Comparison of the CAD mass spectra of the studied phosphonium ions clearly points to the importance of m/z 169 ion assigned to the phosphirenylium cation **11**$^+$. Attempts to observe cation/molecule clusters [or P-alkylation (P-arylation)] with **3**$^+$ by reaction with Et_3S^+, Et_3O^+ and the

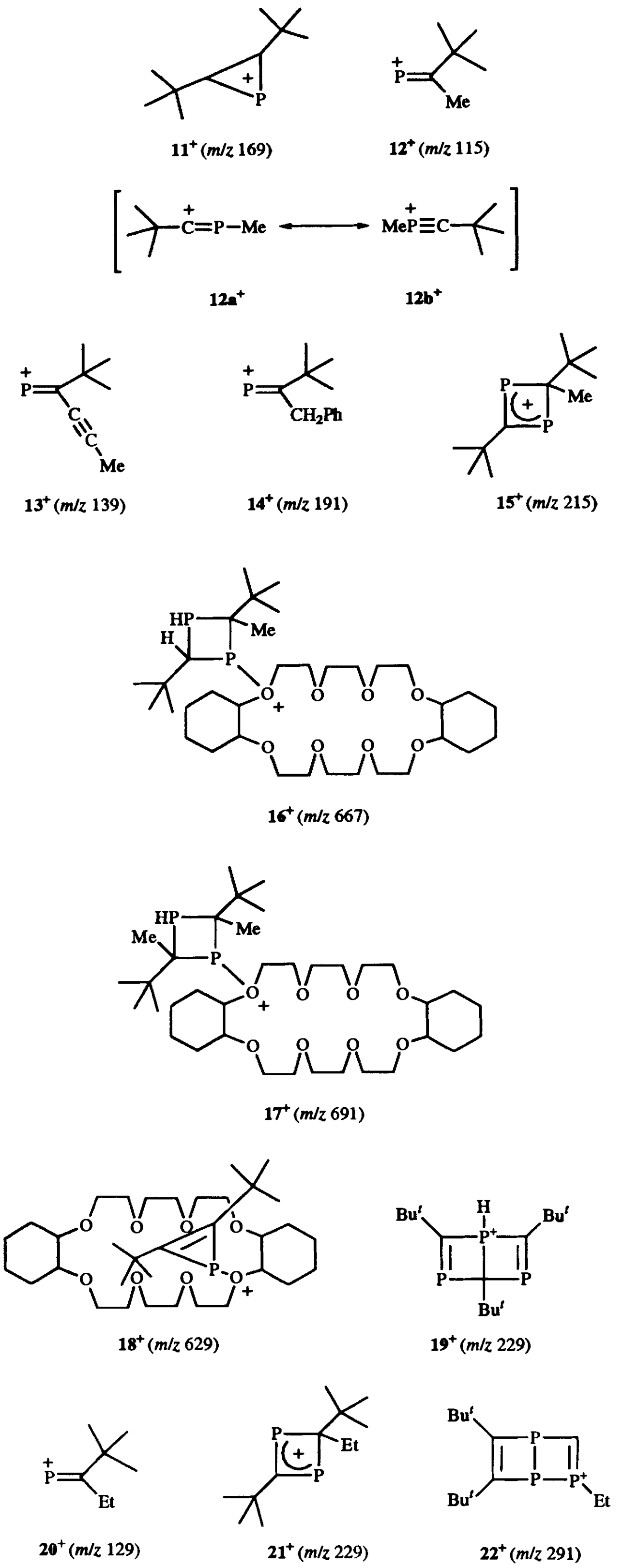

Fig. 7 Fragment ions and their clusters produced in the normal FD or FAB mass spectra and/or by collisional decomposition of phosphonium ions shown in Fig. 2

trityl cation were unsuccessful, instead oxidation was observed in several cases. Similarly, it was not possible to detect a diphosphonium dication or an intact monocation from the dication salts.

Experimental

2,4,6,8-Tetra-*tert*-butyl-1,3,5,7-tetraphosphacubane was prepared by the metal-mediated cyclotetramerization approach recently described by Regitz and co-workers.[16]

Monophosphonium salts $\mathbf{3}^+\mathbf{(OTf)}^-$ and $\mathbf{5}^+\mathbf{(OTf)}^-$ were available from our previous studies.[1,2] Syntheses and NMR studies of other phosphonium salts used in this investigation are described in refs. 2 and 3.

Samples of $Et_3O^+SbCl_6^-$, $Et_3S^+BF_4^-$, $Ph_3C^+BF_4^-$, dicyclohexano-24-crown-8, 15-crown-5 and sulfolane were purchased from Aldrich and used without additional purification.

Typically, *ca.* 10 mg of the phosphonium triflate was dissolved in 1 cm^3 of dry $CDCl_3$. The crown ether was slowly added (3–4 small drops) and the sample vigorously mixed (vortex). In experiments involving oxonium salts and trityl tetrafluoroborate, dry dichloroethane or methylene chloride was used as solvent. For samples studied with the VG Autospec instrument, a concentrated solution of the phosphonium salt (*ca.* 15 mg in 0.5 cm^3 of CH_2Cl_2) was used. A suitable drop was quickly deposited *via* a pipette on the probe tip followed by a drop of the liquid matrix (crown or sulfolane).

A Finnigan-Matt 95Q hybrid mass spectrometer (at BF Goodrich) was used for the MS studies with $\mathbf{3}^+\mathbf{(OTf)}^-$. The low energy collisional activation procedures were as recently described,[17,18] and the FAB and FD conditions used with $\mathbf{3}^+\mathbf{(OTf)}^-$ were analogous to our previously described methods.[6] FAB mass spectra and high energy CAD mass spectra for the other phosphonium salts were acquired on a VG Autospec trisector EBE instrument at the University of Akron. In this tandem MS E-1 and B serve as MS-1 and E-2 as MS-2.

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