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# Gas phase chemistry of the 2-*tert*-butyl-3-phenylphosphirenylium cation: novel onium ions by nucleophilic attack at phosphorus and *de novo P*-spiro bicyclic phosphonium ions *via* [4 + 2$^+$] cycloaddition with dienes

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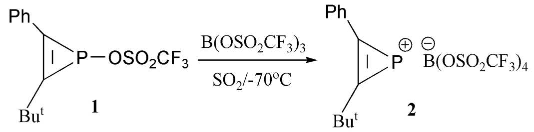
***Received 4th October 2002, Accepted 14th November 2002***
***First published as an Advance Article on the web 17th December 2002***

The 2-*tert*-butyl-3-phenylphosphirenylium ion **13** is formed in abundance in the gas phase from 1-chloro-1*H*-phosphirene **6** upon 70 eV electron ionization. Collision-induced dissociation (CID) and ion–molecule reactions followed by CID of the product ions were performed *via* pentaquadrupole mass spectrometry to probe the structure and reactivity of **13** towards representative nucleophiles and dienes. Under CID conditions, **13** produces a variety of fragment ions mainly *via* dissociation processes that are preceded by isomerizations. In ion–molecule reactions, **13** reacts readily with ethers, sulfides, pyridine and aniline to form hitherto unknown oxonium, sulfonium and azonium ions *via* nucleophilic attack at phosphorus. With butadiene, isoprene, 1-acetoxybutadiene, and with Danishefsky's diene (1-methoxy-3-silyloxybuta-1,3-diene), **13** undergoes [4 + 2$^+$] cycloaddition at phosphorus to generate novel *P*-spiro bicyclic phosphonium ions. With butadiene and isoprene, a second [4 + 2] cycloaddition occurs which generates *P*-spiro tricyclic phosphonium ions. Whereas **13** also reacts readily with 1-acetoxybutadiene *via* [4 + 2$^+$] cycloaddition, most of the nascent *P*-spiro cycloadducts are unstable and dissociate by the loss of either a neutral ketene or acetic acid molecule. B3LYP/6-31G(d,p) calculations were performed to gain insight into the structures of the product ions. The present study constitutes the first successful attempt to unravel the chemistry of **13**, a unique 2π-Hückel phosphirenylium ion for which no direct solution chemical reactivity data are as yet available. The present findings also create a parallel with the solution reactivity of 1-halo-1*H*-phosphirenes and 1-triflato-1*H*-phosphirenes as precursors to phosphirenylium ions.

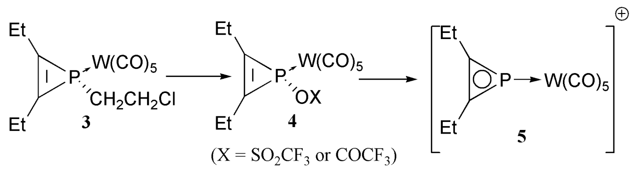
## Introduction

The first persistent phosphirenylium ion was synthesized as a [B(OTf)$_4$]$^-$ salt **2** by Laali, Regitz and their students by ionization of the triflate **1** with B(OTf)$_3$ in liquid SO$_2$ at low temperature (Scheme 1).[1] Multinuclear NMR studies and theory confirmed the aromatic character of this 2π-Hückel cation.[1] *Ab initio* theoretical studies estimated a resonance energy of 38 kcal mol$^{-1}$ for the phosphirenylium ion.[2] Theoretical studies have also underscored the importance of liquid SO$_2$ as solvent to lower the ionization barrier and for counterion complexation, which would further lower the barrier to ionization.[2]



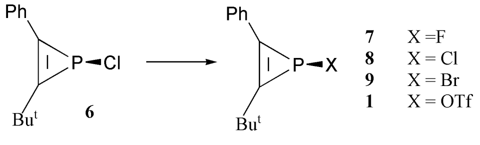
**Scheme 1**

Starting with a pentacarbonyltungsten precursor **4** which was in turn prepared from **3**, phosphirenylium ion **5**, in which the remaining lone-pair at phosphorus is coordinated with W(CO)$_5$ was synthesized (Scheme 2).[3]



**Scheme 2**

Despite these successes in preparing phosphirenylium ions, their insufficient stability has precluded direct chemical reactivity studies in solution, in particular in reaction with nucleophiles and in cycloaddition reactions. In the solution chemistry of phosphirenes, several examples of nucleophilic displacement reactions at phosphorus are known. For example, halophosphirenes of type **6** serve as precursor to the three halophosphirenes **7**–**9** and the triflatophosphirene† **1** (Scheme 3).[4–6]



**Scheme 3**

It was also reported that **6** fails to react with PhNMe$_2$ or pyridine whereas the more ionic triflate **1** does react (Scheme 4).[5,7] Examples of cycloadditions of phosphirenes with dienes in which the three-membered ring is preserved are rare.[4,6] For instance, an activated phosphirene complex reacted with 2,3-dimethylbutadiene *via* [4 + 2] cycloaddition across the phosphirene double bond to form a 6,3-fused bicyclic compound (Scheme 5).[6]

The gas phase provides a suitable environment in which to study the intrinsic stability and solvent- and counter-ion-free properties and reactivity of ions,[8] and to perform fast screening for potential ionic reactants and model reactions.[9] Ions, which may be transient and highly reactive species in solution, are

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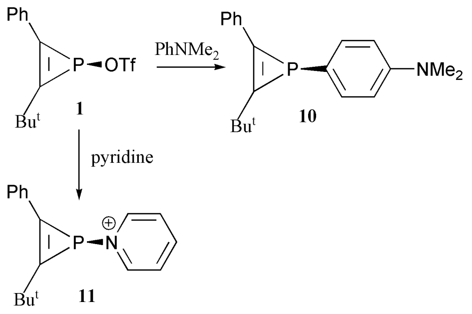
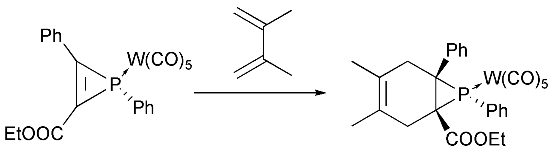
† The IUPAC name for triflato is trifluoromethanesulfonato.

DOI: 10.1039/b209696j



Scheme 4



Scheme 5

often stable and long-lived in the gas phase, and after mass selection, their intrinsic reactivity can be conveniently gauged *via* multiple-stage mass spectrometric (MS) techniques.

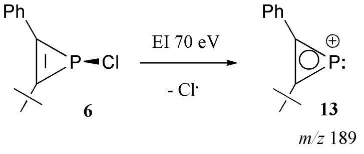
Recent studies have shown that gas-phase studies employing ion–molecule reactions can be successfully applied to low-coordination organophosphorus cations. Thus several long-lived phosphenium ions $R_2P^+$ were successfully generated and isolated in the gas phase, and their intrinsic reactivity was probed by various MS techniques.[10] We have recently applied multiple-stage MS techniques to form and investigate the intrinsic chemistry of the 3-dimethylamino-1,1-dimethyl-1*H*-azaphosphiren-1-ium ion (**11**), the first member of the hitherto unknown class of azaphosphirenium ions and the first *N*,*P*-analogue of the aromatic cyclopropenyl cation.[11]

Herein we report that long-lived three-membered ring 2-*tert*-butyl-3-phenylphosphirenylium ions **13** can be formed in abundance in the gas phase from 1-chloro-1*H*-phosphirene **6** *via* 70 eV electron ionization. We have subsequently used collision-induced dissociation (CID) and ion–molecule reactions followed by CID of the major product ions to examine its reactivity towards representative nucleophiles and dienes. We report on the formation of novel oxonium, sulfonium and azonium ions *via* nucleophilic attack at phosphorus of **13** and on the generation of *de novo* *P*-spiro bicyclic and *P*-spiro tricyclic phosphonium cations *via* mono (and bis) [4 + 2$^+$] cycloaddition with dienes.

The present study constitutes therefore the first successful attempt to unravel the chemistry of this unique 2π-Hückel phosphorus cation for which no direct solution chemical reactivity data are as yet available. The present findings also create a parallel with the solution reactivity of 1-halo-1*H*-phosphirenes and 1-trifluoroacetoxy-1*H*-phosphirenes as precursors to phosphirenylium ions.

## Results and discussion

1-Chloro-1*H*-phosphirene **6** was used to form the gaseous and stable phosphirenylium ion **13** of *m*/*z* 189 *via* 70 eV electron ionization (Scheme 6). Fig. 1 displays the geometry and charge distribution for the unique 2π-Hückel phosphirenium ion **13** as optimized by B3LYP/6-31G(d,p) calculations. The P–C bond lengths are 1.76 and 1.73 Å, respectively, with the P–C–Ph bond being slightly longer. These values compare closely with those of the model 2-methylphosphirenylium cation calculated at the MP2/6-31+G* level.[2] The computed ring C–C bond length (1.38 Å) is longer in **13** than in the 2-methylphosphirenylium cation (1.361 Å). It is also noteworthy that the positive charge is extensively delocalized into the phenyl ring of **13**. The geometrical features and charge delocalization reinforce previous findings regarding aromaticity in phosphirenylium cations.[1,2]



Scheme 6

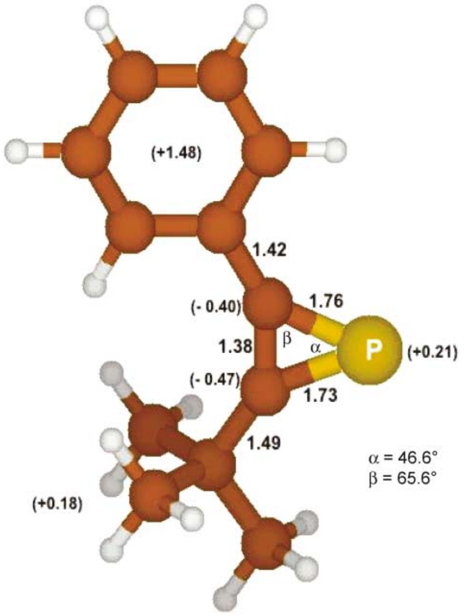


**Fig. 1** Geometry and charge distribution for phosphirenium ion **13** as optimized by B3LYP/6-31G(d,p) calculations.

The stable **13** was then mass-selected and dissociated by 15 eV collisions with argon (Fig. 2). Except for methyl loss (*m*/*z* 174), no favorable direct bond cleavages were observed, and **13** formed, upon CID, a great variety of product ions likely *via* the loss of $CH_3$ (*m*/*z* 174), $PH_2$ (*m*/*z* 156), $C_3H_6$ (*m*/*z* 147), $PHCH_3$ (*m*/*z* 142), $PH_2CH_3$ (*m*/*z* 141), $C_4H_8$ (*m*/*z* 133), $C_6H_6$ (*m*/*z* 111), $C_6H_8$ (*m*/*z* 109), and $PC_5H_7$. Loss of $PC_5H_7$ yields the most intense low-energy CID product ion of **13**, likely $PhCH_2^+$ of *m*/*z* 91. Collision-induced structural rearrangements must therefore precede most dissociations of **13**.

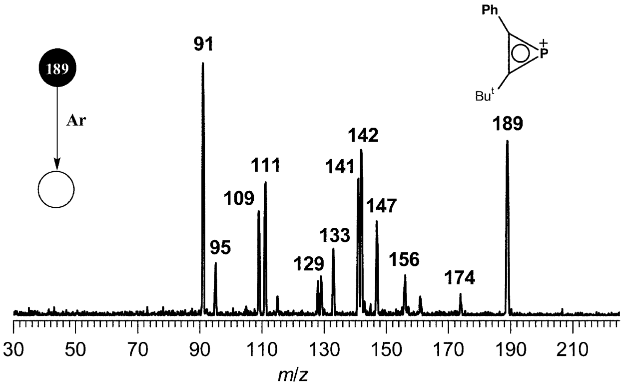
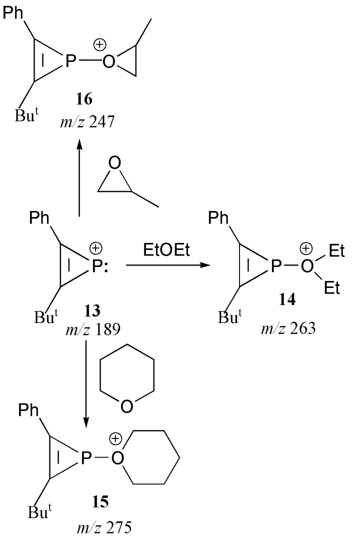


**Fig. 2** Product ion mass spectrum for 15 eV collision-induced dissociation (with argon) of **13** (*m*/*z* 189).

### Reaction with oxygen nucleophiles

In representative cases for oxygen nucleophiles, **13** reacts efficiently with diethyl ether, tetrahydropyran and propylene oxide (Scheme 7) to produce the corresponding oxonium ions **14** (*m*/*z* 263), **15** (*m*/*z* 275), and **16** (*m*/*z* 247). The constitution of these P–O adducts was confirmed *via* sequential MS$^3$ experiments

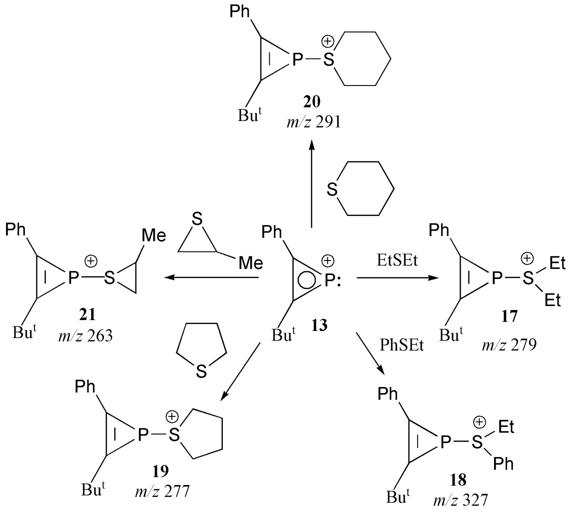


Scheme 7

(spectra not shown) through which all adducts were observed to dissociate, upon substantial 10–15 eV collision activation (which eliminates loosely bound species), back to **13** by the expected cleavage of the weakest P–O bond.

### Reaction with sulfur nucleophiles

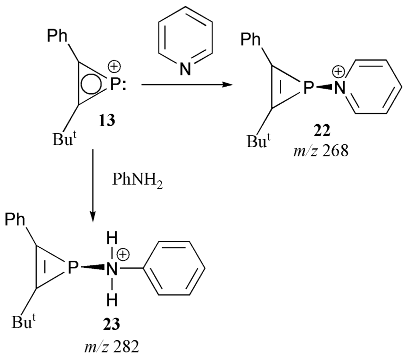
The *m*/*z* 189 ion **13** reacts with a variety of acyclic and cyclic sulfides (Scheme 8), namely diethyl sulfide, ethyl phenyl sulfide, thiolane, thiane (Fig. 3a), and thiirane, to form the corresponding sulfonium ions **17** (*m*/*z* 279), **18** (*m*/*z* 327), **19** (*m*/*z* 277), **20** (*m*/*z* 291), and **21** (*m*/*z* 263). Under CID conditions, these adducts mainly dissociate back to the reactant ion **13** of *m*/*z* 189.



Scheme 8

### Reaction with nitrogen nucleophiles

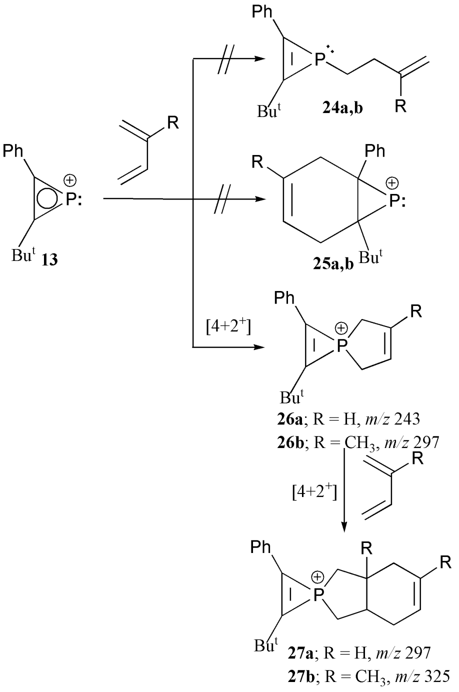
With pyridine and aniline (Fig. 3b), **13** reacts readily to form the respective adducts, *viz.* the azonium ions **22** of *m*/*z* 268 and **23** of *m*/*z* 282 (Scheme 9). Under CID conditions, these adducts mainly dissociate back to the reactant ion **13** of *m*/*z* 189, as exemplified in Fig. 4 for the pyridine–**13** adduct. As depicted in Scheme 4, **1** was found to react with $PhNMe_2$ in solution to give **10**.[5,7] Although using the gas-phase MS data we are unable to differentiate between *C*-attack at the aromatic ring *versus* attack at nitrogen for aniline, theoretical calculations at the B3LYP/6-31G(d,p) level point to attack at nitrogen forming the ammonium ion adduct **23** (stable and formed *via* a −24.7 kcal mol$^{-1}$ exothermic reaction) as opposed to the *p*-benzenium ion adduct, which was found by the calculations to be unstable.



Scheme 9

### Cycloaddition reactions with dienes

With the simplest s-*cis* diene, buta-1,3-diene, **13** reacts readily to form both the mono- and bis-adduct of *m*/*z* 243 and *m*/*z* 297 (Scheme 10). As indicated by B3LYP/6-31G(d,p) calculations (Fig. 5), and in accordance with previous findings for the phosphenium ion $(CH_3O)_2P^+$ both in the gas phase[12] and in solution,[13] the mono-adduct of *m*/*z* 243 results from [4 + 2$^+$] cycloaddition at phosphorus, which forms the *P*-spiro bicyclic phosphonium ion **26a** (a 3-phosphoniaspiro[2.4]hepta-1,5-diene cation derivative) *via* a −34.6 kcal mol$^{-1}$ exothermic reaction. The alternative cycloadduct **25a** *via* a less thermodynamically favorable [4 + 2] cycloaddition across the C=C double bond of **13** (Fig. 5) and the acyclic adduct **24a** *via* a simple *P*-addition (Scheme 10) were both found to be unstable. The cycloadduct **25a** isomerizes during geometry optimization to an interesting "cage-like" phosphorus cation **28a** (Fig. 5) in a −19.5 kcal mol$^{-1}$ exothermic reaction, whereas the acyclic adduct **24a** dissociates back to the reactants. Furthermore, the alternative [4 + 2] cycloaddition that would form **26a** is also kinetically disfavored because its transition state involving the phosphirenium double bond appears highly crowded, although a precedent exists for a thermal [4 + 2] cycloaddition as shown in Scheme 5.[6] The bis-adduct **27a** of *m*/*z* 297 is presumably



Scheme 10

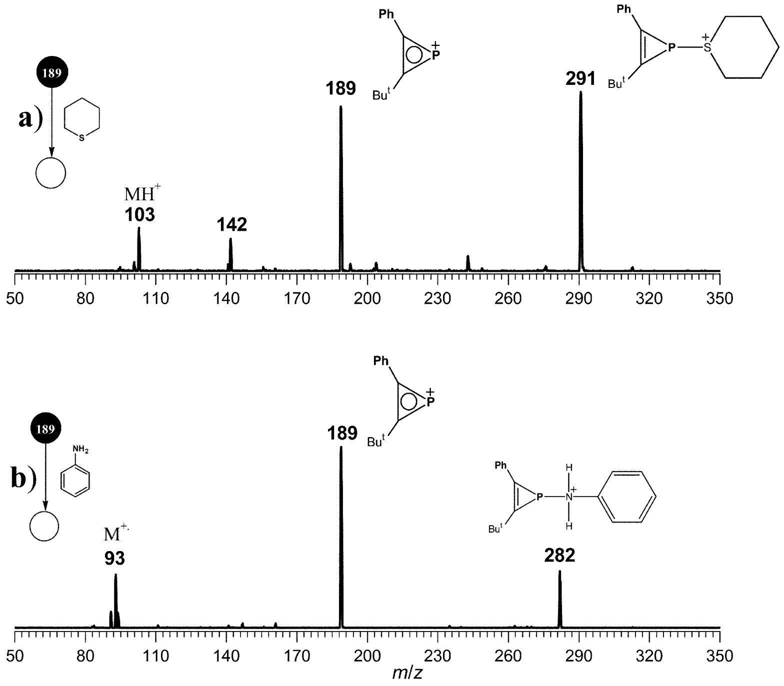


**Fig. 3** Product ion mass spectrum for reactions of **13** (*m*/*z* 189) with (a) thiane (102 u) and (b) aniline (93 u). MH$^+$ and M$^{+\cdot}$ are protonated and ionized molecules of the reactants formed *via* proton transfer and charge exchange reactions, respectively. The *m*/*z* 142 ion is the main fragment of **13** produced under the very low energy collisions (near 1 eV) used for ion–molecule reactions.

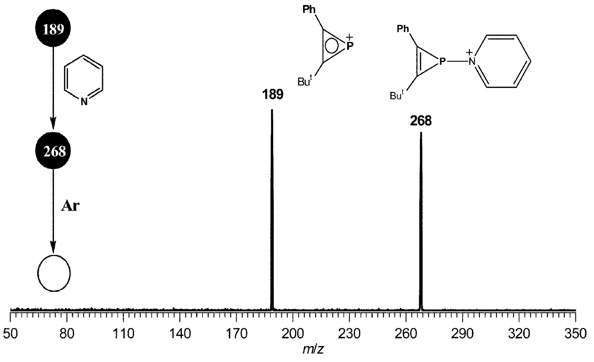
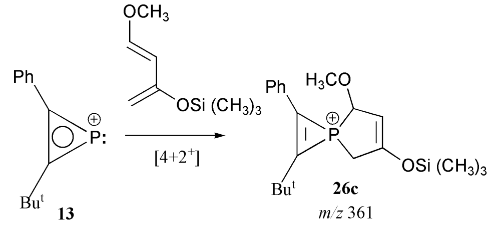


**Fig. 4** Sequential product ion mass spectrum for 15 eV collision-induced dissociation with argon of the pyridine–**13** adduct (*m*/*z* 268).

formed (as indicated by the B3LYP/6-31G(d,p) calculations, (Fig. 5) *via* a subsequent "charge-remote" [4 + 2$^+$] cycloaddition that occurs overall exothermically by as much as −77.6 kcal mol$^{-1}$ across the cyclopentene double bond of **26a** (Scheme 10). The alternative double cycloaddition across the three-membered ring C=C bond (**29a**) is much less thermodynamically favored (−57.7 kcal mol$^{-1}$). Such a cycloadduct is likely also to be kinetically less favored due to steric congestion.

Cation **13** reacts similarly and efficiently with isoprene to form the mono- and bis-cycloadducts of *m*/*z* 257 and *m*/*z* 325 (Fig. 6a). As with butadiene, it is proposed that the *P*-spiro phosphonium adduct **26b** is formed *via* [4 + 2$^+$] cycloaddition and the bis-adduct **27b** is generated *via* a subsequent [4 + 2$^+$] cycloaddition across the cyclopentene double bond (Scheme 10).

With Danishefsky's diene (1-methoxy-3-silyloxybuta-1,3-diene), **13** reacts to form the mono [4 + 2$^+$] adduct **26c** of *m*/*z* 361 (Scheme 11) to a great extent, but no substantial formation of a bis-adduct is noted. The cycloadducts are observed to dissociate under CID conditions back to **13** of



**Scheme 11**

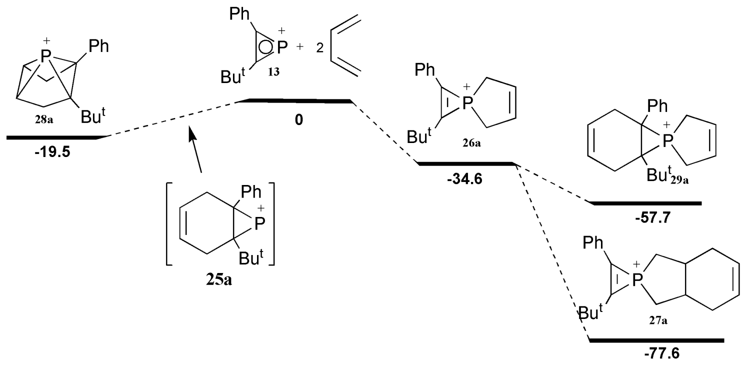


**Fig. 5** B3LYP/6-31G(d,p) potential energy surface diagram for alternative mono and bis [4 + 2$^+$] cycloadditions of **13** with buta-1,3-diene. The alternative acyclic adduct **24a** (Scheme 10) for simple addition at phosphorus and the cycloadduct **25a** for cycloaddition across the C=C bond are both found by the calculations to be unstable; during geometry optimization **25a** isomerizes without an energy barrier to **28a**, whereas **24a** dissociates back to the reactants. Relative energies are given in kcal mol$^{-1}$.

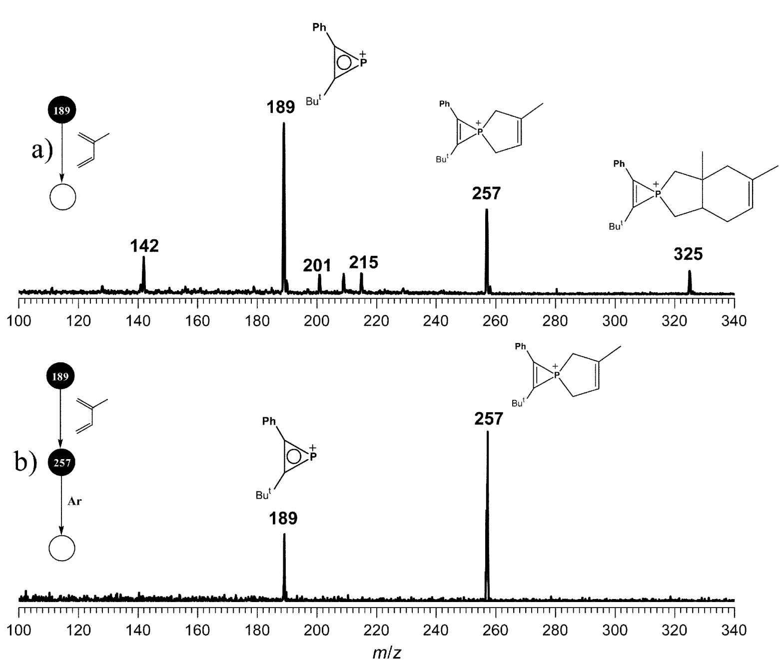


**Fig. 6** (a) Product ion mass spectrum for the reaction of **13** (*m*/*z* 189) with isoprene (68 u). (b) Sequential product ion mass spectrum for CID of the *m*/*z* 257 product ion.

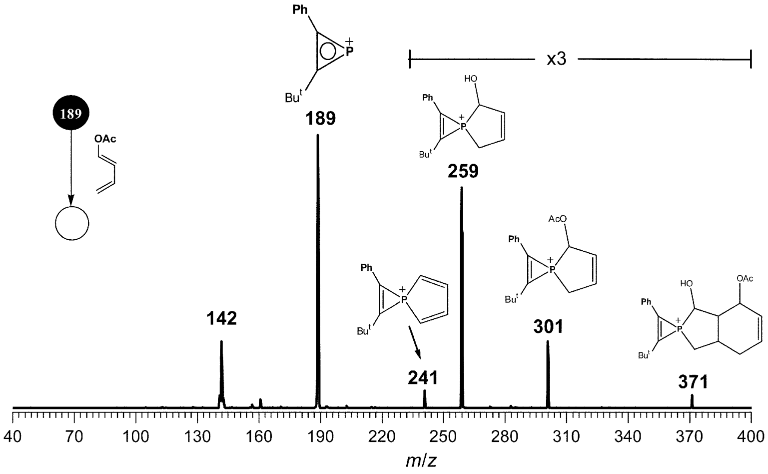


**Fig. 7** Product ion mass spectrum for the reaction of **13** (*m*/*z* 189) with 1-acetoxybuta-1,3-diene (112 u).

*m*/*z* 189 (retro-cycloaddition), as exemplified in Fig. 6b by the sequential product ion mass spectrum of the isoprene–**13** cycloadduct.

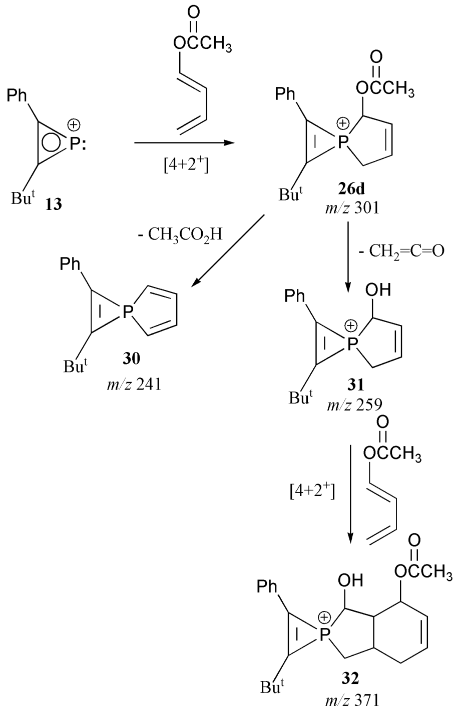
With 1-acetoxybuta-1,3-diene, **13** reacts to form the [4 + 2$^+$] cycloadduct **26d** of *m*/*z* 301 (Fig. 7). But in this particular case, even under the very mild near 1 eV low energy collisions used for the ion–molecule reactions, most of the nascent cycloadducts of *m*/*z* 301 dissociate either by ketene loss to form **31** of *m*/*z* 259 or by acetic acid loss to form **30** of *m*/*z* 241 (Scheme 12). This rich dissociation chemistry, similar to that recently observed for 1-acetoxybuta-1,3-diene [4 + 2$^+$] cycloadducts with acylium ions,[14] appears to rule out loosely bonded and acyclic adducts. In turn, **31** of *m*/*z* 259 undergoes presumably a second [4 + 2] cycloaddition[15] with 1-acetoxybuta-1,3-diene across the cyclopentene double bond to form **32** of *m*/*z* 371 (Scheme 12).

### Comparative discussion

1-Chloro-1*H*-phosphirene **6** serves as a convenient precursor for generation of gaseous phosphirenylium ion **13** which is rather stable under CID conditions towards direct bond cleavage dissociation. Therefore, dissociations occur after substantial collisional activation and are preceded by collision-induced isomerizations. Ion–molecule reactions demonstrate phosphorus reactivity towards a host of oxygen and sulfur nucleophiles generating novel oxonium and sulfonium derivatives. In reaction with pyridine, in line with the solution chemistry of **1**, a pyridinium ion is formed. In reaction with aniline, an ammonium ion is formed *via* attack at nitrogen, which appears to occur predominantly as suggested by the B3LYP/6-31G(d,p) calculations. The reactions with dienes demonstrate the feasibility to generate novel *P*-spiro bicyclic and, in some cases, *P*-spiro tricyclic phosphonium cations *via* [4 + 2$^+$] cycloaddition at phosphorus followed by a second [4 + 2] cycloaddition across the cyclopentene double bond. In solution, under the experimental conditions outlined in Scheme 1, it is unlikely that cycloaddition with **13** could compete efficiently with diene oligomerization in the presence of super Lewis acids used to ionize the P–X precursor. A more viable approach, which we plan to test, is to use the highly ionic P–OTf derivative **1** without employing Lewis acids.

## Experimental and methods

The neutral substrates used for ion–molecule reactions were high purity reagents which were used as received. 1-Chloro-1*H*-phosphirene was available in our laboratory from previous



Scheme 12

studies (K. K. L.). Gaseous **13** of *m*/*z* 189 was produced from **6** by 70 eV EI, mass selected, reacted, and its product ions analyzed *via* double- ($MS^2$) and triple-stage ($MS^3$) pentaquadrupole mass spectrometric experiments[16] performed with an Extrel [Pittsburgh, PA] pentaquadrupole ($Q_1q_2Q_3q_4Q_5$) mass spectrometer, which is described in detail elsewhere.[17] For the $MS^2$ ion–molecule reactions, $Q_1$ was used to mass select **13** for further reactions in $q_2$ with a selected neutral reagent. Ion translational energies were set to near 1 eV as calibrated by the *m*/*z* 39:41 ratio in neutral ethylene/ionized ethylene reactions.[18] Product ion mass spectra were acquired by scanning $Q_5$, while operating $Q_3$ and $q_4$ in the broad band rf-only mode. Multiple collision conditions were used in $q_2$, as indicated by typical beam attenuations of 50–70%, which increases reaction yields and promotes collisional quenching of both the reactant and product ions.[16]

For the $MS^3$ experiments, a $q_2$-product ion of interest was mass-selected by $Q_3$ for further 15 eV collision-induced dissociation (CID) with argon in $q_4$, while scanning $Q_5$ to record the mass spectrum. The 15 eV collision energies were taken as the voltage differences between the ion source and the collision quadrupoles. The indicated pressures in each differentially pumped region were typically $2 \times 10^{-6}$ (ion-source), $8 \times 10^{-6}$ ($q_2$) and $8 \times 10^{-5}$ ($q_4$) Torr, respectively.

Total energies of optimized geometries with no symmetry constraints were calculated at the B3LYP/6-31G(d,p) level of theory[19] run on GAUSSIAN98.[20] Details of the optimized structures are available from the authors upon request.

## Acknowledgements

This work was supported by the São Paulo State Research Foundation (FAPESP) and the Brazilian National Research Council (CNPq). A travel fellowship to K. K. L. from FAPESP facilitated this joint project.

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