Trends in the Unimolecular Reactions of Triaryl Pnictogen Radical Cations $Ar_3E^{•+}$ (E = N, P, As, Sb, Bi): Reductive Elimination versus E−C Bond Cleavage

Hans-Friedrich Grützmacher* and Dirk Kirchhoff

Fakultät für Chemie, Universität Bielefeld, P.O.B 10 01 31, D-33501 Bielefeld, Germany

Hansjörg Grützmacher

Laboratorium für Anorganische Chemie, ETH Zentrum, CH-8092 Zürich, Switzerland

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The unimolecular reactions of the molecular ions $\mathbf{M}^{•+}$ of the triphenyl pnictogens $(C_6H_5)_3E$ (**1**, E = N; **2**, E = P; **3**, E = As; **4**, E = Sb; **5**, E = Bi) have been investigated using mass-analyzed ion kinetic energy (MIKE) spectrometry to select ions of low internal excess energy. Molecular ions of triphenylamine **1** both of high and low internal energy prefer fragmentation by losses of one and two H atoms, which proceeds by a well-known reaction between two phenyl ligands resulting in fragment ions of an azafluorene structure. In contrast, the molecular ions of the heavier triphenyl pnictogens **3**, **4**, and **5** dissociate at high and low internal energies almost completely by generating ions $C_6H_5E^{•+}$ ($\mathbf{B}^{•+}$; E = As, Sb, Bi). Ionized triphenyl phosphane **2** is intermediate, showing loss of H as the main reaction at low internal energy. The ions $\mathbf{B}^{•+}$ (E = As, Sb, Bi) are generated from molecular ions of low internal energy in a one-step process without ions $(C_6H_5)_2E^+$ ($\mathbf{A}^+$; E = As, Sb, Bi) being intermediates. The formation of $\mathbf{B}^{•+}$ by successive cleavages of the relatively weak $E-C_{aryl}$ bonds and sequential losses of two phenyl radicals, which is discussed in the literature, is definitely excluded. Direct formation of $\mathbf{B}^{•+}$ from $\mathbf{M}^{•+}$ entails reductive elimination of $C_6H_5E^{•+}$ under ligand coupling to yield biphenyl as the neutral product. Biaryl ions have been detected earlier in 70 eV mass spectra of triaryl pnictogens, and in the case of tris(4-ethylphenyl)-arsane **6** and 4-methylphenylbisphenylarsane **7**, the formation of biaryl-derived ions is the main reaction in the MIKE spectra of the molecular ions, giving positive evidence for the reductive elimination process. Formation of $\mathbf{B}^{•+}$ at low and high excess energies with exclusion of the formation of intermediate $\mathbf{A}^+$ requires a fast and effortless rearrangement of the molecular ions into the structure of a complex which is well prepared for biaryl loss. It is assumed that this complex contains the biphenyl moiety and the fragment C_6H_5E rather loosely bound to one of the benzene rings. The fast isomerization of the heavier triaryl pnictogen radical cations explains also the puzzling phenomenon known for a long time that in the case of **3**, **4**, and **5** the appearance energy AE of ions $\mathbf{B}^{•+}$, generated by loss of two aryl radicals, is distinctly below the AE of ions $\mathbf{A}^+$, generated by loss of only one aryl radical.

Introduction

The EI mass spectra of triphenylamine $(C_6H_5)_3N$ (**1**) and its heavier element homologues triphenyl phosphane $(C_6H_5)_3P$ (**2**), triphenyl arsane $(C_6H_5)_3As$ (**3**), triphenyl stibane $(C_6H_5)_3Sb$ (**4**), and triphenyl bismuthane $(C_6H_5)_3Bi$ (**5**) have been known for years,[1] and the fragmentations of their molecular ions have been discussed primarily in context of a variation of the bond energy *D*(E−C) of the element E to carbon C of the elements ("pnictogens") of group 15 of the periodic table of chemical elements. The intensity of the molecular ion $(C_6H_5)_3E^{•+}$ decreases and that of the fragment ion $C_6H_5E^{•+}$ increases in the 70 eV mass spectrum for the series E = N, P, As, Sb, Bi, and this has been attributed to a corresponding decrease of *D*(E−C) which favors a sequential loss of two aryl ligands. Further, the fragment ions $C_6H_5E^{•+}$ were considered to be especially stable in the case of heavier pnictogens.[1,2] With the exception of **2**, which has been studied in some detail by Williams et al.[3] using specifically deuterated derivatives, no extended investigation of the reactions of ionized triaryl derivatives of the heavier pnictogens using modern techniques of tandem mass spectrometry is available. This is in contrast to the renewed interest in the existence and reactions of neutral fragments of organoelement compounds of group 15, i.e., of "p-block" elements.[4] In particular the existence and reactions of

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[1] (a) Bowie, J. J.; Nussey, B. *Org. Mass Spectrom.* **1970**, *3*, 933. (b) Zeeh, B.; Thompson, J. B. *Tetrahedron Lett.* **1969**, 111. (c) Rake, A. T.; Miller, J. M. *Org. Mass Spectrom.* **1970**, *3*, 237. (d) Spalding, T. R. *Org. Mass Spectrom.* **1976**, *11*, 1019. (c) Glidewell, C. *J. Organomet. Chem.* **1976**, *116*, 199.

[2] (a) Hendrick, K.; Mickiewicz, M.; Wild, S. B. *Austr. J. Chem.* **1975**, *28*, 1455. (b) Hendrick, K.; Mickiewicz, M.; Roberts, N.; Shewshuk, E.; Wild, S. B. *Aust. J. Chem.* **1975**, *28*, 1473.

[3] Williams, D. H.; Ward, R. S.; Cooks, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 966.

10.1021/om0104058 CCC: $20.00

low-valent organoelement derivatives of the type Ar−E have been studied. Thus, neutral aryl nitrenes Ar−N and aryl phosphandiyls Ar−P are definitely known,[4] but the existence of the corresponding derivatives of the heavier pnictogens Ar−As, Ar−Sb, and Ar−Bi is still questionable. These fragments are only known as parts of complexes and components of ylidic bond systems.[5]

As mentioned before,[1,2] the ionized species $C_6H_5E^{\bullet +}$ are easily prepared in the gas phase and in fact give rise to the base peak in the mass spectra of the heavier triaryl pnictogens, in agreement with the proposed easy decomposition of the molecular ions by loss of two phenyl radicals.[1,2] However, the appearance of diffuse peaks of "metastable transition" in the mass spectra of triaryl derivatives of the heavier pnictogens was mentioned[1] which could by attributed to the direct formation of $C_6H_5E^{\bullet +}$ from the molecular ion. This indicates that the mechanisms of the decomposition of the ionized triaryl pnictogens may be more complicated than assumed. Although several rearrangement processes of the molecular ions of ionized triaryl pnictogens have been suggested to rationalize the fragment ions of the 70 eV mass spectra,[1,2] the mechanism of these rearrangements and their energetic requirements are not known. This is of importance because the mechanisms of formation of organoelement species with low coordination especially of heavy main group elements are relevant for the use of these species as precursors in MOCVD processes. Mass spectrometry can provide some insight into the fragmentation reactions of organoelement compounds. This and the general interest in the formation and reactivity of reactive organoelement species of heavier elements stimulated us to study the gas-phase ion chemistry of the triphenyl pnictogens **1**−**5** again with special emphasis on the As compound **3** using the methods of tandem mass spectrometry.

Results and Discussion

The EI mass spectra of **1**−**5** are available from the NIST library of mass spectra included in the NIST WebBook of Chemistry.[6] The mass spectra obtained in this work are in excellent agreement with these published spectra and therefore are not shown explicitly here. Table 1 gives a summary of relevant peaks in their 70 eV EI mass spectra.

As discussed before,[1,2] the relative intensity of the molecular ions $\mathbf{M}^{\bullet +}$ decreases and that of the fragment ions $C_6H_5E^{\bullet *}$ ($\mathbf{B}^{\bullet +}$) increases distinctly in the series E = N > P > As > Sb > Bi, while the relative intensity of the fragment ion $(C_6H_5)_2E^{\bullet *}$ ($\mathbf{A}^+$), which is supposed to be an intermediate for the formation of $\mathbf{B}^{\bullet +}$,[1] is always rather small and has a maximum in the mass spectrum of **4** (E = Sb). In addition, abundant ions [**A**-2H]$^+$ and of the ligand $C_6H_5^+$ are observed in almost all spectra with the exception of the mass spectrum of **5** (E = Bi). The mass spectrum of **5** (E = Bi) displays [**A**-2H]$^+$ < 0.5% and a very large signal for Bi^+. Further, in the mass spectra of **1** and **2** significant peaks due to the ions [**M**-H]$^+$ and [**M**-2H]$^{\bullet +}$ are observed which are much less abundant or absent for the higher homologues. As noted earlier,[1] the observation of notable signals at *m*/*z* 154 in the spectra of **3**, **4**, and **5** is of particular interest. Exact mass determination was performed and shows that this peak is always due to ions $C_{12}H_{10}^{\bullet +}$, which have to arise from C−C bond formation between two C_6H_5 ligands. This is evidence for a rearrangement process that may be also involved in the formation of fragment ions $\mathbf{B}^{\bullet +}$. A summary of these fragmentation routes of ionized **1**−**5** is given in Scheme 1. More information about the preferred decomposition routes of ions with low internal energy derived from **1**−**5** is obtained from the MIKE spectra of $\mathbf{M}^{\bullet +}$, $\mathbf{A}^+$, [**A**-2H]$^+$, and $\mathbf{B}^{\bullet +}$ presented in Tables 2−5.

Scheme 1

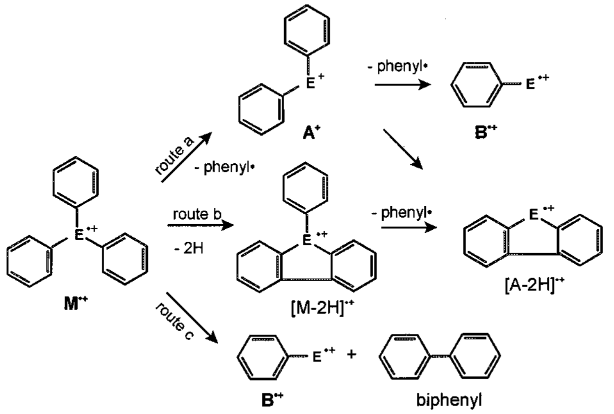

Table 1. Partial 70 eV Mass Spectra (% relative intensity) of Triphenyl Element Compounds $(C_6H_5)_3E$: 1, E = N; 2, E = P; 3, E = As; 4, E = Sb; 5, E = Bi

ion	1	2	3	4	5
$\mathbf{M}^{\bullet +}$ $(C_6H_5)_3E^{\bullet +}$	100	100	29	13	<0.5
[M-H]$^+$	45	13			
[M-2H]$^{\bullet +}$	8	2			
$\mathbf{A}^+$ $(C_6H_5)_2E^+$	7	8	7	17	8
[A-2H]$^+$	34	67	27	10	<0.5
$\mathbf{B}^{\bullet +}$ $C_6H_5E^{\bullet +}$	3	33	100	100	100
$(C_6H_5)_2^{\bullet +}$	1	2	7	47	11
$C_6H_5^+$	79	2	6	26	14
$E^{\bullet +}$			1	7	98

Table 2. MIKE Spectra (% relative intensity of total fragment ions) of Molecular Ions $\mathbf{M}^{\bullet +}$ of Triphenyl Element Compounds $(C_6H_5)_3E$: 1, E = N; 2, E = P; 3, E = As; 4, E = Sb; 5, E = Bi

	$\mathbf{M}^{\bullet +}$ [$(C_6H_5)_3E^{\bullet +}$]				
fragment ion	$\mathbf{M}^{\bullet +}$ (**1**)	$\mathbf{M}^{\bullet +}$ (**2**)	$\mathbf{M}^{\bullet +}$ (**3**)	$\mathbf{M}^{\bullet +}$ (**4**)	$\mathbf{M}^{\bullet +}$ (**5**)
[M-H]$^+$	89	53			
[M-2H]$^{\bullet +}$	11				
[M-C_6H_6]$^{\bullet +}$		32	5	<1	40
$\mathbf{B}^{\bullet +}$; $C_6H_5E^{\bullet +}$		15	91	99	57
[M-HE]$^+$		<1	4	<1	3

The MIKE spectra of $\mathbf{M}^{\bullet +}$ are quite simple and reveal a clear trend along the group 5 of the PS for the preferred reactions of these radical cations. The metastable $\mathbf{M}^{\bullet +}$ of **1** fragments solely by loss of one and two H atoms (route b, Scheme 1), whereas that of **2** undergoes loss of C_6H_6 and generation of the ion $C_6H_5P^{\bullet +}$ besides loss of H. Elimination of H is not observed for metastable $\mathbf{M}^{\bullet +}$ of **3**, **4**, and **5**. The genera-

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[4] (a) Mathey, F. *Angew. Chem.* **1987**, *99*, 285. (b) Li, X.; Weissmann, S. I.; Lin, T. S.; Gaspar, P. P.; Cowley, A. H.; Smirnov, A. I. *J. Am. Chem. Soc.* **1994**, *116*, 7899. (c) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 827. (d) Nguyen, M. T.; Van Keer, A.; Vanquickenborne, L. G. *J. Org. Chem.* **1996**, *61*, 7077.

[5] For example see: Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445.

[6] NIST Chemistry WebBook, NIST Standard Reference Database Number 69, February 2000 (http://webbook.nist.gov./chemistry).

Table 3. MIKE Spectra (% relative intensity of total fragment ions) of Fragment Ions A^+ [$(C_6H_5)_2E^+$] of Triphenyl Element Compounds: 1, E = N; 2, E = P; 3, E = As; 4, E = Sb; 5, E = Bi

	ion **A**$^+$ [$(C_6H_5)_2E^+$]				
fragment ion	**A**$^+$ (**1**)	**A**$^+$ (**2**)	**A**$^+$ (**3**)	**A**$^+$ (**4**)	**A**$^+$ (**5**)
[A-H]$^{\bullet+}$	94	9	1		
[A-2H]$^+$		82	94	33	
[A-E]$^{\bullet+}$			2	67	<1
[A-$C_{12}H_{10}$]					99
[A-HE]$^+$			2		
[A-H_2E]$^{\bullet+}$		8	1		
[A-HCE]$^+$	6				

Table 4. MIKE Spectra (% relative intensity of total fragment ions) of Fragment Ions [A-2H]$^+$ [$(C_6H_4)_2E^+$] of Triphenyl Element Compounds: 1, E = N; 2, E = P; 3, E = As; 4, E = Sb

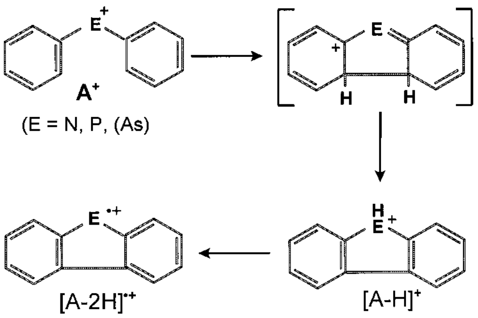
	ion [**A-2H**]$^+$ [$(C_6H_4)_2E^+$]			
fragment ion	**A**$^+$ (**1**)	**A**$^+$ (**2**)	**A**$^+$ (**3**)	**A**$^+$ (**4**)
[A-2H-H]$^{\bullet+}$	90	32	15	
[A-2H-C_2H_2]$^+$	4	34		
[A-E]$^{\bullet+}$		41	85	100
[A-HCE]$^+$	6	3		

Table 5. MIKE Spectra (% relative intensity of total fragment ions) of Fragment Ions $B^{\bullet+}$ [$C_6H_4E^{\bullet+}$] of Triphenyl Element Compounds: 2, E = P; 3, E = As; 4, E = Sb; 5, E = Bi

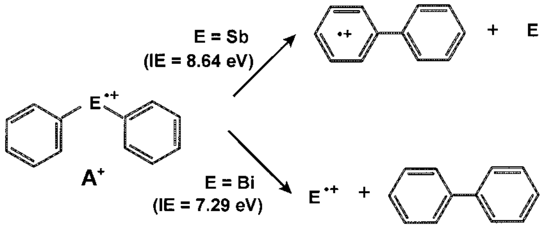
	ion **B**$^{\bullet+}$ [$C_6H_4E^+$]			
fragment ion	**B**$^{\bullet+}$ (**2**)	**B**$^{\bullet+}$ (**3**)	**B**$^{\bullet+}$ (**4**)	**B**$^{\bullet+}$ (**5**)
[B-H]$^+$	100	100	87	
[B-E]$^+$			9	
[B-C_6H_5]$^+$			1	100

tion of the ion **B**$^{\bullet+}$ is almost the only process found in the MIKE spectra of ionized **3** and **4**, while metastable **M**$^{\bullet+}$ of **5**$^{\bullet+}$ fragments also abundantly by loss of C_6H_6. Note that the formation of a fragment ion **A**$^+$ by loss of a $C_6H_5^{\bullet}$ radical is not observed in the MIKE spectra for any **M**$^{\bullet+}$. Therefore, the loss of a phenyl radical (route a, Scheme 1) is not the energetically favored process, even in the case of the Bi derivative **5**, disproving the earlier explanation of the mass spectra of $(C_6H_5)_3E^{\bullet+}$. Instead of a cleavage of the E−C bond, the ionized triphenyl derivatives $(C_6H_5)_3E^{\bullet+}$ with E = N and P prefer interactions between the C_6H_5 ligands, which eventually result in the losses of H or C_6H_6, while the molecular ions $M^{\bullet+}$ of the heavier pnictogens As, Sb, and Bi definitely dissociate in a single step directly to fragment ions $C_6H_5E^{\bullet+}$ of type **B**$^{\bullet+}$ (route c, Scheme 1).

Scheme 2



Scheme 3



Furthermore, the MIKE spectra of ions **A**$^+$, generated by loss a phenyl radical, do not show any signal for the formation of ions **B**$^{\bullet+}$ by loss of a (second) phenyl radical (Table 3). Thus, ions **A**$^+$ are not an important precursor of the abundant ions **B**$^{\bullet+}$ observed in the EI mass spectra of **2**−**5**, and a sequential loss of two phenyl radicals (route a) can be excluded as a main route of the fragmentation of the ionized triphenyl pnictogens. Metastable ions **A**$^+$ derived from amine **1** lose almost exclusively H, while those from **2** and **3** eliminate mainly H_2. Williams et al. have shown that ions **A**$^+$ derived from phosphane **2** eliminate specifically HD, if one of the phenyl groups is deuterated.[3] This agrees with the C−C bond formation between the two phenyl groups and elimination of one H atom from each phenyl to generate a 9-phosphafluorenyl cation (Scheme 2). In contrast, deuterated ions derived from **3** eliminate H_2, HD, and D_2 in a statistical ratio, indicating extensive H/D exchange between the phenyl groups.[1a] However, it is not clear at which stage this H migration occurs.

Interestingly, metastable ions **A**$^+$ from stibane **4** and bismuthane **5** fragment by elimination of the central pnictogen E center either as a neutral atom or atomic ion. Both processes are in fact identical[1d] because the ionization energy IE of Sb of 8.64 eV[5] is above and the IE of Bi of 7.29 eV[5] is below the IE of biphenyl of 8.16 eV.[5] Thus, according to the rule of Audier and Stephenson, the charge remains in both cases with different fragmentation products (Scheme 3). This reductive elimination of the central pnictogen atom and formation of a biphenyl radical cation is already observed in the MIKE spectrum of **A**$^+$ derived from arsane **3**, although only as a minor process. Nevertheless, this process is clearly typical for the derivatives of the heavier pnictogens As, Sb, and Bi.

To supplement the MIKE spectra of **A**$^+$, the MIKE spectra of the ions [**A**-2H]$^+$ derived from **2**−**4** are presented in Table 4. While the intensity of ions [**A**-2H]$^{\bullet+}$ exceeds that of **A**$^+$ in the EI spectra of **2**−**4**, no such ions are found in the EI spectrum of **5**. Again the preferred decomposition route changes systematically along the group 5 elements. On the one side the loss of H, which is the strongly dominant fragmentation of [**A**-2H]$^+$ from amine **1**, decreases from phosphane **2** to arsane **3** and is absent in the MIKE spectrum of [**A**-2H]$^+$ from stibane **4**.[7] On the other side, elimination of E, which is the only process of [**A**-2H]$^+$ in the case of **4**, decreases on going from **3** to **2** and is absent in the MIKE spectrum of [**A**-2H]$^+$ derived from **1**. This elimination of E is in agreement with a heterofluorene structure of the ions [**A**-2H]$^{\bullet+}$ in all cases (Scheme 1).

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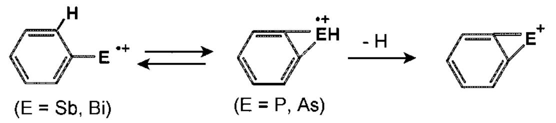
[7] The MIKE spectra of [**A**-2H]$^{\bullet+}$ derived from **2**−**4** exhibit a sharp signal at the position expected for loss of H. However, by separate experiments (changing the instrument and mode of scanning) it can be shown that this is an artifact peak arising from the intense loss of H_2 from metastable **A**$^+$ in the first field-free region of the Mikromass VG AutoSpec mass spectrometer. Because of this artifact signal, a small signal for loss of H may be masked.

Scheme 4



B$^{\bullet+}$

Actually, the elimination of As atoms has already been reported for the mass spectrometric fragmentation of 9,10-diarsenaanthracene.[8]

Last, the fragment ions observed in the MIKE spectra of ions **B**$^{\bullet+}$ from **2**–**5** are shown in Table 5. The only reaction observed in the spectra of **B**$^{\bullet+}$ derived from **2** and **3** is the loss of H. This reaction is also observed in the spectrum of **B**$^{\bullet+}$ derived from **4**, but in addition a distinct signal of $C_6H_5^+$ is detected. The same fragmentation, but with charge retention at Bi, is the only abundant process for metastable ions **B**$^{\bullet+}$ from **5**. Ions **B**$^{\bullet+}$ of a structure $C_6H_5E^{\bullet+}$ may be compared to ionized carbene analogues in the sense that they expose an empty and a singly occupied orbital at E. Hence, the elimination of H from **B**$^{\bullet+}$ in the case of E = P and As can be attributed to a reaction sequence consisting of insertion of E into a neighboring C–H bond of the phenyl group and subsequent E–H cleavage and generating a bicyclic ion with a three-membered ring containing the heteroatom at the apex (Scheme 4). This insertion reaction is expected to be energetically less favorable in the case of E = Sb and Bi.

The most interesting unimolecular reactions of the triaryl pnictogens **2**–**5** are certainly (i) the formation of ions **B**$^{\bullet+}$, which apparently occurs by an energetically favorable one-step process according to the MIKE spectra of **M**$^{\bullet+}$, and (ii) the decomposition of the ions **A**$^{+}$ from **3**–**5** into the central pnictogen atom E and a biphenyl molecule with charge retention on either of the fragments depending on the relative IE. Both processes consist of a reductive elimination under the formation of C_6H_5E or of the center E, respectively, by C–C coupling of the two phenyl ligands. The proof for the formation of biphenyl as the neutral product during the generation of ion **B**$^{\bullet+}$ from **M**$^{\bullet+}$ of **2**–**5** is only circumstantial, however, because neutral products are not detected in MIKE spectra. If the IE of the evolving biphenyl $R-C_6H_4-C_6H_4-R$ is lowered by substituents R below the IE of the diyl fragment $R-C_6H_4-E$, the charge should remain with the biaryl product of this fragmentation according to the rule of Audier and Stephensen. Therefore, the biaryl product would appear in the MIKE spectrum as an biaryl ion and would provide positive evidence for a reductive elimination of the central $R-C_6H_4-E$ from the parent radical cation $(R-C_6H_4)_3E^{\bullet+}$. A suitable compound for this experiment is tris(4-ethylphenyl) arsane **6**, and the MIKE spectra of the **M**$^{\bullet+}$ of the unsubstituted compound **3** and of **6** are shown in Figure 1 for comparison.

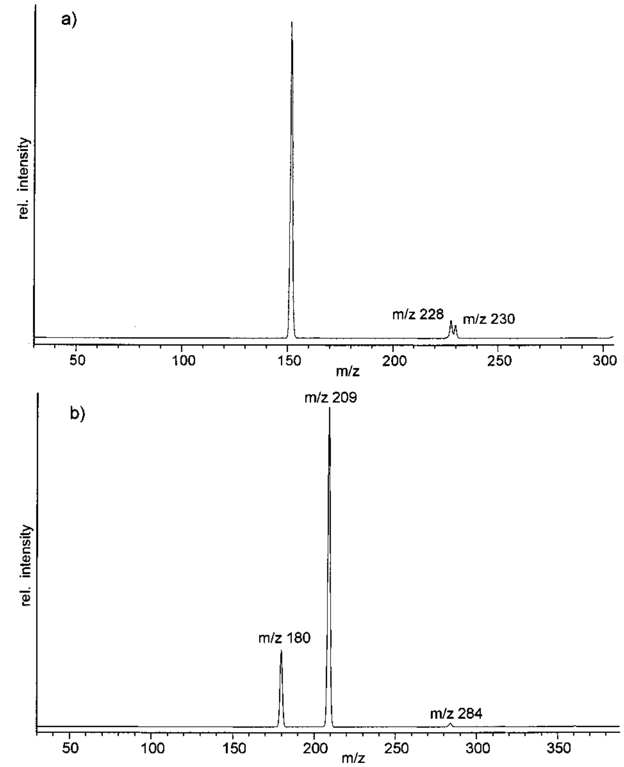


Figure 1. MIKE spectrum of (a) triohenyl arsane **3** and (b) tris(4-ethylphenyl) arsane **6**.

As discussed before, the MIKE spectrum of **3** displays only one strong signal for ion **B**$^{\bullet+}$ at *m*/*z* 152. In contrast, the MIKE spectrum of **6** contains two intense signals, one at *m*/*z* 180 owing to the expected ion **B**$^{\bullet+}$, $C_2H_5-C_6H_4-As^{\bullet+}$, while the second and more intense signal at *m*/*z* 209 arises from the ion $C_{16}H_{17}^+$. This ion corresponds to the ion [biaryl-H]$^+$ of bis(4-ethylphenyl), which is the expected product of the reductive elimination process. The mechanism of the formation of the ions $C_{16}H_{17}^+$ is not definitely known.[9,10] An obvious possibility is that the diyl fragment $C_2H_5-C_6H_4-As$ abstracts a H atom from the benzylic position bis(4-ethylphenyl) radical cation before leaving the product complex. Anyway, the experiment proves unambiguously a C–C bond formation between two of the aryl ligands in the radical cation of **6** before fragmentation (Scheme 5).

In a further experiment the fragmentations of **M**$^{\bullet+}$ of 4-methylphenyldiphenylarsane **7** were analyzed. This unsymmetrically substituted compound can generate two fragment ions of type **B**$^{\bullet+}$, namely, $C_6H_5-As^{\bullet+}$, *m*/*z* 152, and $CH_3-C_6H_4-As^{\bullet+}$, *m*/*z* 166, and two different biaryls, namely, biphenyl and 4-methylbiphenyl, which may yield ions *m*/*z* 154 and 168, respectively. However, only the IE of the substituted biphenyl is probably low enough to allow for charge retention, and H-abstraction from this radical cation gives rise to ions $C_6H_5-C_6H_4-CH_2^+$, *m*/*z* 167. If the reductive elimination of the central aryl–As fragment occurs without a significant substituent effect, the intensity of the ions (*m*/*z* 166 + 154) vs ion (*m*/*z* 152 + 168 + 167) in the mass spectrum of **7** and in the MIKE of **M**$^{\bullet+}$ should appear in a ratio 1:2. The 70 eV mass spectrum of **7** contains signals of all the predicted ions at *m*/*z* 320 (M$^{\bullet+}$, relative intensity 54%, corrected for ^{13}C contribution), 168 (63.0%), 167 (34.2%), 166 (30.9%), 154 (16.5%), and 152 (99.8%).

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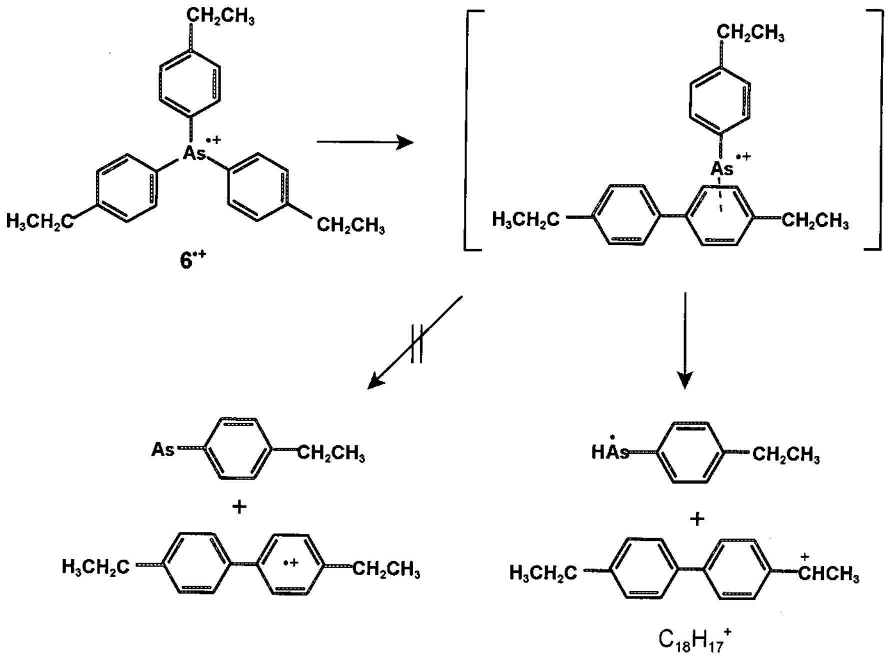
(8) Vermeer, H.; Weustink, R. J. M.; Bickelhaupt, F. *Tetrahedron Lett.* **1978**, *35*, 155.

(9) There is evidence from the mass spectrometric behavior of other alkylphenyl–As compounds (refs 9, 14) that the complex (biaryl·C_6H_5-As$^{\bullet+}$) rearranges by insertion of the As fragment into a benzylic C–H bond before dissociation. This would explain the absence of any intact biaryl ions in the MIKE spectra.

(10) Kirchhoff, D. Dissertation, Universität Bielefeld, 1999.

Scheme 5



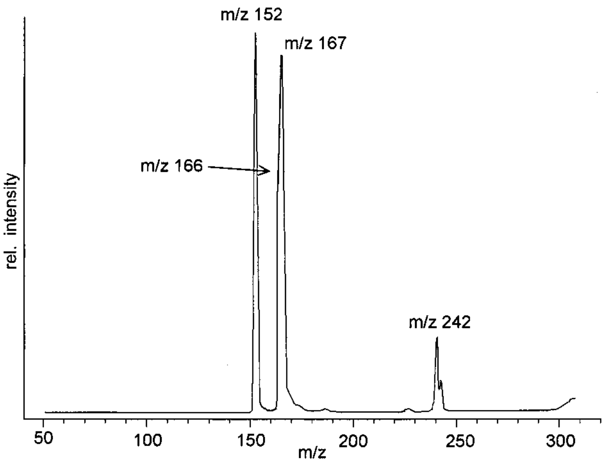


Figure 2. MIKE spectrum of 4-methylphenyldiphenylarsane **7**.

Thus, at high internal energy the fragmentation of $\mathbf{7}^{\bullet+}$ by reductive elimination of the group C_6H_5As to generate ions *m/z* 152, 168, and 167 is favored by a factor of about 4 over elimination of the group $CH_3{-}C_6H_4As$, yielding ions *m/z* 154 and 166. The MIKE spectrum of the molecular ion shown in Figure 2 displays a large signal at *m/z* 152 and a nonresolved signal at *m/z* 166 and 167 besides two smaller peaks at *m/z* 242 and 244. The ion *m/z* 167 arises from the ionized 4-methylbiphenyl, from which the leaving fragment C_6H_5As abstracts an H atom. The ions *m/z* 152 and 166 correspond to the radical cations $\mathbf{B}^{\bullet+}$ ($C_6H_5As^{\bullet+}$ and $CH_3C_6H_4As^{\bullet+}$). Neither the 4-methylbiphenyl radical cation *m/z* 168 nor the biphenyl radical cation *m/z* 154 is detected in the MIKE spectrum. The intensity ratio of the observed ions can be estimated only because the signals *m/z* 166 and 167 overlap. But again formation of the ions (*m/z* 152 + 167) by reductive elimination of C_6H_5As is clearly favored over elimination of CH_3 C_6H_4As (*m/z* 166) from $\mathbf{7}^{\bullet+}$ by at least a factor of 3. If the formation of all these ions is truly competitive,[11] this would indicate that an electron-donating substituent is preferably retained in the biaryl fragment.

The rearrangement and fragmentation of the radical cations of the triaryl main group 5 element compounds **1**−**5** by reductive elimination have to compete with the direct cleavage of the E−C bond, resulting in ion $\mathbf{A}^+$ and an aryl radical (route a, Scheme 1), and with a C−C bond formation between two aryl ligands followed by elimination of one and/or two H atoms (route b, Scheme 1). This latter process is known from the mass spectra of many organic compounds containing a geminal diphenyl moiety. Instructive examples are diphenyl methane and diphenyl ether, which exhibit large signals for sequential losses of H atoms in their mass spectra.[6] In the case of the triphenyl pnictogens investigated here, this fragmentation route is dominant for the amine radical cation $\mathbf{1}^{\bullet+}$ of low internal energy (observed in the MIKE spectrum) and of high internal energy (detected in the 70 eV mass spectrum). The preferred fragmentations of the radical cation of the phosphane $\mathbf{2}^{\bullet+}$ containing sufficient excess energy for a fast decomposition within the ion source are the formation of ions $[\mathbf{A}\text{-}2H]^+$ and formation of ion $\mathbf{B}^{\bullet+}$ by the reductive elimination process. According to the reactions of the metastable molecular ion $\mathbf{2}^{\bullet+}$ and the metastable fragment ion $\mathbf{A}^+$, the ions $[\mathbf{A}\text{-}2H]^+$ arise from two fragmentation sequences. The first one proceeds by elimination of one and two H atoms followed by loss of a phenyl radical, and the second one consists of the loss of a phenyl radical followed by loss of one and two H atoms. The latter route is very likely more important. Therefore, in the case of the phosphorus derivative **2** elimination of H (and 2H) and of a phenyl radical compete with each other. However, it is clear from the fragmentation of metastable molecular ion $\mathbf{2}^{\bullet+}$ of low internal energy that reductive elimination of the aryl−E fragment

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[11] The dissociation energies are not known for the radical cations, but can be estimated for As, Sb, and Bi derivatives from the data of Table 6 (see text) from AE($\mathbf{A}^+$) − IE(M): $D(As{-}C_{aryl}{}^{\bullet+}) = 196$ kJ/mol; $D(Sb{-}C_{aryl}{}^{\bullet+}) = 168$ kJ/mol; and $D(Bi{-}C_{aryl}{}^{\bullet+}) = 43$ kJ/mol.

Table 6. Ionization Energy (IE) and Appearance Energy (AE) of Ions $(C_6H_5)_2E^+$ (A^+) and $C_6H_5E^{\bullet+}$ ($B^{\bullet+}$) for Triphenyl Pnictogens 1−5 (IE and AE in eV)[a]

	1	2	3	4	5
IE(M)	6.80 ± 0.05	7.44 ± 0.05	7.32 ± 0.05	7.26 ± 0.05	7.45 ± 0.05
AE(**A**$^+$)			9.35 ± 0.10	9.0 ± 0.1	7.9 ± 0.1
AE(**B**$^{\bullet+}$)			8.2 ± 0.1	8.7 ± 0.1	7.75 ± 0.10

[a] All data taken from ref 12.

competes also effectively in this case with the other two fragmentation routes. This indicates that already for **2**$^{\bullet+}$ the activation energy for the reductive elimination is similar or smaller than the P−C$_{aryl}$ bond energy.[11] Although the dissociation energy D(E−C$_{aryl}$) certainly decreases in the case of the molecular ions **3**$^{\bullet+}$, **4**$^{\bullet+}$, and **5**$^{\bullet+}$, the reductive elimination becomes by far the dominant reaction of the radical cations of the triphenyl derivatives of the heavier pnictogens, both for ions of small and large amounts of internal energy. This is significant because by the principles of the QET or RRKM theory the "simple" cleavage of a weak bond is strongly favored by a large frequency factor and is expected to compete successfully with a supposedly slow rearrangement process at sufficiently high internal energies of the decomposing ion.[12] It follows that before fragmentation most of the molecular ions of **3**$^{\bullet+}$−**7**$^{\bullet+}$ and some of **2**$^{\bullet+}$ must have isomerized immediately in the ion source of the mass spectrometer into isomers that favor a fast fragmentation into **B**$^{\bullet+}$ and a biaryl at all internal energies of the decomposing ion. There is another piece of evidence present in the literature that supports the assumption of a preceding and facile isomerization process of the molecular ions of **3**−**5**. The IE of these molecules and the appearance energy AE of the corresponding ions **A**$^+$ and **B**$^{\bullet+}$ have been obtained by Potapov et al.[13] using photoionization techniques, and their data, quoted in ref 6, are presented in Table 6.

The puzzling result from these data is that formation of ion **B**$^{\bullet+}$, which formally requires cleavage of two E−C$_{aryl}$ bonds, always needs less energy than formation of ion **A**$^+$ by cleavage of only one E−C$_{aryl}$ bond. This anomaly has been known for more than 25 years, and the solution to this old enigma is ostensibly that ions **A**$^+$ and **B**$^{\bullet+}$ are generated from different isomers of the ionized triphenyl pnictogens. The data of Table 6 can be used to estimate the upper limit for the activation energy of the isomerization process of the molecular ions **3**$^{\bullet+}$, **4**$^{\bullet+}$, and **5**$^{\bullet+}$ of conventional structure into the complex [**3***]$^{\bullet+}$, [**4***]$^{\bullet+}$, and [**5***]$^{\bullet+}$ by the difference AE(**B**$^{\bullet+}$) − IE(M), since the measured AE is determined by the highest energy barrier on the route from the neutral molecule to the dissociation products, i.e., by the barrier either of the isomerization or of the dissociation of the complex into ion **B**$^{\bullet+}$ and biphenyl. The results are **3**$^{\bullet+}$ → [**3***]$^{\bullet+}$ 85 kJ/mol (0,88 eV); **4**$^{\bullet+}$ → [**4***]$^{\bullet+}$ 139 kJ/mol (1,44 eV); and **5**$^{\bullet+}$ → [**5***]$^{\bullet+}$ 29 kJ/mol (0,3 eV). These activation energies are indeed rather small, in particular for the Bi derivative, and well below the dissociation energy D(E−C$_{aryl}{}^{\bullet+}$) of the parent radical cation, which can be estimated from the difference AE(**A**$^+$) − IE(M).[11]

It is an obstacle of the experimental methods applied that more precise structural information of the species investigated cannot be obtained. Conventionally, more insight into the structures and isomerization processes of the radical cations of **1**−**5** may be obtained by theoretical methods, but a detailed analysis of the hypersurface of these rather large radical ions using adequate ab initio methods is beyond the scope of this study. However, on the basis of our previous experimental studies and theoretical considerations on $[X_2E{\cdot}C_6H_6]$[14,15] and other aryl−As radical cations[10,16] and on ab initio calculations on related group 14 and 15 element systems performed by others[17] the assumption of stable radical cation biaryl complexes is reasonable. In these systems the aryl−E moiety is bonded in a multihapto fashion (presumably η^2 for E = P, η^4 for E = As, and η^6 for E = Sb, Bi) to an arene ring. Preliminary theoretical investigations show that all of these complexes correspond to stable species on the hypersurface and are more stable than the conventional structures in certain cases for E = As, Sb, and Bi. This is very likely also true for the "nonclassical" isomers [**3***]$^{\bullet+}$, [**4***]$^{\bullet+}$, and [**5***]$^{\bullet+}$ of the radical cations of the arsane **3**, stibane **4**, and bismuthane **5**. It is thus not surprising that from these low-energy isomers, which are structurally well prepared, a facile loss of biaryl is observed.

Furthermore, the order of stability between the conventional and complex structures of the radical cations of the triphenyl pnictogens and the associated variation of the reactivity of these radical cations is plausible. A formal transformation of the conventional structure $(C_6H_5)_3E$ into the complex structure $[C_6H_5{-}C_6H_5{\cdot}C_6H_5E]$ requires the cleavage of two E−C$_{aryl}$ bonds and the formation of a C$_{aryl}$−C$_{aryl}$ bond besides complexing the C_6H_5E fragment. The C$_{aryl}$−C$_{aryl}$ bond is strong, and the energy gained by its formation is constant for all triphenyl pnictogens. In contrast, the dissociation energy D(E−C$_{aryl}$) decreases strongly in going from the N derivative to the Bi derivative.[10] Therefore it is anticipated that the conversion of $(C_6H_5)_3E^{\bullet+}$ into the complex ion $[C_6H_5{-}C_6H_5{\cdot}C_6H_5E]^{\bullet+}$ becomes even exothermic for the heavier main group 5 elements even if the binding energy of the C_6H_5E fragment is neglected. Obviously a "crossing" in stability occurs for the As derivative. In considering the trend of the unimolecular reactions of the ionized triaryl pnictogens, the mass spectrum of **1** shows that bond formation between two phenyl ligands and losses of H and H_2 are the favored reactions. A bond formation between the phenyl ligands requires charge and spin localization in these groups to promote an internal aromatic sub-

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stitution. The IE of the element hydrides EH_3 decreases from NH_3 to BiH_3 by about 1 eV.[18] In contrast, the IE *increases* almost 0.6 eV by going from **1** to **2** and then remains more or less constant. The particularly low IE of **1** is of course the result of a charge delocalization over the extended π system of the lone pair p electrons of the N atom and the three phenyl ligands. Evidently, the higher IE for the triphenyl derivatives of the heavier main group 5 elements indicates less charge delocalization.[19] As a consequence the radical cations of these derivatives are less reactive with respect to bond formation between the ligands, apart from other effects due to the molecular geometry. This leaves only a dissociation of the $E-C_{atryl}$ bond and formation of ions $\mathbf{A}^+$ as a likely process competing with the exothermic isomerization of the molecular ions into the complex structure. However, the rather low abundance of $\mathbf{A}^+$ despite the weak $E-C_{aryl}$ bond for E = As, Sb, and Bi and a large frequency factor for this type of fragmentation shows that $E-C_{aryl}$ bond dissociation has little chance to prevail over isomerization and dissociation of the complex ion $[C_6H_5-C_6H_5{\cdot}C_6H_5E]^{\bullet+}$ into ion $\mathbf{B}^{\bullet+}$ and biphenyl. Since rearrangement of the molecular ions is handicapped by a small frequence factor[11] and is therefore an inherently slow process, the activation energy for the isomerization of the radical cations of **3**, **4**, and **5** must be indeed rather small. This is true, however, only for the radical cations, and it is of interest to speculate that a reductive elimination of an aryl−E fragment and formation of a diaryl can proceed also in solution if the heavier triaryl pnictogens are oxidized in solution. Indeed, in 1988 an efficient synthesis of diaryls was described by D. H. R. Barton et al. in which a ligand coupling is induced in triaryl bismuthanes and triarylstibanes when a Pd(0) catalyst is generated in situ from Pd(II).[20] This work extends earlier work in which Cu was used to induce the ligand coupling.[21] Although the mechanism of this reaction is still unclear, radical cations of the Sb and Bi compounds generated during the reduction of the catalyst salt are possible intermediates.

Experimental Section

Pure triphenyl derivatives **1**−**5** of the pnictogens are commercially available and were used without further purification. Tris(4-ethylphenyl)arsane **6** was prepared by Grignard reaction of 4-ethylphenylmagnesium bromide in diethyl ether/petroleum ether with $AsCl_3$ under standard reaction conditions.[22] 4-Methylphenyl-diphenylarsane **7** was prepared by the Grignard reaction of 2 equiv of phenylmagnesium bromide with dichloro-4-methylphenylarsane using analogous reaction condition as before. The arsanes **6** and **7** were purified by vacuum distillation and characterized by ^1H NMR spectroscopy and EI-mass spectrometry.

Mass Spectrometry. EI mass spectra were obtained by using a Micromass VG AutoSpec mass spectrometer, an electron energy of 70 eV, and an accelerating voltage of 8 kV. The compounds were introduced into the ion source either in pure form or absorbed at Na_2SO_4 powder using a solid sample probe at a suitable sample temperature to ensure an ion beam of sufficient intensity. The fragmentation of metastable ions was analyzed using a VG ZAB-2F mass spectrometer operated at 70 eV electron energy and 6 kV accelerating voltage. The samples were introduced into the ion source as described before. To obtain the MIKE spectra, the selected ions were focused magnetically into the second field-free region of the ZAB-2F instrument following the magnetic sector, and the fragment ions were recorded by variation of the deflecting voltage of the electrostatic analyzer. The MIKE spectra shown are the mean of 30−50 scans. All signals observed in the MIKE spectra are narrow and Gaussian-shaped peaks, and the relative intensity of the fragment ions in the MIKE spectra was calculated from the peak areas using the Origin program[23] to fit the experimental peak shapes.

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(18) The following IE's were taken from ref 6: $IE(NH_3) = 10.88$ eV; $IE(PH_3) = 10.60$ eV; $IE(AsH_3) = 10.51$ eV; $IE(SbH_3) = 10.02$ eV; $IE(BiH_3) \approx 10.1$ eV; and $IE((C_6H_5)_3N = 6.75$ eV; $IE((C_6H_5)_3P = 7.44$ eV; $IE((C_6H_5)_3As = 7.32$ eV; $IE((C_6H_5)_3Sb = 7.26$ eV; $IE((C_6H_5)_3Bi \approx 7.45$ eV; see also Table 6.

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