Methylidynearsine (HC$\equiv$As): synthesis and direct characterization by UV-photoelectron spectroscopy and mass spectrometry†‡

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The dehydrohalogenation of gaseous dichloromethylarsine on solid base led to chloromethylidenearsine and, at higher temperature of the base, to methylidynearsine, the third unsubstituted heteroalkyne unambiguously synthesized up to now.

Only two unsubstituted heteroalkynes, hydrogen cyanide and methylidynephosphine, have been prepared up to now: Scheele synthesized the first one in 1782[1] and Gier characterized the phosphorus derivative in 1961.[2] For the compound corresponding to the next element of the column 15 of the periodic table, the methylidynearsine **1**, the ionization potentials,[3] force constants and bond lengths,[4] the gas-phase proton affinity[5] or basicity[6] have only been investigated from a theoretical point of view.

Furthermore, few substituted arsaalkynes have been isolated. The tri-*tert*-butylphenylarsaalkyne, a compound stabilized by a bulky substituent, was synthesized by Märkl and Sejpka in 1986.[7] The first kinetically non-stabilized arsaalkynes, the ethylidyne-[8] and propylidynearsine[9] were then described. To the best of our knowledge, no other derivative has been characterized up to now except complexed derivatives.[10]

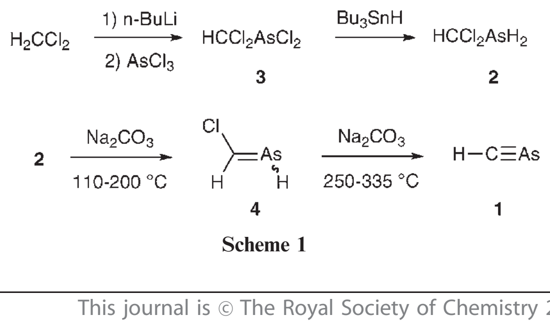
We report here the synthesis of methylidynearsine **1** formed in a three-step reaction: the synthesis of the dichloromethyldichloroarsine **3**, its chemoselective reduction in the corresponding dichloromethylarsine **2** followed by a bisdehydrohalogenation on a solid base in a vacuum gas–solid reaction (VGSR) (Scheme 1).[11] The characterization was performed in the gas phase by UV photoelectron spectroscopy (UV-PES) and high resolution mass spectrometry (HRMS).

The fast addition of arsenic trichloride on the lithium salt of dichloromethane diluted in a pentane–diethyl ether–THF solution cooled at low temperature (−110 °C) led to a mixture of arsenic trichloride, dichloromethyldichloroarsine **3** and bis(dichloromethyl)chloroarsine. Dichloroarsine **3** was purified by selective trapping *in vacuo* in a cell cooled at −20 °C (yield: 24%) and then characterized by ^{1}H and ^{13}C NMR spectroscopy and HRMS.

The second step, the reduction reaction, was performed by slow addition of dichloroarsine **3** diluted in tetraglyme on tributyl tin hydride in excess. During and after the addition, the formed dichloromethylarsine **2** was distilled off *in vacuo* from the reaction mixture. Arsine **2** was purified in the gaseous phase by trap-to-trap distillation (yield: 32%) and characterized by UV-photoelectron, ^{1}H and ^{13}C NMR spectroscopy and HRMS. The UV-photoelectron spectrum of dichloromethylarsine **2**, (Fig. 1(a)) displays a first sharp band at 9.65 eV with a right-side shoulder at 10.2 eV; the massif centered at 11.6 eV has two well distinguished bands at 11.3 (left-side) and at 11.8 eV (right-side), the higher energy ionization is observed at 12.5 eV. By mass spectrometry, the molecular ion was observed (calc. for $HC^{35}Cl_2AsH_2$: 159.8828, found: 159.883) (see details on the PE and mass spectra in ESI‡). This arsine is kinetically very unstable, even at low temperature (−80 °C), and should be kept in liquid nitrogen in pure form or at low temperature (−50 °C) when diluted in a solvent.

Arsine **2** was then vaporized on solid sodium carbonate in VGSR conditions.[11] The gaseous flow condensed with a cosolvent was then analyzed by ^{1}H NMR spectroscopy. Up to a temperature of 200 °C of the base, the signals corresponding to small amounts of arsine **2** were observed in the presence of unidentified oligomeric products.

This gaseous flow was then directly analyzed by UV photoelectron spectroscopy. On the spectrum corresponding to a temperature of 200 °C for the base, (Fig. 1(b)) the first PE band is slightly shifted to the lower energy and appears at 9.5 eV, two new bands at 10.4 and 11.2 eV are well distinguished and the collapsing of the



Scheme 1

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‡ Electronic supplementary information (ESI) available: Synthesis of **1–4**, calculated geometrical parameters, ionization potentials and mass spectra of compounds **2** and **4**. See DOI: 10.1039/b806771f

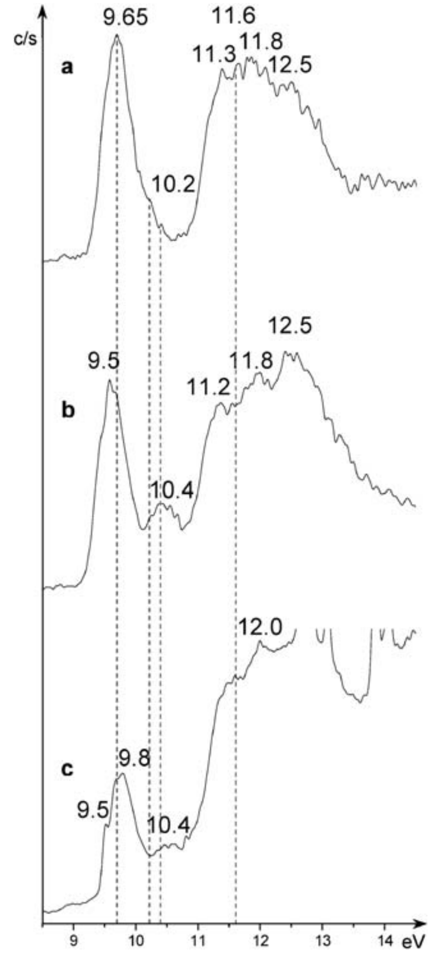

Fig. 1 PES spectra of (a) $ClCH_2AsH_2$ **2**, (b) **2** vaporized on Na_2CO_3 at 200 °C (c) **2** vaporized on Na_2CO_3 at 335 °C.

11.6 eV band intensity is obvious. The relative intensity of the first band and the massif around 12.5 eV is also changed.

The VGSR reactor was then connected to the ionization chamber of a high-resolution mass spectrometer. For a temperature of the base of 110 °C, the characterization of a compound with a $^{35}ClCHAsH$ formula was performed. It corresponds to a monodehydrohalogenation product and was attributed to chloromethylidenearsine **4** (calc. for $^{35}ClCHAsH$: 123.9061, found: 123.906). The main fragments correspond to the loss of a chlorine atom (*m*/*z* 90) and HCl (*m*/*z* 89).

Similar experiments were performed using a higher temperature of the base. By UV-PE spectroscopy and with the carbonate heated to 335 °C (Fig. 1(c)), the appearance of ionizations at 9.8 and 12.0 eV and the collapse of the shoulder at 11.3 eV corresponding to the precursor **2** are clearly observed. In this case, the relative intensity of the first band and the massif around 12.5 eV was completely inversed. The two previously observed bands at 9.5 and 10.4 eV are now weaker. By mass spectrometry and for a base temperature of 250 °C, the molecular ion corresponding to CHAs and attributed to arsaalkyne **1** was observed (calc. for HCAs: 87.9294, found: 87.929) (Fig. 2). Carbon dioxide (*m*/*z* 44) formed in the dehydrohalogenation reactions was also observed on the spectra.

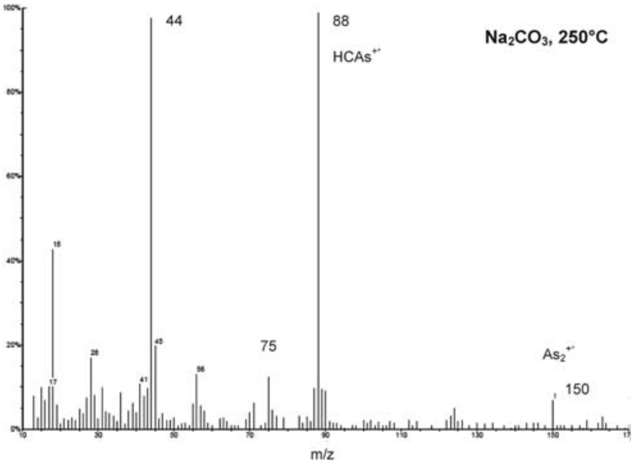

Fig. 2 Mass spectrum of **2** vaporized on Na_2CO_3 at 250 °C.

The comparison of theoretical and experimental IPs is necessary for a reliable identification of the compounds on the PE spectra. This has been carried out using time-dependent density functional theoretical methods (TD-DFT).[12] The experimental data were compared to the IP *ab initio* estimated by Outer Valence Green's Function (OVGF),[13] CASPT2 calculations[14] and so-called "corrected" IPs which are the less rigorous "shifting" of calculated Kohn–Sham energies[15] (Tables 1 and 2).

For the arsaalkene **4**, the first four IPs at 9.5, 10.4, 11.2 and 12.5 eV correspond to the $\pi_{C=As}$ ionization, followed by the arsenic and the chlorine lone pair ionizations, respectively. Considering the "naked" molecule of $CH_2{=}AsH$ ($\pi_{C=As}$ 9.7 eV; n_{As} 10.3 eV),[16] the 0.2 eV lowering of the $\pi_{C=As}$ IP is explained as a compromise between the σ-withdrawing stabilizing effect of the chlorine atom and its more important π destabilizing donor effect. The arsenic lone pair is only slightly influenced (0.1 eV stabilization) by chlorine atom in β position. Distinction between *E* and *Z* isomer by UV-PES is not easy (Table 3S. ESI‡) considering that the *Z* isomer is

Table 1 Calculated and experimental ionization potentials (IPs) for *E* and *Z* isomers of **4** (all values in eV)

	$-\varepsilon^{K-S}$		"Corrected"		CASPT2		TDDFT		OVGF		
MO	*E*	*Z*	*E* (x = 2.56)	*Z* (x = 2.55)	*E*	*Z*	*E*	*Z*	*E*	*Z*	Exptl.
A″ ($\pi_{C=As}$)	6.94	6.95	9.5[b]		9.20	9.21	9.31[a]	9.32[a]	9.16	9.18	**9.5**
A′ (n_{As}, n_{Cl})	8.17	8.04	10.73	10.59	10.49	10.38	10.52	10.42	10.52	10.36	**10.4**
A′ (n_{Cl})	8.92	9.04	11.48	11.59	11.25	11.36	11.19	11.31	11.32	11.45	**11.2**
A″	10.27	10.25	12.83	12.8	12.41	12.40	12.57	12.57	12.65	12.64	**12.5**

[a] Value of ΔSCF. [b] Experimental value.

Table 2 Calculated and experimental ionization potentials (IPs) for **1** (all values in eV)

MO	$-\varepsilon^{K-S}$	"Corrected" ($x = 2.38$)	CASPT2	TDDFT	OVGF	Exptl.
$\pi_{C\equiv As}$	7.42	9.8[b]	10.09	10.165[a]	9.82	**9.8**
n_{As}	9.75	12.13	12.16	12.69	13.07	**12.0**

[a] Value of ΔSCF. [b] Experimental value.

calculated to be more stable than the *E* one by only 0.18 kcal mol^{-1} and, that the IP calculated values are very close.

For the methylidynearsine **1**, the first band at 9.8 eV corresponds to the removal of one electron from the carbon–arsenic triple bond, and the second one at 12.0 eV to the arsenic lone pair ionization.

Quite good agreement between theoretical and experimental ionization potential data is thus observed for methylidynearsine **1** and chloromethylidenearsine **4**, but, for the second ionic state of compound **1**, TD-DFT (B3LYP/6-311G**) and OVGF calculations are less satisfactory than the CASPT2 and "corrected" method for these molecules.

The experimental and theoretical data for methylidynearsine **1**, emphasize an electronic similarity of arsenic and phosphorus triple-bonded to the carbon atom, a more diffuse character of the $\pi_{C\equiv As}$ orbital originating from the 2pπ–4pπ overlap and a weaker energy of this triple bond relative to the phosphorus analogue (2pπ–3pπ).[17] Moreover, the destabilization of the $\pi_{C\equiv As}$ compared to the $\pi_{C\equiv P}$ (0.99 eV) is slightly more important than the corresponding lone pair destabilization (0.86 eV, n_{As} *vs.* n_P). This observation can be explained as the compromise between a slightly smaller electronegativity of the arsenic atom compared to the phosphorus one, and an increasing s-character of the arsenic lone pair. In fact, this last value is close to the ionization potentials difference of atoms ($\Delta_{IP} = 0.69$ eV, $IP_P = 10.48$ eV; $IP_{As} = 9.79$ eV). The same order of magnitude of the two first ionic states separation in methylidynearsine **1** (2.0 eV) as observed previously for $HC\equiv P$ (2.07 eV) has to be remarked.

On the other hand, compounds **1** and **4** present a very high reactivity in the condensed phase and attempts to characterize these species diluted in a solvent by low temperature (−100 °C) ^1H NMR spectroscopy were unsuccessful. Only yellow-brown insoluble compounds were observed on heating the products condensed with a cosolvent (CD_2Cl_2–CCl_3F) on a cold finger (77 K) and that before the melting of solvents (≈ −100 °C). In similar experimental conditions, the NMR spectra of the much more kinetically stable methylidynephosphine were recorded with a sample diluted in deuterochloroform and cooled at −30 °C.[18]

In summary, the methylidynearsine has been synthesized by bisdehydrohalogenation of the dichloromethylarsine on solid sodium carbonate and its UV photoelectron and mass spectra have been recorded. The very high reactivity of this compound shows, once again, how challenging the synthesis of such compounds is. This approach to the third unsubstituted heteroalkyne characterized up to date paves the way to the preparation of various other arsaalkynes.

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Notes and references

1 The first synthesis of hydrogen cyanide, previously called "Berlin Blue acid", is reported in *History of cyanide*, N. Bunce and J. Hunt, http://www.physics.uoguelph.ca/summer/scor/articles/scor176.htm.

2 T. E. Gier, *J. Am. Chem. Soc.*, 1961, **83**, 1769–1770.

3 A. Chrostowska, V. Lemierre, A. Dargelos, J.-M. Sotiropoulos and J.-C. Guillemin, *Appl. Organomet. Chem.*, 2004, **18**, 690–693.

4 E. Kurita, H. Matsuura and K. Ohno, *Spectrochim. Acta, Part A*, 2004, **60**, 3013–3023.

5 O. Mo, M. Yanez, J.-C. Guillemin, El. H. Riague, J.-F. Gal, P.-C. Maria and C. Poliart, *Chem.–Eur. J.*, 2002, **8**, 4919–4924.

6 L. L. Lohr and A. C. Scheiner, *THEOCHEM*, 1984, **18**, 195–200.

7 G. Märkl and H. Sejpka, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 264–265.

8 J.-C. Guillemin, L. Lassalle, P. Dréan, G. Wlodarczak and J. Demaison, *J. Am. Chem. Soc.*, 1994, **116**, 8930–8936.

9 L. Lassalle, S. Legoupy and J.-C. Guillemin, *Inorg. Chem.*, 1995, **35**, 5694–5697.

10 D. Seyferth, J. S. Merola and R. S. Henderson, *Organometallics*, 1982, **1**, 859–866; P. B. Hitchcock, C. Jones and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1994, 2061–2062; M. Finze, E. Bernhardt, H. Willner and C. W. Lehmann, *Angew. Chem., Int. Ed.*, 2004, **43**, 4160–4163 and references therein.

11 For a review on the VGSR technique, see J.-M. Denis and A.-C. Gaumont, *Gas-Phase Reactions in Organic Synthesis*, Gordon & Breach Science Publishers, Amsterdam, 1997, pp. 195–235.

12 (*a*) R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218–8224; (*b*) M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys.*, 1998, **108**, 4439–4449.

13 (*a*) W. von Niessen, J. Schirmer and L. S. Cederbaum, *Comput. Phys. Rep.*, 1984, **1**, 57–125; (*b*) J. V. Ortiz, *J. Chem. Phys.*, 1988, **89**, 6348–6352.

14 *MOLCAS* Version 5, Lund University, Sweden, 2000.

15 (*a*) A. J. Arduengo, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Hermann, N. L. Jones, M. Wagner and R. West, *J. Am. Chem. Soc.*, 1994, **116**, 6641–6649; (*b*) H. Muchall, N. Werstiuk, J. Pitters and M. S. Workentin, *Tetrahedron*, 1999, **55**, 3767–3778; (*c*) H. Muchall, N. Werstiuk, B. Choudury, J. Ma, M. S. Workentin and J. Pezacki, *Can. J. Chem.*, 1998, **76**, 238–240; (*d*) H. Muchall, N. Werstiuk and B. Choudury, *Can. J. Chem.*, 1998, **76**, 221–227; (*e*) H. Muchall and P. Rademacher, *J. Mol. Struct.*, 1998, **471**, 189–194.

16 A. Chrostowska, A. Dargelos, V. Lemierre, J.-M. Sotiropoulos, P. Guenot and J.-C. Guillemin, *Angew. Chem., Int. Ed.*, 2004, **43**, 873–875.

17 D. C. Frost, S. T. Lee and C. A. McDowell, *Chem. Phys. Lett.*, 1973, **23**, 472–475.

18 J.-C. Guillemin, T. Janati, P. Guenot, P. Savignac and J.-M. Denis, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 196–198; J.-C. Guillemin, T. Janati and J.-M. Denis, *J. Org. Chem.*, 2001, **66**, 7864–7868.