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New routes to diarsenes and arsaphosphenes involving fluorinated arsines

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Abstract

The stable diarsene ArAs=AsAr (**1**) and arsaphosphene ArAs=PAr (**6**) (Ar = 2,4,6-tri-*tert*-butylphenyl) have been synthesized in excellent yields from the difluoroarsine $ArAsF_2$ by reaction with $ArAs(Li)SiMe_3$ (for **1**) and with ArP(H)Li followed by *t*-BuLi (for **6**). Compound **1**, previously prepared by other routes, as well as the new compound **6** were characterized by single-crystal X-ray diffraction (*d*(As=As) 2.2634(3) Å, *d*(P=As) 2.141(5) Å). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diarsene; Arsaphosphene; Fluorinated arsines; Fluoroarsinylphosphine

1. Introduction

Considerable interest has been directed toward the synthesis of doubly bonded derivatives of Group 15 elements during the last two decades; various derivatives of the type –E=E′– (E, E′ = P, As, Sb, Bi) have been synthesized [1].

The three main methods which have been used for the preparation of diarsenes –As=As– or arsaphosphenes –As=P– are dechlorination reactions by lithium compounds [2], magnesium or potassium [3] (route a), dehydrochlorination reactions with DBU [4] or lithium compounds [5] (route b) and dechlorosilylation reactions involving disilylphosphines or disilylarsines [6] or lithium silylphosphides [4a,7] (route c) (Scheme 1).

The yields in diarsenes and arsaphosphenes reported in the literature vary from 7 to 72%. One problem is in some cases the formation of by-products due to the alkylation or the reduction of phosphorus or arsenic precursors.

We present here a new method of synthesis of diarsene and arsaphosphene using fluoroarsines. We have substituted phosphorus and arsenic by the 2,4,6-tri-*tert*-butylphenyl group, previously used for stabilization of the first diphosphene by Yoshifuji [8], in order to establish a comparison between structural data within a complete series of diphosphene, arsaphosphene and diarsene substituted by the same group on phosphorus and arsenic.

2. Results and discussion

2.1. Diarsene 1

The bis(2,4,6-tri-*tert*-butylphenyl)diarsene (**1**) is synthesized by reaction between the difluoroarsine **2** [9] and the lithium silylarsinide **3**. The intermediate **4** cannot be isolated, immediately losing fluorotrimethylsilane to lead to the diarsene **1** in an excellent yield of 75% (Scheme 2).

It is not necessary to isolate **3** which is prepared by successive addition of butyllithium, chlorotrimethylsilane and butyllithium to the arsine **5**. Thus, the reaction can be performed in one pot from the arsine **5**. **1** has been obtained previously by Weber by reaction of $ArAsCl_2$ and magnesium (61% yield) [3a], and as a by-product in the reaction between $ArAsCl_2$ and $C_5Me_5(CO)_2FeAs(SiMe_3)_2$ (10% yield) [6b,6c].

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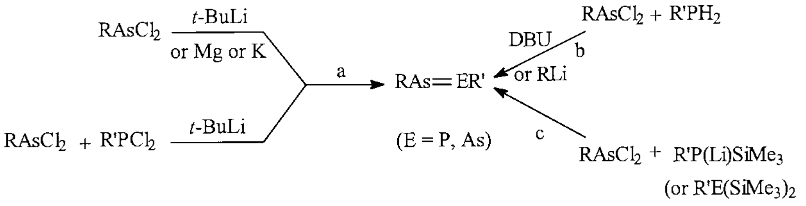


Scheme 1.

2.2. Arsaphosphene **6**

The bis(2,4,6-tri-*tert*-butylphenyl)arsaphosphene (**6**) has been synthesized by a two step dehydrofluorination reaction involving the intermediate formation of the fluoroarsinylphosphine **7** in nearly quantitative yield from the difluoroarsine **2** and the lithium phosphide **8**. **7** was obtained in the form of two diastereoisomers which present rather close ^{31}P and ^{19}F chemical shifts (**7a**, 85%; δ^{31}P -30.5, δ^{19}F -126.4 ppm, ${}^{1}J_{PH}$ 218.1 Hz; **7b**, 15%; δ^{31}P -43.7, δ^{19}F -113.4 ppm, ${}^{1}J_{PH}$ 211.6 Hz) but very different ${}^{2}J_{PF}$ (**7a** 89.0 Hz, **7b** 34.6 Hz).

Addition of *tert*-butyllithium to **7** in pentane afforded the arsaphosphene **6** (Scheme 3).

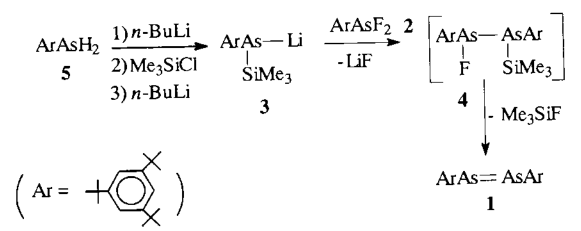
Arsaphosphene **6** can be obtained directly from **2** and **8** without isolation of **7**. It displays a ^{31}P signal at 524.5 ppm, in the expected field for such a derivative (generally from 520 to 670 ppm [1c,10]).

Orange and orange–red crystals of diarsene **1** and arsaphosphene **6** are thermally stable and can be handled in air without decomposition.

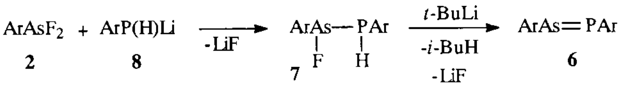
2.3. X-ray structure analysis of **1** (Fig. 1) and **6** (Fig. 2)

Four diarsenes have been characterized by X-ray analysis [2b,3b,4c]. They featured As=As distances between 2.224(3) [4c] and 2.285(3) Å [3b]. The As=As bond length of **1** (2.2634(3) Å) is in the middle of the range. The shortening in relation to the standard As–As single bond (2.34–2.45 Å) is about 8%.

The As–P double-bond length of **6** (2.141(5) Å) is also close to the As–P distance reported for the two arsaphosphenes previously structurally characterized (2.124(2) Å in $(Me_3Si)_2CH{-}As{=}PAr$ [4b] and 2.134 (2) Å in $2,6\text{-}Trip_2C_6H_3As{=}PMes$ (Trip = $2,4,6\text{-}i\text{Pr}_3C_6H_2$) [5]). The shortening is about 8.5% in relation to the standard As–P bond (2.33 Å), roughly halfway between diarsenes (~8%) and diphosphenes (generally 9–9.5%). The synthesis of a complete homologous series of ArE=E′Ar derivatives (E, E′ = P, As) allows comparison of their structural data and determination of their most significant features (Table 1). The AsP double-bond length is exactly midway between the values found for As–As and P–P double bonds. A decrease is observed in the C–E–E′ bond angle from



Scheme 2.



Scheme 3.

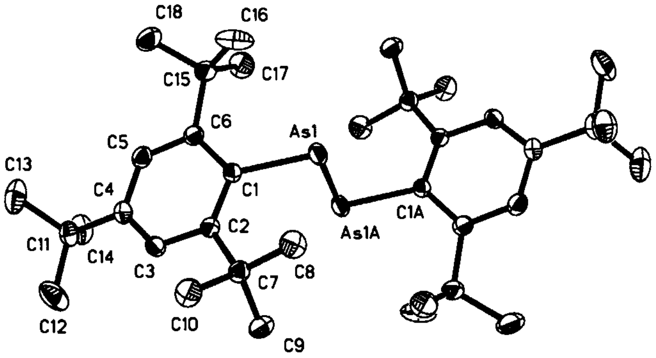


Fig. 1. Molecular structure of **1**. The thermal ellipsoids are drawn at 50% probability.

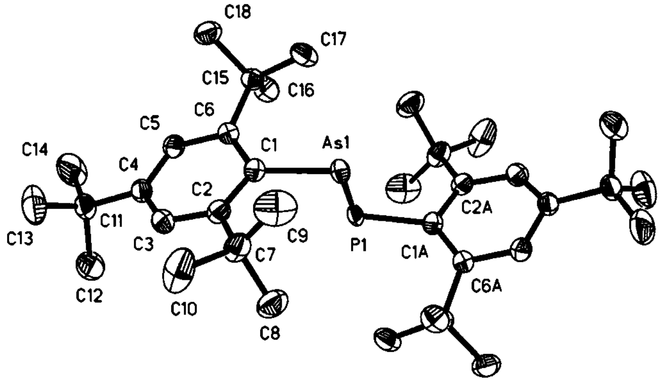


Fig. 2. Molecular structure of **6**. The thermal ellipsoids are drawn at 50% probability.

Table 1
Selected bond lengths, bond angles and torsion angles for **1**, **6** and ArP=PAr [8]

ArAs=AsAr (**1**)		ArP=AsAr (**6**)		ArP=PAr	
As=As	2.2634(3)	P=As	2.141(5)	P=P	2.034(2)
$\mathrm{AsC_1}$	2.0006(12)	$\mathrm{P{-}C_{1A}}$	1.893(4)	$\mathrm{P{-}C_1}$	1.862(2)
		$\mathrm{As{-}C_1}$	1.9976(10)		
$\mathrm{C_1AsAs_A}$	97.46(3)	$\mathrm{C_1AsP}$	98.59(9)	$\mathrm{C_1{-}P{-}P_A}$	102.8(1)
$\mathrm{AsC_1C_6}$	119.49(8)	$\mathrm{C_{1A}PAs}$	100.8(3)		
$\mathrm{AsC_1C_2}$	121.32(9)	$\mathrm{AsC_1C_2}$	120.89(12)		
		$\mathrm{AsC_1C_6}$	120.35(12)		
		$\mathrm{PC_{1A}C_{2A}}$	116.5(3)		
		$\mathrm{PC_{1A}C_{6A}}$	124.3(3)		
$\mathrm{C_1AsAs_AC_{1A}}$	180.0	$\mathrm{C_1AsPC_{1A}}$	175.2(4)	$\mathrm{C_1PP_AC_{1A}}$	172.2(1)

102.8(1)° (CPP in ArP=PAr [8]) to 100.8(3)° and 98.59(9)° (CPAs and CAsP in **6**) and 97.46(3)° (CAsAs in **1**) reflecting as expected the increasing p character of the σ and π bonding and s character of the lone pair. By contrast, the torsion angle CEE′C′ increases from diphosphene (172.2(1)°) [8], to arsaphosphene (175.2(4)°) and to diarsene (180.0°). A similar trend has been reported in a series of diphosphene, diarsene, distibene and dibismuthene [3b]. As expected, all of them are in a *E* configuration.

3. Experimental

All reactions were carried out under nitrogen or argon with carefully dried solvents. NMR spectra (^{1}H, ^{13}C, ^{19}F (CF_3COOH), ^{31}P (H_3PO_4)) were recorded on Bruker AC 80 and AC 200 respectively at 80.130, 50.323, 188.298 and 81.015 MHz; mass spectra were obtained from a Hewlett–Packard HP 5989 spectrometer in the electron-impact mode (70 eV). Melting points (m.p.) were measured on a Leitz microscope.

*3.1. Preparation of diarsene **1***

To $ArAsH_2$ (1.10 g, 3.41 mmol) in 15 ml of THF at −78°C was added dropwise a solution of *n*-BuLi in hexane (2.34 ml, 3.74 mmol, 1.6 M). The reaction mixture turned green. After 45 min at this temperature, 0.47 ml (3.78 mmol) of Me_3SiCl was added giving a yellow solution. THF and hexane were evaporated in vacuo and replaced by 15 ml of THF. To this solution cooled at −78°C were added 2.24 ml (3.58 mmol) of a solution of *n*-BuLi in hexane. The reaction mixture was then transferred via cannula to a solution of $ArAsF_2$ (1.23 g, 3.44 mmol) in THF (10 ml) at −78°C giving an orange suspension. The solvents were removed in vacuo and the residue was dissolved in pentane; inorganic salts were filtered out and the filtrate was concentrated. Recrystallization from pentane gave 1.01 g (77%) of **1**; m.p. 174°C. ^{1}H-NMR ($CDCl_3$): δ_{ppm} 1.36 (s, 18H, *p*-*t*-Bu); 1.41 (s, 36H, *o*-*t*-Bu); 7.43 (s, 4H, arom H). ^{13}C-NMR ($CDCl_3$): δ_{ppm} 31.5 (*p*-C(CH$_3$)$_3$); 34.2 (*o*-C(CH$_3$)$_3$); 34.8 (*p*-C(CH$_3$)$_3$); 39.1 (*o*-C(CH$_3$)$_3$); 122.4 (*m*-CH); 141.9 (*ipso*-C); 148.8 (*p*-C); 154.5 (*o*-C). MS (EI, *m*/*z*;%): 640, (1) [M$^+$]; 584, (2) [M − *t*-Bu + 1]; 395, (1) [ArAs=As]; 319, (22) [ArAs − 1]; 57, (100) [*t*-Bu].

*3.2. Synthesis of fluroarsinylphosphine **7***

A solution of *n*-BuLi in hexane (1.58 ml, 2.53 mmol, 1.6 M) was added to $ArPH_2$ (0.64 g, 2.30 mmol) in 10 ml of THF under stirring at −78°C. The solution became brown and was transferred to a solution of $ArAsF_2$ (0.8 g, 2.30 mmol) in THF (15 ml) at −78°C. Then the reaction mixture was warmed to room temperature and solvents were removed in vacuo. The residue was dissolved in pentane and LiF was filtered out; ^{31}P and ^{19}F-NMR analysis showed the formation of two diastereoisomers in the ratio 85:15. Only the major one could be obtained in pure form by recrystallization from pentane as pale yellow crystals (0.51 g, 36%); m.p. 141°C. ^{1}H-NMR: δ_{ppm} 1.26–1.36 (m, 54H, *p*- and *o*-*t*-Bu (ArP and ArAs)); 5.03 (dd, $^1J_{PH}$ 217.2 Hz, $^3J_{HF}$ 3.0 Hz, 1H, PH); 7.25 (d, $^4J_{PH}$ 2.3 Hz, 2H, arom H (ArP)); 7.36 (s, 2H, arom H (ArAs)). ^{31}P-NMR: δ_{ppm} −30.5 (dd, $^1J_{PH}$ 218.1 Hz, $^2J_{PF}$ 89.0 Hz); ^{19}F-NMR: δ_{ppm} −126.5 (d, $^2J_{PF}$ 89.0 Hz); ^{13}C-NMR: δ_{ppm} 31.4, 31.7 (*p*-C(CH$_3$)$_3$ (ArP and ArAs)); 33.9 (broad s, *o*-C(CH$_3$)$_3$ (ArP and ArAs)); 34.7, 35.0 (*p*-C(CH$_3$)$_3$ (ArP and ArAs)); 38.0 (*o*-C(CH$_3$)$_3$ (ArP and ArAs)); 122.8, 123.8 (*m*-C (ArP and ArAs)); 150.0, 150.8 (*p*-C (ArP and ArAs)); 154.6, 154.9 (*o*-C (ArP and ArAs)). MS (EI, *m*/*z*,%): 616, (1) [M$^+$]; 339, (2) [ArAsF]; 319, (6) [ArAs − 1]; 277, (18) [ArPH]; 275, (12) [ArP − 1], 264, (15) [ArAs − *t*-Bu + 1], 208, (32) [ArAs − 2*t*-Bu + 2]; 57, (100) [*t*-Bu].

3.3. Preparation of arsaphosphene **6**

To a solution of **7** (0.5 g, 0.80 mmol) in pentane (10 ml) cooled at −78°C, was added a solution of one equivalent of *t*-BuLi in pentane (0.47 ml, 1.7 M). The reaction mixture became red and then was slowly warmed to room temperature; the solvent was evaporated in vacuo, LiF was filtered out and the residue was extracted with 15 ml of pentane. **6** crystallized in the form of orange red crystals (0.35 g, 75%); m.p. 173°C. ^{1}H-NMR: δ_{ppm} 1.36 (s, 18H, *p*-*t*-Bu (ArAs and ArP)); 1.43, 1.45 (2s, 2 × 18H, *o*-*t*-Bu (ArAs and ArP)); 7.39 (d, $^4J_{PH}$ 1.1 Hz, 2H, arom H (ArP)); 7.44 (s, 2H, arom H (ArAs)). ^{31}P-NMR: δ_{ppm} 524.5. ^{13}C-NMR: δ_{ppm} 31.5 (*p*-C(CH_3)$_3$ (ArP and ArAs)); 34.1 (d, $^4J_{CP}$ 3.6 Hz, *o*-C(CH_3)$_3$ (ArP)); 34.4 (*o*-C(CH_3)$_3$ (ArAs)); 34.7 (*p*-*C*(CH_3)$_3$ (ArP and ArAs)); 38.7, 39.0 (*o*-*C*(CH_3)$_3$ (ArP and ArAs)); 122.1, 122.6 (*m*-C (ArP and ArAs)); 148.7, 148.9 (*p*-C (ArP and ArAs)); 153.8 (*o*-C (ArAs)); 154.6 (d, $^2J_{CP}$ 5.9 Hz, *o*-C (ArP)); MS (EI, *m*/*z*, %): 596, (6) [M$^+$]; 539, (1) [M − *t*-Bu]; 319, (6) [ArAs − 1]; 208, (32) [ArAs − 2*t*-Bu + 2]; 57, (100) [*t*-Bu].

Table 2
Crystal data and structure refinement for **1** and **6**

Empirical formula	$C_{36}H_{58}As_2$ (**1**)	$C_{36}H_{58}AsP$ (**6**)
Formula weight	640.66	596.72
Temperature (K)	193(2)	193(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	9.9082(2)	9.9274(2)
b (Å)	10.1943(2)	10.2828(2)
c (Å)	10.6758(2)	10.5872(2)
α (°)	94.5880(10)	93.9980(10)
β (°)	109.1560(10)	109.0350(10)
δ (°)	116.9730(10)	117.6710(10)
Volume (Å^3), *Z*	873.64(3), 1	872.66(3), 1
Density (calculated) (Mg m^{-3})	1.218	1.135
Absorption coefficient (mm^{-1})	1.933	1.041
F(000)	340	322
Crystal size (mm)	0.6 × 0.5 × 0.1	0.3 × 0.5 × 0.6
θ range for data collection (°)	2.10–30.51	2.11–31.05
Limiting indices	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $-15 \leq l \leq 15$	$-14 \leq h \leq 13$ $-14 \leq k \leq 14$ $-14 \leq l \leq 15$
Reflections collected	15792	13216
Independent reflections	5298 ($R_{int} = 0.0257$)	4960 ($R_{int} = 0.0282$)
Completeness to θ = 30.51° (%)	99.4	88.7
Absorption correction	Semi-empirical	None
Max. and min. transmission	1.000000 and 0.781077	
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5298/0/181	4960/54/190
Goodness-of-fit on F^2	0.978	1.079
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0257$, $wR_2 = 0.0644$	$R_1 = 0.0318$, $wR_2 = 0.0878$
R indices (all data)	$R_1 = 0.0319$, $wR_2 = 0.0663$	$R_1 = 0.0372$, $wR_2 = 0.0900$
Largest difference peak and hole (e Å^{-3})	0.742 and −0.251	0.393 and −0.233

3.4. X-ray data collection and structure refinement

Crystal data for **1** and **6** are presented in Table 2. All data were collected at low temperature on a Bruker-AXS CCD 1000 diffractometer with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods by means of SHELXS-97 [11] and refined with all data on F^2 by means of SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. The inversion centre between the P and the As atoms in **6** leads to a disorder, which has been refined with the help of ADP and distance restraints with an occupancy of 0.5 for each atom by ignoring the symmetry (PART-1).

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC nos. 145883 (**1**) and 145884 (**6**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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