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Communications

From the New Arsaalkene ArAs=C(Br)SiMe$_3$ to the First Stable Arsaallene, ArAs=C=CR$_2$ (Ar = 2,4,6-Tri-*tert*-butylphenyl, CR$_2$ = Fluorenylidene)

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Summary: The first stable arsaallene, ArAs=C=CR$_2$ **1** *(Ar = 2,4,6-tri-tert-butylphenyl, CR$_2$ = fluorenylidene), has been synthesized by a one-pot procedure involving the successive addition of n-butyllithium and fluorenone to the new arsaalkene ArAs=C(Br)SiMe$_3$, which presents a Z configuration and a short As=C bond length (1.789(3) Å). An X-ray crystallographic structure determination of air and thermally stable* **1** *proves its allenic geometry (AsC(1)C(2) bond angle 169.72(19)°, angle between the fluorenylidene plane and the C(15)AsC(1)C(2) mean plane 79.3°) with very short As=C(1) and C(1)=C(2) double-bond lengths (1.754(2) and 1.314(3) Å).*

Over the last 20 years very intense research has been devoted to low-coordinate species of the group 15 elements, particularly those with a $\lambda^3\sigma^2$ phosphorus atom such as −P=X (X = group 14 and 15 elements). The phosphaalkenes −P=C< have been particularly well-studied, and many of them have been synthesized.[1] More recently, various types of phosphaallenes or phosphacumulenes −P=C=X (X = CR$_2$, NR, PR, O, S, C=PR, C=CR$_2$)[1c,2] have also been prepared. In contrast, arsenic analogues are less well-known. Such a difference between phosphorus and arsenic is, of course, due to many factors, particularly the lack of arsenic NMR, which requires the isolation of pure compounds for their analysis, whereas ^{31}P NMR is a powerful tool that allows the determination of structures in complex mixtures. Thus, only a few arsaalkenes −As=C< have been prepared[3] and, very recently, some *C*-haloarsaalkenes have been obtained.[4−6] Only two stable allenic derivatives of arsenic, the arsaphosphaallene ArP=C=AsAr (Ar = 2,4,6-tri-*tert*-butylphenyl)[5] and the diarsaallene ArAs=C=AsAr,[6] have been reported. Two transient allenic or cumulenic species have been postulated: the arsaallene HAs=C=CH$_2$[7] and the arsabutatriene TsiAs=C=C=CPh$_2$ (Tsi = (Me$_3$Si)$_3$C).[8]

We describe here the synthesis of the first arsaallene, monomeric ArAs=C=CR$_2$ (**1**), in a one-pot procedure from the new arsaalkene ArAs=C(Br)SiMe$_3$ (**4**).

Arsenic is substituted by the well-known stabilizing supermesityl group (Ar = 2,4,6-tri-*tert*-butylphenyl);[9] the terminal carbon atom of the allenic structure is included in a fluorenylidene group chosen for its ability to favor crystallization and to stabilize low-coordinate compounds such as phosphaalkenes due to its steric hindrance.[10]

With the arsaalkene **3** as starting material, prepared as previously described,[4] the new arsaalkene **4**[11] was obtained by successive reaction with *n*-butyllithium and chlorotrimethylsilane (Scheme 1).

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[1] (a) For reviews see: Lochschmidt, S.; Schmidpeter, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1986**, *29*, 73. (b) Appel, R.; Knoll, F. *Adv. Inorg. Chem.* **1989**, *33*, 259. (c) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 1990; p 157. (d) Markovskii, L. N.; Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019. (e) Weber, L. *Eur. J. Inorg. Chem.* **2000**, 2425.

[2] For a review, see: Escudié, J.; Ranaivonjatovo, H.; Rigon, L. *Chem. Rev.* **2000**, *100*, 3639.

[3] For a review, see: Weber, L. *Chem. Ber.* **1996**, *129*, 367.

[4] Ramdane, H.; Ranaivonjatovo, H.; Escudié, J.; Knouzi, N. *Organometallics* **1996**, *15*, 2683.

[5] Ranaivonjatovo, H.; Ramdane, H.; Gornitzka, H.; Escudié, J.; Satgé, J. *Organometallics* **1998**, *17*, 1631.

[6] Bouslikhane, M.; Gornitzka, H.; Escudié, J.; Ranaivonjatovo, H.; Ramdane, H. *J. Am. Chem. Soc.* **2000**, *122*, 12880.

[7] HAs=C=CH$_2$ has been postulated as an intermediate in the heating of alkynylarsane H$_2$AsC≡CH on solid sodium carbonate (VGSR conditions) to afford the arsaalkyne As≡CMe (Guillemin, J. C.; Lassale; L.; Dréan, P.; Wlodarczak, G.; Demaison, J. *J. Am. Chem. Soc.* **1994**, *116*, 8930). However, in contrast to the case of its phosphorus analogue (Guillemin, J. C.; Janati, T.; Denis, J.-M. *J. Chem. Soc., Chem. Commun.* **1992**, 415. Guillemin, J. C.; Janati, T.; Denis, J.-M.; Guénot, P.; Savignac, P. *Tetrahedron Lett.* **1994**, *35*, 245), attempts to characterize it have been unsuccessful.

[8] Märkl, G.; Reithinger, S. *Tetrahedron Lett.* **1990**, *31*, 6331.

[9] Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

[10] (a) Yoshifuji, M.; Takahashi, H.; Shimura, K.; Toyota, K.; Hirotsu, K.; Okada, K. *Heteroat. Chem.* **1997**, *8*, 375. (b) Van der Knaap, T. A.; Bickelhaupt, F. *Chem. Ber.* **1984**, *117*, 915. (c) Chentit, M.; Sidorenkova, H.; Choua, S.; Geoffroy, M.; Ellinger, Y.; Bernardinelli, G. *J. Organomet. Chem.* **2001**, *634*, 136.

[11] A 1.6 M solution of *n*-BuLi in hexanes (1.2 mL, 1.92 mmol) was added under N$_2$ to a solution of **3** (0.90 g, 1.83 mmol) in Et$_2$O (10 mL) at −90 °C. After 30 min, 0.25 mL (1.97 mmol) of Me$_3$SiCl was added to the orange solution of ArAs=C(Br)Li. After removal of Et$_2$O and hexanes in vacuo from the brown solution, 25 mL of pentane was added, and LiCl was filtered out. Recrystallization of the residue from pentane gave 0.68 g (76%) of yellow crystals of **4**. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.28 (s, 9 H, SiMe$_3$), 1.35 (s, 9 H, *p*-*t*-Bu), 1.44 (s, 18 H, *o*-*t*-Bu), 7.44 (s, 2 H, arom H). ^{13}C NMR (CDCl$_3$, 62.896 MHz): δ −0.6 (SiMe$_3$), 32.5 (*p*-C(*C*H$_3$)$_3$), 33.9 (*o*-C(*C*H$_3$)$_3$), 35.1 (*p*-*C*(CH$_3$)$_3$), 38.1 (*o*-*C*(CH$_3$)$_3$), 122.2 (*m*-C of Ar), 145.9 (ipso C of Ar), 149.9 (*p*-C of Ar), 152.7 (*o*-C of Ar), 187.4 (As=C). MS (EI/70 eV; *m*/*z*): 484 (M, 3), 405 (M − Br, 1), 319 (ArAs − 1, 100), 276 (ArAs=C − isobutene, 8), 263 (ArAs − *t*-Bu, 21), 57 (*t*-Bu, 81). Anal. Calcd for C$_{22}$H$_{38}$AsBrSi: C, 54.43; H, 7.89. Found: C, 54.30; H, 7.93.

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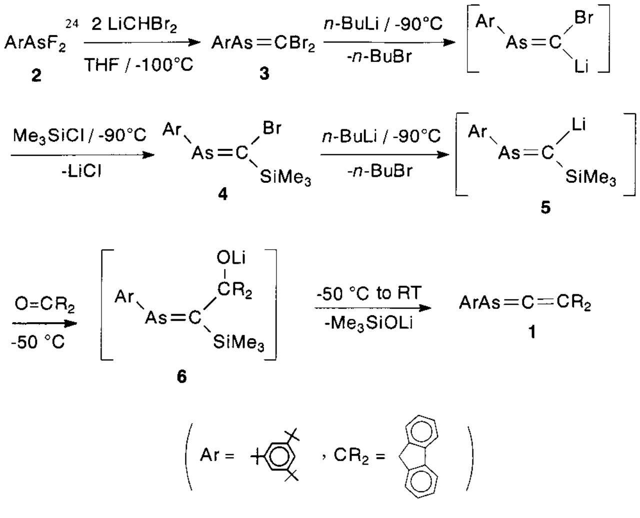
Scheme 1



Only the *Z* stereoisomer **4** was obtained, in agreement with the expected mechanism of the reaction involving, in our case, the Br/Li exchange from the less hindered site,[12] i.e., the *E* bromine atom; such a stereochemistry has previously been reported in phosphorus analogues[13] and was proved for **4** by an X-ray structure determination (Figure 1).[14-17] **4** has a short As═C(1) bond (1.789(3) Å) (shortening of 10% in comparison to the AsC(2) single bond (1.971(4) Å)). Slightly longer As═C bond lengths have been observed in the acyclic arsaalkenes −As═C< substituted by alkyl or aryl groups (generally 1.79−1.83 Å and up to 1.876 Å).[18]

The air-stable **4** can be functionalized by means of Li/Br exchange, as shown in Scheme 1. Reaction of the intermediate organolithium reagent **5** with fluorenone is followed by a Peterson elimination of Me_3SiOLi to give the arsaallene **1**[19] in nearly quantitative yield (Scheme 1).

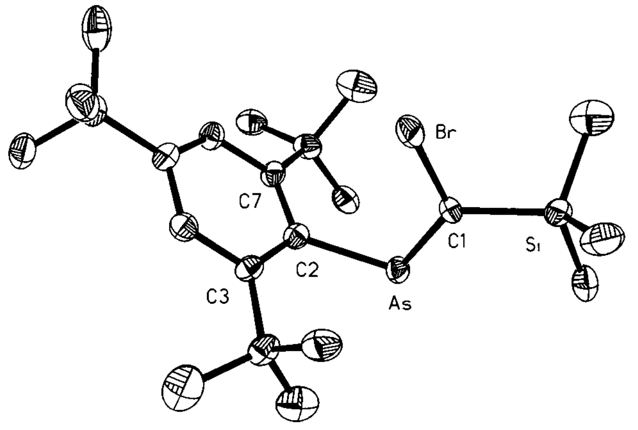


Figure 1. Solid-state structure of **4** (ellipsoids are drawn at the 50% probability level). Selected bond lengths (Å) bond angles and torsion angles (deg): AsC(1) = 1.789(3), AsC(2) = 1.971(3), C(1)Si = 1.873(4), C(1)Br = 1.906(3); C(1)AsC(2) = 100.97(14), AsC(1)Si = 122.12(18), AsC(1)-Br = 125.83(19), BrC(1)Si = 111.94(17), C(2)AsC(1)Br = 1.3, C(2)AsC(1)Si = −177.5, C(1)AsC(2)C(3) = −86.8, C(1)-AsC(2)C(7) = 81.4, angle between AsC(1)BrSi and Ar mean planes 93.6.

The intermediates in the reaction are most likely the arsaalkenes **5** and **6**. The elimination of Me_3SiOLi from **6** occurs spontaneously on warming the reaction mixture to room temperature. In phosphorus chemistry, a similar Peterson-type reaction was used for the synthesis of phosphaallenes $ArP{=}C{=}CR_2$[10c] and $ArP{=}C{=}C(Ph)R'$ ($R' = H$, Me).[20]

The arsaallene **1** is remarkably stable toward air and moisture. Colorless crystals were recovered unchanged after they had been kept for some days in air at room temperature. The allenic structure of **1** was easily confirmed by ^{13}C NMR spectroscopy, with a signal at 255.8 ppm due to the sp-hybridized carbon atom. Such a low-field shift is characteristic of this type of allenic structure: for example, 233.44 ppm in $ArP{=}C{=}CR_2$[10c] and 237.6 ppm in $ArP{=}C{=}CPh_2$[21] and more generally from 233 to 247 ppm.[1c,2] Carbon 2 (see the numbering in Figure 2) of the fluorenylidene group (129.1 ppm) lies also in the expected range (128.1 and 128.3 ppm in $ArP{=}C{=}CR_2$[10c] and $ArP{=}C{=}CPh_2$,[21] respectively).

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[12] Br/Li exchange from the less hindered site does not always occur since, depending on the experimental conditions and on the structure of the reagent, mixtures of *Z* and *E* isomers are sometimes obtained. (a) Köbrich, G.; Ansari, F. *Chem. Ber.* **1967**, *100*, 2011. (b) Oku, A.; Harada, T.; Hattori, K.; Nozaki, Y.; Yamaura, Y. *J. Org. Chem.* **1988**, *53*, 3089. (c) Harada, T.; Katsuhira, T.; Oku, A. *J. Org. Chem.* **1992**, *57*, 5805. (d) Grandjean, D.; Pale, P. *Tetrahedron Lett.* **1993**, *34*, 1155.

[13] (a) Goede, S. J.; Bickelhaupt, F. *Chem. Ber.* **1991**, *124*, 2677. (b) Yoshifuji, M.; Kawanami, H.; Kawai, Y.; Toyota, K.; Yasunami, M.; Niitsu, T.; Inamoto, N. *Chem. Lett.* **1992**, 1053. (c) Van der Sluis, M.; Wit, J. B. M.; Bickelhaupt, F. *Organometallics* **1996**, *15*, 174. (d) Ito, S.; Toyota, K.; Yoshifuji, M. *Chem. Commun.* **1997**, 1637. (e) Niecke, E.; Nieger, M.; Schmidt, O.; Gudat, D.; Schoeller, W. W. *J. Am. Chem. Soc.* **1999**, *121*, 519.

[14] Crystal data for **1** and **4** are as follows. **1**: $C_{32}H_{37}As$, $M_r = 496.54$, monoclinic, $P2_1/n$, $a = 10.0510(6)$ Å, $b = 20.3953(12)$ Å, $c = 13.4192(7)$ Å, $\beta = 107.380(1)°$, $V = 2625.3(3)$ Å^3, $Z = 4$, $\rho_c = 1.256$ Mg m^{-3}, $F(000) = 1048$, $\lambda = 0.710\,73$ Å, $T = 193(2)$ K, μ(Mo Kα) = 1.312 mm^{-1}, crystal size 0.1 × 0.3 × 0.4 mm^3, $1.88° \le \theta \le 26.37°$, 19 834 reflections (5372 independent, $R_{int} = 0.0503$), $T_{min} = 0.833\,509$, $T_{max} = 1.0$, 307 parameters, R1($I > 2\sigma$(I)) = 0.0354, wR2(all data) = 0.0787, largest electron density residue 0.428 e Å^{-3}. **4**: $C_{22}H_{38}AsBrSi$, $M_r = 485.44$, monoclinic, $P2_1/c$, $a = 9.6357(19)$ Å, $b = 12.498(3)$ Å, $c = 20.452(4)$ Å, $\beta = 94.640(3)°$, $V = 2455.0(8)$ Å^3, $Z = 4$, $\rho_c = 1.313$ Mg m^{-3}, $F(000) = 1008$, $\lambda = 0.710\,73$ Å, $T = 193(2)$ K, μ(Mo Kα) = 3.064 mm^{-1}, crystal size 0.05 × 0.1 × 0.3 mm^3, $1.91° \le \theta \le 24.71°$, 14 860 reflections (4186 independent, $R_{int} = 0.0931$), $T_{min} = 0.571\,648$, $T_{max} = 1.0$, 238 parameters, R1($I > 2\sigma(I)$) = 0.0417, wR2(all data) = 0.1038, largest electron density residue 0.431 e Å^{-3}. Data for both structures were collected at low temperature using oil-coated shock-cooled crystals on a Bruker-AXS CCD 1000 diffractometer. Semiempirical absorption corrections were employed.[15] The structures were solved by direct methods (SHELXS-97)[16] and refined using the least-squares method on F^2.[17] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$.

[15] SADABS, Program for data correction; Bruker-AXS.

[16] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[17] Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

[18] Power, P. P. *Chem. Rev.* **1999**, *99*, 3465.

[19] To a solution of **4** (0.88 g, 1.81 mmol) in THF cooled to −90 °C was added 1 equiv of a 1.6 M solution of *n*-BuLi in hexanes; then a solution of fluorenone (0.32 g, 1.78 mmol) was added at −50 °C. The reaction mixture became dark green. After removal of THF in vacuo, 30 mL of pentane was added and LiF was filtered. Recrystallization from pentane gave colorless crystals of **1** (0.74 g, 82%, mp 116−120 °C dec). ^1H NMR ($CDCl_3$, 250 MHz): δ 1.31 (s, 9 H, *p-t*-Bu), 1.76 (s, 18 H, *o-t*-Bu), 7.25 and 7.31 (2 dt, 2 × 2 H, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.2$ Hz, H on C(5)C(12) and C(6)C(11) (see numbering in Figure 2)), 7.47 (s, 2 H, arom H of Ar), 7.66 and 7.67 (2 dd, 2 × 2 H, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.2$ Hz, H on C(4)C(13) and C(7)C(10)). ^{13}C NMR ($CDCl_3$, 62.896 MHz): δ 31.3 (*p*-C(CH$_3$)$_3$), 34.7 (*o*-C(CH$_3$)$_3$), 34.9 (*p*-C(CH$_3$)$_3$), 38.5 (*o*-C(CH$_3$)$_3$), 119.9 (C(7)C(10)), 122.7 (*m*-C of Ar), 124.9 (C(4)C(13)), 126.9 and 128.3 (C(5)C(6)C(11)C(12)), 129.1 (C═CR$_2$), 133.7 (ipso-C of Ar), 137.3 and 138.5 (C(3)C(8)C(9)C(14)), 149.8 (*p*-C of Ar), 154.4 (*o*-C of Ar), 255.8 (═C═). MS (EI/70 eV; *m*/*z*): 496 (M, 1), 439 (M − *t*-Bu, 1), 383 (M − *t*-Bu − isobutene, 5), 319 (ArAs − 1, 6), 251 (M − Ar, 21), 176 (C═CR$_2$, 11), 57 (*t*-Bu, 100). Anal. Calcd for $C_{32}H_{37}As$: C, 77.40; H, 7.51. Found: C, 77.21; H, 7.66.

[20] Yoshifuji, M.; Sasaki, S.; Inamoto, N. *Tetrahedron Lett.* **1989**, *30*, 839.

[21] Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809.

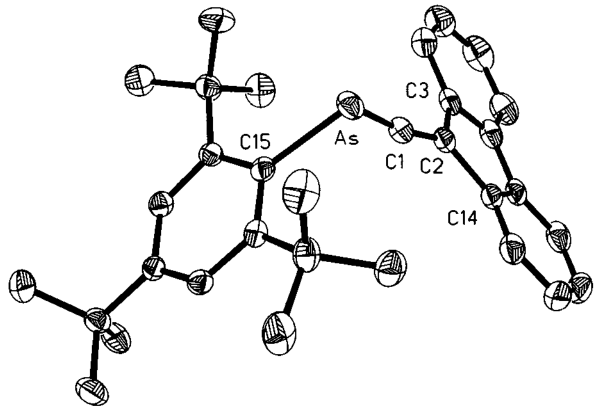

Figure 2. Solid-state structure of **1** (ellipsoids are drawn at the 50% probability level). Selected bond lengths (Å) bond angles and torsion angles (deg): AsC(1) = 1.754(2), C(1)C(2) = 1.314(3), C(2)C(3) = 1.489(3), C(2)C(14) = 1.485(3), AsC(15) = 1.996(2); AsC(1)C(2) = 169.72(19), C(1)AsC(15) = 101.94(9), C(1)C(2)C(3) = 127.8(2), C(1)C(2)C(14) = 127.0(2), C(15)AsC(1)C(2) = 176.

The X-ray structure of $\mathbf{1}^{14-17}$ is shown in Figure 2. The main features are the AsC(1)C(2) bond angle (169.7(2)°),[22] which is rather close to the ideal 180°, and the angle between the fluorenylidene plane and the C(15)AsC(1)C(2) mean plane (79.3°), which proves the heteroallene bonding system. **1** contains a very short As=C(1) bond (1.754(2) Å), comparable to that observed in the diarsaallene ArAs=C=AsAr (1.758(2) Å).[6] The shortening in comparison to the As=C bond of its precursor **4** (0.035 Å) is partly due to the smaller bond radius of the sp-hybridized carbon atom in **1** instead of a sp^2-hybridized carbon in **4**. A shortening of about 11% is observed in comparison with the As−C(15) single bond (1.996(2) Å), which lies in the normal range for such a bond (generally 1.97−2.00 Å).[3] The C(1)C(2) bond length (1.314(3) Å) lies also in the normal range.[23]

In conclusion, the first stable arsaallene **1** has been obtained in a straightforward one-pot procedure from another low-coordinate species of arsenic, the functionalizable arsaalkene **4**, which appears to be a promising reagent in low-coordinate arsenic chemistry.

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) In the phosphaallene ArP=C=CPh$_2$, the P−C−C bond angle is similar. (a) 167°: Appel, R.; Fölling, P.; Josten, B.; Siray, M.; Winkhaus, V.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 619. (b) 168.0(3)°: Yoshifuji, M.; Toyota, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T.; Nagase, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1985**, *25*, 237.

(23) Similar values are reported for the corresponding C=C bond length in ArP=C=CPh$_2$ (1.31,[22a] 1.327(5) Å[22b]) and in ArP=C=CR$_2$ (1.336(4) Å[10c]).

(24) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582.