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The First Stable Arsaphosphaallene, ArP=C=AsAr

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*Summary: The first arsaphosphaallene, ArP=C=AsAr (**1**; Ar = 2,4,6-tri-tert-butylphenyl), has been synthesized by debromofluorination of the (phosphaalkenyl)fluoroarsane **5** by n-butyllithium at low temperature and characterized by NMR (δ_P +159.7 ppm, δ_C +299.5 ppm) and X-ray analysis. A ^1H NMR study between +55 and −60 °C allowed the determination of the rotation barrier of Ar groups.*

During the last 15 years, many studies have been devoted to low-coordinate species of group 15 elements. Impressive progress has been made, particularly for phosphorus compounds. Phosphaalkenes, −P=C<, for example, are now well-known.[1] More recently, stable phosphacumulenes, −P=C=X [2] (X = CR$_2$,[2a−i] NR,[2j−l] PR,[2a,b,d,m−p] O,[2q] C=PR,[2g,r] C=CR$_2$[2s]), have been synthesized. In marked contrast, the field of arsenic analogues has been less investigated. Relatively few acyclic arsaalkenes, −As=C<, have been isolated,[3] and stable arsacumulenes are still unknown since Märkl's arsabutatriene spontaneously forms a head-to-tail dimer by cycloaddition of the As=C double bonds.[4]

We report here the preparation and isolation of the first heterocumulene of arsenic, incorporating a $\sigma^2\lambda^3$ phosphorus atom, the arsaphosphaallene ArP=C=AsAr (**1**; Ar = 2,4,6-tri-*tert*-butylphenyl).

The reaction of *n*-butyllithium at −100 °C with ArP=CBr$_2$ (**2**)[5] followed by addition of ArAsF$_2$[6] afforded the (phosphaalkenyl)fluoroarsane **5**.[7] Only one stereoisomer was formed, although it is impossible to determine from NMR data which one was obtained. How-

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(1) For reviews see: (a) Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1986**, *29*, 73. (b) 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. (c) Appel, R.; Knoll, F. *Adv. Inorg. Chem.* **1989**, *33*, 259. (d) Markovskii, L. N.; Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019.

(2) For a review on phosphacumulenes, −P=C=X, see ref 1b. See also: (a) Appel, R.; Fölling, P.; Josten, B.; Siray, M.; Winkhaus, V.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 619. (b) Yoshifuji, M.; Sasaki, S.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1989**, 1732. (c) Appel, R.; Winkhaus, V.; Knoch, F. *Chem. Ber.* **1986**, *119*, 2466. (d) Yoshifuji, M.; Niitsu, T.; Shiomi, D.; Inamoto, N. *Tetrahedron Lett.* **1989**, *30*, 5433. (e) Yoshifuji, M.; Sasaki, S.; Inamoto, N. *Tetrahedron Lett.* **1989**, *30*, 839. (f) Yoshifuji, M.; Toyota, K.; Okamoto, Y.; Asakuro, J. *Chem. Lett.* **1990**, 2311. (g) Märkl, G.; Kreitmeier, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1360. (h) Märkl, G.; Reithinger, S. *Tetrahedron Lett.* **1988**, *29*, 463. (i) Märkl, G.; Herold, U. *Tetrahedron Lett.* **1988**, *29*, 2935. (j) Kolodiazhnyi, O. I. *Phosphorus Sulfur* **1983**, *18*, 39; *Tetrahedron Lett.* **1982**, *23*, 4933. (k) Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809. Yoshifuji, M.; Niitsu, T.; Toyota, K.; Inamoto, N.; Hirotsu, K.; Odagaki, Y.; Higuchi, T.; Nagase, S. *Polyhedron* **1988**, *7*, 2213. (l) Niitsu, T.; Inamoto, N.; Toyota, K.; Yoshifuji, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2736. (m) Karsch, H. H.; Reisacher, H.-U.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 618. (n) Yoshifuji, M.; Toyota, K.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1984**, 689. (o) Karsch, H. H.; Köhler, F. H.; Reisacher, H.-U. *Tetrahedron Lett.* **1984**, *25*, 3687. (p) Gouygou, M.; Koenig, M.; Escudié, J.; Couret, C. *Heteroat. Chem.* **1991**, *2*, 221. (q) Appel, R.; Paulen, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 785. (r) Yoshifuji, M.; Toyota, K.; Yoshimura, H. *Chem. Lett.* **1991**, 491. (s) Märkl, G.; Sejpka, H.; Dietl, S.; Nuber, B.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1003.

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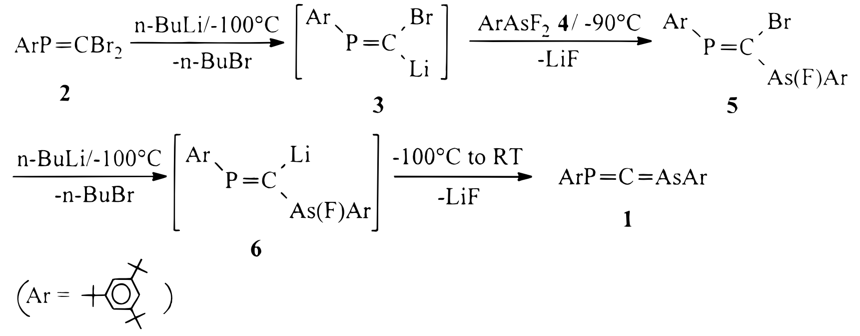
Scheme 1



ever, we suggest that, from the most probable mechanism, it is the *Z* isomer. The halogen–metal exchange of **2** with *n*-butyllithium must occur from the least hindered side, i.e., at the *E* bromine atom, to give the carbenoid intermediate **3**, which reacts with difluoroarsane **4** to furnish **5** (*Z*). A similar stereochemistry was reported by Bickelhaupt and co-workers [5] in the synthesis of ArP=CHBr from **2**. In the ^{1}H and ^{13}C NMR spectra of **5**, two signals are observed for the two *o*-*t*-Bu substituents on the Ar group bonded to phosphorus. This is, of course, due to the hindered rotation of this Ar group. In contrast, only one signal, a doublet (coupling with fluorine), is observed for the *o*-*t*-Bu substituents on the Ar group bonded to arsenic, for which the free rotation is observed.[7] Addition of *n*-butyllithium to **5** at −90 °C led to the organolithium intermediate **6**, which lost LiF to give in nearly quantitative yield the expected arsaphosphaallene **1** (Scheme 1).[8]

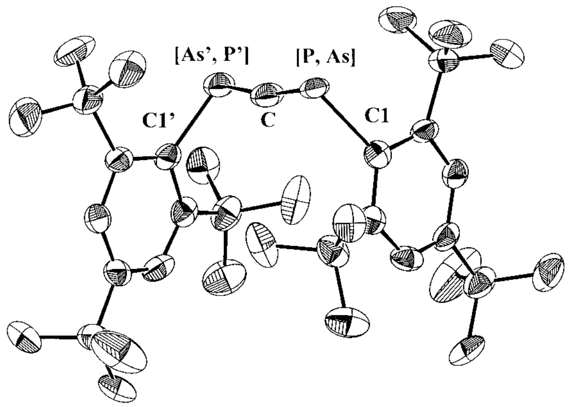


Figure 1. Molecular view of **1** in the solid state. Bond lengths and bond angles could not be determined exactly (see text and ref 9).

1 crystallized from pentane in the form of air-stable, yellow crystals. The X-ray analysis[9] (Figure 1) gives information about half of the molecule; the whole molecule is formed by a 2-fold axis of symmetry. Because of this symmetry and other problems mentioned in ref 9, the phosphorus and arsenic atom positions are not defined exactly. However, although no bond angles or bond distances can be discussed,[9] the general aspect of **1** with the presence of the central allenic carbon bonded to two ArP or ArAs groups can be evidenced. The NMR spectra of **1** were also consistent with the assigned structure,[8] particularly the ^{13}C signal characteristic of an allenic carbon (δ_C 299.54, d, $^{1}J_{CP}$ = 75.1 Hz) and the low-field chemical shift in the ^{31}P NMR spectrum (δ_P 159.7). The ^{1}H NMR spectrum at room temperature

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(7) Synthesis of **5**: A solution of n-BuLi, 1.6 M in hexane (3.4 mL, 5.36 mmol), was added slowly to a solution of ArP=CBr$_2$ (**2**;[5] 2.40 g, 5.36 mmol) in Et_2O (25 mL) cooled to −100 °C. The reaction mixture turned yellow-orange. After 30 min of stirring at −100 °C, 1 equiv of $ArAsF_2$ (1.92 g, 5.36 mmol) in Et_2O (10 mL) was slowly added. The reaction mixture was gradually warmed to room temperature. After removal of Et_2O in vacuo from the light yellow solution, pentane was added. The LiF was filtered, and crude **5** was isolated by evaporation of the filtrate. **5** was recrystallized from Et_2O (1.02 g, 27%, mp 138–140 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.28 (s, 18H, *p*-*t*-Bu of ArP and ArAs); 1.31 (s, 9H, *o*-*t*-Bu of ArP); 1.33 (s, 9H, *o*-*t*-Bu of ArP); 1.50 (d, $^{6}J_{H-F}$= 1.1 Hz, 18H, *o*-*t*-Bu of ArAs); 7.32 (d, $^{4}J_{H-P}$ = 1.5 Hz, 2H, arom H of ArP); 7.39 (s, 2H, arom H of ArAs). ^{31}P NMR ($CDCl_3$) δ_P 308.7 (d, $^{3}J_{P-F}$ = 23.3 Hz). ^{19}F NMR ($CDCl_3$, CF_3COOH external standard): δ_F −95.6 (d, $^{3}J_{F-P}$ = 23.3 Hz). ^{13}C NMR ($CDCl_3$): δ_C 31.30 (*p*-(CH_3)$_3$C of ArP and ArAs); 32.74 (d, $^{4}J_{C-P}$ = 7.5 Hz, *o*-(CH_3)$_3$C of ArP); 33.06 (d, $^{4}J_{C-P}$ = 7.2 Hz, *o*-(CH_3)$_3$C of ArP); 34.14 (d, $^{5}J_{C-F}$ = 4.0 Hz, *o*-(CH_3)$_3$C of ArAs); 34.19 (*p*-(CH_3)$_3$*C* of ArP and ArAs); 37.92, 38.04, 38.29 (*o*-(CH_3)$_3$*C* of ArP and ArAs), 122.14, 122.42, 122.71 (*m*-C of ArP and ArAs); 138.50 (d, $^{1}J_{C-P}$ = 69.3 Hz, C ipso of ArP); 142.60 (broad s, C ipso of ArAs); 150.72, 151.74, 152.39, 153.51, 155.97 (*o*-C and *p*-C, ArP and ArAs); 167.50 (dd, $^{1}J_{C-P}$ = 99.2 Hz, $^{2}J_{C-F}$ = 5.9 Hz, P=C–As). MS EI: *m*/*z* 706 (M, 1); 686 (M − F − 1, 1); 649 (M − *t*-Bu, 13); 629 (M − *t*-Bu −F − 1, 9); 461 (M − Ar, 11); 405 (M − Ar − tBu + 1, 2); 385 (M − Ar − *t*-Bu − F, 2); 319 (ArAs − 1, 1); 57 (*t*-Bu, 100). Anal. Calcd for $C_{37}H_{58}AsBrFP$: C, 62.80; H, 8.26. Found: C, 62.99; H, 8.21.

(8) Synthesis of **1**: A solution of *n*-BuLi, 1.6 M in hexane (0.35 mL, 0.56 mmol), was added slowly to a solution of **5** (0.40 g, 0.56 mmol) in Et_2O (10 mL) cooled to −78 °C. After slow warming to room temperature, a light brown solution was obtained. Et_2O was removed in vacuo, pentane was added, and LiF was filtered. Recrystallization at −20 °C from pentane gave 0.30 g of **1** (88%, mp 198 °C dec) in the form of hexagonal transparent yellow crystals. ^{1}H NMR ($CDCl_3$, 200 MHz): δ (25 °C) 1.27, 1.28 (2s, 2 × 9H, *p*-*t*-Bu of ArP and ArAs); 1.34 (broad s, 2 × 18H, *o*-*t*-Bu of ArP and ArAs); 7.24 (d, $^{4}J_{H-P}$ = 1.4 Hz, 2H, arom H of ArP); 7.28 (broad s, 2H, arom H of ArAs). ^{31}P NMR ($CDCl_3$): δ_P 159.7. ^{13}C NMR ($CDCl_3$): δ_C 31.54, 31.58 (2s, *p*-(CH_3)$_3$C of ArP and ArAs); 33.47 (d, $^{4}J_{C-P}$ = 7.1 Hz, *o*-(CH_3)$_3$C of ArP); 33.61 (*o*-(CH_3)$_3$C of ArAs); 34.91 (*p*-(CH_3)$_3$*C* of ArP and ArAs); 38.22 (broad s, *o*-(CH_3)$_3$*C* of ArP and ArAs); 121.72, 122.07 (2s, *m*-CH of ArP and ArAs); 129.34 (d, $^{1}J_{C-P}$ = 74.5 Hz, ipso-C of ArP); 134.58 (d, $^{3}J_{C-P}$ = 19.0 Hz, ipso-C of ArAs); 149.31, 149.55 (2s, *p*-C of ArP and ArAs); 153.31 (broad s, *o*-C of ArP and ArAs); 299.54 (d, $^{1}J_{C-P}$ = 75.1 Hz, P=C=As). MS EI: *m*/*z* 608 (M, 2); 552 (M − *t*-Bu + 1, 30); 495 (M − 2*t*-Bu + 1, 100); 438 (M − 3*t*-Bu + 1, 10); 275 (ArP − 1, 3). UV (cyclohexane): λ_{max} (ϵ) 274 nm (45 634) ($\pi \rightarrow \pi^*$), 374 nm (1267) ($n \rightarrow \pi^*$). Anal. Calcd for $C_{37}H_{58}AsP$: C, 72.98; H, 9.61. Found: C, 72.51; H, 9.59.

displays a single, broad signal for the *o*-*tert*-butyl parts of the two Ar groups.[10] This single broad signal cannot be explained by an inversion at phosphorus or arsenic or by a rotation about the P═C and As═C double bonds.[11] Rather, this phenomenon is due to rotation of Ar groups, slowed down because of the steric congestion. A dynamic ^{1}H NMR study between −60 °C (hindered rotation)[12] and +55 °C (synchronous rotation of Ar groups)[12] allowed determination of the rotation barrier of these Ar groups. This barrier can be calculated from the evolution of both the signals of aromatic protons (Tc = 274 K, $\Delta G^* = 13.57$ kcal/mol) and of *t*-Bu groups ($T_c = 287$ K, $\Delta G^* = 13.67$ kcal/mol). This surprisingly high value (13.6 kcal/mol) shows the severe steric congestion in **1** caused by the two huge Ar groups, despite the (at first sight) great distance between them. This steric hindrance explains why **1** is so stable toward oxygen and moisture that it can be kept for weeks in open air. Similar values of rotation barriers have been obtained by Yoshifuji in the diphosphaallene ArP═C═PAr.[13]

The chemical behavior of **1** is now under investigation.

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(9) **Crystal data for 1:** $C_{37}H_{58}AsP$, $M_r = 608.72$, monoclinic, *C*2/*c*, $a = 9.696(2)$ Å, $b = 18.264(4)$ Å, $c = 20.230(4)$ Å, $\beta = 93.44(3)°$, $V = 3576(1)$ Å^3, $Z = 4$, ρ_c 1.131 Mg m^{-3}, $F(000) = 1312$, $T = 173(2)$ K, μ (Mo Kα) = 1.017 mm^{-1}, crystal size 0.4 × 0.3 × 0.1 mm, $4.8° < 2\theta < 46.0°$, 9136 reflections collected, 2483 independent ($R_{int} = 0.0815$), refinements of 226 parameters using 94 restraints, large electron density residue 1.957 e Å^{-3}, R1(for $F > 2\sigma(F)$) = 0.1072 and wR2 = 0.2926 (all data) with $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. Diffraction data for compound **1** were collected on a STOE-IPDS diffractometer. Mo Kα radiation ($\lambda = 0.710\,73$ Å) was used. The structure was solved with direct methods (SHELXS-96)[14] and refined against F^2 using all data (SHELXL-97).[15] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions using the riding model. The space group is *C*2/*c*, and the phosphorus atom and the arsenic atom are on symmetry-equivalent positions. Both atoms were refined with an occupancy of 0.5, ignoring the symmetry center using the command PART −1. The structure could not be refined satisfactorily, with a peak of height more than 1.9 e Å^{-3} remaining on the difference electron density map. The difference peak might be interpreted as an alternative position of a phosphorus atom or an arsenic atom. The disorder is also present in the possible space groups with lower symmetry. Moreover, R1 (0.1072) and wR2 (0.2926) are still not satisfactory. By looking at the reciprocal space using the program RECIPE,[16] it was possible to find two orientations of a nonmerohedric twin with the matrix 1,0,0,0−1,0,−$^2/_9$,0,−1, but it was not possible to clean the data in a satisfactory way. Recrystallization gave the same problems. For this reason we will not discuss the structure in detail and have not deposited coordinates.

(10) A similar broad signal was observed at room temperature for *o*-*t*-Bu groups in the diphosphaallene ArP═C═PAr (Ar = 2,4,6-tri-*tert*-butylphenyl) by Appel.[2a]

(11) Stable stereoisomers of phosphaalkenes[1] and of arsaalkenes[3] have been obtained and isolated; the *Z*/*E* isomerization has never been observed at room temperature.

(12) ^{1}H NMR ($CDCl_3$, 200 MHz): δ (55 °C) 1.30 and 1.31 (2s, 2 × 9H, *p*-*t*-Bu of ArP and ArAs), 1.37 and 1.38 (2s, 2 × 18H, *o*-*t*-Bu of ArP and ArAs), 7.27 (d, $^4J_{PH} = 1.6$ Hz, 2H, arom H of ArP), 7.30 (s, 2H, arom H of ArAs); δ (−60 °C) 1.06 (s, 18H, one *o*-*t*-Bu of ArP and one *o*-*t*-Bu of ArAs), 1.27 and 1.28 (2s, 2 × 9H, *p*-*t*-Bu of ArP and ArAs), 1.55 and 1.58 (2s, 2 × 9H, *o*-*t*-Bu of ArP and ArAs), 7.19 and 7.34 (2s, 2 × 1H, arom H of ArP), 7.24 and 7.37 (2s, 2 × 1H, arom H of ArAs).

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