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The First Diarsaallene ArAs═C═AsAr (Ar = 2,4,6-Tri-*tert*-butylphenyl)

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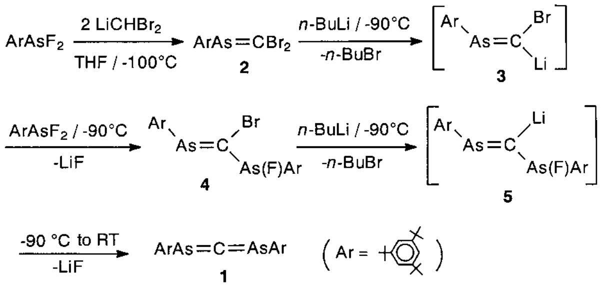
A very intensive research has been devoted on the last 20 years to the low-coordinate species of groups 14, 15, and 16 elements. Almost all of the possible E═E′ derivatives (E, E′ = Si, Ge, Sn, Pb, N, P, As, Sb, Bi, O, S, Se), which are heavy homologues of alkenes, amines, or ketones, have been isolated or at least characterized.

A new challenge was the synthesis of compounds of the type E═C═E′ with two cumulative double bonds and one or two doubly bonded heavy elements of groups 14 or 15 which can be considered as "heavy allenes".[1] Although the E_{14}═C double bond is extremely reactive, some E_{14}═C═X derivatives (E = Si, X = C,[2] N,[3] P,[4] O;[5] E = Ge, X = C,[6] P;[7] E = Sn, X = N)[8] have been isolated or at least physicochemically characterized; however >Si═C═N−,[3] >Si═C═O[5] and >Sn═C═N−[8] compounds, should be considered as silylenes or stannylenes complexes rather than sila- or stannaallenes. In the field of E_{15}═C═X compounds (X = C, N, P, O, S), many phosphorus derivatives have been obtained.[1,9] By contrast, in the case of arsenic, only two transient arsaallene HAs═C═CH_2[10] and arsabutatriene TsiAs═C═C═CPh_2[11] (Tsi = $(Me_3Si)_3C$) have been postulated as intermediates and only one stable allenic derivative of arsenic has been obtained so far, namely the arsaphosphaallene ArAs═C═PAr[12] (Ar = 2,4,6-t-$Bu_3C_6H_2$). However, mainly due to its special symmetry, the X-ray analysis of the latter could not be satisfactorily performed.

Scheme 1



We report in this paper the preparation and the structural parameters of the first allenic compound with two $\lambda^3\sigma^2$ arsenic atoms, the diarsaallene ArAs═C═AsAr **1**.

The synthesis of **1** (Scheme 1) involves the preliminary preparation of the new air-stable arsaalkene **4**[13] by reaction of *n*-BuLi with ArAs═CBr_2[14] in Et_2O at −90 °C followed by addition of $ArAsF_2$.[15] Only one stereoisomer was formed, probably the *Z*-isomer since the halogen−metal exchange from **2** with *n*-BuLi must occur at the least hindered side, that is at the *E*-bromine atom, to give the carbenoid intermediate **3**; such a stereochemistry has been proved to occur predominantly in similar reactions from ArP═CX_2 (the phosphorus analogue of **2**) and *n*-BuLi.[16]

Whereas many phosphaalkenes −P═C< have been reported,[9,17] the corresponding acyclic transient or stable arsaalkenes −As═C< are relatively rare thus far.[18,19] **4** is the first one with an arsenic on the sp^2 carbon. Owing to the presence on this carbon of a bromine atom easily substitutable by a lithium atom, a functionalization could occur conferring a great interest to **4** in low-coordinate arsenic chemistry.

Debromofluorination of **4** by *n*-BuLi gives in good yield the arsaallene **1** via the intermediate **5** (Scheme 1).[20] Air-stable pale yellow crystals of **1** were obtained from pentane. NMR data[20] of **1** were consistent with the assigned structure, particularly the

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(20) A 1.6 M solution of *n*-BuLi in hexanes (0.65 mL, 1.04 mmol) was added to a solution of **4** (0.78 g, 1.04 mmol) in Et_2O (25 mL) at −78 °C; the reaction mixture was then allowed to warm to room temperature. After removal of Et_2O in vacuo, pentane was added, and LiF was filtered out. Recrystallization from pentane gave 0.52 g of pale yellow crystals of **1** (78%, mp 164−166 °C). ^1H ($CDCl_3$, 200 MHz) (25 °C): δ 1.28 (s, 18 H, p-*t*-Bu), 1.34 (s, 36 H, *o*-*t*-Bu), 7.27 (s, 4H, arom H). (−60 °C): δ 1.05 (s, 18 H, *o*-*t*-Bu), 1.27 (s, 18 H, *p*-*t*-Bu), 1.55 (s, 18 H, *o*-*t*-Bu), 7.21 (broad s, 2 H, arom H), 7.35 (broad s, 2 H, arom H). ^{13}C NMR: δ 31.5 (p-$C(CH_3)_3$), 33.7 (o-$C(CH_3)_3$), 34.8 (p-$C(CH_3)_3$), 38.4 (o-$C(CH_3)_3$), 121.9 (*m*-CH), 134.9 (ipso-C), 149.1 (*p*-C), 153.2 (*o*-C), 296.5 (═C═). MS, EI (*m/z*): 652 (M, 1), 596 (M − *t*-Bu + 1, 2), 539 (M − 2 *t*-Bu + 1, 18), 231 (Ar − CH_2, 100). UV/vis (cyclohexane) λ_{max} (ϵ) 282 nm (97674), 388 nm (838). Anal. Calcd for $C_{37}H_{58}As_2$: C, 68.09; H, 8.96; Found C, 67.92; H 7.87.

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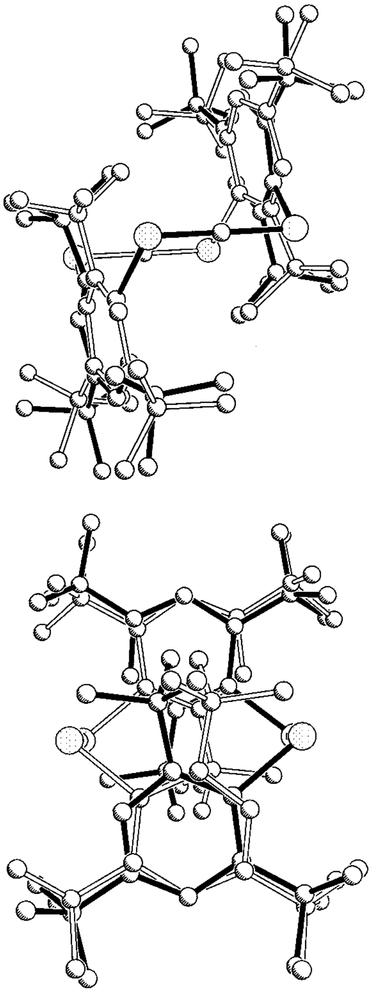

Figure 1. Representation of the disorder of **1**.

characteristic very low field ^{13}C signal at 297.5 ppm for the allenic carbon close to those reported for phosphaallenes ArP=C=AsAr (299.5 ppm),[12] ArP=C=GeMes$_2$ (280.9 ppm),[7] ArP=C=Si(Ph)-Tip (269.1 ppm),[4] and ArP=C=PR (275−277 ppm).[1,9]

The ^{1}H NMR spectrum of **1** at room temperature displays a broad singlet for the ortho *tert*-butyl groups which can only be explained by a slow rotation of the Ar groups in gear mode since the rotation around the As=C double bond or the inversion of arsenic should occur at higher temperatures. A dynamic ^{1}H NMR study between −60 °C and +60 °C allowed determination of the rotation barrier of Ar groups around the As−C(2) single bond from the evolution of ortho *tert*-butyl groups (two singlets at −60 °C and one singlet at +60 °C; $T_C = 273$ K) and of the aromatic protons (two broad singlets at −60 °C and one singlet at +60 °C; $T_C = 260$ K). This high barrier (12.9 kcal/mol) reflects the great steric hindrance caused by the large Ar groups. Rather similar values have been obtained for ArP=C=AsAr (13.6 kcal/mol)[12] and by Yoshifuji for ArP=C=PAr[21] while we could expect a much easier rotation of Ar groups in **1** than in ArP=C=PAr due to longer As−C and As=C bonds than P−C and P=C bonds. The close ΔG^* values determined in these three heteroallenes can be explained by the C(Ar)As=C bond angle in **1** (96.9(4) and 97.8(8)°) smaller than the corresponding C(Ar)P=C bond angle in ArP=C=PAr (99.9(4) and 100.3(4)°),[22] increasing the steric hindrance.

1 crystallizes with a disorder of the whole molecule[23] (see Figure 1). The molecule representing the major part of the disorder (68%) is shown in Figure 2. **1** displays a nearly linear AsCAs skeleton (175.6(6)°: major part of the disorder (68%) and 176.2(13)°: minor part (32%)).[23] A more significant deviation from linearity to reduce the interaction between the two Ar groups was observed for the PCP moiety in the diphosphaallene ArP=C=PAr (172.6(5)°).[22] The As=C bond lengths (1.7584(9) and 1.7575(17) Å) are the shortest ones ever reported, much shorter than in acyclic arsaalkenes with a sp^2-hybridized carbon atom (1.794−1.876 Å).[24] This shortening is due to the smaller bond radius of the sp-hybridized carbon atom and also to the special electronic characteristics of the heteroallene moiety. A shortening of 12% is observed in relation with As(1)−C(2) (2.021(11) and 2.015(15) Å) (the standard As−C single bond lengths are in the range 1.97−2.00 Å).[18] The torsion angle C(2)As(1)As(1a)C(2a) (77.6(6) and 78.3(9)°) is smaller than the corresponding angle in ArP=C=PAr (83.0°).[22] The C(2)As(1)C(1) bond angle (97.4(7) and 97.6(9)°) is at the lower limit for such an angle which ranges from 94.3 to 116.2°[24] in various arsaalkenes (105.0 (4)°[19b] in R$_2$C=AsAr (R$_2$C = 1,8-di-*tert*-butyl-9-fluorenylidene) which has the same Ar group on arsenic). All these data prove that the AsCAs moiety possesses a heteroallene bonding system.

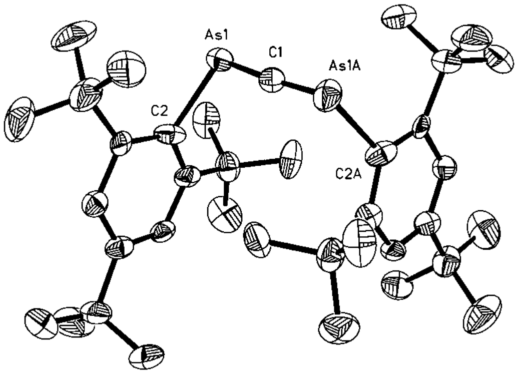

Figure 2. Solid-state structure of **1** (ellipsoids are drawn at 50% probability level) representing the major part of the disorder (68%). Selected bond lengths (Å) and angles (°): As(1)C(1) 1.7584(9), As(1)C(2) 2.021(11), As(1)C(1)As(1a) 175.6(6), C(1)As(1)C(2) 97.4(7), C(2)As(1)As(1a)C(2a) 77.6(6).

The study of the reactivity of **1** is now under active investigation.

Acknowledgment. Thanks are due to Regine Herbst-Irmer (University of Göttingen, Germany) for discussions about the X-ray structure.

Supporting Information Available: Representative procedure and physicochemical data for **4**, tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, hydrogen coordinates, and view of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] Crystal data for **1**: $C_{37}H_{58}As_2$, M = 652.67, orthorhombic, *Pccn*, $a = 19.6100(5)$ Å, $b = 10.0342(2)$ Å, $c = 18.3205(4)$ Å, $V = 3604.9(14)$ Å^3, $Z = 4$, $\rho_c = 1.203$ Mg m^{-3}, $F(000) = 1384$, $\lambda = 0.71073$ Å, $T = 193(2)$ K, μ (Mo Kα) = 1.875 mm^{-1}, crystal size 0.1 × 0.1 × 0.1 mm, $2.08° \leq \Theta \leq 24.71°$, 35441 reflections (3067 independent, $R_{int} = 0.0465$) were collected at low temperature using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer. A semiempirical absorption correction was employed[25] ($T_{min} = 0.868428$, $T_{max} = 1.000000$). The structure was solved by direct methods (SHELXS-97),[26] and 354 parameters were refined using the least-squares method on F^2.[27] A disorder of the whole molecule was observed. Recrystallization did not solve the problem because the two molecules occupy the same volume in the crystal (see Figure 1). After discussions with Dr. Regine Herbst-Irmer, we excluded the possibility of a twinned system. The disorder was refined anisotropically by using 345 distances and ADP restraints with the occupancies of 0.68 and 0.32. Largest electron density residue: 0.628 e Å^{-3}, R_1 (for $F > 2\sigma(F)$) = 0.0672 and $wR_2 = 0.2047$ (all data) with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$.

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