Notiz / Note

Synthesis and Crystal Structure of an Arsolyl Anion and Preparation of an Arsinogallate

Shawn C. Sendlinger, Brian S. Haggerty, Arnold L. Rheingold, and Klaus H. Theopold*

Department of Chemistry & Biochemistry, University of Delaware,
Newark, Delaware 19716, U.S.A.

Received December 21, 1990

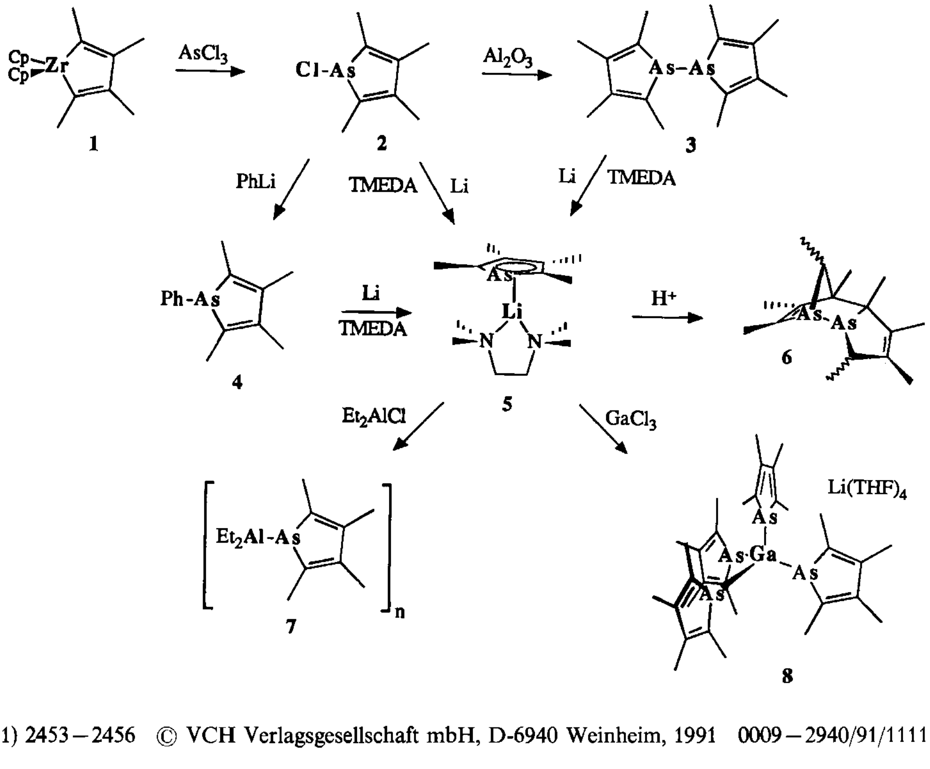
Key Words: Arsolyl anion / Heteroaromatics / Gallium compounds / Arsoles

The permethylated arsolyl anion $C_4Me_4AsLi(TMEDA)$ (**5**) has been prepared; its crystal structure (determined by X-ray diffraction) revealed an aromatic heterocycle comparable to the homologous pyrrolyl and phospholyl anions.

As part of our efforts to prepare novel precursors for the III-V semiconductors (e.g. gallium arsenide, indium phosphide) we have explored the use of phospolyl and arsolyl moieties as ligands for group-13 metals[1]. Together with the pyrrolyl anion these heterocycles constitute a homologous series to be compared with the isoelectronic family of heterobenzenes (C_5H_5N, C_5H_5P, C_5H_5As etc.)[2]. Herein we report convenient syntheses of several permethylated arsole derivatives, the crystal structure of the lithium salt of the $[C_4Me_4As]^-$ anion, and its exemplary use in the preparation of a novel arsinogallate containing four arsolyl ligands coordinated to gallium.

As in our recent work on the permethylphospholyl ion[3], we have adopted the synthetic methodology reported by Fagan et al. involving zirconium-mediated alkyne coupling and transfer to main-group electrophiles[4]. Reaction of $Cp_2ZrC_4Me_4$ (**1**) with $AsCl_3$ yielded chloroarsole **2** (Scheme 1)[5]. In contrast to the analogous chlorophosphole (C_4Me_4PCl)[3], **2** suffered extensive decomposition upon sublimation. However, it could be isolated in good yield (80%) by extraxtion and recrystallization from pentane. **2** formed yellow needles which melted around room temperature (m.p. ≈ 20°C); it also decomposed with a halflife of ca. 3 days. Attemps to purify it by column chromatography on alumina led to its conversion to 1,1′-biarsole (**3**)[6], which was isolated in 40% yield. Reduction of either **2** or **3** with lithium yielded C_4Me_4AsLi, albeit in erratic yields and accompanied by formation of elemental arsenic. Eventually we found that the most reliable synthesis of the anion consisted of the conversion of **2** into the previously prepared phenylarsole **4** (by reaction of **2** prepared in situ with 1.0 equivalents of phenyllithium,

Scheme 1



Chem. Ber. **124** (1991) 2453–2456 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1991 0009–2940/91/1111–2453 $ 3.50+.25/0

85% yield), followed by reductive cleavage with lithium metal. Extraction with Et_2O completely removed the byproduct PhLi and gave analytically pure C_4Me_4AsLi in quantitative yield. Addition of 2.0 equivalents of TMEDA to an Et_2O solution of the lithium salt and cooling to −30°C yielded clear colorless needles of $C_4Me_4AsLi(TMEDA)$ (**5**).

The crystal structure of **5** is shown in Figure 1. The crystal consists of monomeric molecules featuring η^5 coordination of the heterocycle to lithium. Saturation of the coordination sphere of the lithium is effected by the two nitrogen donors of the TMEDA chelate. The five-membered ring is essentially planar; the arsenic atom is displayed toward lithium by 0.024 Å from the plane defined by C(1), C(2), C(3), and C(4). The carbon–carbon distances within the arsolyl ring [C(1)–C(2) 1.406, C(2)–C(3) 1.428, C(3)–C(4) 1.367 Å] are very similar and serve as structural evidence for significant delocalization. In addition, the arsenic–carbon bonds [As–C(1) 1.903, As–C(4) 1.890 Å] are intermediate in length between single (1.97 Å)[7] and double (1.79 Å)[8] bonds between these elements and close to the 1.85 Å measured in arsabenzene[2]. The C(1)–As–C(4) angle of 87.0° is consistent with high p character of the bonding, as expected for the heavier group-15 elements. The structural features support the assignment of aromatic character to the arsolyl anion. A comparison with the two structurally characterized arsolyl complexes of transition metals, $(\eta^5\text{-}Ph_4C_4As)Mn(CO)_3$[9] and $(\eta^5\text{-}2,5\text{-}Me_2H_2C_4As)_2Fe$[10], revealed no significant differences in the bond distances and angles of the heterocycles, indicating a fair insensitivity to the effects of π bonding.

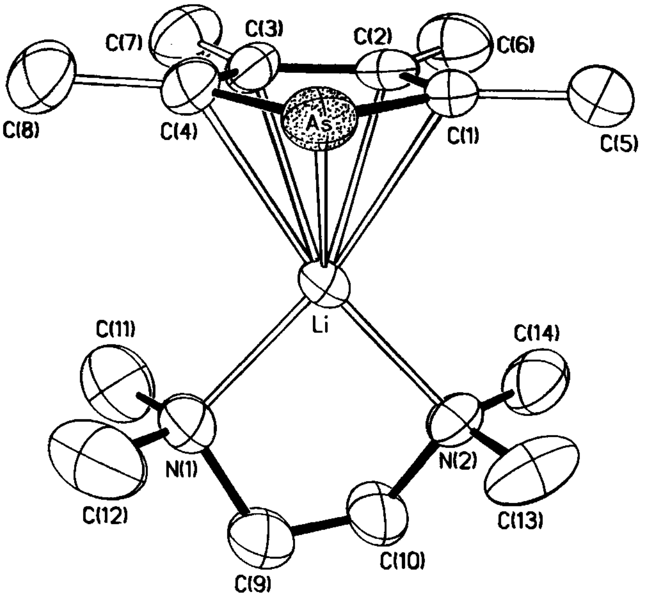


Figure 1. Molecular structure of $Me_4C_4AsLi(TMEDA)$ (**5**). Selected bond distances [Å] and angles [°]: As–C(1) 1.903(10), As–C(4) 1.890(8), C(1)–C(2) 1.406(10), C(2)–C(3) 1.428(13), C(3)–C(4) 1.367(12), As–Li 2.596(12), C(1)–Li 2.415(15), C(2)–Li 2.407(15), C(3)–Li 2.442(14), C(4)–Li 2.502(16), N(1)–Li 2.119(16), N(2)–Li 2.097(16); C(1)–As–C(4) 87.0(4), As–C(1)–C(2) 110.8(7), C(1)–C(2)–C(3) 114.2(8), C(2)–C(3)–C(4) 116.2(7), C(3)–C(4)–As 111.7(7), N(1)–Li–N(2) 85.0(5)

Table 1 shows a direct comparison of the structural parameters of the permethylated pyrrolyl, phospholyl, and arsolyl anions. The structures of neither Me_4C_4NLi nor H_4C_4NLi are known, however, in light of the close structural resemblance between the lithium and transition metal derivatives of phospholyl and arsolyl ligands, respectively, the parameters of the iron complex $(\eta^5\text{-}Me_4C_4N)_2Fe(HNC_4Me_4)_2$ are given[11]. The observed trends clearly parallel those found for the series of heterobenzenes.

Table 1. Comparison of the structural parameters of the permethylated pyrrolyl, phospholyl, and arsolyl anions

	$[Me_4C_4N]^-$	$[Me_4C_4P]^-$	$[Me_4C_4As]^-$
X-C	1.393(3)	1.751(4)	1.897(9)
X-C_{sp2}	1.36	1.83	1.97
X=C_{sp2}	1.28	1.68	1.79
X-C in C_5H_5X	1.37	1.73	1.85
C_1-C_2,C_3-C_4	1.411(4)	1.396(5)	1.387(11)
C_2-C_3	1.413(4)	1.424(7)	1.428(13)
C_1-X-C_4	106.2(2)	90.5(2)	87.0(4)
C_1-X-C_5 in C_5H_5X	117	101	97

Protonation of **5** with $HBF_4 \cdot Et_2O$ gave the arsole dimer **6**. By analogy to similar phosphole chemistry[12] **6** was presumably formed by a Diels-Alder reaction between two molecules of 2*H*-arsole, which in turn resulted from a tautomerization of the first formed 1*H*-arsole. Reaction of **5** with Et_2AlCl gave a colorless solid, to which, on the basis of spectroscopic and analytical data, we assign the formula $[Et_2AlAsC_4Me_4]_n$ (**7**). In line with many other compounds with covalent bonds between group-13 and group-15 elements[13] **7** most likely is a head-to-tail dimer ($n = 2$) by virtue of Lewis acid base interactions between aluminium and arsenic. Finally, reaction of $GaCl_3$ with an excess of **5** produced clear colorless rhombs of the arsinogallate $[Li(THF)_4]^+[(\eta^1\text{-}Me_4C_4As)_4Ga]^-$ (**8**) in 53% yield. The structure suggested in Scheme 1 is consistent with all spectroscopic and analytical data and the anticipated η^1 bonding mode is based on the related structure of $[K(18\text{-crown-}6)]^+[(\eta^1\text{-}Me_4C_4P)_2InCl_2]^-$[1]. The recently reported $[Li(THF)_4]^+[Ga(AsPh_2)_4]^-$ serves as further precedent[14]. While **7** and **8** may be considered precursors for the III-V alloys AlAs and GaAs, their low vapor pressures probably preclude their use in chemical vapor deposition (CVD) processes.

Parts of this research were carried out at Cornell University and were supported by grants from *AKZO Corporate Research America, Inc.* and the *New York State Science and Technology Foundation.*

Experimental

NMR: Bruker WM 300. – IR: Mattson Alpha Centauri. – MS: Kratos MS-9. – Elemental analysis: Oneida Research Services, Whitesboro, NY 13492, USA.

1,1-Bis(η^5-cyclopentadienyl)-2,3,4,5-tetramethyl-1-zirconacyclopentadiene (**1**) was prepared according to a published procedure[4]. Cp_2ZrCl_2 (13.51 g, 46.22 mmol) was dissolved in ca. 150 ml of THF. The solution was cooled to −78°C while being purged with nitrogen. *n*BuLi (46.22 ml of a 2.0 M pentane solution, 92.44 mmol) was slowly added with a syringe. The mixture was allowed to stir for 30 min, and then 2-butyne (5.0 g, 92.44 mmol) was added by a cannula. After stirring for 15 min, the mixture was allowed to warm to room temp. and was left to stir for ca. 12 h. The solvent was removed, and the red product was extracted with toluene, filtered, and recrystallized at −30°C. Yield 13.7 g (90%). – ^{1}H-NMR ([D_6]benzene): δ = 6.05 (s, 10H), 1.93 (s, 6H), 1.80 (s, 6H).

1-Chloro-2,3,4,5-tetramethylarsole (**2**): A solution of zirconacycle **1** (2.79 g, 8.47 mmol) in ca. 50 ml pentane was cooled to −30°C. Arsenic(III)chloride (1.54 g, 8.47 mmol) was added resulting in an immediate color change from deep red to light yellow. The mixture was filtered, the solvent removed, and the resulting yellow oil was recrystallized from pentane at -30°C as yellow needles. This material is moderately unstable at room temp. in pure form or in solution. Yield 1.48 g (80%), m.p. ≈ 20°C. – IR (neat, NaCl plates): $\tilde{\nu}$ = 2974 cm^{-1} (s), 2853 (m), 2728 (w), 1619 (w), 1581 (w), 1437 (s), 1381 (m), 1063 (m). – ^{1}H NMR ([D$_8$]THF): δ = 2.04 (s, 6H), 1.85 (s, 6H). – ^{13}C NMR ([D$_8$]THF): δ = 147.70 (s), 141.97 (s), 14.43 (s), 13.69 (s). – MS (70 eV): *m/z* (%) 183 (4.6) [$C_8H_{12}As^+$].

$C_8H_{12}AsCl$ (218.6) Calcd. C 43.96 H 5.53
Found C 44.05 H 5.59

2,2′,3,3′,4,4′,5,5′-Octamethyl-1,1′-biarsole (**3**): Chloroarsole **2** (2.0 g, 9.15 mmol) was dissolved in diethyl ether and was eluted through a small plug of alumina. Removal of solvent and recrystallization from pentane at -30°C gave yellow rhombs. Yield 0.67 g (40%), m.p. 53–55°C. – IR (KBr): $\tilde{\nu}$ = 2969 cm^{-1} (s), 2907 (s), 2849 (s), 1606 (w), 1437 (s), 1374 (m), 1302 (w), 1199 (vw), 1119 (m), 1060 (m), 999 (w), 957 (m), 898 (w), 770 (w). – ^{1}H NMR ([D$_6$]benzene): δ = 1.90 (s, 12H), 1.72 (s, 12H). – ^{13}C NMR ([D$_6$]benzene): δ = 142.95 (s), 139.54 (s), 15.43 (s), 14.49 (s). – Electrochemistry (THF): irreversible reduction at ca. -2.2 V (vs Fc+/Fc).

$C_{16}H_{24}As_2$ (366.2)
Calcd. C 52.49 H 6.61 Found C 52.09 H 6.41
Mol. mass Calcd. 366.0312 Found 366.0303 (MS)

1-Phenyl-2,3,4,5-tetramethylarsole (**4**) has been previously prepared[4]. A solution of zirconacycle **1** (1.27 g, 3.85 mmol/l) in 40 ml of pentane was cooled to -30°C. AsCl$_3$ (0.71 g, 3.9 mmol) was added dropwise. The mixture was filtered and cooled to -30°C. PhLi (2.15 ml of a 1.8 M cyclohexane/diethyl ether solution, 3.9 mmol) was added dropwise. The mixture was filtered, the solvent removed, and the resulting solid was eluted over a small plug of alumina with pentane. The solvent was removed leaving a slightly yellow oil. Yield 0.81 g (85%). – IR (neat, NaCl plates): $\tilde{\nu}$ = 3044 cm^{-1} (w), 2924 (s), 2851 (m), 1570 (w), 1433 (m), 1375 (m), 1063 (m), 1022 (w), 999 (w), 735 (m), 694 (m). – ^{1}H NMR ([D$_8$]THF): δ = 7.29–7.18 (m, 5H), 1.96 (s, 6H), 1.88 (s, 6H). – ^{13}C NMR ([D$_8$]THF): δ = 144.8 (s), 141.9 (s), 138.6 (s), 133.7 (s), 129.3 (s), 129.0 (s), 14.9 (s), 14.7 (s).

2,3,4,5-Tetramethylarsolyl Anion, Lithium Salt: Reduction of phenylarsole **4** (0.50 g, 1.92 mmol) with excess lithium dispersion in THF resulted in a color change to deep red. Filtration, removal of solvent, and washing of the resultant white powder with diethyl ether removed all traces of PhLi and gave the lithioarsole in 100% yield (0.36 g). M.p. >380°C. – IR (KBr): $\tilde{\nu}$ = 2917 cm^{-1} (s), 2855 (s), 1443 (m), 1383 (m), 484 (s). – ^{1}H NMR ([D$_8$]THF): δ = 2.17 (s, 6H), 1.83 (s, 6H). – ^{13}C NMR ([D$_8$]THF): δ = 144.97 (s), 125.95 (s), 18.07 (s), 14.67 (s).

$C_8H_{12}AsLi$ (190.05) Calcd. C 50.56 H 6.36
Found C 50.39 H 6.44

(η^5-2,3,4,5-Tetramethylarsolyl) (N,N,N′,N′-tetramethylethylenediamine)lithium (**5**): Me$_4$C$_4$AsLi (see above) (1.0 g, 5.26 mmol) was slurried in 50 ml of diethyl ether with an excess of TMEDA (9.28 mmol) present. After stirring for several hours, the solvent was removed. Recrystallization from diethyl ether at -30°C gave the product as clear needles. Yield 1.45 g (90%), m.p. >380°C. – IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (s), 2939 (s), 2907 (s), 2847 (s), 2801 (s), 2778 (s), 2706 (w), 1460 (w), 1441 (m), 1406 (w), 1358 (w), 1296 (m), 1289 (m), 1262 (w), 1250 (w), 1182 (w), 1159 (m), 1130 (m), 1099 (m), 1068 (m), 1034 (s), 1018 (m), 949 (m), 870 (w), 835 (w), 793 (m), 775 (w), 592 (w), 492 (s), 475 (s). – ^{1}H NMR ([D$_8$]THF): δ = 2.28 (s, 4H), 2.24 (s, 6H), 2.14 (s, 12H), 1.89 (s, 6H). – ^{13}C NMR ([D$_8$]THF): δ = 145.4 (s), 126.2 (s), 58.5 (s), 46.0 (s), 18.2 (s), 14.8 (s).

$C_{14}H_{28}AsLiN_2$ (306.25) Calcd. C 54.91 H 9.22 N 9.14
Found C 55.29 H 9.15 N 8.88

Crystal Structure Determination of **5**[15]: A colorless crystal of **5** (0.36 × 0.36 × 0.36 mm) was obtained from Et$_2$O. 3007 data were collected on a Nicolet R3m/μ diffractometer with a graphite monochromator using Wyckoff scans (2θ scan range: 4–48°) and Mo radiation [μ(Mo-K_α) = 20.1 cm^{-1}]. Of these, 1505 independent reflections had $I > 5\sigma(I)$. The ratio of minimum to maximum transmission was 1.11, obviating an absorption correction. The structure was solved by direct methods and refined by block-matrix methods. All non-hydrogen atoms, except for C(9′) and C(10′), were refined anisotropically; the ethano bridge [i.e. C(9) and C(10)] was slightly disordered, and C(9′) and (10′) exhibited occupancies of 11%, thus anisotropic refinement was deemed unwarranted. All hydrogen atoms were included as idealized contributions. The data reduction was performed with the programs contained in the SHELXTL library (version 5.1). The weighting scheme employed was $w^{-1} = \sigma^2(F_o) + gF_o^2$ with $g = 0.01$. Crystal data: $C_{14}H_{28}AsLiN_2$. M = 306.25, monoclinic, space group $P2_1/n$, a = 9.010(3), b = 15.867(6), c = 12.689(2) Å, $\beta = 107.93(2)^0$, U = 1724.6(9) Å^3, λ(Mo-K_α) = 0.71073 Å, D_c = 1.18 g cm^{-3}, Z = 4. N_o/N_v = 8.75, R = 0.058, R_W = 0.059, GOOF 1.446, residual electron density 0.49 eÅ^{-3}. Atomic coordinates and isotropic thermal parameters are given in Table 2.

Table 2. Atomic coordinates (× 10^4) and isotropic thermal parameters (Å^2 × 10^3) of **5**

Atom	x	y	z	U[a)]
As	2335.5(10)	3115.5(6)	1017.5(7)	63.0(4)
Li	3938(15)	2050(8)	2479(12)	57(6)
N(1)	5635(8)	1235(4)	2190(6)	68(3)
N(2)	3185(8)	978(4)	3135(5)	61(3)
C(1)	2074(9)	3150(5)	2449(7)	56(3)
C(2)	3478(10)	3371(4)	3258(7)	53(3)
C(3)	4748(9)	3519(5)	2831(7)	53(3)
C(4)	4429(9)	3437(5)	1711(7)	60(3)
C(5)	540(10)	2995(6)	2632(9)	88(5)
C(6)	3582(13)	3495(6)	4438(7)	87(5)
C(7)	6318(10)	3828(6)	3595(8)	88(5)
C(8)	5558(11)	3628(6)	1087(8)	88(5)
C(9)	5191(20)	386(7)	2449(20)	100(9)
C(10)	4504(19)	355(8)	3314(18)	88(8)
C(9′)	5738(51)	542(30)	3199(37)	20(15)
C(10′)	3923(54)	205(30)	2595(39)	22(15)
C(11)	7181(13)	1487(8)	2845(10)	117(6)
C(12)	5567(14)	1194(8)	1035(9)	126(7)
C(13)	1710(12)	706(6)	2354(8)	103(5)
C(14)	3002(11)	1063(6)	4207(7)	91(5)

[a)] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

3,4,5,6,7,8,9,10-Octamethyl-1,2-diarsatricyclo[5.2.1.0^{2,6}]deca-4,8-diene (**6**-*endo*): Protonation of **5** (0.60 g, 3.16 mmol) with HBF$_4$ (0.685 g of an 85% Et$_2$O solution, 3.60 mmol) at -30°C in a diethyl ether slurry produced a clear solution after having warmed to room temp. The solvent was removed and the resulting white solid was extracted with pentane, filtered, and recrystallized at -30°C to give colorless crystals. Yield 0.40 g, (70%), m.p. 97–101°C. – IR (KBr): $\tilde{\nu}$ = 2945 cm^{-1} (s), 2922 (s), 2863 (s), 1449 (m), 1370 (m), 1182 (w), 1136 (w), 1082 (w), 1059 (w), 1016 (w), 976 (w), 740 (w), 669 (w). –

^1H NMR: Peaks for **6**-*endo* predominate, however, a small amount of **6**-*exo* (vide infra) is also present, (CD_2Cl_2): δ = 2.28 (m, 1H), 2.12 (q, 1H, *J* = 7.1 Hz), 1.851 (m, 3H), 1.671 (m, 3H), 1.529 (m, 3H), 1.435 (s, 3H), 1.169 (s, 3H), 1.167 (d, 3H, *J* = 7.4 Hz), 0.901 (d, 3H, *J* = 7.2 Hz). – ^{13}C NMR (CD_2Cl_2): δ = 144.77 (s), 136.91 (s), 133.44 (s), 69.50 (s), 59.84 (s), 51.76 (s), 37.48 (s), 23.40 (s), 21.12 (s), 19.12 (s), 18.93 (s), 15.75 (s), 15.12 (s), 14.65 (s), 13.65 (s).

$C_{16}H_{26}As_2$ (368.23)
Calcd. C 52.19 H 7.12 Found C 51.80 H 7.05
Mol. mass Calcd. 368.04685 Found 368.0475 (MS)

3,4,5,6,7,8,9,10-Octamethyl-1,2-diarsatricyclo[5.2.1.0^{2,6}]deca-4,8-diene (**6**-*exo*): Heating of an NMR tube containing predominately the octamethyl-2*H*-arsole dimer **6** to 95°C for ca. 16 h resulted in decreased peak intensities for **6**-*endo* and increased peak intensities for **6**-*exo*. Before a complete conversion was reached, other resonances began to appear in the ^1H-NMR spectrum, probably due to decomposition. – ^1H-NMR (CD_2Cl_2): δ = 2.67 (m, 1H), 2.001 (q, 1H, *J* = 7.1 Hz), 1.871 (m, 3H), 1.593 (m, 3H), 1.570 (s, 3H), 1.365 (s, 3H), 1.327 (s, 3H), 1.267 (d, 3H, *J* = 7.4 Hz), 1.064 (s, 3H), 1.000 (d, 3H, *J* = 7.3 Hz). = ^{13}C NMR (CD_2Cl_2): δ = 146.84 (s), 139.69 (s), 137.48 (s), 133.70 (s), 68.71 (s), 54.00 (s), 49.59 (s), 37.95 (s), 24.55 (s), 21.55 (s), 19.06 (s), 18.99 (s), 17.08 (s), 16.37 (s), 15.85 (s), 14.30 (s).

1-(Diethylaluminio)-2,3,4,5-tetramethylarsole (**7**): Diethylaluminum chloride (3.73 ml of a 1.0 M solution in hexane, 3.73 mmol) was placed in 50 ml of diethyl ether. The mixture was cooled to −30°C. Me_4C_4AsLi (0.71 g, 3.74 mmol) was added as a solid with stirring. The mixture was stirred for 1 d after which time the solution was cloudy white. It was filtered, the solvent was removed, and the resulting white powder was triturated several times with pentane. Yield 0.70 g, (70%), m.p. 196–200°C. – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (s), 2861 (s), 2787 (w), 2720 (w), 1445 (m), 1406 (m), 1371 (m), 1262 (w), 1227 (w), 1188 (w), 1125 (w), 1090 (w), 1065 (w), 1022 (w), 988 (m), 951 (m), 920 (m), 795 (w), 768 (w), 637 (s), 608 (s), 532 (w), 486 (m). – ^1H NMR ([D_8]THF): δ = 2.02 (s, 6H), 1.83 (s, 6H), 1.01 (t, 6H, *J* = 8.2 Hz), −0.12 (q, 4H, *J* = 8.2 Hz). – ^{13}C NMR ([D_8]THF): δ = 144.40 (s), 140.13 (s), 15.29 (s), 14.50 (s), 9.05 (s), −0.38 (s). – MS (70 eV): *m/z* (%) 183 (84.4) [$C_8H_{12}As^+$], 85 (8.7) [Et_2Al^+].

$C_{12}H_{22}AlAs$ (268.2) Calcd. C 53.74 H 8.27
Found C 53.39 H 7.89

Tetrakis(tetrahydrofuran)lithium Tetrakis(2,3,4,5-tetramethyl-1-arsolyl)gallate (III) (**8**): Gallium(III) chloride (0.154 g, 8.77×10^{-4} mol) was added to a slurry of Me_4C_4AsLi (0.75 g, 3.95 mmol) in 50 ml of diethyl ether at −30°C. After stirring for 15 h the mixture was cloudy yellow. It was filtered, the solvent was removed, and the product was recrystallized from THF giving clear colorless rhombs. Yield 0.51 g (53%), m.p. 260°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2973 cm^{-1} (s), 2899 (s), 2849 (s), 1506 (w), 1443 (s), 1372 (w), 1190 (w), 1119 (m), 1047 (s), 920 (m), 891 (s), 679 (w), 507 (w), 486 (m), 437 (m). – ^1H NMR ([D_8]THF): δ = 2.102 (s, 6H), 1.750 (s, 6H) and resonances for free THF. – ^{13}C NMR ([D_8]THF): δ = 143.71 (s), 137.10 (s), 17.78 (s), 15.02 (s) and resonances for free THF.

$C_{48}H_{80}As_4GaLiO_4$ (1097.5) Calcd. C 52.53 H 7.35
Found C 52.21 H 7.11

CAS Registry Numbers

1: 84101-39-3 / **2**: 135004-32-9 / **3**: 135064-33-0 / **4**: 113111-17-4 / **5**: 135004-37-4 / **6**: 135004-34-1 / **7**: 135004-35-2 / **8**: 135004-39-6 / $AsCl_3$: 7784-34-1 / Et_2AlCl: 96-10-6 / $GaCl_3$: 13450-90-3 / Cp_2ZrCl_2: 1291-32-3 / 2,3,4,5-tetramethylarsolyl anion, lithium salt: 135004-36-3 / 2-butyne: 503-17-3

---

[1] T. Douglas, B. S. Haggerty, A. L. Rheingold, K. H. Theopold, *Polyhedron* **9** (1990) 329.

[2] C. Elschenbroich, A. Salzer, *Organometallics*, p. 162, VCH, Verlagsgesellschaft, Weinheim 1989.

[3] T. Douglas, K. H. Theopold, *Angew. Chem.* **101** (1989) 1394; *Angew. Chem. Int. Ed. Engl.* **28** (1989) 1367.

[4] P. J. Fagan, W. A. Nugent, *J. Am. Chem. Soc.* **110** (1988) 2310.

[5] The analogous 1,5-$Ph_2H_2C_4PCl$ has been reported in G. Märkl, H. Hauptmann, *Angew. Chem.* **84** (1972) 439; *Angew. Chem. Int. Ed. Engl.* **11** (1972) 441.

[6] For the crystal structure of 2,2′,5,5′-tetramethyl-1,1-biarsole see A. J. Ashe, III, W. M. Butler, T. R. Diephouse, *Organometallics* **2** (1983) 1005.

[7] K. Hedberg, E. W. Hughes, J. Waser, *Acta Crystallogr. Sect. B*, **14** (1961) 369.

[8] $(d_{C=C} + d_{As=As})/2$, see ref.[2], p. 165, for $d_{As=As}$ = 2.24 Å.

[9] E. W. Abel, I. W. Nowell, A. G. J. Modinos, C. Towers, *J. Chem. Soc., Chem. Commun.* **1973**, 258.

[10] C. L. Chiche, J. Galy, G. Thiollet, F. Mathey, *Acta Crystallogr., Sect B*, **36** (1980) 1344.

[11] N. Kuhn, E.-M. Horn, R. Boese, N. Augart, *Angew. Chem.* **100** (1988) 1433; *Angew. Chem. Int. Ed. Engl.* **27** (1988) 1368.

[12] C. Charrier, H. Bonnard, G. de Lauzon, F. Mathey, *J. Am. Chem. Soc.* **105** (1983) 6871.

[13] A. H. Cowley, R. A. Jones, *Angew. Chem.* **101** (1989) 1235; *Angew. Chem. Int. Ed. Engl.* **28** (1989) 1208.

[14] C. J. Carrano, A. H. Cowley, D. M. Giolando, R. A. Jones, C. M. Nunn, J. M. Power, *Inorg. Chem.* **27** (1988) 2709.

[15] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55612, the names of the authors, and the journal citation.

[421/90]