

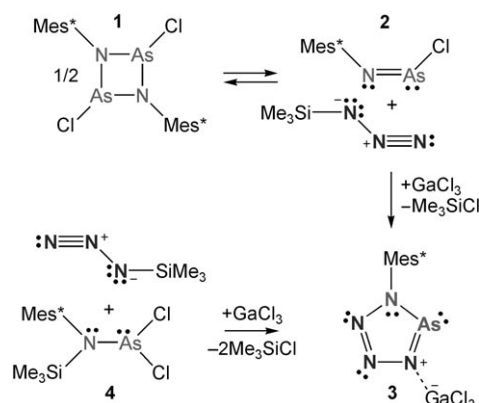
Tetrazarsoles—A New Class of Binary Arsenic–Nitrogen Heterocycles**

Axel Schulz* and Alexander Villinger

Triazadiphosphole^[1] was recently prepared from $(\text{Me}_3\text{Si})_2\text{N}-\text{N}(\text{SiMe}_3)\text{PCl}_2$ ^[2] and GaCl_3 under mild conditions in a formal GaCl_3 -assisted [3+2] cycloaddition. The second example of a binary azaphosphole, the tetrazaphosphole,^[3] was formed in the reaction of Me_3SiN_3 with $\text{Mes}^*\text{N}=\text{P}(\text{Cl})$ ($\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$), again catalyzed by GaCl_3 . Both reactions only succeed when GaCl_3 is added, because GaCl_3 triggers the elimination of Me_3SiCl and kinetically stabilizes the heterocycle at the end of the reaction sequence by adduct formation (yields for both reactions are greater than 95 %).

To our knowledge, binary five-membered arsenic–nitrogen heterocycles composed of only these two elements are not yet known, and hence we tried to apply the GaCl_3 -assisted [3+2] cycloaddition to the arsenic species.^[4a] In analogy to the azaphosphole synthesis, two routes seemed promising: 1) The reaction of $(\text{Me}_3\text{Si})_2\text{N}-\text{N}(\text{Me}_3\text{Si})\text{AsCl}_2$ with GaCl_3 , which, however, led to $(\text{ClSiMe}_2)_2\text{N}-\text{N}(\text{SiMe}_3)\text{AsMe}_2$, after an intriguing intrinsic Cl/methyl exchange.^[4b] 2) Utilization of “disguised” kinetically stabilized iminoarsanes that give high yields of the desired tetrazarsole (Scheme 1). Herein, we provide an interesting extension of the GaCl_3 -assisted formal [3+2] cycloaddition to the chemistry of arsenic, which led to the isolation of the first binary arsenic–nitrogen five-membered heterocycle, a tetrazarsole.

We started with an investigation of the equilibrium between cyclic diarsadiazane (**1**) and its monomer, the iminoarsane (**2**; Scheme 1), by means of temperature-dependent ¹H NMR spectroscopy. The dimer was first described by Burford et al., and the authors speculated on its reversible dissociation.^[5] The white crystalline dimer **1** readily dissolves in CH_2Cl_2 , but the initially colorless solution slowly turns red, the color of the monomeric species. To derive thermochemical data for the dimer–monomer equilibrium, ¹H NMR spectra were collected between 233 and 298 K, yielding a value of 2.2 kJ mol^{-1} for the enthalpy of monomerization.^[6a]



Scheme 1. Synthetic routes to tetrazarsoles.

A dimer/monomer ratio of 1:1.7 was found at 298 K, corresponding to a free enthalpy $\Delta G^\circ = -2.6 \text{ kJ mol}^{-1}$.

If one equivalent of Me_3SiN_3 (relative to the monomer) and subsequently one equivalent of GaCl_3 are added at -40°C to **1** and **2** in equilibrium, the red color of the monomer immediately disappears, and one new colorless species is formed, according to ¹H and ¹³C NMR studies. Indeed, the end of the reaction (complete formation of the new species) can be titrated utilizing the distinct color change.^[6a,c]

The same species is obtained in the reaction of Me_3SiN_3 and $\text{Mes}^*\text{N}(\text{SiMe}_3)\text{AsCl}_2$ in CH_2Cl_2 at -40°C when a solution of GaCl_3 in CH_2Cl_2 is added (Scheme 1). In this case, the reactive species, the iminoarsane **2**, is generated in situ by GaCl_3 -assisted elimination of Me_3SiCl . The workup for both procedures is the same. The reaction mixture is allowed to warm to ambient temperature over a period of one hour. The solution is then concentrated in vacuo to incipient crystallization and stored in a freezer at -25°C . After crystallization and drying in vacuo, **3** remains as colorless crystals (yield: 92–98 %).^[6a,c] Pure, dry **3** is stable at temperatures up to 190–195 °C (decomposition), is neither heat nor shock sensitive, and decomposes very slowly at ambient temperatures in the solid state and in solvents, releasing N_2 gas. Colorless crystals of **3** rapidly turn yellow when traces of water or oxygen are present.

X-ray structure analysis of **3** confirms the formation of the desired tetrazarsole derivative (Scheme 1). This compound crystallizes as colorless needles in the monoclinic space group $P21/c$ with four molecules per unit cell.^[6b] As depicted in Figure 1, the AsN_4 ring is planar, like in the pentazoles,^[7] triazadiphospholes,^[1] and tetrazaphospholes (**5**),^[3] and the structural features of **3** and **5** are very similar. The AsN_4 ring is slightly distorted, with two longer N–N bonds ($d(\text{N1}-\text{N2}) =$

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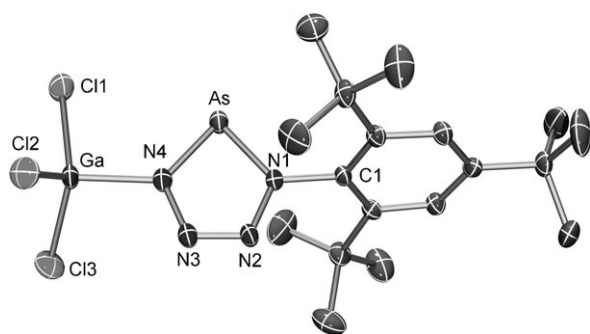


Figure 1. ORTEP drawing of the crystal structure of **3**. Thermal ellipsoids are shown with 50% probability at 173 K (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: As–N4 1.784(2), As–N1 1.805(2), N1–N2 1.349(3), N1–C1 1.458(4), N2–N3 1.286(3), N3–N4 1.366(3), N4–Ga 1.964(2), Ga–Cl3 2.1463(9), Ga–Cl1 2.1499(9), Ga–Cl2 2.1503(9); N4–As–N1 82.8(1), N2–N1–C1 117.3(2), N2–N1–As 115.2(2), C1–N1–As 127.4(2), N3–N2–N1 113.2(2), N2–N3–N4 114.0(2), N3–N4–As 114.8(2), N3–N4–Ga 117.4(2), As–N4–Ga 127.7(1), N4–Ga–Cl3 105.15(7), N4–Ga–Cl1 101.48(7), Cl3–Ga–Cl1 114.61(4), N4–Ga–Cl2 106.33(7), Cl3–Ga–Cl2 113.70(4), Cl1–Ga–Cl2 113.97(4).^[6b]

1.349(2) and $d(\text{N3–N4})=1.366(3)$; **5**: 1.355(5) and 1.374(5) Å) and one very short N–N bond ($d(\text{N2–N3})=1.286(3)$; **5**: 1.286(5) Å). These N–N bonds of 1.28–1.38 Å are substantially shorter than the sum of the covalent radii ($d_{\text{cov}}(\text{N–N})=1.48$ and $d_{\text{cov}}(\text{N=N})=1.20$),^[8] which indicates partial double-bond character for all the N–N bonds, with the N2–N3 bond having a bond order close to two. Although both **3** and **5** seem predisposed to the release of molecular nitrogen, the arsenic analogue is stable at ambient temperatures, and no significant release of molecular nitrogen was observed, in contrast to **5**.^[3] Obviously, the “naked” AsN₄ ring is better kinetically protected in the sandwich between the large aryl and GaCl₃ units (Figure 2).

Partial double-bond character can also be assumed for the two As–N bonds ($d(\text{As–N1})=1.784(2)$ and 1.805(2) Å) of the AsN₄ ring ($d_{\text{cov}}(\text{N–As})=1.91$ and $d_{\text{cov}}(\text{N=As})=1.71$ Å; 1.82–1.84 Å in cations of 1,3,2-diazarsolenes^[8,9]). In contrast to the well-known iminophosphanes,^[10] little is known about the corresponding compounds containing As=N bonds.^[5,9,11] The first fully characterized compound with an As=N bond ($d(\text{As–N})=1.714(7)$ and 1.745(7) Å) was *N,N*-bis(2,4,6-tri-*tert*-butylphenyl)amino-iminoarsane, prepared by Lappert et al. in 1986.^[12]

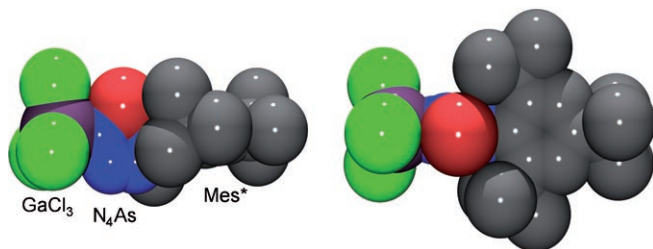


Figure 2. Space-filling representation of **3** (left: AsN₄ ring in the plane of the page, right: turned by 90°); Cl green, Ga purple, N blue, As red, C gray.

The Ga–N bond length of 1.964(2) Å is in the typical range for GaCl₃ adducts (1.990(4) in **5**). The N–As–N angle of 82.8(1)° (88.2(2)° in **5**) is very small compared to the As–N–N (114–116°) and N–N–N angles (113–114°). In the crystal, all AsN₄ rings are parallel to each other; the same holds true for the Mes* groups, which, however, are almost perpendicular to the AsN₄ rings (Figure 3). The short As–N and N–N bonds,

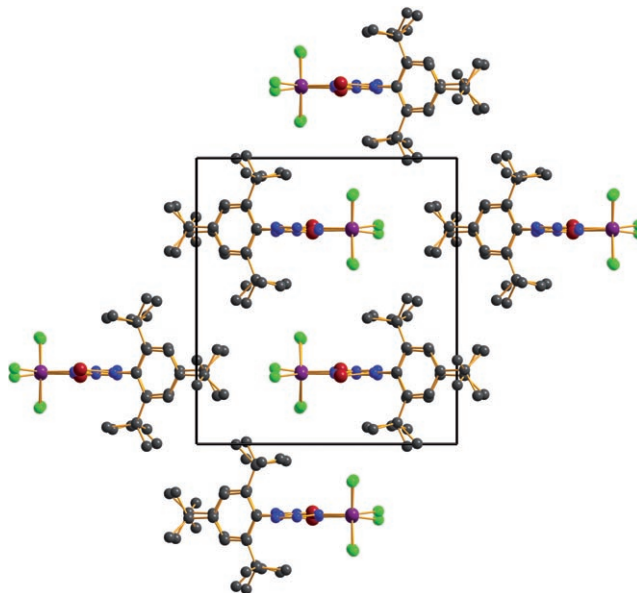
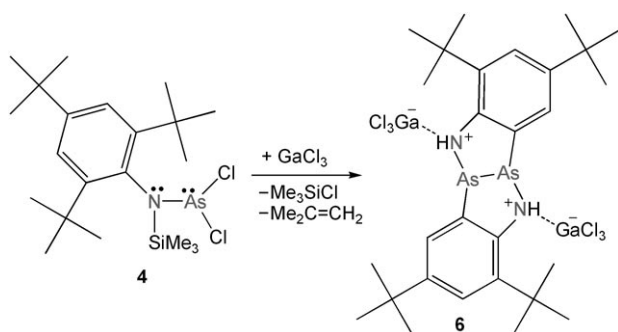


Figure 3. View along the *c* axis of **3**. Color code as in Figure 2.

together with the planarity, indicate the presence of a strongly delocalized 6 π -electron system, which is supported by molecular orbital (MO) and natural bond orbital (NBO) calculations.^[6c,13,14] As expected, according to NBO analysis the σ and π As–N bonds within the AsN₄ ring of **3** are strongly polarized (σ : 20/80 and π : 22/78%) with partial charges of +1.21 at arsenic and –0.53 and –0.84 *e* at N1 and N4, respectively, while the bonds between the adjacent nitrogen atoms of the ring are almost ideally covalent ($q(\text{N2})=q(\text{N3})=0.00$). We calculate a charge of +0.12 *e* at the exocyclic carbon atom (C1) and +1.44 *e* at the gallium center. The computed charge transfer in this Lewis base–acid adduct (**3**) is 0.14 *e* (**5**: 0.15 *e*).

Finally, we wanted to answer the question of what happens when GaCl₃ is added to **4** without the 1,3-dipole Me₃SiN₃ (Scheme 2).^[6a–c] It can be assumed that in the first reaction step, Me₃SiCl is also eliminated upon adding GaCl₃, but the very reactive iminoarsane (formally a dipolarophile) cannot be quenched with Me₃SiN₃, and hence it slowly attacks the *tert*-butyl group of the Mes* moiety, finally yielding the GaCl₃ diadduct **6** (Scheme 2). The formation of **6** was unequivocally confirmed by X-ray crystallography and NMR spectroscopy.^[6a–c] Compound **6** crystallizes as colorless blocks in the monoclinic space group *C2/c* with four molecules per unit cell.^[6b] The molecular structure of **6** (Figure 4) shows it to be a formal dimer, with two nonplanar five-membered rings connected by a long As–As bond



Scheme 2. Reaction of **4** with GaCl_3 without Me_3SiN_3 .

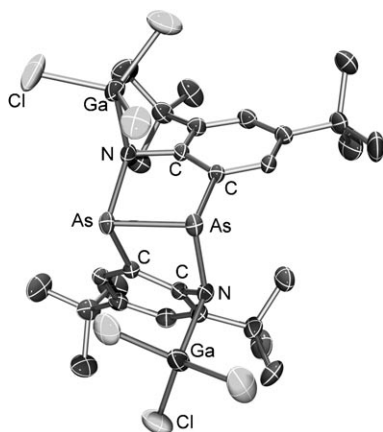


Figure 4. ORTEP drawing of the crystal structure of **6**. Thermal ellipsoids are shown with 50% probability at 173 K (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: As–C 1.947(3), As–N 1.999(2), As–As 2.4174(7), N–C 1.451(3), N–Ga 2.018(2); C–As–N 95.4(1), C–As–As 89.92(7), N–As–As 86.90(6), C–N–As 114.5(2).^[6b]

(2.4174(7); for comparison: 2.2560(5) in base-stabilized amidodiarsenes^[15] and 2.433(2) Å in $\text{Me}_2\text{As}=\text{AsMe}_2$ ^[16]).

In summary, we have reported a simple synthetic route to the first tetrazarsole, which was isolated as a GaCl_3 -stabilized adduct in high yield (greater than 90%). Compound **3** was fully characterized and has an electronic structure that is related to those of aromatic hydrocarbons that have $4n+2$ π electrons and therefore formally obey the Hückel rule. The tetrazarsole can formally be regarded as the [3+2] cycloaddition product of $[\text{Mes}^*\text{N}=\text{As}]^+$ and N_3^- ions. This cycloaddition only occurs if Me_3SiCl elimination is induced by the Lewis acid GaCl_3 , releasing the dipolarophile. Without a 1,3-dipolar molecule, GaCl_3 still triggers the Me_3SiCl elimination, but the very reactive iminoarsane is not quenched, and in an intermolecular process a cyclic diarsane is formed, while one *tert*-butyl group is removed.

Experimental Section

General information is included in the Supporting Information.^[6]

3: M.p. 190–195°C (dec.). Elemental analysis (%): calcd $\text{C}_{18}\text{H}_{29}\text{AsCl}_3\text{GaN}_4$ (552.44 g mol^{-1}): C 39.13, H 5.29, N 10.14; found:

C 39.17, H 5.56, N 9.97. $^1\text{H NMR}$ (25°C, CD_2Cl_2 , 300 MHz): δ = 1.04 (s, 18H, *o*-*t*Bu), 1.38 (s, 9H, *p*-*t*Bu), 7.66 ppm (s, 2H, CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (25°C, CD_2Cl_2 , 75 MHz): δ = 31.5 (C8, $(\text{CH}_3)_3$), 33.5 (C6, $(\text{CH}_3)_3$), 35.9 (C7, $\text{C}(\text{CH}_3)_3$), 37.6 (C5, $\text{C}(\text{CH}_3)_3$), 125.1 (C3), 132.7 (C2), 146.8 (d, C1), 154.5 ppm (C4) (see Figure S1^[6] in the Supporting Information). Raman (75 mW, 25°C, 3000 scans): $\tilde{\nu}$ = 3111 (1), 2969 (9), 2936 (7), 2911 (10), 2786 (2), 2755 (2), 2713 (1), 1596 (2), 1466 (1), 1442 (1), 1285 (1), 1244 (2), 1198 (1), 1178 (1), 1146 (1), 1007 (1), 924 (1), 821 (2), 772 (1), 594 (1), 574 (1), 523 (2), 451 (1), 404 (1), 358 cm^{-1} (2). IR (ATR, 25°C, 32 scans): $\tilde{\nu}$ = 2962 (s), 2867 (m), 1596 (m), 1568 (w), 1474 (m), 1421 (m), 1395 (m), 1363 (s), 1271 (m), 1235 (m), 1215 (m), 1198 (w), 1128 (w), 1030 (m), 1015 (s), 963 (m), 927 (w), 880 (m), 771 (m), 712 cm^{-1} (s). MS (EI, *m/z*, > 5%): 43 (12) $[\text{C}_3\text{H}_7]^+$, 57 (20) $[\text{C}_4\text{H}_9]^+$, 69 (20), 91 (20) $[\text{NAsH}_2]^+$, 112 (14), 230 $[\text{Mes}^*\text{H}-\text{Me}]^+$, 246 (100) $[\text{Mes}^*\text{H}]^+$, 261 (17) $[\text{Mes}^*\text{NH}_2]^+$.

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