

Heterocycles

Isolation of 1,4-Diarsinine-1,4-diide and 1,4-Diarsinine Derivatives

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Dedicated to Professor Holger Braunschweig on the occasion of his 60th birthday

Abstract: 1,4-Diarsinine-1,4-diide compound $[(ADC^{Ph})As]_2$ (**5**) ($ADC^{Ph} = [C(DippN)]_2CPh$, $Dipp = 2,6-iPr_2C_6H_3$) with a planar C_4As_2 ring fused between two 1,3-imidazole scaffolds has been isolated as a red crystalline solid. Compound **5**, formally comprising an 8π -electron C_4As_2 ring, is antiaromatic and undergoes $2e$ -oxidation with $AgOTf$ to form the 6π -electron aromatic system $[(ADC^{Ph})As]_2(OTf)_2$ (**6**).

Benzene derivatives containing heavier main-group elements (E) in an unsaturated $C_{6-n}E_n$ ring are highly appealing synthetic targets because of their intriguing electronic structure, reactivity, and physical properties.^[1] The close resemblance between benzene (C_6H_6) and pyridine (C_5H_5N) is well-known, the stability of heavy heteroarenes C_5H_5E , however, decreases according to $E = P > As > Sb > Bi$.^[2] This is because of the weak $C=E$ π -interaction, making these species highly reactive. The first breakthrough was made by Märkl in 1966 with the isolation of 2,4,6- $Ph_3C_5H_2P$.^[3] Over the years numerous stable compounds featuring one or more phosphorus atoms in a six-membered unsaturated ring have been reported.^[4] In contrast, analogous stable arsenic (as well as Sb and Bi) species remained extremely rare.^[5] In 1971, Ashe reported the parent arsabenzene **I** (Figure 1),^[4f] while in 1969, Jutzl^[6] and Bickelhaupt^[7] independently described the synthesis of 9-arsanthracene **II**. In 2001,^[8] Ashe and co-workers also reported 1-arsanaphthalenes **III**. While **I** was found to be

a distillable liquid, **II** and **III** could not be isolated as monomers because of their high propensity to form Diels–Alder dimers. Very recently, Dostál et al. isolated a 1-arsanaphthalene monomer **IV** and demonstrated its diene-like reactivity.^[9]

Phosphorus analogs of pyrazine (1,4-diazabenzene) remained rather rare species and no stable examples of 1,4-diarsinine **V** or **VI** are known to date. While Kalb described the synthesis of the parent 9,10-diarsanthracene **VII** already in 1921,^[10] it was, however, later shown to be a Diels–Alder dimer.^[11] Despite the significant potential of polycyclic aromatic hydrocarbons (PAHs) containing heavy main-group elements in materials science,^[12] no stable example of a 1,4-diarsinine derivative is known to date. Very recently, we have developed a conceptually new approach to access stable cyclic main-group compounds that relies on the use of anionic dicarbenes (ADCs) as key structural motifs.^[4i,13]

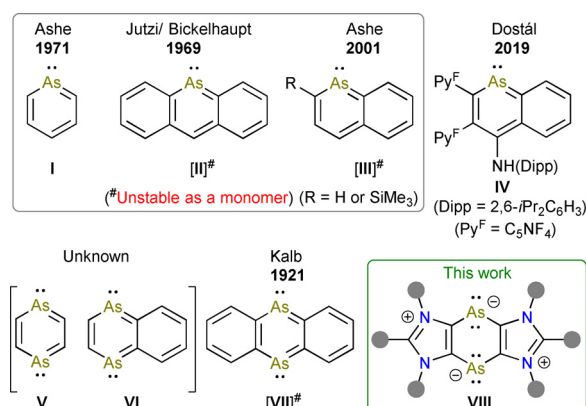


Figure 1. Selected examples of arsenic $\lambda^3\sigma^2$ -heterocycles.

Herein we report the synthesis, structure, and reactivity of 1,4-diarsinine-1,4-diide **VIII** and the corresponding $2e$ -oxidized species (**VIII**)²⁺, the 1,4-diarsinine derivative, containing a C_4As_2 ring fused between two 1,3-imidazole units.

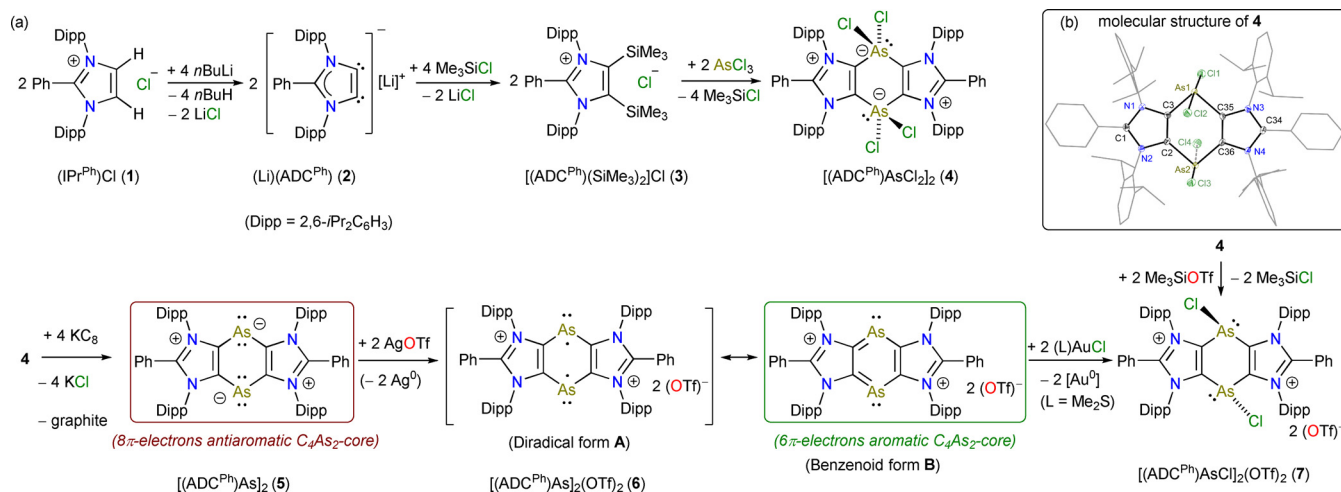
The desired precursor $[(ADC^{Ph})AsCl_2]_2$ (**4**) ($ADC^{Ph} = [C(DippN)]_2CPh$, $Dipp = 2,6-iPr_2C_6H_3$) was prepared by reacting C_4,C_5 -bis-silylated-1,3-imidazolium chloride **3**^[4i] with $AsCl_3$ as a colorless crystalline solid (Scheme 1).^[14] Like $(NHC)AsCl_3$,^[15] $(NHC = N\text{-heterocyclic carbene})$ **4** may be considered as a hypervalent arsenic(+3) compound with four-coordinated arsenic atoms. Treatment of **4** with 4 equivalents of KC_8 affords **5** as a red crystalline solid in 96% yield. Each of the arsenic atoms of **5** is in a formal oxidation state of

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Scheme 1. a) Synthesis of 4–7. b) Solid-state molecular structure of 4. Thermal ellipsoids are displayed at the 50% probability level. H atoms and CH₂Cl₂ molecules are omitted. Aryl substituents are depicted as wire-frame models for clarity.

+1 and has two lone pairs of electrons, as in the NHC–arsinide compounds (NHC)AsR (R = H or an aryl group).^[16] The planar C₄As₂ ring of **5** with a formal 8π-electron count should be, according to Hückel’s rule, antiaromatic (see below).^[17] Therefore, its 2e-oxidation to the corresponding 6π-electron species should be a favorable process. Indeed, **5** reacts with AgOTf to quantitatively form **6** as a yellow crystalline solid (Scheme 1). Further oxidation of **6** is also viable with (Me₂S)AuCl to yield **7**, which is also accessible on treatment of **4** with Me₃SiOTf.

Compounds **4–7** are stable under an inert gas atmosphere. The ¹H and ¹³C{¹H} NMR spectra of **4–7** (see the Supporting Information) exhibit expected signals for the ADC^{Ph} moieties, which are fully consistent with their solid-state molecular structures established by single-crystal X-ray diffraction. **4** (Scheme 1), **5**, **6**, and **7** (Figure 2) comprise a C₄As₂ framework. Each of the arsenic atoms of **4** is four-coordinated and has two chloride substituents. The As1–Cl2 (2.592(1) Å) and As2–Cl4 (2.647(1) Å) bonds are longer than the As1–Cl1 (2.355(1) Å) and As2–Cl3 (2.336(1) Å) bonds. The latter is within the range of those of (IPr)AsCl₃ (2.171(1)–2.484(2) Å).^[15] The As–C bond lengths (Table 1) of **4** (1.947(3)–1.957(3) Å) are smaller than that of (IPr)AsCl₃ (2.018(3) Å),^[15] which is consistent with the stronger σ-donor property of C4 carbenes.^[18] The C–C bond lengths

(1.361(4), 1.364(4) Å) and the N–C–N bond angles (106.4(2), 107.5(2)°) of the C₃N₂ ring of **4** are comparable with those of **1** (1.353(2) and 106.4(2)°).^[19] The six-membered C₄As₂ ring of **5** and **6** (Figure 2) is almost planar. The C–C bond lengths of **5** (1.383(2)–1.384(2) Å) and **6** (1.395(7), 1.398(7) Å) are larger than those of **4** (Table 1). The As–C bond lengths of **5** (1.918(2)–1.923(2) Å) and **6** (1.856(5)–1.877(5) Å) are slightly smaller than those of **4**. The shortening of As–C bonds of **6** as compared to those of **5** may be attributed to the aromatic character of **6**. The As–C bond lengths of **5** are smaller than those of **4**, suggesting π-conjugation of the lone pairs of As atoms to the adjacent carbon atoms of the C₄As₂ framework (see Figure 4). The As–C bonds of **5** and **6** are longer than typical As=C double bonds (1.816–1.827 Å) in non-conjugated acyclic arsaalkenes^[20] but shorter than the calculated C–As single bond length (1.96 Å)^[21] and those measured for a 1,4-dihydro-1,4-diaarsinine species [(RC)₂As(Me)]₂ (R = CO₂tBu, 1.962–1.979 Å) containing a non-conjugated C₄As₂ ring.^[22] The elongation of C–C and the shortening of As–C bonds of **5** and **6** concerning **4** suggest delocalization of π-electrons over the C₄As₂ ring of the former.^[4i,13]

The calculated nucleus independent chemical shift (NICS) values for the C₄As₂ ring of **5** (NICS(1)_{zz} = +17.49) and **6** (NICS(1)_{zz} = –15.00) indicate antiaromatic and aromatic character, respectively.^[23] This is also manifested in the

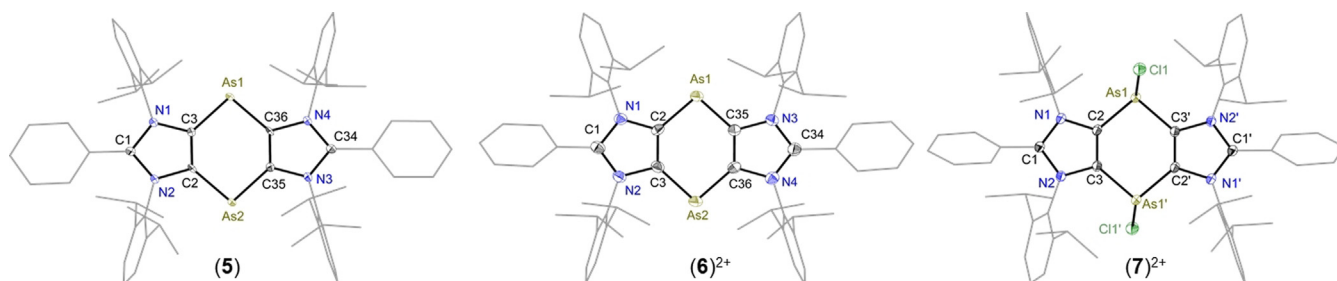
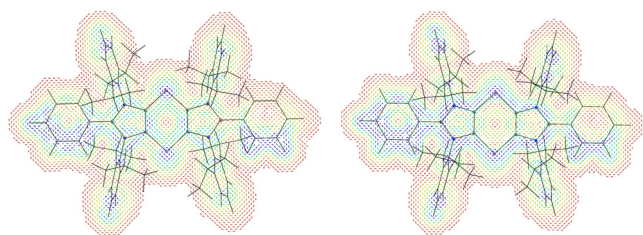


Figure 2. Molecular structures of **5**, **6**²⁺, and **7**²⁺. Aryl substituents are shown as wire-frame models. Only one of the three molecules per unit cell is shown for **5**, H atoms and solvent molecules are omitted. The OTf anions for **6** and **7** have been omitted. Thermal ellipsoids for the C₆N₄As₂ core are shown at the 50% probability level.

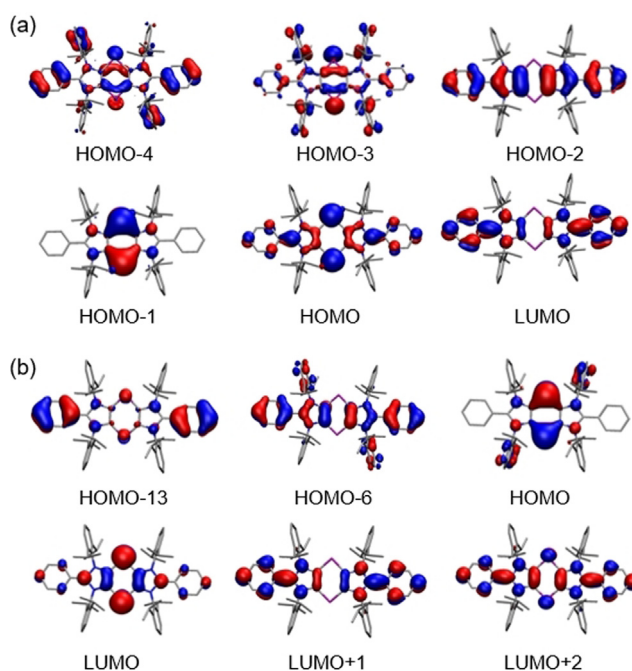
Table 1: Selected bond lengths (Å) and angles (°) of **4–7**.

	4	5	6	7
As–C	1.947(3)–	1.918(2)–	1.856(5)–	1.938(9),
	1.957(3)	1.923(2)	1.877(5)	1.942(1)
C–C	1.361(4),	1.383(2)–	1.395(7),	1.361(2)
	1.364(4)	1.384(3)	1.398(7)	
N–C	1.391(4)–	1.389(2)–	1.390(6)–	1.395(2),
	1.406(3)	1.397(2)	1.409(6)	1.398(2)
N–C'	1.349(4)–	1.363(2)–	1.342(7)–	1.346(2),
	1.359(4)	1.367(2)	1.356(7)	1.353(2)
C–As–C	95.1(1),	92.6(1)–	93.3(2),	95.0(1)
	95.2(1)	93.2(1)	94.5(2)	
C–C–As	130.2(2)–	132.9(2)–	132.0(4),	131.4(1),
	131.5(2)	133.8(1)	133.6(4)	131.9(2)

anisotropy of the induced current density (ACID)^[24] and the magnetically induced current density (MICD)^[25] analysis of **5** and **6** (Figures S38–S41). According to MICD (Figure 3), **5** has local conjugation over the imidazole rings, while the conjugation in **6** spans over the periphery of all three rings. The ¹³C{¹H} NMR signal for the C₄As₂ carbon nuclei of **6** (169.6 ppm) appeared at downfield relative to that of **5** (154.7 ppm), which can be rationalized by a ring-current effect from 6 π -electrons in the former.

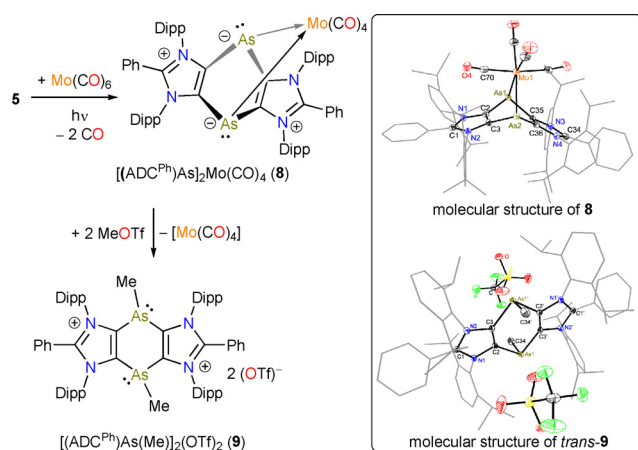
**Figure 3.** MICD profiles of **5** (left) and **6**²⁺ (right) calculated in a plane placed 0.5 Å above the molecular plane at the BP86-D3BJ/def2-TZVPP computational level. Red to dark blue represents weak to strong current density in a range between 0 to 0.001 atomic units.

The DFT-optimized structures of **5** and **6** (Figure S33) at the BP86-D3BJ/def2-SVP level of theory are in good agreement with their solid-state molecular structures (Figure 2). The HOMO–4 and HOMO–3 of **5** are the σ -type lone-pair orbitals at the arsenic atoms, while the HOMO–1 and HOMO are the other two lone-pair orbitals of π -symmetry (Figure 4a). The HOMO of **5** becomes the LUMO of **6** (Figure 4b). The HOMO and HOMO–1 of **6** are also the π -symmetry orbitals mainly located at the C₄As₂ ring. To further shed light on the electronic structures of **5** and **6**, we also performed CASSCF(12,12) calculations. The active space is comprised of 12 electrons distributed in 12 orbitals originating from the π - and π^* -orbitals of arsenic and carbon atoms of the C₄As₂ framework along with the σ - and σ^* -orbitals of the arsenic atoms (see the Supporting Information). The singlet is the ground state for both **5** and **6** with the singlet–triplet energy gap (ΔE_{S-T}) of 15.2 and 29.0 kcal mol⁻¹, respectively. HOMO (**5**: 0.94e; **6**: 1.45e) and LUMO (**5**: 0.66e; **6**: 0.85e) show fractional occupations. The CI vector coefficients indicate a weak diradical character for **5** (11.7%) and **6**

**Figure 4.** Kohn–Sham molecular orbitals (isovalue 0.03) of **5** (a) and **6**²⁺ (b) at BP86-D3BJ/def2-TZVPP level of theory. H atoms were omitted for clarity.

(7.4%).^[26] The quantum theory of atoms in molecules (AIM) analysis points toward strongly polarized As–C bonds for **5** and **6**, which is in line with positive partial charges at the arsenic atom of 0.33e (**5**) and 0.78e (**6**). The lower conjugation in **5** than **6** can be assessed by the Wiberg Bond Indices (WBI), which are 1.05 au and 1.13 au, respectively. The UV/Vis–NIR spectrum of **5** exhibits two main absorptions at λ_{\max} = 985 and 890 nm, which based on TD-DFT analysis may be assigned to H→L and H→L+5 transitions (Table S9), respectively. The UV/Vis spectrum of **6** shows two absorptions at λ_{\max} = 414 and 451 nm, which are related to the H–1→L and H–5→L transitions, respectively.

Treatment of **5** with Mo(CO)₆ under UV-irradiation led to the formation of [[(ADC^{Ph})As]₂[Mo(CO)₄]] (**8**) as a brown crystalline solid (Scheme 2). The solid-state molecular structure of **8** (Scheme 2) reveals a distorted octahedral geometry at the molybdenum atom. The arsenic atoms of the C₄As₂ ring, having a fold angle of 60.3(1)° between the C₂As₂ planes, bind to the Mo atom in a *cis*-fashion. In addition to the anticipated NMR signals for the ADC^{Ph} moieties, the ¹³C-¹H NMR spectrum of **8** exhibits two resonances at δ = 224.1 and 217.1 ppm for the axial and equatorial CO ligands. Similarly, the IR spectrum of **8** shows four CO stretching bands as expected for a *cis*-(L)₂M(CO)₄ complex, which may be assigned as A₂¹ (medium, 1976 cm⁻¹), B₁ (shoulder, 1938 cm⁻¹), A₁¹ (very strong, 1850 cm⁻¹), and B₂ (very strong, 1815 cm⁻¹).^[27] The As–Mo bonds (2.785(2), 2.802(2) Å) of **8** are longer than those of (Ph₃As)₂Mo(CO)₄,^[28] which may be due to steric reasons. Each of the arsenic atoms of **8** has trigonal pyramidal geometry with a sum of the angles of ca. 271°, consistent with the presence of a lone pair of electrons. The reaction of **8** with MeOTf yielded the



Scheme 2. Synthesis and structures (inset) of **8** and **9**.

methylated product **9** (Scheme 2), with the concomitant loss of the Mo(CO)_4 fragment. The ^1H NMR spectrum of **9** exhibits a singlet at 0.90 ppm for the As-CH_3 groups along with the resonances for the ADC^{Ph} units. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** shows no signal in the 170–240 ppm region, indicating the absence of CO groups. The X-ray diffraction analysis of a sample of **9** disclosed the presence of two different types of crystals, which were found to be *cis* and *trans* stereoisomers of **9** (Figures S31 and S32). Each of the arsenic atoms is three-coordinated and has a distorted trigonal pyramidal geometry. The As-C_{Me} (1.893(8)–1.955(8) Å) and As-C_{ADC} (1.939(8)–1.971(8) Å) bond lengths compare well with those of R_3As ($\text{R} = \text{alkyl or aryl}$) derivatives (1.947(5), 1.960(8) Å).^[29] The C=C bond lengths (av. 1.36 Å) of the imidazole units are similar to that of **1** (1.353(2) Å). Thus, **9** may be described as an arsine-functionalized 1,3-imidazolium dication.

In conclusion, the first 1,4-diarsinine-1,4-diide (**5**) and 1,4-diarsinine (**6**) derivatives have been reported as crystalline solids. Experimental and computational findings suggest that the planar C_4As_2 ring of **5** and **6**, formally containing 8 π - and 6 π -electrons, respectively, is antiaromatic and aromatic. Preliminary reactivity studies of **5** and **6** corroborate these descriptions. Further investigations are currently underway to explore the coordination chemistry of **5** and **6** as well as their applications in materials science.

Deposition numbers 2070342, 2070343, 2070344, 2070345, 2070346, 2070347 and 2070348 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aromaticity · arsenic · diarsinine · dicarbene · heterocycle

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