Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
DOI: 10.1002/zaac.202100006
ARTICLE

On thio-substituted N-heterocyclic arsines

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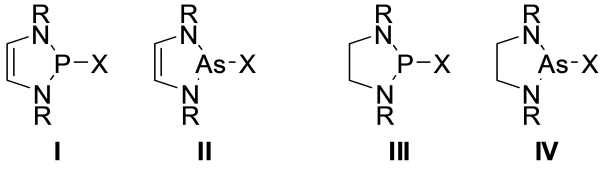
Dedicated to Professor Dr. Christoph Janiak on the occasion of his 60th birthday

Metathesis of N-heterocyclic chloroarsines with sulfur-based nucleophiles furnished thio-substituted 1,3,2-diazarsolidines and 1,3,2-diazarsolenes. Crystallographic and NMR spectroscopic studies revealed that a thiocyanato-diazarsolene exhibits a salt-like structure composed of weakly interacting thiocyanate and arsenium ions, while the remaining products formed neutral molecules. The structural data indicate that the heterocyclic framework induces an elongation of exocyclic As–S bonds that is more prominent in diazarsolenes than in diazarsolidines and parallels the bond polarisation effect established for N-heterocyclic phosphines. The NMR data suggest that diazarsolenes undergo facile inversion of the pyramidal configuration at arsenic, which was successfully modelled by DFT studies.

Introduction

1,3,2-Diazaphospholenes **I** (Scheme 1) are a class of N-heterocyclic phosphines that have gained attention for their special bonding situation, which induces a unique polarization of the exocyclic P–X bond.[1] The specific reactivity arising from this effect propelled not only unusual stoichiometric reactions, involving e.g. the activation of P–C or P–H bonds, but was also decisive for the discovery of novel catalytic transformations that are currently emerging into interesting synthetic tools in organic synthesis.[2] In the wake of these developments, also homologous 1,3,2-diazarsolenes **II**[3] have moved into focus and were, like their phosphorus congeners, shown to be capable of mediating catalytic hydroboration.[2a,4] The actually catalytically active species – a benzannulated analogue of a secondary diazarsolene (**II**, X = H) – being unstable, chloro- or alkoxy-substituted derivatives were employed as pre-catalysts.[4] Because arsenic is commonly deemed a thiophilic chemical element, we anticipated that thio-substituted N-heterocyclic arsines (**II**, X = SR) might likewise be readily accessible compounds whose superior resilience toward hydrolysis should grant easy handling and might make these species likewise potentially interesting pre-catalysts. In this context, it was of interest whether a similar hyperconjugation mechanism as in **I**[1] enables tuning the polarity of the exocyclic As–S bond. To tackle this question, we set out to synthesize thio-substituted diazarsolenes **II** and diazarsolidines **IV**[3a,5] and evaluate their structural features, knowing that this approach had proven effective in case of the lighter homologues.[1]



Scheme 1. Molecular structures of 1,3,2-diazaphospholenes **I**, 1,3,2-diazarsolenes **II**, 1,3,2-diazaphospholidines **III** and 1,3,2-diazarsolidines **IV** (R = alkyl, aryl, X = various substituents, e.g. H, Cl, Cp, C≡CR, OR, SR).

Results and Discussion

Syntheses. The synthesis of thio-functionalised N-heterocyclic arsines was accomplished by metatheses of chloro-substituted precursors with suitable sulfur-based nucleophiles (Scheme 2).

The chloro-arsines employed comprise previously known diazarsolidine **1a**[3a] and diazarsolenes **2a-b**[3] as well as newly synthesized **2c**. NMR spectroscopic studies indicated that reactions of all starting materials with sodium thiocyanate (**3**), potassium tert-butyl-xanthogenate (**4**) and sterically encumbered sulfhydryl silane **5** proceeded in a similar manner, even if isolation of analytically pure products was not in all cases feasible. Thus, clean thiocyanato- and xanthogenato-substituted N-heterocyclic arsines **6** and **7** were only obtained from reactions of **3** with **2a** and of **4** with **2c**, respectively, whereas

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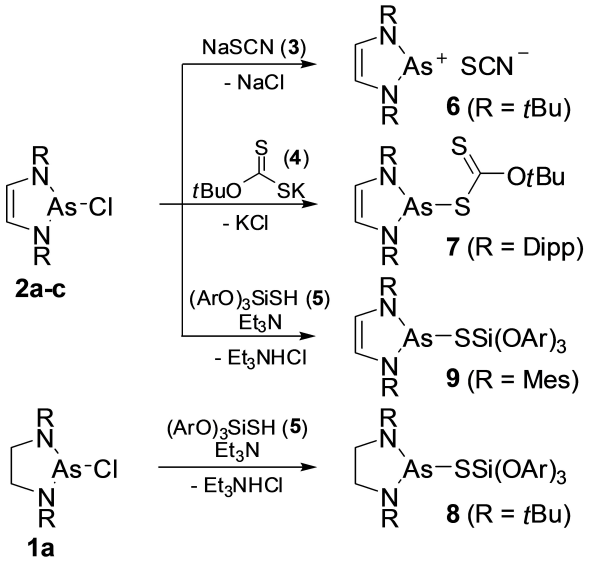
Supporting information for this article is available on the WWW under https://doi.org/10.1002/zaac.202100006



Scheme 2. Synthesis of thio-substituted N-heterocyclic arsies **6**–**9** (Ar = Dipp, R = *t*Bu (**1a**, **2a**), Mes (**2b**), Dipp (**2c**); Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-diisopropylphenyl).

all further attempts yielded products contaminated by varying amounts of unreacted starting materials that could not be separated. Likewise, base assisted dehydrohalogenation proceeded smoothly in reactions of **5** with **1a** and **2b** to furnish orthosilicothioates **8** and **9**, respectively. The new products were identified and characterized by analytical and spectroscopic data and single-crystal XRD studies.

Crystallographic studies. The crystals of **2c** and **7**–**9** comprise discrete molecular entities (Figures 1–3), whereas crystalline **6** is best described as ionic compound containing weakly interacting diazarsolenium cations and thiocyanate anions (Figure 4). A similar composition had also been established for the corresponding phosphorus homologue (**10**).[6]

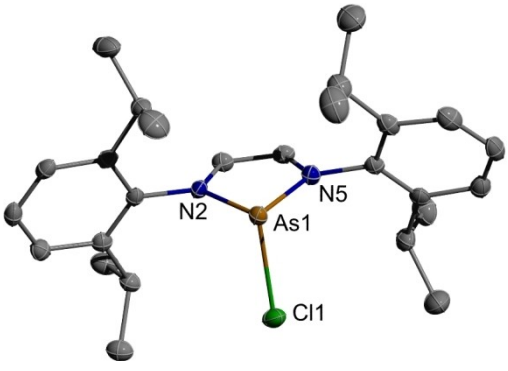


Figure 1. Representation of the molecular structure of one of two crystallographically independent molecules of **2c** in the crystal. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances and angles are listed in Table 1.

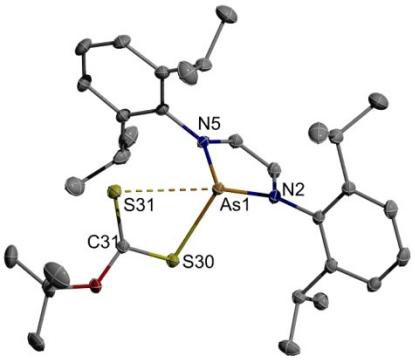


Figure 2. Representation of the molecular structure of **7** in the crystal. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level and only one of two positions of disordered iPr-groups is shown. Selected distances and angles are listed in Table 1.

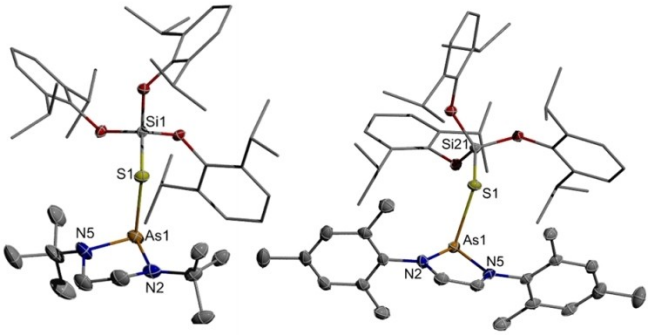


Figure 3. Representation of the molecular structures of **8** (left, one of two crystallographically independent molecules shown) and **9** (right) in the crystal. For clarity, hydrogen atoms were omitted, carbon atoms of Dipp-substituents drawn using a wire model, and only one of two positions of disordered iPr groups is displayed. Thermal ellipsoids are drawn at the 50% probability level. Selected distances and angles are listed in Table 1.

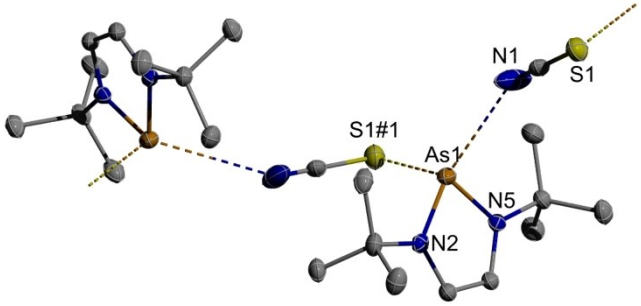


Figure 4. Representation of the molecular structure of two formula units of **6** in the crystal. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances and angles are listed in Table 1.

The conformational features of all molecules studied comply with established characteristics, viz. the prevalence of twisted

and envelope-shaped ring conformations in diazarsolidines and diazarsolenes, and of a planar ring in the diazarsolenium cation, respectively.[3] The As–N distances match those in known N-heterocyclic arsines and arsenium ions extending from 1.79 to 1.84 Å.[3,4] Taken together, the distances in all N-heterocyclic arsines and arsenium ions (see Table 1) are slightly below the reported 'standard' As–N distance of 1.858 Å,[7] which might be taken as an indication of above-average As–N (hyper) conjugation in the five-membered rings. However, the observed distances show neither a clear-cut dependence on the nature of the exocyclic substituent nor a pronounced shortening upon its abstraction as had been noticed for homologous diazaphospholenes (**I**) and diazaphospholidines (**III**).[1,8] A forthright interpretation of trends in terms of electronic effects is currently out of reach and requires presumably a larger body of experimental data.

The intermolecular interactions in diazarsolenium thiocyanate **6** induce, like in its lighter homologue **10**,[6] a one-dimensional stacking of anions and cations. However, apart from this superficial similarity, the packing motifs in both compounds are quite different. Whereas the anions in **10** connect to two adjacent phosphenium cations exclusively via their sulfur atoms, the closest interaction in **6** links the N-terminus of the anion to the arsenic centre in one adjacent cation (N···As 3.137(4) Å), and the S-Terminus engages in a weaker contact (S···As 3.5701(11) Å) to a second cation. Because both distances significantly exceed standard bond lengths (As–N 1.858 Å, As–S 2.266 Å[7]), it is deemed unlikely that the contacts imply a significant covalent contribution with concomitant charge transfer. However, the preference of the cation to approach the N- rather than the S-terminus of the thiocyanate is neither well in accord with a pronounced thiophilicity of the arsenic centre. The reasons for the different interaction modes in **6** and **10** are not immediately evident.

The molecular N-heterocyclic arsines **7**–**9** exhibit exocyclic As–S distances between 2.415(1) and 2.467(1) Å (Table 1) clearly exceeding the standard single bond distance of 2.266 Å.[7] Although a similar structure correlation analysis of substituent effects as in the diazaphospholene system[1] is impeded by the scarcity of the available data, direct comparison of the distances in **8** and **9** carrying an identical orthosilicothioato-substituent at As can provide at least some qualitative insight. The deviation in As–S distances between **8** (2.417(1), 2.440(1) Å) and **9** (2.463(1) Å) is attributable to two effects, viz. a change from a diazarsolidine to a more unsaturated diazarsolene architecture in the heterocycle, and the formal exchange of NMes for N*t*Bu substituents. As suggested by a comparison of the As–Cl distances in **2c** (2.366–2.373 Å) and **2a** (2.6527(4) Å[3b]) and **1c** (2.3027(8) Å[9]) and **1a** (2.375(2), 2.3911(5) Å[3a]), the more electron releasing N-alkyl groups induce a similar elongation of the exocyclic bonds as in the diazaphospholene[1] and diazaphospholidine systems,[8] respectively. In this setting, the lengthened As–S distance in **9** supports the hypothesis that a diazarsolene unit likewise exert a stronger polarising effect on an exocyclic As–S bond than a backbone-saturated diazarsolidine moiety, and that this effect outweighs the influence of the N-substituents operating into the reverse direction.

A further noteworthy feature of the molecular structure of **7** is the presence of a secondary interaction between the thiocarbonyl-sulfur and arsenic atoms (As···S 2.9818(4) Å) at a distance that is intermediate between the As1–S30 single bond (2.4666(3) Å) and the sum of the van-der-Waals radii (3.73 Å[10]). The alignment of this contact roughly opposite to one of the As–N bonds (S31–As1–N2 162.18(3)°) suggests an interpretation as either a σ-hole interaction between the sulfur atom and an electron-depleted region on arsenic, or weak n(S)···σ*(As–N) hyperconjugation. Note that the second interpretation is well in accord with the slight lengthening of the As1–N2 (1.846(1) Å)

Table 1. Selected distances (in Å) and angles (in °) for **2c**, **6**–**9**.

[a]	**2c**[b]	**6**	**7**	**8**[b]	**9**
As–N2	1.814(2)	1.802(2)	1.8463(9)	1.817(3)	1.8251(18)
As–N5	[1.815(2)]	1.810(3)	1.8341(9)	[1.820(3)]	1.8266(17)
	1.818(2)			1.850(3)	
	[1.818(2)]			[1.838(3)]	
As–S/Cl	2.3663(6)	[c]	2.4666(3)	2.4146(8)	2.4628(6)
	[2.3730(6)]			[2.4402(9)]	
S–C/Si	–	1.649(4)	1.736(1)	2.0869(11)	2.0806(7)
				[2.0951(12)]	
C=X[d]	–	1.364(4)	1.657(1)	–	–
N–As–N	85.40(8)	85.5(1)	84.88(4)	87.98(13)	84.86(8)
	[85.31(8)]			[87.90(13)]	
Σ(XAsY)	288.9(2)	–	287.3(1)	287.0(3)	283.9(2)
	[289.4(2)]			[287.1(4)]	
Σ(XNY)	360.0(5)	360.0(7)	358.4(2)	352.2(7)	359.8(5)
	[359.8(5)]	360.0(6)	360.0(2)	[354.6(7)]	359.5(5)
	360.0(5)			345.6(7)	
	[360.0(5)]			[354.4(7)]	

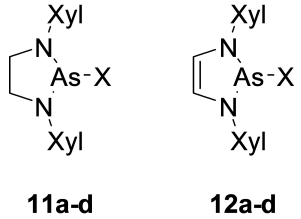
[a] Σ(XAsY) and Σ(XNY) denote the sum of bond angles around the As and N atoms and C=X the distances to the second sulfur atom in the xanthogenato or the nitrogen atom in the thiocyanato unit. [b] numbers in brackets refer to a second crystallographically independent molecule. [c] closest intermolecular distances: As–S 3.5701(11) and As–N 3.137(4) Å. [d] X = N (**6**), S (**7**).

compared to the As1–N5 distance (1.834(1) Å), and that the same phenomenon had previously been observed in dithiocarboxyl-substituted phenylarsines.[11]

Spectroscopic studies. The ^{1}H and ^{13}C NMR data of the new N-heterocyclic arsines show for the most part no peculiarities, but two features deserve some comments. Firstly, both the ^{1}H and ^{13}C NMR signals of the CH-moieties in the diazarsolene ring of **6** display a distinctive deshielding with respect to the corresponding signals of the neutral arsines **2c**, **7**, **9**. A similar effect is also known in the diazaphospholene system and was explained as a consequence of cation formation.[12] Following this argumentation, the deshielding in case of **6** supports then the hypothesis that the ionic structure established in the solid state persists in solution.

Secondly, the observation of two distinguishable ^{1}H NMR signals for the methylene protons in the NCH_2CH_2N-backbone of diazarsolidines **1c** and **8** implies that the pyramidal coordination geometry at the arsenic atom is stable with respect to configuration inversion on the NMR time scale. In contrast, the ^{1}H and ^{13}C NMR spectra of diazarsolenes **2c** and **7** reveal an equivalence of both *ortho*-isopropyl groups in each NDipp-substituent that is incompatible with the presence of a configurationally stable molecule and suggests rather a fluxional structure characterised by rapid (on the NMR time scale) inversion at the As-centre. A similar dynamics may also be presumed for **9**, although it can in this case not be ruled out that the equivalence of *ortho*- and *meta*-positions in the NMes-group is caused by rotation of the sterically less demanding substituent around the N–C bond. In total, these findings imply that the unsaturated π-electron system in the diazarsolene ring facilitates inversion of the pyramidal coordination at the arsenic atom.

Computational studies. The influence of the N-heterocyclic architecture on the inversion process was further studied by DFT calculations. To save computation time, all investigations were performed on model diazarsolidines **11** and diazarsolenes **12** (Scheme 3) featuring N-2,6-xylyl instead of computationally expensive N-Dipp substituents, and bulky triarylorthosilicothioato and *tert*-butylxanthogenato substituents in **7**–**9** were mimicked by simpler methylthio and methylxanthogenato groups, respectively. The ground-state molecular geometries of chloro-, methylthio- and xanthogenato-substituted model compounds obtained after energy optimisation were found in qualitatively good agreement with the crystallographic data of **2c** and **7**–**9**, notwithstanding some deviations in bond angles and torsional angles that are obviously attributable to decreased steric congestion in the model compounds. Because earlier computational studies on trivalent pnictogen hydrides and halides EX_3 (E = N, P, As, Sb; X = H, F, Cl, Br) had shown that the inversion may proceed via closed-shell transition states featuring either trigonal planar (C_{3v}) or T-shaped (C_{2v}) geometries,[14] transition state searches were performed from different starting geometries. Last, but not least, inversion barriers for AsF_3 and $AsCl_3$ were re-calculated at the same computational level for comparison.



Scheme 3. Molecular structures of model compounds **11a–d**/**12a–d** (Xyl = 2,6-dimethylphenyl, X = H, Cl, SMe, SC(S)OMe, see Table 2).

The lowest transition structures located for **11a-c** and **12a–c** are closed-shell states that are characterised by a distinct asymmetry in N–As–X angles (with ranges of 86–90° and 143–169°, see Figure 5) and qualify like those of the arsenic trihalides[14] as T-shaped. The transition structures of **11d** and **12d** are very similar, but feature an approximately symmetrically η^2-coordinated xanthogenato-unit, and may be classified as pseudo-T-shaped. The energies summarised in Table 2 reveal that configuration inversion at the arsenic atom requires in all N-heterocyclic arsines except **11a** lower energies than in parent arsine or arsenic trichloride and trifluoride, respectively. Inversion barriers in diazarsolenes are generally lower than in diazarsolidines and show further a strong dependence on the exocyclic substituent X, ΔG^{298}(TS) decreasing in both series in the succession X = H > SMe > Cl > SC(S)OMe.

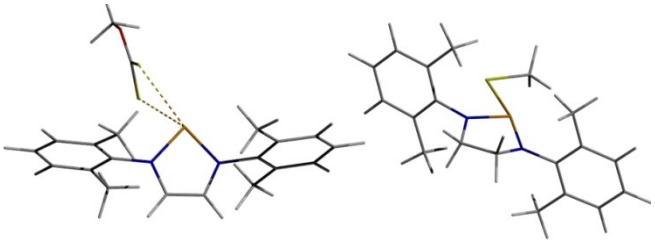


Figure 5. Wireframe representations showing the computed transition structures for the inversion of the pyramidal configuration at arsenic in **11c** (right) and **12d** (left).

Table 2. Computed Gibbs free energies of the energetically lowest transition structures for configuration inversion in diazarsolidines **11a–d**, diazarsolenes **12a–d**, and AsX_3 (X = H, F, Cl) computed at the ωB97x-D/def2-tzvp/ωB97x-D/def2-svp level of theory.

compound	X	ΔG^{298}(TS)[a]
11a	H	214.1
11b	Cl	121.5
11c	SMe	137.6
11d	SC(S)OMe	77.5
12a	H	70.3
12b	Cl	48.7
12c	SMe	63.0
12d	SC(S)OMe	46.7
AsH_3	–	165.3
AsF_3	–	190.1
$AsCl_3$	–	182.8

[a] in kJ mol^{-1} relative to the molecular ground state.

NBO analyses[15] suggest describing the bonding in the transition states of **11a–c/12a–c** as a σ-bonding 3-centre-4-electron interaction in the X–As–N 'axis' that instigates a shift of electron density from the central to the terminal atoms and is counterbalanced by an increased π-electron donation from the N-centred lone pairs to the As-atom. The substituent-dependent trends in inversion barriers reflect in this picture different apicophilicities[16] of exocyclic substituents X: low apicophilicity of X implies a high degree of covalency in the As–X bond, which weakens the opposite As–N bond (evidenced by an appropriate bond lengthening) and induces thus an overall energetic destabilisation of the transition state.

The inversion of **11d/12d** differs from that of the remaining molecules as it involves cooperative action of both sulfur atoms in the xanthogenato-unit, which change their bonding state during the process. This reaction is accordingly best pictured as an intramolecular substitution that is already foreshadowed in the molecular structure of the ground states which reveal a similar secondary interaction between the arsenic and the non-bonded sulfur atoms as was observed in crystalline **7**.

Conclusions

2-Thio-substituted 1,3,2-diazarsolidines and 1,3,2-diazarsolenes are accessible by metathesis of 2-chloro-substituted precursors with sulfur nucleophiles. A thiocyanato-diazarsolene exhibits a similar salt-like structure as its phosphorus-based congener, while orthosilicothioato and xanthogenato substituted species form neutral molecules. All molecular N-heterocyclic arsines studied exhibit a similar tendency for elongation of exocyclic As–S or As–Cl bonds as had previously been established for diazaphospholidines and diazaphospholenes. Although the scarcity of available data precludes a more detailed analysis, there is evidence that the bond lengthening effect is, like in the phosphorus congeners, stronger in the more unsaturated diazarsolenes. The hypothesis that the diazarsolene framework facilitates configuration inversion at arsenic was substantiated by computational studies.

Experimental Section

All manipulations were carried out in an atmosphere of dry argon or nitrogen using standard vacuum line techniques or in glove boxes. Solvents were dried prior to use by common procedures. NMR spectra were recorded at 303 K on Bruker Avance 400 (^{1}H 400.1 MHz, ^{13}C 100.6 MHz) or Avance 250 (^{1}H 250.1 MHz, ^{13}C 62.9 MHz) spectrometers. NMR chemical shifts were referenced to TMS using the signals of the residual protons or carbon atoms of the deuterated solvent (^{1}H: $\delta(CDCl_3)=7.24$, $\delta(CD_2Cl_2)=5.32$, $\delta(DMSO\text{-}d_6)=2.50$) as secondary references. Elemental analyses were obtained with an Elementar Micro Cube elemental analyser. The synthesis of N-heterocyclic arsines **1a** and **2a,b**[3] and silanethiol **5**[17] were carried out as described.

Crystal structure determinations. Single-crystal X-ray diffraction data for **2c**, **6**–**9** were collected on a Bruker Kappa APEX II Duo diffractometer equipped with a KRYO-FLEX cooling device with Mo-K_α radiation ($\lambda=0.71073$ Å) at 100(2) K. Crystals were selected under Paratone-N oil, mounted on nylon loops, and immediately placed in a cold stream of N_2. The structures were solved by direct methods (SHELXS-2014[18]) and refined with a full-matrix least squares scheme on F^2 (SHELXL-2014[18]). Numerical absorption corrections were applied. Non-hydrogen atoms were refined anisotropically. Further crystallographic data and details on the structure solution are given in the Supporting Information and cif-files. CCDC-2053020 to CCDC-2053024 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational studies were carried out with the Gaussian16 suite of programs.[19] Calculations were performed on isolated molecules (in the gas phase) using the ωB97X-D functional[20] and an ultrafine grid for numerical integrations. Molecular structures of ground and transition states were first energy optimized using a def2-svp basis set.[21] Searches for transition structures were performed from various starting geometries and converged always to the same geometry. Harmonic frequencies calculated at the same level allowed identifying the optimized structures as local minima (only positive eigenvalues of the Hessian matrix) or transition states (one negative eigenvalue) on the potential energy surface, and stability tests qualified the resulting densities of transition structures as stable. Gibbs free Energies at stationary states were computed by combining electronic energies recalculated with a def2-tzvp basis set[21] with the corrections derived from the frequency calculation with the smaller basis set.

2-Chloro-1,3-bis(2,6-diisopropylphenyl)-1,3,2-diazarsolene (**2c**). Lithium granules (0.15 g, 22 mmol) were added to a cooled (-78 °C) solution of bis-(2,6-diisoprophylphenyl)diazabutadiene (3.77 g, 10 mmol) in THF (40 mL). The mixture was then allowed to warm slowly (within 12 h) to room temperature. The resulting red solution was cooled to −78 °C and Et_3NHCl (3.03 g, 22 mmol) and Et_3N (1.39 mL, 10 mmol) were added. When the solution had become colourless, $AsCl_3$ (0.84 mL, 11 mmol) was added. The solution was allowed to warm to room temperature and then stirred for additional 12 h. Volatiles were removed in vacuum. The residue was treated with hexane (100 mL). The resulting suspension was filtered. The filtrate was evaporated to dryness to yield the product as a colourless solid (yield 4.14–4.48 g, 85–92%, m.p. 153 °C). Single crystals were obtained from hexane. – ^{1}H NMR ($CDCl_3$): δ = 7.37 (m, 2 H, *p*-C_6H_3), 7.27 (m, 4 H, *m*-C_6H_3), 6.58 (s, 2 H, NCH), 3.29 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, CH), 1.31 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.22 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH_3). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 147.2 (*o*-C), 135.6 (*i*-C), 128.8 (*p*-C), 124.2 (*m*-C), 123.4 (NCH), 28.6 (CH), 25.3 (CH_3), 24.7 (CH_3). MS (EI): m/z (%) = 486.2 (37%, M^+), 451.2 (100%, M^+ – Cl). – $C_{26}H_{36}AsClN_2 \cdot 0.5$ LiCl (508.16 g/mol): calcd. C 61.45 H 7.14 N 5.51, found C 61.36 H 7.29 N 5.29.

2-Thiocyanato-1,3-di-*tert*-butyl-1,3,2-diazarsolene (**6**). Method A: A solution of **2a** (103 mg, 0.40 mmol) in pentane (20 mL) was added dropwise to a suspension of NaSCN (30 mg, 0.40 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 12 h. Further NaSCN (60 mg, 0.8 mmol) was added and the mixture sonicated for 15 min in an ultrasound bath. The mixture was concentrated to approx. half of its original volume and filtered. The filtrate was evaporated to dryness to furnish the product as a yellow solid (77 mg, yield 69%). Single crystals were grown from hexane. – ^{1}H NMR ($CDCl_3$): δ = 8.10 (s, 2 H, NCH), 1.79 (s, 18 H, CH_3). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 131.7 (NCH), 62.3 (NC), 31.7 (CH_3). – $C_{11}H_{20}AsN_3S$ (301.28 g/mol): calcd. C 43.95 H 6.69 N 13.95, found C 44.39 H 6.98 N 13.15.

Method B: NaSCN (165 mg, 2.00 mmol) was added to a solution of 1,3-di-*tert*-butyl-1,3,2-diazarsolidinium-trifluormethylsulfonate[3b] (200 mg, (0.50 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 12 h during which the colour changed from colourless to yellow.

The remaining solid was removed by filtration and the clear solution evaporated to dryness to afford the product as yellow solid (136 mg, 88%).

2-*tert*-Butylxanthogenato-1,3-bis(2,6-diisopropylphenyl)-1,3,2-diazarsolene (7). A solution of **2c** (244 mg, 0.50 mmol) in hexane (30 mL) was added dropwise to a stirred solution of potassium *tert*-butylxanthogenate (94 mg, 0.50 mmol) in CH_2Cl_2 (10 mL) and hexane (10 mL). Stirring was continued for 1 h after the addition was complete, and the mixture was then concentrated under reduced pressure to approx. one quarter of its original volume. Solids were removed by filtration and the filtrate evaporated to dryness to furnish a yellow solid (139 mg, yield 46%). Single crystals were grown from hexane. ^{1}H NMR ($CDCl_3$): δ = 7.22 (m, 6 H, *m/p*-C_6H_3), 6.48 (s, 2 H, NCH), 3.26 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, CH), 1.51 (s, 9 H, CH_3), 1.33 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.22 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH_3). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 163.1 (CS_2), 147.0 (*o*-C), 136.7 (*i*-C), 125.1 (NCH), 123.9 (*p*-CH), 123.2 (*m*-CH), 88.9 (OC), 28.8 (CH), 28.1 (CH_3), 23.4 (CH_3). – $C_{31}H_{45}AsN_2OS_2$ (600.76 g/mol): calcd. C 61.98 H 7.55 N 4.66, found C 61.08 H 7.60 N 4.49.

2-Tris(2,6-diisopropylphenoxy)silylthio-1,3-di-*tert*-butyl-1,3,2- diazarsolidine (8). Silanethiol **5** (0.32 g, 0.50 mmol) was added to a solution of **1a** (0.15 g, 0.50 mmol) and Et_3N (70 µl, 0.50 mmol) in Et_2O (10 mL). The mixture was stirred for 1 h and then evaporated to dryness. The residue was extracted with pentane (20 mL). The filtered extract was concentrated to about half its original volume and stored at −30 °C to furnish the product as colourless crystals (yield 134 mg, 30%). – ^{1}H NMR ($CDCl_3$): δ = 7.04 (m, 6 H, *m*-C_6H_3), 6.94 (m, 3 H, *p*-C_6H_3), 3.44 (sept, 6 H, $^3J_{HH}$ = 6.8 Hz, CH), 3.24 (m, 2 H, NCH_2), 3.15 (m, 2 H, NCH_2), 1.21 (s, 18 H, CH_3), 1.05 (d, 36 H, $^3J_{HH}$ = 6.8 Hz, CH_2). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 148.5 (*o*-C), 138.9 (*i*-C), 123.7 (*m*-CH), 122.8 (*p*-CH), 54.9 (NC, 48.6 (NCH_2), 29.6 (CH), 27.1 (CH_3), 24.3 (CH_3). – $C_{46}H_{73}AsN_2O_3SSi$ (837.17 g/mol): calcd. C 66.00 H 8.79 N 3.35, found: C 65.40 H 8.79 N 2.87.

2-*Tris*(2,6-diisopropylphenoxy)-silylthio-1,3-bis(2,4,6-tri-methylphenyl)-1,3,2-diazarsolene (9). The synthesis was carried out as described for **8** using **2b** (12 mg, 30 µmol), Et_3N (10 µL, 30 µmol) and silanethiol **5** (17 mg, 30 µmol) to furnish 16 mg (yield 58%) of a colourless solid. – ^{1}H NMR (C_6D_6): δ = 7.01 (m, 9 H, *m/p*-C_6H_3), 6.76 (s, 4 H, *m*-CH), 5.90 (s, 2 H, NCH), 3.68 (sept, 6 H, $^3J_{HH}$ = 6.8 Hz, CH), 2.28 (s, 12 H, *o*-CH_3), 2.15 (s, 6 H, *p*-CH_3), 1.08 (d, 36 H, $^3J_{HH}$ = 6.8 Hz, CH_2) $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 149.5 (*i*-C), 139.8 (*o*-C), 137.4 (*p*-C), 137.0 (*i*-C), 136.1 (*o*-C), 129.5 (*m*-CH), 123.6 (*m*-CH), 122.8 (*p*-CH), 121.9 (NCH), 27.3 (CH), 23.7 (CH_3), 20.5 (*o*-CH_3), 19.0 (*p*-CH_3).

Acknowledgements

We thank Barbara Förtsch for elemental analyses, and Dr. Wolfgang Frey (Institut für Organische Chemie) for collecting X-ray data sets. The computational studies were supported by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no INST 40/467-1 FUGG (JUSTUS cluster). Open access funding enabled and organized by Projekt DEAL.

Keywords: arsenic · sulfur · nitrogen heterocycles · inversion

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Manuscript received: January 5, 2021
Revised manuscript received: February 3, 2021
Accepted manuscript online: February 3, 2021

