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Biradicaloids

A Mixed Arsenic–Phosphorus Centered Biradicaloid**

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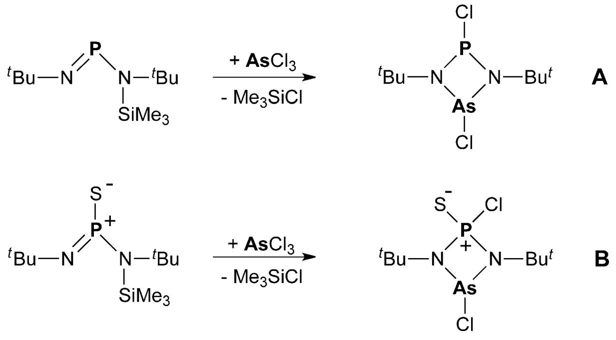
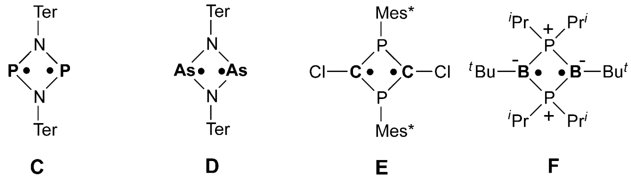
Abstract: *Main-group singlet biradicaloids have been thoroughly investigated in the past two decades, especially derivatives of cyclobutane-1,3-diyl. However, in each of the known examples, the radical centers are identical. Therefore, we sought to prepare a mixed dipnictadiazanediyls with P and As bearing the radical character. To achieve this goal, the unprecedented cyclodichloro arsaphosphadiazane [ClP(μ-NTer)$_2$AsCl] had to be prepared first. Treatment of [ClP(μ-NTer)$_2$AsCl] with a halide-abstracting agent led to the novel cyclic cation [P(μ-NTer)$_2$AsCl]$^+$, while reduction with magnesium afforded the first arsaphosphadiazanediyl [P(μ-NTer)$_2$As].*

1,3-Dichloro-1,3-diphospha-2,4-diazanes, [ClP(μ-NR)]$_2$, are well known and were mentioned first as early as 1894, when Michaelis and Schroeter investigated the reaction of aniline (R = Ph) with phosphorous chloride.[1] Ever since then their reactivity has been extensively explored.[2–4] The chemistry of their heavy analogues, arsenic, antimony, and bismuth, is much less explored. For example, the preparation of a dichlorocyclodibismadiazane, [ClBi(μ-NR)]$_2$, was reported only in 2010.[5] Similarly, reports on mixed cyclodipnictadiazanes are scarce,[4] and there is no fully characterized example.[6] Scherer and Schnabl reported on the preparation of a cyclo-1-arsa-3-phospha-2,4-diazane (**A**, Scheme 1).[7] The second example of an N$_2$AsP-cyclic system was also reported by Scherer et al. containing arsenic(III) and phosphorus(V) centers (**B**, Scheme 1).[8]

Following our interest in small cyclic molecules containing exclusively Group 15 elements, we recently succeeded in the synthesis of cationic Group 15 heterocycles[9–11] and singlet biradicaloids, namely diphosphadiazanediyl and diarsadiazanediyl (species **C** and **D** in Scheme 2).[12,13] There are several other singlet biradicaloids, and especially systems derived from cyclobutanediyl have been thoroughly investigated since Niecke et al. isolated [(μ-CCl)PMes*]$_2$ (**E**, Mes* = 2,4,6-^{t}Bu-C$_6$H$_2$) and Bertrand et al. reported [(μ-B^{t}Bu)P^{i}Pr$_2$]$_2$ (species **F** in Scheme 2).[14,15] For further insight, biradicals[16–24] and small inorganic heterocycles were recently reviewed in detail.[6,25,26]



Scheme 1. Cycloarsaphosphadiazanes prepared by Scherer et al.[7,8]



Scheme 2. Selected homoatomic singlet biradicaloids.

To isolate and investigate a mixed (heteroatomic) biradicaloid, the 1-arsa-3-phospha-2,4-diazane-1,3-diyl [P(μ-NR)$_2$As], which contains two different radical centers, we had to find a synthetic route to the sterically encumbered 1,3-dichloro-1-arsa-3-phospha-2,4-diazane [ClP(μ-NR)$_2$AsCl], which could be reduced with magnesium to give the new biradicaloid [P(μ-NR)$_2$As]. Furthermore we were interested in studying chloride abstraction by Lewis acids from [ClP(μ-NR)$_2$AsCl] affording either arsenium and/or phosphenium ions.

Reduction of 1,3-dichlorocyclodiphosphadiazane ([ClP(μ-NR)]$_2$) with magnesium yields the biradicaloid only when bulky terphenyl (maximal cone angle $\Theta_{\max} = 232°$) or hypersilyl groups (210°) prevent dimerization, which was found for smaller groups (less steric strain), such as dimethylphenyl (199°) or *tert*-butyl (160°) groups.[27] Hence, we decided to choose the terphenyl substituent for the preparation of [ClP(μ-NR)$_2$AsCl] (Scheme 3, R = Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl). Since the terphenyl substituted aminoiminophosphane **1** is readily available,[28] the potassium salt of bis(terphenylimino) phosphide (**2**)[29] was employed in the conversion with AsCl$_3$, exploiting the formation of KCl as driving force. As shown by ^{31}P NMR spectroscopy, a mixture of the cyclic *cis* (10 %, δ = 243 ppm, cf. δ = 226 ppm in ([ClP(μ-NTer)]$_2$) and *trans* isomer (90 %, δ = 269 ppm, cf. δ = 264 ppm in [ClP(μ-NTer)]$_2$) of [ClP(μ-NTer)$_2$AsCl] (**3**)

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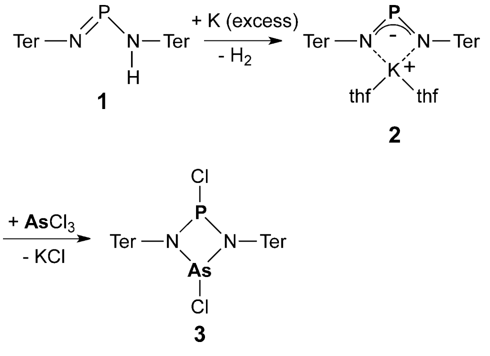
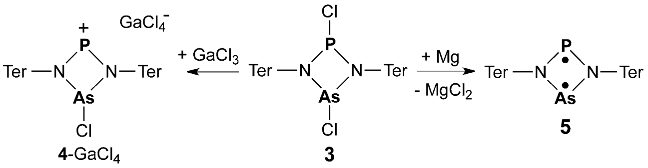


Scheme 3. Preparation of **2** from **1**.

were obtained and isolated in good yields (68%), yet no intermediate formation of the open-chain Ter-N-P-N(Ter)-$AsCl_2$ system was detected. The isomers of **3** were investigated by means of DFT computations (pbe1pbe/6-31G(d,p)) revealing the *cis* isomer to be the lowest lying isomer. The *trans* isomer is only slightly less favorable by 1.3 $kJ\,mol^{-1}$ and the open chain isomer Ter-N-P-N($AsCl_2$)-Ter is less favorable by 38.0 $kJ\,mol^{-1}$, in accord with our experimental data.[29]

Chloride abstraction from **3** by addition of gallium chloride affords the red phosphenium salt (**4**-$GaCl_4$) in nearly quantitative yield (Scheme 4). Variable temperature ^{31}P NMR spectroscopy ($\delta = 385$ ppm, cf. $\delta = 366$ ppm for P^+ and $\delta = 204$ ppm for P−Cl in $[ClP(\mu\text{-}NTer)P]^+$)[9] and X-ray studies (Figure 1) indicate, that the chloride ion is selectively cleaved from the phosphorus center, forming a phosphenium ion. In addition, a rather short As−Cl distance is observed (2.170(2) Å, cf. 2.2605(7) in $[(\mu\text{-}NTer)AsCl]_2$). Clearly, by delocalization of the nitrogen lone pairs (LP) into the empty p atomic orbitals (AO) of the P^+ ion, the positive charge on the P^+ center can be better stabilized than a positive charge on a possible As^+ center, this assumption in accord with NBO analysis data. This formal p-LP(N)→p-AO(P) hyperconjugation accounts for a significant π-bond character along the N-P-N unit (see below). Also there is no exchange of the Cl^- ion between the P and As atom of the four-membered ring in solution, which can be detected on the NMR time scale, in accord with computation indicating that the P^+ centered species $[ClAs(\mu\text{-}NTer)P]^+$ is favored by 42.3 $kJ\,mol^{-1}$ over the As^+ centered ion $[ClP(\mu\text{-}NTer)As]^+$. Interestingly, an excess of halide-abstraction reagent $GaCl_3$ will lead to the digallate anion $[Cl_3Ga\text{-}Cl\text{-}GaCl_3]^-$ but not to the dication.



Scheme 4. Preparation of **4** and **5**.

In the light of the halide abstraction, it was interesting to see, if reduction also leads 1) to the expected biradicaloid at all and 2) (if yes) to a larger spin density at the arsenic atom.

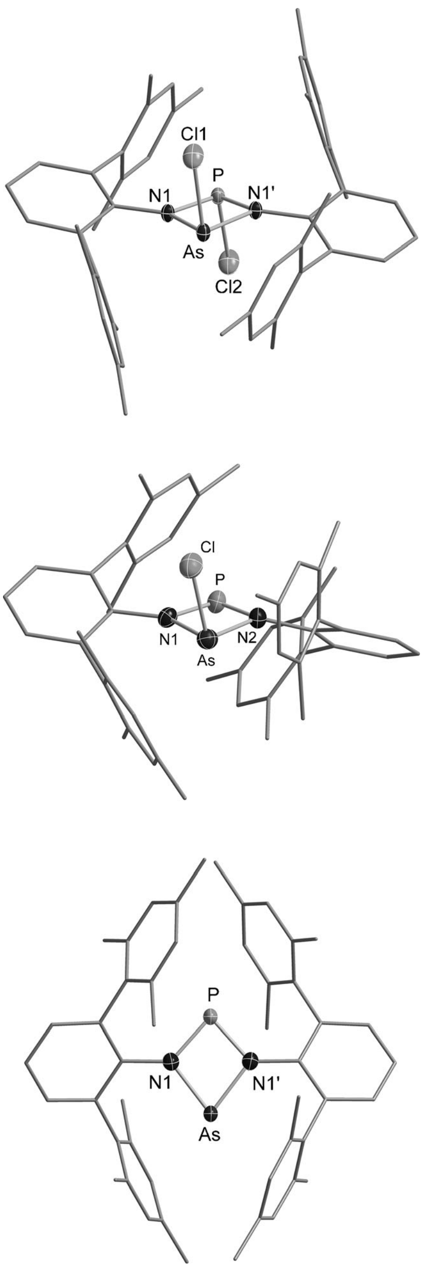


Figure 1. Molecular structures of **3** (top), $\mathbf{4}^+$ (middle), and **5** (bottom). Thermal ellipsoids are set at 50% probability (173 K).

Indeed, reduction of **3** results in the formation of arsaphosphadiazanediyl **5** in very good yields (82%). The reaction can be followed visually by the color change from pale yellow (color of the starting material **3**) to deep red-violet **5**. Violet crystals of **5** rapidly become yellow when traces of water or oxygen are present. Like **3** and **4**, biradicaloid **5** can be prepared in bulk and is thermally stable up to well above 200 °C and decomposes without melting (T_{dec}: **2** 226, **3** 235 °C, **4** 214, and **5** 210 °C). Herein we want to focus on compound **5** which is the first heteroatomic biradicaloid. ^{31}P NMR spectroscopy is not really suitable to monitor the reduction process and to distinguish between **3** (cf. $\delta[^{31}P] = 243$ *cis* isomer, $\delta = 269$ ppm *trans* isomer) and **5** ($\delta = 269$ ppm) as the *trans* isomer of **3** and **5** resonate almost at the same frequency.

UV/Vis measurements revealed two strong bands at 550 and 376 nm (λ_{max}) in accord with time-dependent DFT computations. These bands are slightly hypsochromic shifted compared to $[(\mu\text{-NTer})\text{As}]_2$ (560, 378 nm), however the difference is small and hence the optically perceived color is almost identical. The band at 560 nm arises from a π_{Ph}–$\pi_{\text{4ring,in-plane}}{}^*$ (HOMO−1→LUMO + 1) transition, while the absorption at 376 can be attributed to a π_{4ring}–$\pi_{\text{4ring}}{}^*$ (HOMO→LUMO, Figure 2) transition.

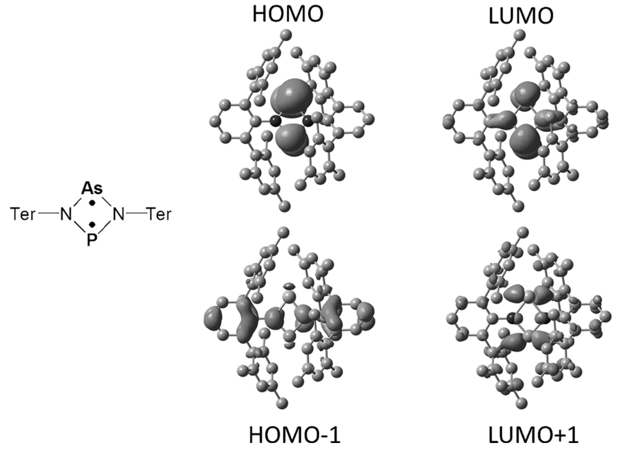


Figure 2. Molecular orbitals of **5**.

X-ray diffraction studies of crystals from the reaction sequences as illustrated in Scheme 4 revealed the formation of the unprecedented heteroatomic biradicaloid **5** (Figures 1 and Figure 2). Compound **5** crystallizes isotypic to $[(\mu\text{-NTer})_2\text{E}]_2$ (E = P, As) in the monoclinic space group *C*2/*c* with four molecules per unit cell. The most prominent structural feature is the kite shaped (deltoid) planar four-membered N_2PAs ring with two equal P–N (1.714(3), cf. $\Sigma r_{\text{cov}}(\text{P–N}) = 1.82$ Å)[30] and As–N distances (1.889(2), cf. $\Sigma r_{\text{cov}}(\text{As–N}) = 1.92$ Å) displaying only a small amount of double bond character ($\Sigma r_{\text{cov}}(\text{P=N}) = 1.62$ Å, $\Sigma r_{\text{cov}}(\text{As–N}) = 1.74$ Å) in accord with the bond lengths found for $[(\mu\text{-NTer})\text{E}]_2$ (E=P 1.716(1),[12] E = As: 1.867(2) Å). It is interesting to compare the transannular As···P distance of 2.790(2) Å, which is significantly shorter than the sum of the van der Waals radii (3.65 Å) but much longer than the sum of the covalent radii (2.32 Å), with those of **3** and **4**. Among all three considered species (**3**, **4**, and **5**, Table 1) the transannular distance slightly decreases upon abstraction of chloride from dichloroarsaphosphadiazane **3** and increases upon reduction. It is noteworthy to mention, that the metric parameters of the NPN and NAsN moieties of **5** resemble those of the corresponding homoatomic biradicaloids **C** and **D** (Scheme 2, Table 1). However, small changes are observed for the NPN angle, which is slightly increased (83.2 vs. 80.5°), while the NAsN angle is decreased (74.1 vs. 78.5°). Also the transannular distance reveals a similar elongation compared to the sum of the covalent radii (**5**: 16 %, **C**: 18 %, and **D**: 19 %), thus a quite similar reactivity can be expected.

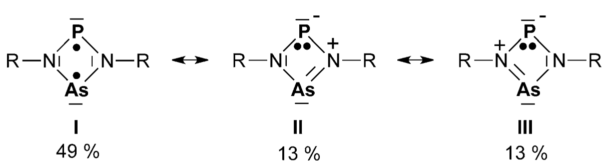
Table 1: Experimental details for compounds **3**, **4** and **5** and for comparison **C** and **D**.

Parameter	3[b]	4[c]	5	C	D
T_{dec} [°C]	235	214	210	224	245
$\delta(^{31}\text{P})$	242.9 268.8	385.1	268.8	276.4	–
E···E [Å][a]	2.768(8)	2.762(2)	2.790(2)	2.619(1)	2.884(1)
N-P [Å]	1.698(9)	1.650(4) 1.668(4)	1.714(3)	1.715(1) 1.718(1)	–
N-As [Å]	1.904(4)	1.952(4) 1.939(4)	1.889(2)	–	1.863(2) 1.857(2)
N-P-N [°]	85.2(3)	87.9(2)	83.2(2)	80.5(1)	–
N-As-N [°]	74.3(1)	72.6(2)	74.1(1)	–	78.5(1)

[a] E = As and P for **2**, **4**, and **5**; E = P for **C** and E = As for **D**. [b] Owing to positional disorder, the P–Cl distance was restrained to 2.111(9) Å, *d*(As-Cl) = 2.27(1) Å. [c] *d*(As-Cl) = 2.170(2) Å.

The biradical character of **5** can be derived from computations of the electronic structure (UHF, CASSCF(2,2); MO, NAO, NOON) calculations especially from the coefficients of the leading wave functions of multi-reference CASSCF(2,2) calculations displaying two dominant contributions to the CI wave function for the ^{1}A state: $\Phi(^1\text{A}) = 0.93\,|\pi_1{}^2\pi_2{}^2\pi_3{}^2\rangle - 0.37\,|\pi_1{}^2\pi_2{}^2\pi_4{}^2\rangle$.[29] A good measure for the biradical character is $\beta = 2\cdot c_1{}^2/(c_1{}^2 + c_2{}^2)$,[31] which amounts to 0.28 (28 %) for **5** (cf. $[(\mu\text{-NTer})\text{P}]_2$ (25 %) and $[(\mu\text{-NTer})\text{As}]_2$ (32 %). Also the natural orbital occupation numbers (HOMO: 1.407 and LUMO: 0.593) clearly indicate open shell singlet biradical character.[32] The frontier orbitals of **5** are mainly located on the four-membered ring (Figure 2), with the HOMO and LUMO being mainly transannular antibonding (HOMO) and bonding orbitals (LUMO), respectively. Yet a striking difference to homoatomic biradicaloids is, that owing to symmetry breaking in the heteroatomic biradicaloid, the HOMO has larger coefficients on the As than on the P atom. On the other hand, the LUMO has larger coefficients on the P atom.

Natural bond orbital (NBO) analysis data[33] give a large negative partial charge for both N atoms (−1.18 *e*), whereas the phosphorus atom carries a large positive charge (+1.04 *e*) and the As center a slightly smaller one (+0.98 *e*). However, strong polarization occurs mainly in the σ bonding system, while the π bond system features occupations numbers in accord with Lewis formula **I** in Scheme 5 ($2p\pi(\text{N}) = 1.74$, $3p\pi(\text{P}) = 1.10$, and $4p\pi(\text{As}) = 1.16\ e$; $\Sigma p\pi = 5.74\ e$). The natural resonance theory (NRT)[34] was used to determine the major Lewis formulae and their percentage weightings in the resonance scheme. The leading resonance structures display a 6π electron four-membered ring with a Dewar-type bond between the P and As atom and a lone pair localized at each



Scheme 5. Lewis representations (out of 698 structures) of model compound **5** with R = Ph along with their percentage weightings in the resonance scheme.

of the N centers (Lewis representations **I** in Scheme 5). Interestingly, dipolar structures **II** and **III** are considerably less favored and always exhibit the negative charge at the P atom and a delocalized π electronic system along the N-As-N unit. Computations targeting the aromaticity of the N_2PAs heterocycle produced a NICS(0) value of $\delta = -5$ ppm (cf. -6 $[E(\mu\text{-NTer})]_2$ E = P, As), which indicates also the existence of a 6π electron aromatic system. The computed ELF (electron localization function) features some intriguing differences between the two radical centers: As expected, the N−As bonds are more polarized than their N−P counterparts. Furthermore, the lone pairs of P and As are distinctly different. The ELF area of the P lone pair is banana-shaped with a maximum in plane with the four-membered ring (Figure 3). In contrast, the ELF describing the As lone pair is characterized by two maxima, above and below the N_2PAs plane. Therefore, the reactivity on the two radical centers is expected to differ, which was exploited for the following subsequent reactions with a) CS_2 and b) phosphaalkyne ^{t}Bu-CP displaying remarkable regioselectivity. Treatment of biradicaloid **5** with CS_2 led to the formation of 2.1.1 bicyclic species **6a** and **6b** in the ratio 7:1 clearly favoring P−C and As−S over P−S and As−C bond formation (Scheme 6, see Supporting Information). Complete regioselectivity was observed in the reaction of ^{t}Bu-C≡P with **5** yielding exclusively the P−C and As−P bridged addition product **7** (Scheme 6, see Supporting Information).

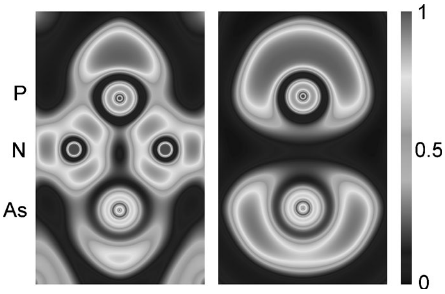
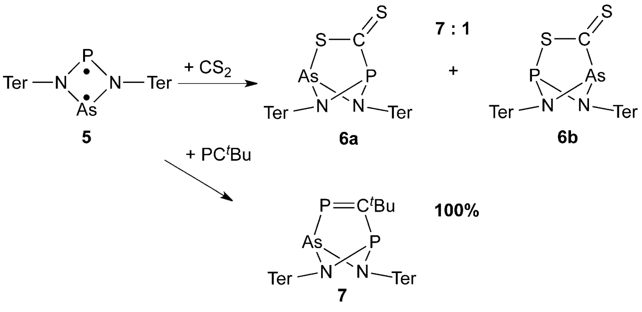


Figure 3. ELF representation in plane of the N_2PAs four-membered ring (left) and perpendicular to it (right, only the section of the four-membered ring is shown).

In conclusion, the synthetic approach to cyclic heterodipnictadiazanes via the potassium salt of bis(terphenylimino)phosphide was successful, making a wide range of cyclic interpnictogen compounds $R_2N_2E_1E_2Cl_2$ (E = Group 15 element) accessible, of which the corresponding cations and reduced species could be generated for E = P, As. We presented the first biradicaloid with different radical centers, biradicaloid **5**, which was readily available by reducing the corresponding dichloroarsaphosphadiazane. Since the reactivity should resemble other biradicaloids, the new species with different radical centers can be a useful building block for the preparation of heteroatomic cage molecules. Because the coefficients of the radical centers are non-equivalent, biradicaloid **5** features remarkable regioselectivity. The present work illustrates an exciting nexus of main-group heterocyclic chemistry with that of reactive heteroatomic biradicaloids; we expect that this approach of introducing different pnictogen radical centers can be extended further to novel combinations of main-group elements for the study of reactivity patterns, evaluation of fundamental properties, and applications in synthesis.



Scheme 6. Activation of small molecules bearing double and triple bonds by biradicaloid **5** leading to regioselective products.

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