

# Cyclic Group 15 Radical Cations\*\*

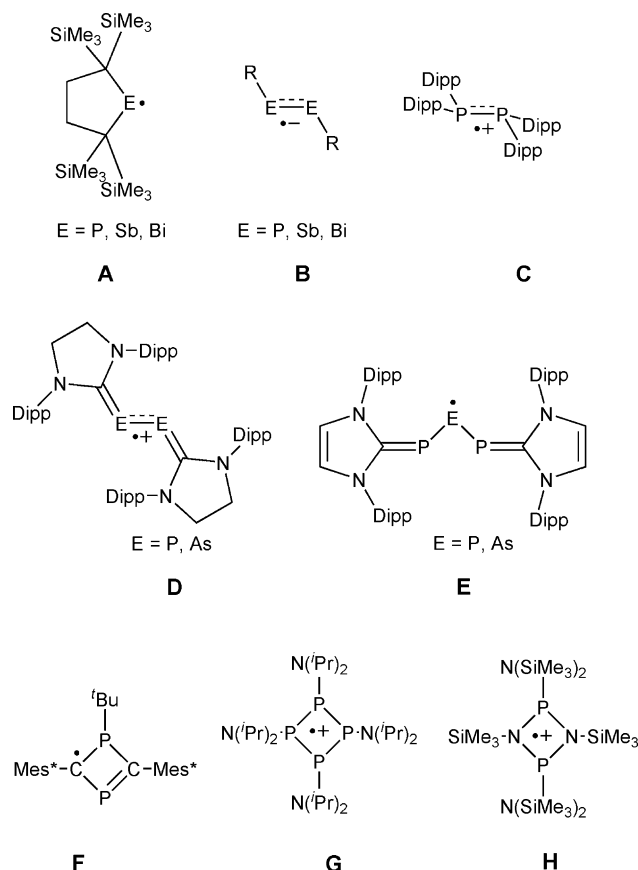
Angelika Brückner, Alexander Hinz, Jacqueline B. Priebe, Axel Schulz,\* and Alexander Villinger

Dedicated to Professor Uwe Rosenthal on the occasion of his 65th birthday

**Abstract:** Singlet cyclo-1,3-dipnicta-2,4-diazane-1,3-diyls of the type  $[E(\mu\text{-N}Ter)_2E]$  (**2**,  $E = P, As$ ,  $Ter = 2,6\text{-dimesitylphenyl}$ ) can undergo a one-electron-oxidation utilizing silver salts of weakly coordinating anions such as  $[AgL_n][B(C_6F_5)_4]$  ( $L =$  donor solvents) to afford the novel cyclic radical cations,  $[E(\mu\text{-N}Ter)_2E]^{\bullet+}$  (**3<sup>+</sup>**). When smaller and more basic anions were employed in the reaction, the anions were found to form covalent bonds to the radical centers yielding dipnictadiazanes,  $[FP(\mu\text{-N}Ter)_2PF]$  (**5**) and  $[(CF_3CO_2)_2P(\mu\text{-N}Ter)_2P(CF_3CO_2)_2]$  (**6**). A two-electron oxidation process, resulting in the formation of dications of the type  $[E(\mu\text{-N}Ter)_2E]^{2+}$ , could not be observed. Computational and EPR data revealed that the spin density is almost completely localized at the two heavier pnictogen centers  $E$  of the former 1,3-dipnictadiazane-1,3-diyls. The bonding situation in the radical cations features a rare example of a transannular one-electron  $\pi$  bond without having a  $\sigma$  bond.

**S**t able and transient radicals of main-group elements attracted great interest in recent years. Such species were reviewed by Power<sup>[1]</sup> and, more recently with focus on carbene-substituted radicals, by Bertrand et al.<sup>[2]</sup> Selected examples for radicals centered on boron,<sup>[3–6]</sup> carbon,<sup>[7,8]</sup> nitrogen,<sup>[9]</sup> phosphorus,<sup>[10,11]</sup> and silicon<sup>[12,13]</sup> can be found. Most recently, Beckmann et al. succeeded in the oxidation of dichalcogenides and the subsequent isolation of radical cations.<sup>[14]</sup>

We are especially interested in radicals centered on Group 15 elements, of which several examples are known to date (Scheme 1). By thermally induced processes of bond breaking or formation, the generation or recombination of P-centered radicals was observed for several cases of diphosphanes and their heavier homologues (**A**).<sup>[15–20]</sup> Bulky arenes as substituents provided enough stabilization to prevent



**Scheme 1.** Selected known stable radicals featuring Group 15 elements in the central molecular scaffold.

radicals from dimerization, which were obtained by oxidation of triarylphosphanes,<sup>[21]</sup> tetraaryldiphosphanes,<sup>[22]</sup> and phosphalkenes.<sup>[23]</sup> Furthermore, dipnictenes were reduced to give radical anions (**B**) and dipnictanes were oxidized by one electron to form the corresponding radical cations (**C** and **D**).<sup>[24,25]</sup> Carbene-substituted radicals were investigated by Bertrand et al.<sup>[26–29]</sup> Only recently, Grützmacher et al. succeeded in the preparation of carbene-substituted  $P_3$  and  $PAsP$  radicals (**E**).<sup>[30]</sup> Radical species featuring cyclobutane derivatives as central structural motif were investigated by Ito, Yoshifuji, and co-workers<sup>[31,32]</sup> displaying a diphosphacyclobutane scaffold (**F**) and by Wang et al. with respect to the oxidation of cyclic diphosphadiazanes and tetraphosphanes (**G**, **H**).<sup>[33]</sup>

Recently, different Group 15 open-shell singlet biradicals **2**, which can be prepared by reduction of the corre-

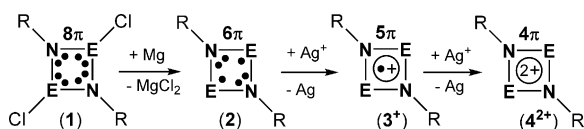
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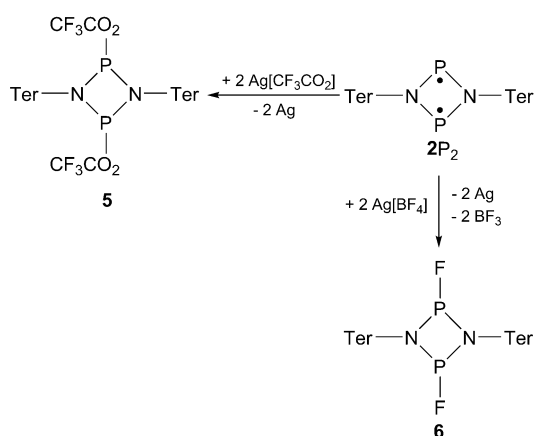
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201502054>.



**Scheme 2.** General preparation of salts containing cyclic radical cations ( $3^+$ ) starting from **1** ( $E = P, As$ ). To isolate radical cation  $3^+$ , weakly coordinating anions have to be used as counterions.

spending dichlorodipnictadiazanes **1**, were reported by our group (Scheme 2).<sup>[34–36]</sup> Since in the mass spectra of the biradicaloids  $[P(\mu\text{-N}Ter)_2P]$  (**2P<sub>2</sub>**),  $[P(\mu\text{-N}Ter)_2As]$  (**2PAs**), and  $[As(\mu\text{-N}Ter)_2As]$  (**2As<sub>2</sub>**) the corresponding molecular cations ( $3^+$ ) could be detected ( $m/z$  716, 760, 804) with surprisingly high intensities, we were intrigued by the idea to carry out the selective oxidation of the dipnictadiazane-1,3-diyls **2** yielding the  $5\pi$  electrons containing radical cations  $3^+$  as shown in Scheme 2.

Oxidation of biradicaloids **2** with typical oxidants such as  $[Ph_3C]^+$  or  $Ag^+$  readily occurred. However, the choice of anion with respect to size and basicity was crucial for the generation of radical cations. If the anion does not feature enough steric bulk and is too basic, it simply will attach to the phosphorus atom introducing polar covalent bonds (Scheme 3). For instance, with silver trifluoroacetate,  $Ag[CF_3CO_2]$ ,  $[(CF_3CO_2)P(\mu\text{-N}Ter)_2P(CF_3CO_2)]$  (**5**) is obtained

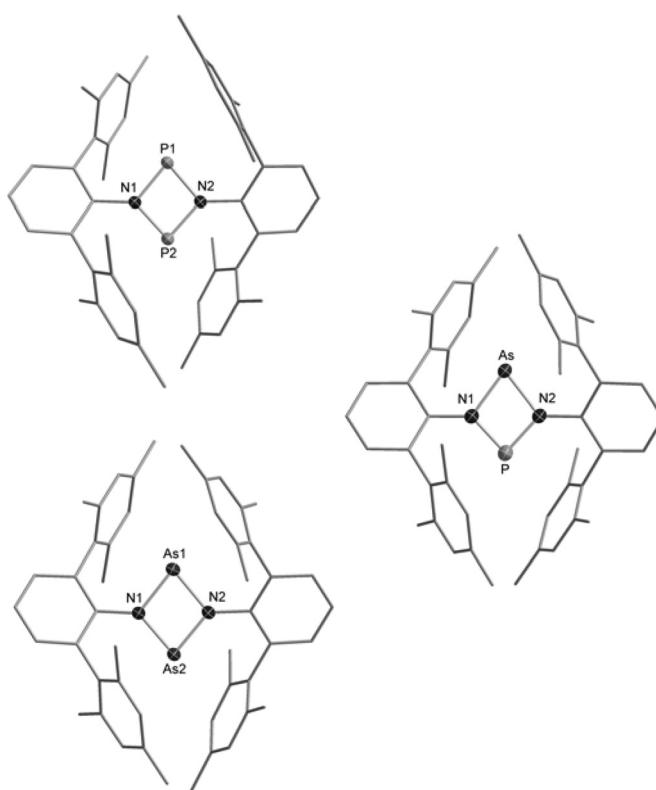


**Scheme 3.** Synthesis of **5** and **6** from **1P<sub>2</sub>** employing silver salts as oxidants.

upon reaction with  $[P(\mu\text{-N}Ter)_2P]$  (**2P<sub>2</sub>**). Analogously, in the reaction of **2P<sub>2</sub>** with  $Ag[BF_4]$ , the anion decomposed into  $BF_3$  and  $F^-$ , which in turn attacked the transient radical cation  $3P_2^+$ , finally yielding the difluorodiphosphadiazane (**6**, see the Supporting Information).<sup>[37,38]</sup> Since the formation of cyclo-dipnictadiazanes (**1**, Scheme 2) was not desired, a bulkier, more stable and weakly coordinating anion, the tetrakis(pentafluorophenyl)borate was utilized. Reaction of **2** with  $[AgL_3]^+ [B(C_6F_5)_4]^-$  ( $L$  = solvents = diethyl ether, toluene, *m*-xylene) was carried out in either diethyl ether or in fluorobenzene. In both cases, elemental silver precipitated and could be filtered off.  $^{31}P$  NMR experiments indicated the formation of radical cations  $3^+$ , since the singlet resonances of

biradicaloids **2P<sub>2</sub>** (276.4 ppm) and **2PAs** (269.9 ppm) vanished, and the reaction mixtures were completely NMR-silent. After concentration of the filtrate, single crystals of salts of the type  $3^+[B(C_6F_5)_4]^-$  containing the radical cations **3P<sub>2</sub><sup>+</sup>**, **3PAs<sup>+</sup>**, and **3As<sub>2</sub><sup>+</sup>** (Scheme 2) could be isolated and fully characterized. It is interesting to note that attempts to generate a possible dication **4<sup>2+</sup>** by two equivalents of the silver salt were not successful, but resulted always in the formation of a crystalline double salt  $3^+[B(C_6F_5)_4]^- \cdot [Ag(Et_2O)_4]^+[B(C_6F_5)_4]^-$ , in which the excess oxidant co-crystallized with the radical cation salt. Similar mixed crystals were obtained when impurities such as  $[Li(Et_2O)_3][B(C_6F_5)_4]$  were present in the silver salt. Moreover, if any starting material contained impurities of chloride species **1**, double salts such as  $[Ter_2N_2E^1E^2Cl][B(C_6F_5)_4]_x \cdot [Ter_2N_2E^1E^2Cl][B(C_6F_5)_4]_{1-x}$  ( $E = P, As$ ) could be isolated (see the Supporting Information). Deep orange (**3P<sub>2</sub><sup>+</sup>**) and red (**3PAs<sup>+</sup>**, **3As<sub>2</sub><sup>+</sup>**) crystals of  $3^+[B(C_6F_5)_4]^-$  rapidly become yellow when traces of water or oxygen are present. All  $3^+[B(C_6F_5)_4]^-$  salts can be prepared in bulk in crystalline yields larger than 65%. They are thermally stable up to well above 220 °C and decompose without melting ( $T_{dec}$ : **3P<sub>2</sub><sup>+</sup>** 226, **3PAs<sup>+</sup>** 234 °C, and **3As<sub>2</sub><sup>+</sup>** 257 °C).

All three  $3^+[B(C_6F_5)_4]^-$  salts crystallize isotypically from diethyl ether in the triclinic space group  $P\bar{1}$  (Figure 1). The most prominent structural feature is the planar four-membered  $N_2E_2$  ring with  $E-N$  distances (Table 1) with a small amount of double-bond character (cf.  $\Sigma r_{cov}(P-N) = 1.82$ ,  $\Sigma r_{cov}(As-N) = 1.92$  Å), and rather short transannular  $E \cdots E$



**Figure 1.** Molecular structure of **3P<sub>2</sub><sup>+</sup>** (top), **3PAs<sup>+</sup>** (middle), and **3As<sub>2</sub><sup>+</sup>** (bottom) at 173 K. Ellipsoids are set at 50% probability.

**Table 1:** Selected spectroscopic and experimental structural data of the radical compounds (bond lengths in Å, angles in °).

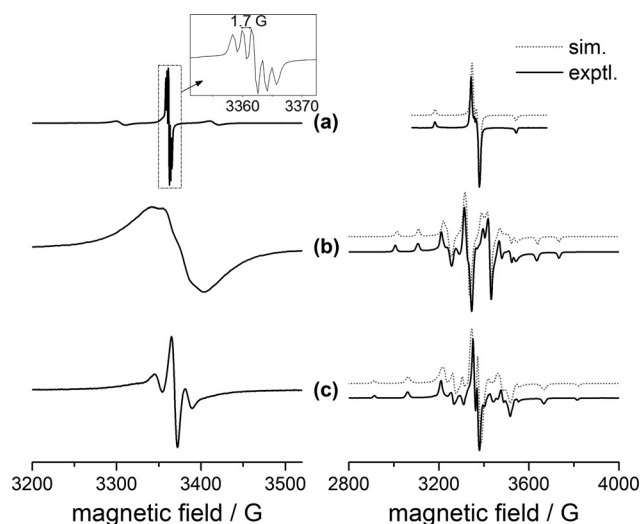
	<b>3P<sub>2</sub><sup>+</sup></b>	<b>3PAs<sup>+</sup></b>	<b>3As<sub>2</sub><sup>+</sup></b>
$\lambda_{\text{max}}$ [nm] <sup>[a]</sup>	471, 372	462, 375	534, 408
$T_{\text{dec}}$ [°C]	226	234	257
P–N <sup>[b]</sup>	1.714	1.716	–
As–N <sup>[b]</sup>	–	1.854	1.853
N–P–N	81.5 <sup>[b]</sup>	83.9	–
N–As–N	–	76.5	78.8 <sup>[b]</sup>
E–N–E <sup>[b]</sup>	98.5	99.8	101.2
E...E	2.597	2.758	2.863

[a] UV/Vis spectra recorded in diethyl ether. [b] averaged values.

distances, which are significantly shorter than the sum of the van der Waals radii ( $\Sigma r_{\text{vdW}}(\text{P}\cdots\text{P}) = 3.60$ ,  $\Sigma r_{\text{vdW}}(\text{As}\cdots\text{As}) = 3.70$  Å) but much longer than the sum of the covalent radii ( $\Sigma r_{\text{cov}}(\text{P}–\text{P}) = 2.22$ ,  $\Sigma r_{\text{cov}}(\text{As}–\text{As}) = 2.42$  Å). It is interesting to note that upon one-electron oxidation, the metric parameters remain almost unchanged (Table 1). Comparing the structural data of **2** with those of **3<sup>+</sup>** reveals only slightly shortened transannular distances (radical cations **3<sup>+</sup>**: P–P 2.5975(6), P–As 2.758(6), and As–As 2.8632(3) Å; cf. singlet biradicaloids **2E**: E=P–P 2.6186(8), P–As 2.790(2), and As–As 2.8839(4) Å), in accord with increasing transannular bonding interaction (see below).<sup>[34–36]</sup>

All three radical cations display intense colors. **3P<sub>2</sub><sup>+</sup>** is deep orange with an absorption maximum at  $\lambda_{\text{max}} = 471$  nm. The As-containing radicals appear to be almost black due to very strong absorption; however, their absorption maxima are found at 462 nm (**3PAs<sup>+</sup>**) and 534 nm (**3As<sub>2</sub><sup>+</sup>**), respectively. In comparison to the singlet biradicaloid starting materials, all absorption bands are shifted hypsochromically ( $\lambda_{\text{max}}$ : **2P<sub>2</sub>** 492, **2PAs** 550, and **2As<sub>2</sub>** 560 nm). The UV/vis spectra mainly display  $\pi$ – $\pi^*$  transitions into the transannular bonding orbital according to TD-DFT computations.

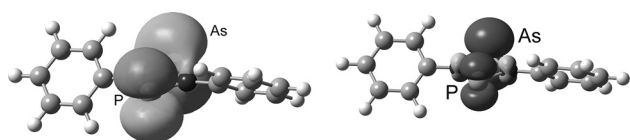
The X-band EPR spectra of all **3<sup>+</sup>** species feature characteristic signals for each of the radical cations (Figure 2). At ambient temperature, a hyperfine structure (hfs) triplet from the coupling of the unpaired electron to the two <sup>31</sup>P nuclei ( $I = 1/2$ ,  $A_{\text{iso}} = 55$  G) is observed for **3P<sub>2</sub><sup>+</sup>** at  $g_{\text{iso}} = 2.003$  which shows additional hfs splitting from the two <sup>14</sup>N nuclei ( $I = 1$ ,  $A_{\text{iso}} = 1.7$  G). In contrast, hfs for **3PAs<sup>+</sup>** and **3As<sub>2</sub><sup>+</sup>** is only poorly resolved (Figure 2). In frozen solution at 100 K, strongly anisotropic EPR spectra are recorded (Figure 2 right). In case of **3P<sub>2</sub><sup>+</sup>**, the <sup>31</sup>P hfs constants differ considerably: While  $A_{xx}$  and  $A_{yy}$  are not resolved,  $A_{zz}$  amounts to 190 and 170 G, respectively. The  $g$  values are in the typical range of non-metal radicals (2.013, 2.003, 1.992).<sup>[1]</sup> The contributions of isotropic and anisotropic hyperfine coupling allow for an estimate of the distribution of the electron in p and s orbitals, which amount to 0.46 $e$  and 0.01 $e$ , respectively, for each P nucleus and thus totaling 0.94 $e$ .<sup>[39]</sup> The size of the hyperfine coupling as well as its anisotropy are very similar to the observations of Grützmacher et al. for compound **E** (Scheme 1, E = P,  $A_{xx} = -3.3$  G,  $A_{yy} = -6.0$  G,  $A_{zz} = 180$  G).<sup>[30]</sup> For **3As<sub>2</sub><sup>+</sup>**, the low-temperature EPR spectrum consists of a strongly anisotropic pattern as well. Owing to the existence of two <sup>75</sup>As nuclei ( $I = 3/2$ ), a pseudo-septet is observed for



**Figure 2.** Left: EPR spectra of **3P<sub>2</sub><sup>+</sup>** (a), **3PAs<sup>+</sup>** (b), and **3As<sub>2</sub><sup>+</sup>** (c) in fluorobenzene solution; right: EPR spectra in frozen solution.

each principal direction. The hfs constants show considerably anisotropy for both of the As atoms (As1:  $A_{zz} = 155$ ,  $A_{yy} = 82.1$ ,  $A_{xx} = 38.3$ ; As2:  $A_{zz} = 147$ ,  $A_{yy} = 36.2$ ,  $A_{xx} = 30.6$  G). The  $g$  values are distributed over a very small range (1.999, 1.993, 1.992) and are consistently smaller than 2. The hfs constants again agree well with those observed by Grützmacher et al. for compound **E** (Scheme 1, E = As,  $A_{xx} = -43$  G,  $A_{yy} = -50$  G,  $A_{zz} = 156$  G).<sup>[30]</sup> The estimate of s and p spin density on the As nuclei resulted in values of 0.02 $e$  and 0.34 $e$ , respectively, hence the spin density on both As nuclei totals 0.72 $e$ .

In case of **3PAs<sup>+</sup>**, the EPR spectrum is most interesting, because conclusions with respect to the electron distribution between the two former radical centers of the open-shell biradicaloid can be drawn. The coupling of the electron to the <sup>75</sup>As nucleus is stronger and more isotropic than to the <sup>31</sup>P nucleus (As:  $A_{xx} = 99.9$ ,  $A_{yy} = 208.1$ ,  $A_{zz} = 71.8$  G; P:  $A_{xx} = 1.0$ ,  $A_{yy} = 96.0$ ,  $A_{zz} = 7.4$  G). Estimating the orbital contributions for both nuclei affords unpaired electron occupation numbers of 0.01 and 0.28 for s(P) and p(P) and 0.02 and 0.36 for s(As) and p(As) atomic orbitals, totaling 0.67. Hence, it can be concluded that 1) the spin density is localized more on the As than on the P atom, and 2) the s-type orbitals of <sup>75</sup>As make a more significant contribution than those of <sup>31</sup>P. These experimental findings can also be rationalized by analysis of the electronic structure utilizing DFT computations at the M062X level of theory for the model compounds [E( $\mu$ -NPh)<sub>2</sub>E]<sup>+</sup> (terphenyl substituted by phenyl). Removal of one electron from the HOMO of **2** by oxidation does not alter the shape of the resulting molecular orbital, and the SOMO of **3<sup>+</sup>** is still of mainly transannular E–E antibonding  $\pi$  character (Figure 3, left). Furthermore, a doubly occupied low-lying, fully bonding  $\pi$  MO is found, with transannular bonding E–E character. Hence, by removing an electron from the dominantly  $\pi^*$ -type orbital (HOMO), a one-electron  $\pi$  bond remains and the unpaired spin density is mainly localized on the two heavy pnictogens (Figure 3, Table 2), which is in accord with the estimates derived from the EPR data.



**Figure 3.** SOMO (left) and spin density distribution in  $3\text{PAst}^+$  (right; mesityl groups omitted for clarity).

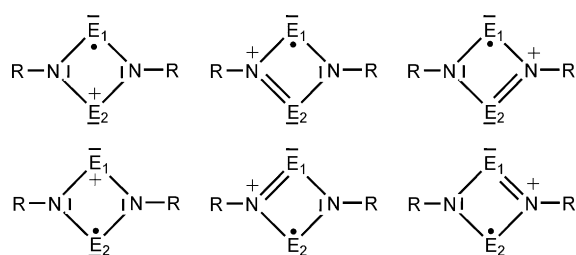
**Table 2:** Computational data<sup>[a,b]</sup> for  $3\text{P}_2^{+}$ ,  $3\text{PAst}^+$ , and  $3\text{As}_2^{+}$  (modelled with phenyl substituents).

	$3\text{P}_2^{+}$	$3\text{PAst}^+$ <sup>[c]</sup>	$3\text{As}_2^{+}$
MSD E1	0.60	0.35 <sup>[c]</sup>	0.64
MSD E2	0.60	0.84 <sup>[c]</sup>	0.64
MSD N	−0.09	−0.08	−0.13
NSD E1	0.58	0.33 <sup>[c]</sup>	0.62
NSD E2	0.58	0.81 <sup>[c]</sup>	0.62
NSD N	−0.07	−0.06	−0.10
q(E1)	1.30	1.36 <sup>[c]</sup>	1.36
q(E2)	1.30	1.28 <sup>[c]</sup>	1.36
q(N)	−1.10	−1.10	−1.13
q(N)	−1.10	−1.10	−1.13
ring charge	0.40	0.44	0.45
BO(E–E)	0.33	0.16	0.31

[a] MSD = Mulliken spin density, NSD natural spin density. [b] NBO charges  $q$  in  $e$ . [c] E1 = P, E2 = As.

Interestingly, the Mulliken spin density in  $3\text{PAst}^+$  amounts to 70.6% for the As atom compared to 29.4% for the P atom (Figure 3), which is in agreement with the experimentally determined values (see above). In accord with these MO data, NBO/NRT computations also indicate the presence of highly localized spin density on both pnictogens atoms (Table 2) along with considerable transannular  $\pi$  bonding interaction (transannular  $\pi$  bond order:  $3\text{P}_2^{+}$ : 0.33,  $3\text{PAst}^+$ : 0.16 and  $3\text{As}_2^{+}$ : 0.31) and the absence of a  $\sigma$  bond. Frenking et al. described a two-electron transannular  $\pi$  bond in  $\text{Ge}_2[\text{Ga}(\text{DDP})]_2$  (DDP =  $\text{HC}(\text{CMeNC}_6\text{H}_3-2,6\text{-iPr}_2)_2$ ) as an unusual example of a bonding situation where two (heavier) main-group atoms are bonded in  $\pi$  fashion without an additional  $\sigma$  bond between them.<sup>[40]</sup> Additionally, delocalization of the lone pairs localized at the two nitrogen centers in  $3^{+}$  must be considered, as illustrated in Figure 4.

In summary, novel stable heterocyclic radical cations of the type  $[\text{R}_2\text{N}_2\text{E}_2]^+$  are presented, which were accessible by oxidation of dipnictadiazanediyls that feature P and As radical centers or even both in one species. In contrast to previously reported four-membered cyclic radicals such as **F**,



**Figure 4.** Lewis representations of radical  $3^{+}$ .

**G**, and **H**, in  $3^{+}$  the spin density is distributed almost exclusively on the two heavy pnictogens of the four-membered ring, the former radical centers of the corresponding open shell singlet biradicaloids. A one-electron transannular  $\pi$  bonding interaction can be discussed. Owing to their high thermal stability and good accessibility, it is expected that such radicals can be used for the activation of small molecules.

**Keywords:** arsenic · group 15 elements · oxidation · phosphorus · radical

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