Biradicaloids

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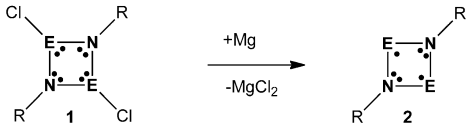
An Arsenic–Nitrogen Biradicaloid: Synthesis, Properties, and Reactivity**

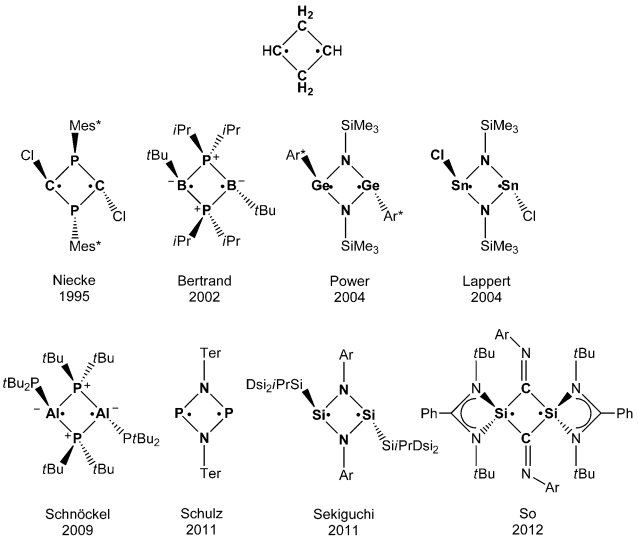
Serhiy Demeshko, Christian Godemann, René Kuzora, Axel Schulz, and Alexander Villinger*

Biradicals are molecules which contain two unpaired electrons in two nearly degenerate non-bonding molecular orbitals.[1] Both electrons can either be antiparallel forming an open-shell singlet state or parallel describing a triplet state.[2] As a result of the two unpaired electrons such biradicals are usually transient species during the process of bond breaking and making. Introduction of steric strain by bulky substituents to prevent bond formation or dimerization, delocalization, and substitution of carbon atoms by suitable main-group elements can lead to a considerable stabilization of such biradicals, however, at the expense of the biradical character, which decreases. Thus the designation of such stabilized species as biradicaloids seems to be more appropriate.[3,4] Singlet biradicals commonly show a relatively small energy gap between their lowest energy singlet and triplet state. The stability of biradicals is increased by increasing the HOMO–LUMO gap leading to a larger singlet–triplet splitting, and lower occupation of the LUMO.[1] However, when the LUMO occupation reaches zero, a closed-shell singlet is finally obtained, and such species cannot be referred to as biradical or biradicaloid, respectively, anymore.

Following our interest in the heterocyclic chemistry of Group 15 elements,[5] we studied the reaction of four-membered rings of the type $[XE(\mu\text{-}NR)]_2$ E = Group 15 element, X = halogen) containing alternating pnictogen(III) and nitrogen centers, with reducing agents such as $[Cp_2Ti(btmsa)]$ (Cp = η-C_5H_5, btmsa = bis(trimethylsilyl)acetylene, $Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3$),[6] $[\{Cp_2TiCl\}_2]$ or Mg.[7] Upon chloride abstraction and reduction (Scheme 1), such *cyclo*-1,3-dipnicta(III)-2,4-diazanes $[ClE(\mu\text{-}NR)]_2$[8] with bulky substituents R (R = terphenyl = Ter = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$)[9] should form remarkably tight ring structures of the type $[E(\mu\text{-}NR)]_2$ featuring two localized radical sites. The only known example, the $[P(\mu\text{-}NR)]_2$ biradicaloid, exhibits two radical centers in the same region of space that strongly resemble elongated single bonds.[7] Biradicaloids of the type $[E(\mu\text{-}NR)]_2$ can be derived from short-lived *cyclo*-butanediyl $[HC(\mu\text{-}CH_2)]_2$ by a formal isolobal replacement of CH by E (Scheme 2). Pioneering work in this field was carried out by Niecke et al. for $[ClC(\mu\text{-}PMes^*)]_2$[10] and later for several derivatives. In addition to these carbon-based 1,3-biradicaloids, an 1,3-dibora-2,4-diphospha-*cyclo*-butane-1,3-diyl compound $[t\text{BuB}(\mu\text{-}P i\text{Pr}_2)]_2$ was reported and systematically studied by Bertrand et al.[11] The groups of Power and Lappert reported the first biradicaloids containing heavier Group 14 elements $[RE(\mu\text{-}NR')]_2$ (E = Sn, Ge; e.g. $[ClSn(\mu\text{-}N\text{-}SiMe_3)]_2$[12] and $[RGe(\mu\text{-}N\text{-}SiMe_3)]_2$ (R = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-$i\text{Pr}_2C_6H_3$)).[13] Recently, Schnöckel's $[RAl(\mu\text{-}Pt\text{Bu}_2)]_2$ (R = $Pt\text{Bu}_2$), Sekiguchi's $[Dsi_2i\text{PrSi}(\mu\text{-}N\text{-}Ar)]_2$[14] (Dsi = $CH(SiMe_3)_2$), and So's amidinate[15] stabilized Si–C biradicaloids extended the area and provided insights into the intermediates of σ-bond formation processes (Scheme 2).[16]



Scheme 1. Synthesis of four-membered E_2N_2 heterocycles bearing two localized radical sites (E = Group 15 element).



Scheme 2. Experimentally known, four-membered heterocyclic biradicaloids derived from *cyclo*-butanediyl.

[*] C. Godemann, R. Kuzora, Prof. Dr. A. Schulz, Dr. A. Villinger
Universität Rostock, Institut für Chemie
Albert-Einstein-Strasse 3a, 18059 Rostock (Germany)
and
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
E-mail: axel.schulz@uni-rostock.de
Homepage: http://www.chemie.uni-rostock.de/ac/schulz
Dr. S. Demeshko
Institut für Anorganische Chemie, Georg-August-Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)

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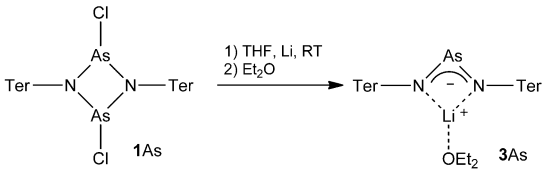
Herein we report the synthesis, structural analysis, and reactivity of a localized singlet As–N biradicaloid **2**As, which is indefinitely stable at room temperature both in solution and in the solid state (Scheme 1). Its biradicaloid character and electronic delocalization are illustrated by theoretical studies and follow-up chemistry. It is expected that such biradicaloids might play a major role in preparative pnictogen–nitrogen chemistry because such species are good starting materials for polycyclic inorganic and organometallic compounds.[8,17,18]

Reactions of bases, such as triethylamine or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and amino dichloroarsanes of the type Ter-N(H)-$AsCl_2$ provide readily access to 1,3-dichloro-2,4-diterphenyl-*cyclo*-1,3-diarsa-2,4-diazane ([ClAs-(μ-NTer)]$_2$) (**1**As, Scheme 1).[19] From the very few available derivatives of **1**As, we chose the terphenyl-substituted species to assure kinetic protection of the desired biradical moiety. Introduction of bulky groups, such as terphenyl[9] and delocalization have been found to be the key to stabilize heavy-element double bonds in low-coordinated reactive species.[4,20,21] A straight forward route to the desired 1,3-diarsa-2,4-diaza-*cyclo*-butane-1,3-diyl [As(μ-NTer)]$_2$ (**2**As) would appear to be to treat three equivalents of activated Mg (twofold excess) with **1**As (Scheme 1) at ambient temperatures in thf (all manipulations were performed under argon).[22] A clean reaction occurred within 12 h as indicated by a color change of the initial yellow to a deep purple solution. After work-up and extraction with benzene at room temperature, compound **2**As was isolated in 92% yield as extremely air-sensitive but highly thermally stable purple crystals (decomposition point 245 °C). The purple color of **2**As vanishes rapidly when traces of H_2O are present.

We also used different reducing agents. While with [Cp_2Ti(btmsa)] and [{Cp_2TiCl}$_2$] **2**As was also obtained (but the work-up is less convenient), the reaction of lithium with **1**As led exclusively to the formation of the diazaarsa allyl system **3**As (Scheme 3) in low yields (10–20%). Two similar 1,3-diazaarsa allyl metal complexes have been isolated by Roesky et al. in the reaction of R(H)NAs=NR with M(N-($SiMe_3$)$_2$)$_2$ (M = Zn, Cd, R = 2,6-diisopropylphenyl)[23] and one cyclic species [$C_6H_4N_2$As·Li(THF)$_2$]$_\infty$ by Paver et al.[24]



Scheme 3. Reaction of **1**As with Li yielding **3**As.

The X-ray diffraction analysis (Figure 1) revealed the perfectly planar As_2N_2 four-membered ring structure of **2**As kinetically protected in the pocket formed by the two terphenyl substituents.[22] The N atoms are in a planar environment and the As–N bond lengths (N1–As2 1.857(2), N1–As1 1.863(2) Å) are almost equal, but a little shorter than expected for single bonds (cf. Σr_{cov}(As–N) = 1.92 Å, Σr_{cov}(As=N) = 1.74 Å;[25] cf. 1.757(2) Å **3**As).[22] The most

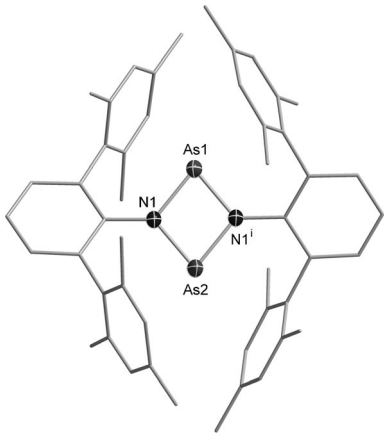
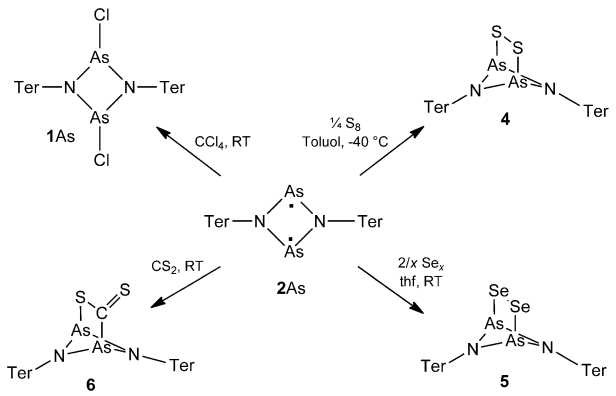


Figure 1. ORTEP diagram of the crystal structure of **2**As (terphenyl groups as wire model). H atoms omitted for clarity. Thermal ellipsoids set at 50% probability at 173 K. Selected bond lengths [Å] and angles [°]: N1–As1 1.863(2), N1–As2 1.857(2), As1···As2 2.8839(4); As2-N1-As1 101.66(8), N1^i-As1-N1 78.5(1), N1-As2-N1^i 78.5(1), As2-N1-As1-N1^i 0.0. Symmetry code i: (i) $-x, y, -z+1/2$.

striking feature is the As···As distance (2.8839(4) Å), which indicates, that there is only a very small transannular As···As interaction. Indeed, this value is about 19% greater than the sum of the covalent radii (2.42 Å).[25] Comparison of the structural data of **1**As (*trans* isomer) with those of **2**As reveal only small differences (cf. As-N 1.862(1)/1.871(1) Å; N-As-N 79.3(1)°). Even the As···As distance is almost identical (**1**As: 2.874(1) vs. **2**As: 2.8839(4) Å). All of these data suggest that **2**As is a biradicaloid. Furthermore, the absence of a signal in the electron paramagnetic resonance (EPR) spectrum, both in solution (20–90 °C) and in the solid state (20–150 °C), indicates that **2**As has a singlet ground state. The existence of a singlet ground state is corroborated by temperature-dependent magnetic measurements for **2**As displaying exclusively diamagnetic behavior between 295 and 2 K ($\chi_M^{dia} = -480 \times 10^{-6}$ cm^3 mol^{-1}).

DFT calculations of the electronic structure support the assumption that **2**As may be referred to as a biradicaloid with six delocalized π electrons (Scheme 1).[22] The aromaticity of the As_2N_2 ring is supported by the calculated NICS(0)[22,26] value of −6 ppm (cf. −6 [P(μ-NTer)]$_2$ (**2**P),[7] −7 ppm for [Li(dme)]$_2^+$[Me_3Si-C(μ-P)]$_2^{2-}$,[10] and +5 ppm in 4π electronic, anti-aromatic [TerN(μ-Si)]$_2$).[27] Full optimization at the UB3LYP/6-31G(d,p) level of theory shows a singlet ground state with a planar As_2N_2. The singlet state of **2**As is 19.3 kcal mol^{-1} lower in energy than the triplet state (UB3LYP/6-311 + G(d,p)//6-31G(d,p)).[22]

The biradical character and reactivity of **2**As was experimentally studied in addition reactions with CCl_4, elemental sulfur and selenium, as well as species containing double bonds, such as CS_2 (Scheme 4). All these reactions are straight forward and high-yielding (over 90%). **2**As readily reacts with mild oxidizing reagents, such as CCl_4, yielding the starting material **1**As. Elemental sulfur and selenium cleanly react with **2**As to give air-, moisture-, and high-temperature stable **4** (T_{decomp} = 281 °C) and **5** (T_{decomp} = 304 °C), respectively, with a dichalcogen bridge between the two radical



Scheme 4. Reactivity of biradicaloid **2**As.

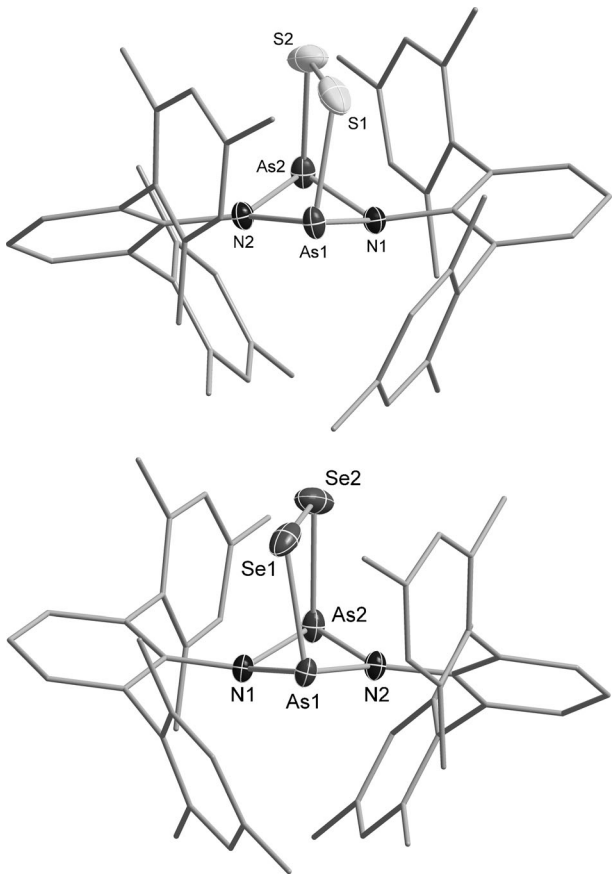


Figure 2. ORTEP diagram of the crystal structure of **4** (top) and **5** (bottom; terphenyl groups as wire model). H atoms omitted for clarity. Thermal ellipsoids set at 50% probability at 173 K. Selected bond lengths [Å] and angles [°]: **4**: As1–N2 1.839(2), As1–N1 1.908(2), As1–S1 2.3187(7), As1···As2 2.7880(3), As2–N1 1.861(2), As2–N2 1.870(2), As2–S2 2.3020(8), S1–S2 2.050(1); N2-As1-N1 78.24(7), N1-As1-S1 90.99(6), As1-S1-S2 97.99(3), N1-As1-As2-N2 143.3(1); **5**: As1-N2 1.847(1), As1-N1 1.910(1), As1-Se1 2.4509(3), As1···As2 2.8143(3), As2-N1 1.861(1), As2-N2 1.870(2), As2-Se2 2.4445(3), Se1-Se2 2.3228(4), N2-As1-N1 78.36(6), N2-As1-Se1 100.27(5), N1-As1-Se1 91.64(5), As1-Se1-Se2 94.52(1), N2-As1-As2-N1 148.0(1).

centers in **2**As (Figure 2). While the reaction with sulfur is finished within minutes, two hours are needed when selenium is utilized as oxidizer. The reaction with elemental tellurium was also attempted but failed owing to decomposition because higher temperatures and long reaction times (60 °C, over two weeks) are needed. Species **4** and **5** are novel, very strained ternary AsNX heterocycles (X = S, Se). For the S and Se species slightly elongated As–X bonds, typical X–X single bonds and narrow N-As-N angles (e.g. N1-As1-N2 **4**: 78.24(7), **5**: 78.36(6)°C) and As-X-X angles at the bridging X atom are found. The As_2N_2 ring is now puckered (N1-As1-As2-N2 **4**: 143.3(1), **5**: 148.0(1)°) and the two As–N distances are slightly different in contrast to **2**As (cf. **2**As: 1.857(2)/1.863(2), **4**: 1.839(2)/1.908(2), **5**: 1.847(1), 1.910(1) Å). Interestingly, the transannular As···As distance is even shorter in **4** (2.7880(3)) and **5** (2.8143(3) Å) than in **2**As (2.8839(4) Å) and is clearly forced by the dichalcogen bridge and not by As···As overlap effects.

The treatment of **2A**s with CS_2 afforded further evidence for its radical-type behavior. A novel crystalline C–S bridged compound **6** was isolated, in which the As_2N_2 four-membered ring remains intact (Figure 3). The structure of **6** was unambiguously deduced from single-crystal X-ray structure

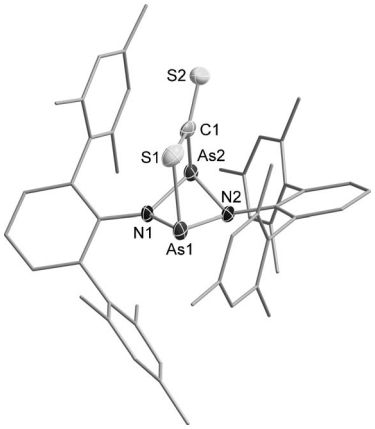


Figure 3. ORTEP diagram of the crystal structure of **6** (terphenyl groups as wire model). H atoms omitted for clarity. Thermal ellipsoids set at 50% probability at 173 K. Selected bond lengths [Å] and angles [°]: As1–N2 1.860(3), As1–N1 1.862(3), As1–S1 2.359(1), As1–As2 2.7776(5), As2–N1 1.864(3), As2–N2 1.930(3), As2–C1 2.014(4), S1–C1 1.727(4), S2–C1 1.619(4); N2-As1-N1 79.4(1), As1-N2-As2 94.2(1), S2-C1-S1 125.5(2), S2-C1-As2 119.7(2), S1-C1-As2 114.8(2), S1-As1-As2 75.29(3), N1-As2-N2 77.6(1), N1-As2-C1 95.1(2), N2-As2-C1 89.06(1), C1-As2-As1 75.6(1), C1-S1-As1 93.2(1), N2-As1-As2-N1 139.8(2).

analysis, which revealed, that one As atom is attached to the C and the second to one S atom of the CS_2 molecule displaying a side-on binding known from transition-metal complexes (e.g. $[(PPh_3)_2Pt(CS_2)]$).[28] While the second exocyclic S atom is still bonded to the C atom with a double bond (S2–C1 1.619(4) Å, Σr_{cov}(S=C) = 1.61 Å, 1.559(3) Å in solid CS2);[29] the distance between S_{bridge}–C (S1–C1 1.727(4), cf. Σr_{cov}(S–C) = 1.78)[25] clearly indicates the presence of a C–S single bond. All other structural parameters are very similar to those discussed for **4** and **5**. Like **2**As, **4**, **5**, and **6** are easily prepared in bulk and almost indefinitely stable when stored in a sealed tube.

In summary a neutral, 6π-electron four-membered heterocycle $[As(\mu\text{-}NTer)]_2$, which can be referred to as a high-temperature stable biradicaloid, is presented for the first time. Biradicaloid **2**As is formed when a bulky substituent, such as the terphenyl group, is utilized to prevent the biradicaloid from dimerization. It was shown that introduction of main-group elements, such as As and N, into hydrocarbon biradicals enables such biradicaloids to be stabilized. Computational and experimental studies of the properties and reactivity allow **2**As to be designated a biradicaloid. Especially, the addition reactions of elemental sulfur and selenium as well as the double bond of CS_2 to give the novel species **4**, **5**, and **6** nicely demonstrate that **2**As exhibits of (some) radical-type behavior.

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