Diradicals Hot Paper

How to cite: *Angew. Chem. Int. Ed.* **2022,** *61,* e202207415
International Edition: doi.org/10.1002/anie.202207415
German Edition: doi.org/10.1002/ange.202207415

Isolation of an Arsenic Diradicaloid with a Cyclic C_2As_2-Core

*Henric Steffenfauseweh, Yury V. Vishnevskiy, Beate Neumann, Hans-Georg Stammler, Diego M. Andrada, and Rajendra S. Ghadwal**

Dedicated to Professor Wolfgang Schnick on the occasion of his 65th birthday

Abstract: Herein, we report on the synthesis, characterization, and reactivity studies of the first cyclic C_2As_2-diradicaloid $\{(IPr)CAs\}_2$ (**6**) (IPr = C{N(Dipp)CH}$_2$; Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$). Treatment of $(IPr)CH_2$ (**1**) with $AsCl_3$ affords the Lewis adduct $\{(IPr)CH_2\}AsCl_3$ (**2**). Compound **2** undergoes stepwise dehydrochlorination to yield $\{(IPr)CH\}AsCl_2$ (**3**) and $\{(IPr)CAsCl\}_2$ (**5a**) or $[\{(IPr)CAs\}_2Cl]OTf$ (**5b**). Reduction of **5a** (or **5b**) with magnesium turnings gives **6** as a red crystalline solid in 90% yield. Compound **6** featuring a planar C_2As_2 ring is diamagnetic and exhibits well resolved NMR signals. DFT calculations reveal a singlet ground state for **6** with a small singlet-triplet energy gap of 8.7 kcal mol^{-1}. The diradical character of **6** amounts to 20% (CASSCF, complete active space self consistent field) and 28% (DFT). Treatments of **6** with $(PhSe)_2$ and $Fe_2(CO)_9$ give rise to $\{(IPr)CAs(SePh)\}_2$ (**7**) and $\{(IPr)CAs\}_2Fe(CO)_4$ (**8**), respectively.

Molecules containing two unpaired electrons in two degenerate (or nearly degenerate) orbitals are regarded as diradicals.[1] Singlet diradicals (or diradicaloids) are of a particular significance because of their intriguing electronic structures[2] and reactivity.[3] On account of their auspicious optical, magnetic, and electronic properties,[4] these open-shell species have become highly sought-after candidates for their applications in the design of advanced molecular materials.[5] Hence, the isolation and exploration of stable organic as well as main-group diradical(oid)s remains a highly avid research topic in fundamental chemistry.[6]

In 1995, Niecke et al. reported the first stable diradicaloid **I** (Figure 1).[7] In 2002, Bertrand et al. isolated a P_2B_2-diradicaloid **II**,[8] while a related aluminum species **III** was reported later by Schnöckel and co-workers.[9] Among Group 14 elements, Power (E = Ge),[10] Lappert (E = Sn),[11] and Sekiguchi (E = Si)[12] reported Niecke-type N_2E_2-diradicaloids **IV-E**. Over the last decade, Schulz and co-workers have isolated cyclic N_2E_2-diradicaloids **V-E** and **VI** (E = P or As)[13] and explored their electronic structures and reactivity.[6m,14] The stability of Niecke-type diradicaloids (**IV-E**)-(**VI**) may be attributed to the captodative (donor–acceptor) effect of nitrogen atoms.[15] Each of the nitrogen atoms of (**IV-E**)-(**VI**) contributes 2e to the N_2E_2-ring, giving rise to a formal Huckel's $4n+2$ π-electron aromatic system.[16] While diradical character and aromaticity are not mutually exclusive,[17] compounds with a large diradical character are expected to be weak (or non-) aromatic.[6,18] In 2017, the research groups of Grützmacher[19] and Ghadwal[20] independently reported two different synthetic routes to a C_2P_2-diradicaloid **VII-P** based on an N-heterocyclic carbene (NHC), i.e. IPr (Figure 1). Note, the arsenic analogue **VII-As** remained, nonetheless, thus far unknown. This is most likely due to the limitation of available synthetic methods and/or the lack of suitable starting materials. Herein, we

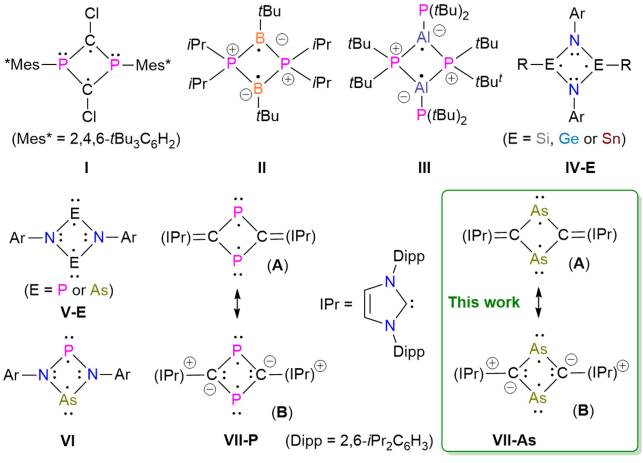
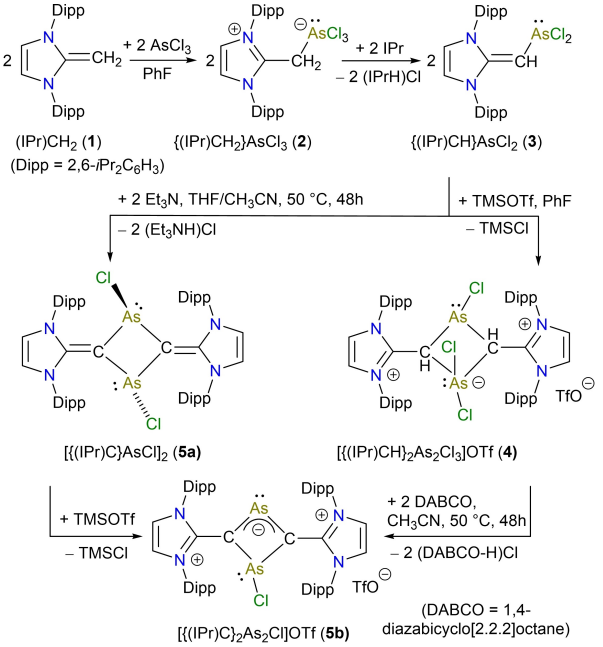


Figure 1. Selected examples of stable main-group singlet diradicals.

[*] H. Steffenfauseweh, Dr. Y. V. Vishnevskiy, B. Neumann, Dr. H.-G. Stammler, Priv.-Doz. Dr. R. S. Ghadwal
Molecular Inorganic Chemistry and Catalysis, Inorganic and Structural Chemistry, Center for Molecular Materials, Faculty of Chemistry, Universität Bielefeld
Universitätsstr. 25, 33615 Bielefeld (Germany)
E-mail: rghadwal@uni-bielefeld.de
Homepage: http://www.ghadwalgroup.de
Dr. D. M. Andrada
Faculty of Natural Sciences and Technology, Department of Chemistry, Saarland University
Campus C4.1, 66123 Saarbrücken (Germany)

report the first C_2As_2-diradicaloid **VII-As** as a red crystalline solid.

Treatment of $(IPr)CH_2$ (**1**) with $AsCl_3$ affords the Lewis adduct $\{(IPr)CH_2\}AsCl_3$ (**2**) as a colorless crystalline solid in 87% yield (Scheme 1). In THF, **2** readily undergoes dehydrochlorination with 1 equiv of IPr base to afford the N-heterocyclic vinyl (NHV)[21] derivative $\{(IPr)CH\}AsCl_2$ (**3**). Compound **3** (lime green) has limited stability in solution as well as in the solid-state. Samples of **3** (both solid as well as solutions) turned dark green on storing them at room temperature overnight. ^{1}H NMR analyses of these samples indicated the formation of an intractable mixture of products including $(IPrCH_3)Cl$ and some residual **3**. This suggests the auto-deprotonation of **3**, which can be rationalized by considering its Lewis basicity, like **1**, owing to the presence of highly polarizable vinylic bond. Nonetheless, **3** can be converted into a thermally stable dimer $[(IPr)CHAsCl\}_2Cl]OTf$ (**4**) on treatment of a freshly prepared PhF solution of **3** with TMSOTf. The dehydrochlorination of **3** is feasible with Et_3N to obtain **5a**, albeit in a low yield (39%). Treatment of an acetonitrile solution of **4** with DABCO at 50 °C for two days affords **5b** as a dark green solid in 90% yield. **5b** is also accessible by reacting **5a** with TMSOTf or KOTf. Compounds **2**–**5** exhibit expected ^{1}H and ^{13}C NMR signals for the IPr moiety (see the Supporting Information). The ^{1}H NMR spectrum of **2** shows a singlet at 3.06 ppm for the CH_2 group. The ^{1}H NMR spectra of **3** (4.54 ppm) and **4** (3.35 ppm) show a singlet for the C*H*As moiety.



Scheme 1. Synthesis of **2**, **3**, **4**, **5a**, and **5b**.

The molecular structures **2** and **4** (Figure 2) exhibit the expected atom connectivity.[22] The C28–As1 bond length of the Lewis adduct **2** (2.015(2) Å) compares well with that of $(IPr)AsCl_3$ (2.018(3) Å).[23] The $C_{(IPr)}$–C bond lengths of **2** (C1–C28: 1.480(2) Å) and **4** (C1–C2: 1.474(1) Å) are larger than that of $(IPr)CH_2$ (**1**) (1.332(4) Å)[24] but consistent with the adducts of **1** with main-group Lewis acids (ca. 1.48 Å).[25] The molecular structure of **5a** (Figure 3) has an inversion center thus the other half of the molecule was symmetry generated. The chlorides were occupied at two positions with a long [As1–Cl1A (2.395(7) Å] and a short [As1–Cl1B (2.309(7) Å] As–Cl bond lengths. The four-membered C_2As_2 ring of **5a** has a plane fold angle of 6.88(6)° from the nearly coplanar peripheral C_3N_2-rings. The C1–C4 (1.381 (1) Å) and C4–As1 (1.909(1) Å) bond lengths of **5a** are smaller compared to those of **2** and **4**, suggesting a modest double bond character (see below for NBO analyses).[21,26]

Treatment of a THF solution of **5a** (or **5b**) with Mg turnings leads to the formation of compound **6** as a red crystalline solid (Scheme 2). **6** is indefinitely stable under inert gas atmosphere but readily decomposes when exposed to air. The ^{1}H and ^{13}C NMR spectra of **6** exhibit well-resolved signals due to the (IPr)C moiety. The ^{1}H NMR spectrum of **6** shows two doublets (Me_2CH), one septet (Me_2CH), and one singlet (NC*H*) for the IPr unit, indicating its highly symmetric structure.

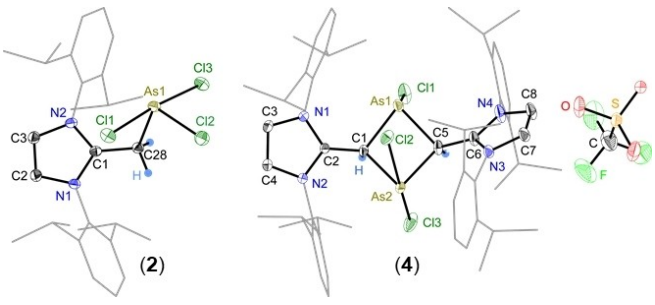


Figure 2. Molecular structures of **2** and **4**. Dipp groups are shown as wire-frame models. H atoms, except of CH or CH_2 moiety, and solvent molecules are omitted for clarity. Thermal ellipsoids are depicted at 50% probability.

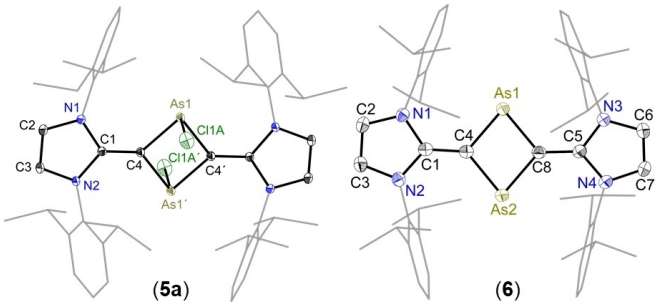
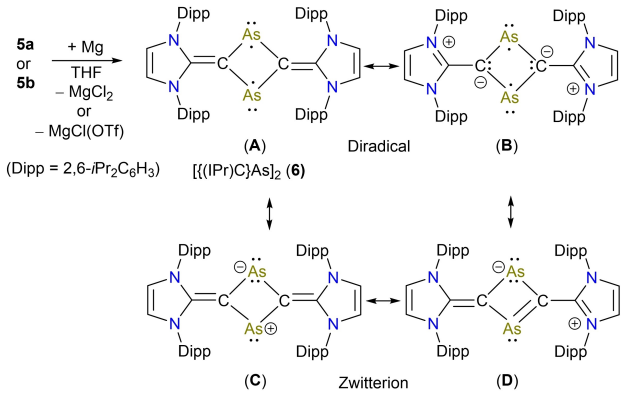


Figure 3. Solid-state molecular structures of **5a** and **6**. Dipp groups are shown as wire-frames and H atoms are omitted for clarity. Thermal ellipsoids are depicted at 50% probability. Selected bond lenghts [Å] and bond angles [°] for **5a**: As–ClA 2.395(7), As–ClB 2.309(7) (structure has one long and one short As–Cl distances, only long one with ClA are shown), As1–C4 1.909(1), C1–C4 1.381(1); Cl1A-As1-C4 97.7(2), C4-As1-C4′ 80.9(1), As1-C4-As1′ 99.1(1). For **6**: As1–C4 1.919(2), As1–C8 1.921(2), As2–C4 1.907(2), As2–C8 1.914(2), C1–C4 1.380(3), C8–C5 1.376(3); C4-As1-C8 79.1(1), C4-As2-C8 79.6(1), As1-C4-As2 100.8(1), As1-C8-As2 100.5(1).



Scheme 2. Reduction of **5a** (or **5b**) with magnesium (turnings) to **6** with representative diradical (**A** and **B**) and zwitterion (**C** and **D**) resonance forms.

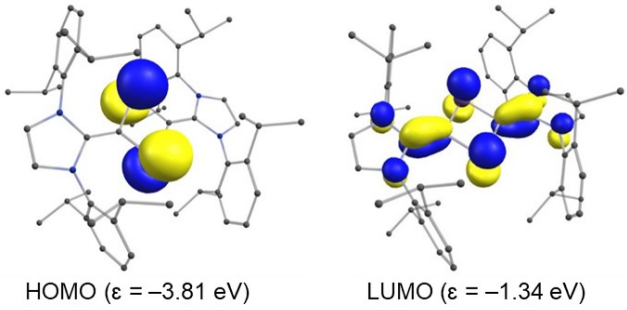


Figure 4. HOMO and LUMO of **6** (0.05 a.u. isosurface, PBE0/def2-TZVP).

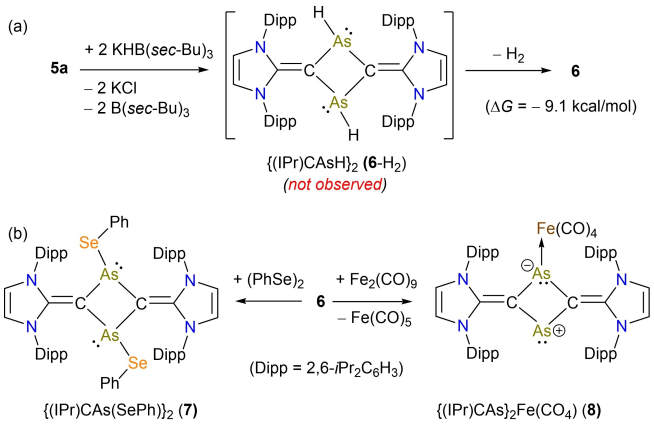
The molecular structure of **6** (Figure 3) features a planar C_2As_2 ring that is twisted by 4.09(9)° and 2.89(10)° from the nearly coplanar peripheral C_3N_2-rings. The trans-annular As1···As2 interatomic distance of **6** (2.948(2) Å) is larger than the sum of the arsenic covalent radii (2.42 Å) but smaller than the sum of the van der Waals radii (3.70).[27] The As1–C4/As1–C8 (1.915(2)/1.921(2) Å) and C1–C4/C5–C8 (1.380(3)/1.376(3) Å) bond lengths of **6** are comparable to those of **5a** (1.909(1), 1.381(1) Å, respectively). They are also similar to those of divinyldiarsene $[(IPr)C(Ph)As]_2$ (1.919(1), 1.376(2) Å) comprising a π-conjugated linear $C_2As_2C_2$-framework.[28]

Further insight into the electronic structure of **6** was obtained by theoretical calculations. The DFT optimized structure of **6** at the RKS-PBEh-3c level of theory (Figure S35) is in good agreement with the XRD structure (Figure 3). We performed NBO (natural bond orbital) analyses for **1**, **2**, **5a**, and **6** (see the Supporting Information). The calculated Wiberg bond indices (WBIs) for the C1–C4 (**5a** 1.41; **6** 1.37) and C4–As1 (**5a** 0.95; **6** 1.02) bonds are consistent with their bond lengths (Figure 3). The NBO charges at the C1 (**5a** 0.40; **6** 0.39), C4 (**5a** –0.98; **6** –0.85), and As (**5a** 1.03; **6** 0.40) atoms indicate strongly polarized C1=C4 bond and partial π-electron density transfer on to the arsenic atoms of the C_2As_2 ring. For comparison, related details of compounds **1** (WBI for C1–C4 1.62) and **2** (WBIs for C1–C4 1.08, C4–As1 0.78) are also provided in the Supporting Information (Tables S5—S7). As previously described for the phosphorus analogue **VII-P** (Figure 1),[19] compound **6** may also be viewed as an NHC-stabilized C_2As_2-cluster.[29]

The HOMO of **6** is a π-type orbital mainly located at the arsenic atoms of the C_2As_2 ring and has trans-annular antibonding combination (Figure 4). The LUMO spans mainly over the $C_2As_2C_2$-framework with some contribution from the nitrogen atoms. Note that the LUMO has trans-annular bonding combination. These features are consistent with Niecke-type singlet N_2E_2-diradicals (**IV-E**)-(**VI**) (Figure 1). The HOMO–LUMO energy gap ($\Delta E_{H\text{-}L}$ = 2.47 eV) of **6** is rather small, suggesting its high reactivity (see below). The UV/Vis spectrum of **6** (Figure S26) exhibits three main absorptions (λ_{max}) at 369, 519, and 655 nm, which based on TD-DFT calculations (Table S11) can be assigned to HOMO−1→LUMO+9, HOMO→LUMO+7/HOMO−1→LUMO, and HOMO→LUMO transitions, respectively.

Despite the closed-shell singlet (**CS**) ground state, the singlet-triplet energy gap ($\Delta E_{S\text{-}T}$ = 8.7 kcal mol^{-1}) calculated for **6** at the PBEh-3c level of theory is fairly small. Interestingly, the broken-symmetry open-shell singlet (**OS**) solution for **6** is calculated to be 0.34 kcal mol^{-1} lower in energy than the **CS** electronic state. The diradical character (y) according to Yamaguchi[30] is calculated to be 28%. The multireference SA-CASSCF(10,8)/def2-TZVP calculations reveal that the ground electronic state S_0 has the active space occupation pattern 22222000 (88%) and 22220200 (10%). The diradical character (β) for the CASSCF electronic structure S_0 amounts to 20%. Like Niecke-type singlet diradicals **IV**–**VII** (Figure 1), **6** may also be regarded as a 6π electron C_2As_2 ring system. However, the calculated nuclear independent chemical shift (NICS) (NICS(1) = −3.4; $NICS(1)_{zz}$ = −0.1) values indicate a rather weak aromatic character of the C_2As_2 ring (Table S12, Figure S42). This is also consistent with the weak ring current at the C_2As_2 ring of **6** as visualized by the ACID (anisotropy of the induced current density) plots (Figure S43).[31] Though aromaticity and diradical character are not mutually exclusive,[17] a rather weak aromaticity of **6** may account for the diradical character.[6,18]

Dihydrogen splitting is considered as a benchmark reaction of diradicals.[32] No change in the ^{1}H NMR spectrum was observed upon exposure of a C_6D_6 solution of **6** to H_2 (1 atm) at room temperature. Warming this solution at 80 °C for 2 h led to the decomposition of **6** as evident by the formation of $(IPr)CH_2$. We attempted an alternative method for the preparation of the hydride **6**-H_2 by reacting **5a** with KHB(*sec*-Bu)$_3$ (Scheme 3a). This reaction, however, afforded **6** and **1** instead of **6**-H_2. We assume that **6**-H_2 is unstable and decomposes into **6** and H_2, which is calculated to be thermodynamically favored by 9.1 kcal mol^{-1}. We also carried out low temperature ^{1}H NMR studies of a reaction of **5a** and KHB(*sec*-Bu)$_3$, which showed the formation of H_2 already at 233 K (Figure S1). At 293 K, the ^{1}H NMR spectrum indicates the presence of **6**, **1**, and H_2 as sole reaction products.



Scheme 3. a) Reaction of **5a** with KHB(*sec*-Bu)$_3$ to **6**. b) Synthesis of **7** and **8**.

Reactions of **6** with $(PhSe)_2$ and $Fe_2(CO)_9$ afford compounds **7** and **8**, respectively (Scheme 3). Compounds **7** and **8** are stable solids and have been characterized by NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction (Figure 5). The molecular structure of **7** shows the presence of SePh substituents at the arsenic atom in *cis*-fashion. In **7**, the C–C (1.377(4)/1.374(4) Å) and C–As (1.927(3)–1.936(3) Å) bond lengths of the C_2As_2 ring are comparable to those of **5a**. As expected for unsymmetrically substituted C_2As_2 ring in **8**, the As1–C4/As1–C8 (1.960(3)/1.964(3) Å) bond lengths are longer than As2–C7/As2–C8 (1.871(3)/1.881(3) Å). Thus, the latter have a partial multiple bond character, while the positive charge is formally distributed over the imidazole rings. The As–Fe bond length of **8** (2.475(1) Å) is larger than that of the electrophilic arsinidene complex {(IPr)CPh}As]Fe(CO)$_4$ (2.367(4) Å)[33] but compares well with four-coordinated nucleophilic arsinidene species (2.48 Å).[34]

In conclusion, the C_2As_2-diradicaloid **6** embedded between NHC (IPr) moieties has been isolated as a crystalline solid and characterized by spectroscopic and X-ray diffraction methods. Calculations suggest a singlet ground state for **6** with a considerably small singlet-triplet energy gap (8.7 kcal mol^{-1}). The calculated diradical character of **6** amounts to 20% (CASSCF) and 28% (PUHF, projection unrestricted Hartree–Fock). Reactivity of **6** has been shown with $(PhSe)_2$ and $Fe_2(CO)_9$, affording compounds **7** and **8**, respectively.

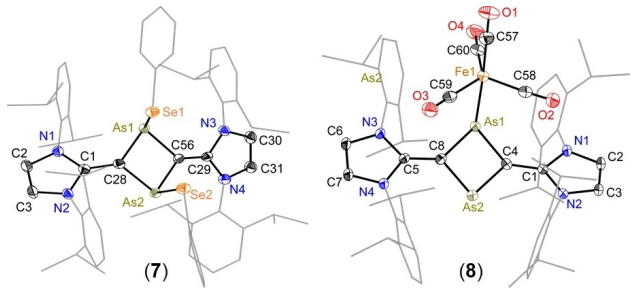


Figure 5. Solid-state molecular structures of **7** and **8**. H atoms have been omitted and aryl groups are shown as wireframe for clarity. Thermal ellipsoids are depicted at 50% probability.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for generous support (GH 129/4-2, GH 129/9-1 and VI 713/1-3). The authors thank Professor Norbert W. Mitzel for continuous support. The HPC facilities at the Universität zu Köln are acknowledged for computing time and programs. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Arsenic · Carbenes · Diradicals · Heterocycles · Vinylidene Ligands

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Manuscript received: May 19, 2022
Accepted manuscript online: June 2, 2022
Version of record online: July 13, 2022