# **CHEMISTRY** A European Journal



# Accepted Article

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To be cited as: Chem. Eur. J. 10.1002/chem.201706060

Link to VoR: http://dx.doi.org/10.1002/chem.201706060

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# Experimental Observation of Thermally Excited Triplet States of Heavier Group 15 Element-Centered Diradical Dianions

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**Abstract:** One-electron reductions of Mes\*As=FI\* (1;  $FI^* = 2,7$ -ditert-butylfluorenylidene, Mes\* = 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and diarsaalkenes [1,2-*b*]-IF(=AsMes\*)<sub>2</sub> (2; IF = indenofluorene) with potassium led to the isolation of the arsenic-centered radical anion salts 1K and 2K, respectively. The diradical dianion salts 2K<sub>2</sub> and 3K<sub>2</sub> were afforded by the reduction of 2 and 2,8-*t*Bu<sub>2</sub>-[2,1-*b*]-IF(=AsMes\*)<sub>2</sub> (3) with an excess amount of KC<sub>8</sub>. The radicals have been investigated by single-crystal X-ray crystallography, EPR and UV-Vis absorption spectroscopy, along with theoretical calculations. The calculations revealed that 2K<sub>2</sub> and 3K<sub>2</sub> feature open-shell singlet ground states with singlet-triplet energy gaps of 2.1 and 1.0 kcal mol<sup>-1</sup>, respectively. They are readily thermally excited to triplet states as demonstrated by EPR spectroscopy. The obtained diradicals represent the first examples of heavier Group 15 element-centered diradicals with experimentally observable triplet states.

Main-group element-based radicals have attracted tremendous attention in contemporary organometallic chemistry because of their importance in biological chemistry, theoretical chemistry and materials science.<sup>[1]</sup> Due to the limited number of energetically accessible valence orbitals in main-group elements, their radicals are highly reactive and unstable under ambient conditions. Despite the challenges, a variety of stable maingroup element-centered radicals have been successfully isolated with the aid of sterically demanding or  $\pi$ -conjugated ligands.<sup>1</sup> Group 15 element-centered radicals have been widely investigated, and phosphorus-centered radicals have been studied the most intensively. Several monoradicals  $^{\left[ 2\right] ,\left[ 3\right] }$  and diradicals<sup>[3d, 3j, 3]</sup> of the phosphorus element have been isolated and fully characterized. However, these diradicals feature large singlet-triplet energy gaps, and their triplet states could not be thermally populated under experimental conditions.

In contrast, there have been a limited number of isolable arsenic-centered radicals (Scheme 1). In 2013, Robinson and coworkers reported the first stable  $As_2^{++}$  radical cation **A** stabilized by two *N*-heterocyclic carbene (NHC) ligands.<sup>[4]</sup> In 2014, Grützmacher and coworkers utilized the phosphinidene

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Supporting information for this article is given via a link at the end of the document. ligand to successfully stabilize the neutral arsenic radical **B**.<sup>[2k]</sup> In comparison to the limited number of arsenic-centered monoradicals, its diradicals are even scarcer. There have been only two stable examples of arsenic-based diradicals ( $C^{[3]}$  and  $D^{[5]}$ ) reported by Schulz and coworkers. It is noteworthy that **C** and **D** only feature some diradical characters, and their triplet states can not be thermally accessible at experimental conditions. In addition, they can further undergo one-electron oxidation to the corresponding radical cations **E** and **F**.<sup>[3i]</sup> Until now, there have been no examples of stable arsenic-based radical anions and diradical dianions, although diarsene<sup>[6]</sup> and phosphaarsene<sup>[7]</sup> radical anions have been investigated by electron paramagnetic resonance (EPR) spectroscopy.



Scheme 1. Isolable arsenic-centered radicals and diradicals

Arsaalkenes, compounds bearing the As=C double bond, are expected to be readily reduced to the radical anions owing to the lower-lying  $\pi^*(As=C)$  orbital when comparing to that of C=C double bond in olefins. This is attributed to smaller overlap of 4p orbitals of the As atom with 2p orbitals of the C atom.<sup>[8]</sup> Considering this property of arsaalkenes and the scarcity of arsenic-based radicals, we were interested in synthesizing stable arsenic-based radical anions and diradical dianions through the reduction of arsaalkenes. Herein, we report the oneelectron reduction of the arsaalkene Mes\*As=FI\* (1; FI\* = 2,7-di-Mes\* 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), tert-butylfluorenylidene, = and diarsaalkene [1,2-b]-IF(=AsMes\*)<sub>2</sub> (2; IF = indenofluorene), affording the radical anions 1K and 2K, respectively. The diarsaalkenes 2 and 2,8-tBu<sub>2</sub>-[2,1-b]-IF(=AsMes\*)<sub>2</sub> (3) could also undergo two-electron reductions to yield the diradical dianions  $2K_2$  and  $3K_2$ , respectively. The solid-state and electronic structures of the obtained radicals were investigated by single crystal X-ray diffraction analysis, EPR and UV-Vis absorption

spectroscopy, in conjunction with density functional theory (DFT) calculations.

Arsaalkene **1** was synthesized according to published procedures.<sup>[9]</sup> Diarsaalkenes **2** and **3** were obtained through the reaction of the *in situ* prepared Mes\*AsCl<sub>2</sub> with the dilithium salt of the corresponding indenofluorenes, following by treatment with an excess amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (see supporting information (SI) for details). The redox properties of **1-3** were evaluated by electrochemical studies (Figures S1–3 in the SI). The cyclic voltammetry reveals that **1** has one reversible reduction peak at -1.78 V, while **2** and **3** feature two reversible reduction peaks (-1.43 and -1.14 V for **2**; -1.98 and -1.42 V for **3**), versus the Ag/AgNO<sub>3</sub> reference electrode. The electrochemical results suggest that compound **1** can undergo one-electron reduction, while **2** and **3** can be one-electron and two-electron reduced.



Scheme 2. Stable arsenic-centered radical anion and diradical dianion salts.

Accordingly, the reduction of 1 with a stoichiometric amount of elemental potassium afforded the radical anion 1K as deep-blue crystals in 45% yield (Scheme 2). The one-electron reductions of 2 and 3 were carried out with one molar equiv. of elemental potassium as the reductant. However, only the reduction of 2 led to the isolation of deep-brown crystals of 2K in moderate yield. We were not able to isolate the crystals of one-electron reduction product of 3. The two-electron reductions of 2 and 3 with an excess amount of KC<sub>8</sub> (three molar equiv.) resulted in the formation of the diradical dianions  $2K_2$  and  $3K_2$  as deep-green crystals in 53% and 36% yields, respectively. All the reduced species of 1-3 are highly moisture- and oxygensensitive, but are stable under an inert atmosphere at ambient temperature for days.

Crystals of **1K** and **2K** were harvested from the concentrated THF solution at -30 °C (Figures S4 and S5).<sup>[10]</sup> The solvated K<sup>+</sup> cation interacts with the fulvene moiety in a  $\eta^5$  mode with a distance of 2.826 Å to the center of the fulvene plane. The As–C bond (1.891(3) Å) to the fulvene group is largely elongated in comparison to that in **1** (1.794(11) Å),<sup>[9]</sup> in line with one-electron addition to the  $\pi^*$  orbital of the As=C double bond. In contrast to **1K**, the K<sup>+</sup> cation of **2K** is coordinated by 18-c-6 and two THF molecules, and there is no direct cation-anion interaction in the structure. The anion moiety is centrosymmetric. The As–C

bonds (1.855(3) Å) to the indenofluorene moiety are longer than that in the neutral compound **1** (1.794(11) Å),<sup>[9]</sup> but shorter than that in the one-electron reduction product **1K** (1.891(3) Å), indicating that the single electron is equally delocalized over the two As=C double bond moieties.

The doubly reduced species  $2K_2$  and  $3K_2$  crystallize in the triclinic space group *P*-1 and orthorhombic space group *Pna*21, respectively (Figure 1). The two K<sup>+</sup> cations in  $2K_2$  coordinate to 18-c-6 and THF molecules, whereas they are trapped by 222-cryptand in  $2K_2$ . The dianion of  $2K_2$  has a symmetric center, and the two As atoms have identical coordination environment, while the two As atoms of  $3K_2$  have slightly different distances to the connected C atoms (1.896(5) and 1.879(5) Å) of the indenofluorene fragment. The distances of the As atoms to C atoms of the indenofluorene moieties in  $2K_2$  (1.888(5) Å) and  $3K_2$  (av. 1.888(5) Å) are comparable with that in 1K (1.891(3) Å), consistent with the result that both  $\pi^*(As=C)$  orbitals are occupied by one single electron.



**Figure 1.** Ellipsoid drawings of the dianion moiety of  $2K_2$  (a) and  $3K_2$  (b) at 30% probability. Hydrogen atoms and THF solvent molecules are omitted for clarity.

The molecular structures of all the reduced species could be well reproduced by DFT calculations at the (U)WB97XD/6-31G(d) level of theory. The singly occupied molecular orbitals (SOMOs) of the radical anions **1K** and **2K** are mainly comprised of As=C antibonding interactions (Figures S6 and S7). The Mulliken spin density distribution reveal that the unpaired electron mainly resides at the As center (0.62) with small contribution from the C atoms of the fluorene moiety in **1K** (Figure S8). Most of the spin density in **2K** is located at two As centers, and there is some contribution from the central phenyl group and the C atoms of the indenofluorene moieties (Figure S9).

In order to determine the ground state of  $2K_2$  and  $3K_2$ , we carried out DFT calculations on their closed-shell singlet (CS), open-shell singlet (OS) and triplet (T) states, and the obtained stationary points were characterized by frequency calculations. For  $2K_2$ , the OS state<sup>[11]</sup> has the lowest energy, and the singlet-triplet gap is 2.1 kcal mol<sup>-1,[12]</sup> which is substantially smaller than

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its phosphorus analogue (6.7 kcal mol<sup>-1</sup>).<sup>[3I]</sup> This suggests that  $2K_2$  has a larger diradical character and its triplet state might be relatively easy to be thermally achieved. The Mulliken spin density distribution reveals that most of the spin density resides at the As centers, meanwhile there is a small amount of density located at the five-membered rings and the central benzene moiety (Figure 2a).



Figure 2. The Mulliken spin density distribution of  $2K_2$  (a) and  $3K_2$  (b) at the open-shell singlet state.

Since the two As=C spin carriers reside at the *meta* positions of the central benzene group, similar to the electronic structures of *meta*-quinodimethanes, we expected that  $3K_2$  might exhibit a triplet ground state.<sup>[13]</sup> However, the calculations reveal that the diradical dianion  $3K_2$  also features an open-shell singlet ground state with a singlet-triplet gap of 1.0 kcal mol<sup>-1</sup>,<sup>12</sup> which is much smaller than that of  $2K_2$ . The spin density mainly resides at the two As atoms, and there is a negligible amount of spin at the central benzene ring (Figure 2b), in strikingly contrast with that of  $2K_2$ .

The different electronic structures between  $2K_2$  and  $3K_2$  are also reflected by the nucleus-independent chemical shift (NICS) values (Table S1).<sup>[14]</sup> The NICS(0) value for the central benzene ring increases from 2, 2K to 2K<sub>2</sub>, suggesting the aromaticity decreases during the reduction processes. This is attributed to the electron delocalization over the central benzene ring leading to an increasing degree of the quinoidal structure upon reduction. In contrast, the aromaticity of the central bezene ring in 3K2 strengthens in comparison to that in 3, but the NICS(o) value for the flanking benzene rings increases substantially from 3 to 3K2 due to the presence of some spin density at these two benzene moieties in the doubly reduced species. In addition, the NICS(0) values of the five-membered rings decrease during reductions, particularly for 2 and its reduced species, they change from antiaromaticity in 2 (3.61) to aromaticity in the doubly reduced form (-1.04).

The EPR spectrum of **1K** in THF solution at room temperature reveals a quartet signal (g = 2.018) with isotropic hyperfine coupling constant (hfc) of  $a({}^{57}As) = 41.8$  G owing to the coupling to one  ${}^{57}As$  (I = 3/2) nucleus (Figure S10), which is much larger

than those in **A** (24 G)<sup>[4]</sup> and **B** (21 G)<sup>[2k]</sup>, further supporting that **1K** is an arsenic-centered radical. The EPR spectrum of **2K** in THF solution at room temperature shows relatively weak signals owing to the coupling with two As nuclei ( $a(^{57}As) = 29.1$  G) (Figure S11). The much smaller coupling constant in comparison to that in **1K** can be interpreted by equal electron delocalization over two As centers. The EPR spectrum of the frozen solution at 88 K exhibits high-resolution anisotropic hyper-couplings (Figure S11), and the *g* factors and hfc tensors were determined as follows:  $g_x = 2.0404$ ,  $g_y = 2.0284$ ,  $g_z = 2.0032$ ,  $a_{xx} = a_{yy} = 26$  G,  $a_{zz} = 124$  G, indicating the spin density mainly resides at the two As centers, consistent with the calculated result.



**Figure 3.** Experimental (black) and simulated (red) EPR spectra of  $2K_2$  (a) and  $3K_2$  (b) obtained in the solid state at room temperature. The peaks labeled with stars are most probably attributed to the monoradical impurity. The insets show the half-field signal.

The EPR spectra of  $2K_2$  and  $3K_2$  were measured in the solid state at room temperature (Figure 3). Strikingly, for both compounds, the half-field signal was observed, supporting its spin-triplet state at the measurement conditions. Therefore, compounds  $2K_2$  and  $3K_2$  represent the first stable heavier Group 15 element-based diradicals featuring observable thermally excited triplet states. The broad peaks centered at g = 2.0054 for  $3K_2$  were simulated, and D = 700 G was obtained from the simulation. The average spin–spin distance was estimated to be 3.4 Å from the D value, which is much shorter than the distance between two As centers (5.8 Å) in the crystal structure, indicating the spin delocalization over the indenofluorene moiety. The EPR spectrum of  $2K_2$  could not be simulated impurity.<sup>[15]</sup>

The UV-Vis absorption spectra of all the reduced species were measured in THF solutions under a nitrogen atmosphere (Figure 4). For the radical anion **1K**, one long wavelength absorption was observed at 624 nm, which is assigned to HOMO( $\beta$ )-LUMO( $\beta$ ) electron transition according to time-

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dependent DFT (TD-DFT) calculations (Figure S12). The spectra of the anion **2K** and the dianions **2K**<sub>2</sub> and **3K**<sub>2</sub> reveal an absorption peak at around 780 nm. For the radical anion **2K**, this absorption is attributed to HOMO( $\beta$ )-LUMO( $\beta$ ) electron transition (Figure S13). In terms of both **2K**<sub>2</sub> and **3K**<sub>2</sub>, they originate from HOMO( $\alpha$ )-LUMO( $\alpha$ ) and HOMO( $\beta$ )-LUMO( $\beta$ ) electron transitions, respectively (Figures S14 and S15). The broad peak at 870 nm in the spectrum of **3K**<sub>2</sub> is tentatively assigned to the monoradical anion impurity, which is confirmed by TD-DFT calculations.



Figure 4. The UV-Vis absorption spectra of 1K, 2K, 2K<sub>2</sub> and 3K<sub>2</sub> obtained in THF solutions under nitrogen atmosphere.

In summary, by utilizing the fluorene and indenofluorene groups as the structural scaffolds, we successfully isolated the arsenic-centered radical anions and diradical dianions. The high stability of these radicals is most probably attributed to partial electron delocalization over the fluorene and indenofluroene moieties. Our work provides the first examples of stable arsenic-centered radical anions synthesized through reduction of the As=C double bonds of arsaalkenes. Strikingly,  $2K_2$  and  $3K_2$  are the first heavier Group 15 element-based diradicals featuring thermally accessible triplet states because of the small singlet-triplet energy gaps. The synthesis of polyradicals based on the R'E=CR<sub>2</sub> (E = Group 15 elements) building block is currently undergoing in our laboratory.

#### Acknowledgements

We thank the National Key R&D Program of China (Grant 2016YFA0300404, X.W.) and the National Natural Science Foundation of China (Grants 21525102, 21690062, X.W. and 21601082, G.T.) for financial support. We are grateful to the High Performance Computing Center of Nanjing University for doing the numerical calculations in this paper on its IBM Blade cluster system.

**Keywords:** Radical • Diradical • Group 15 element • Arsenic • Triplet state

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Layout 1:

## COMMUNICATION

Stable Radical Anions: The stable arsenic-centered radical anion and diradical dianion salts have been successfully synthesized through reductions of the arsaalkene and diarsaalkene precursors. The obtained diradicals represent the first examples of heavier Group 15 element-centered diradicals featuring experimentally observable triplet states.



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Experimental Observation of Thermally Excited Triplet States of Heavier Group 15 Element-Centered Diradical Dianions