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Oxidation of Carbene-Stabilized Diarsenic: Diarsene Dications and Diarsenic Radical Cations

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Supporting Information

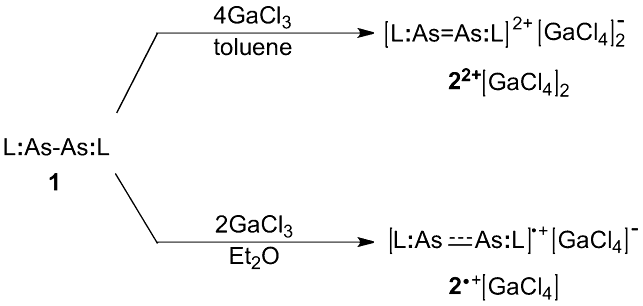
ABSTRACT: Oxidation of carbene-stabilized diarsenic, L:As−As:L [L: = :C{N(2,6-^{i}Pr$_2$C$_6$H$_3$)CH}$_2$] (**1**), with gallium chloride in a 1:4 ratio in toluene affords the dicationic diarsene complex [L:As═As:L]$^{2+}$([GaCl$_4$]$^-$)$_2$ (**2**$^{2+}$[GaCl$_4$]$_2$), while oxidation of **1** with GaCl$_3$ in a 1:2 ratio in Et$_2$O yields the monocationic diarsenic radical complex [L:AsAs:L]$^{•+}$[GaCl$_4$]$^-$ (**2**$^{•+}$[GaCl$_4$]). Strikingly, complex **2**$^{•+}$ is the first arsenic radical to be structurally characterized in the solid state. The nature of the bonding in these complexes was probed computationally and spectroscopically.

Carbene-stabilized diatomic main-group allotropes[1−5] are intriguing, as they provide convenient "zero-oxidation-state" platforms from which further chemistry may be explored. While the first such complex, carbene-stabilized disilicon, L:Si═Si:L [L: = :C{N(2,6-^{i}Pr$_2$C$_6$H$_3$)CH}$_2$], was reported by this laboratory in 2008,[6] subsequent examples of carbene-stabilized diatomic main-group allotropes include P$_2$,[7,8] As$_2$,[9] Ge$_2$,[10] B$_2$,[11] and Sn$_2$.[12] The emerging chemical reactivity of these molecules is as fascinating as it is provocative. For example, L:Si═Si:L was utilized in the synthesis of a "push−pull"-stabilized derivative of the parent silylene (:SiH$_2$)[13] while L:P−P:L functioned as a bidentate ligand in chelating the BH$_2^+$ cation.[14] Might carbene-stabilized diarsenic, L:As−As:L (**1**),[9] similarly possess novel reactivity? Herein we report the syntheses,[15] molecular structures,[15] computational studies,[16] and electron paramagnetic resonance (EPR) spectra of [L:As═As:L]$^{2+}$([GaCl$_4$]$^-$)$_2$ (**2**$^{2+}$[GaCl$_4$]$_2$) and [L:AsAs:L]$^{•+}$[GaCl$_4$]$^-$ (**2**$^{•+}$[GaCl$_4$]). Complex **2**$^{2+}$, a carbene-stabilized diarsene dication, and complex **2**$^{•+}$, a carbene-stabilized monocationic diarsenic radical cation, were both prepared by oxidation of **1** using gallium chloride. Notably, complex **2**$^{•+}$ is the first stable arsenic radical to be structurally characterized.

In contrast to transition metals, the main-group p-block elements do not readily undergo one-electron redox reactions.[17] Regarding the heavier group 15 elements, persistent[18] and stable[18] radicals have been experimentally realized only for phosphorus.[19−24] Bertrand recently reported that carbene−P$_2$ complexes could be oxidized to the corresponding monocationic P$_2^{•+}$ radicals and P$_2^{2+}$ dications using Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ and ferrocenium triflate, respectively.[19] In contrast, the radical chemistry of arsenic, antimony, and bismuth is largely unexplored.[18] Indeed, persistent arsenic-centered radicals have been studied experimentally only by gas-phase electron diffraction[25] and EPR spectroscopy.[20,26]

Although gallium halides reportedly are poor oxidizing reagents,[27] Bertrand's report of the one-electron oxidation of the cyclic (alkyl)(amino)carbene (CAAC)-stabilized parent borylene to the corresponding borinylium complex (H−B$^{•+}$) using GaCl$_3$ is significant.[28] In our laboratory, the reaction of **1** with GaCl$_3$ in a 1:4 ratio in toluene quantitatively resulted in the orange dicationic diarsene complex **2**$^{2+}$[GaCl$_4$]$_2$ (Scheme 1). However, the reaction of **1** with GaCl$_3$ in a 1:2 ratio in Et$_2$O afforded the green monocationic diarsenic radical complex **2**$^{•+}$[GaCl$_4$] in 29.1% yield (Scheme 1). Similarly, AlCl$_3$ and InCl$_3$ were also shown to oxidize **1** to **2**$^{2+}$[ECl$_4$]$_2$ (E = Al, In). Our investigation suggested that the [ECl$_4$]$^-$ (E = Al, Ga, In) counteranions may affect the stability of the dicationic [L:As═As:L]$^{2+}$ fragment in polar solvents. In acetonitrile, while the orange compounds **2**$^{2+}$[ECl$_4$]$_2$ (E = Al, Ga) were stable, orange **2**$^{2+}$[InCl$_4$]$_2$ gradually decomposed with the color changing to green.

Scheme 1. Gallium Chloride Oxidation of L:As−As:L



The compound **2**$^{•+}$[GaCl$_4$] was isolated from the hexane/THF mixed solvent as dark-green crystals. X-ray structural analysis[15] (Figure 1) showed that the As$_2$ core of **2**$^{•+}$ is disordered (only one set of disordered structural data is shown in Figure 1) with an average As−As bond distance of 2.32 Å, which falls between the As−As single bond distance in **1** [2.442(1) Å] and the As═As double bond distance [2.224(2) Å] in RAs═AsR′ [R = 2,4,6-^{t}Bu$_3$C$_6$H$_2$; R′ = CH(SiMe$_3$)$_2$].[29] The average As−C bond distances of 1.92 Å−1.95 Å in **2**$^{•+}$ are somewhat longer than those in **1** [1.881(2) Å].[9] The computed

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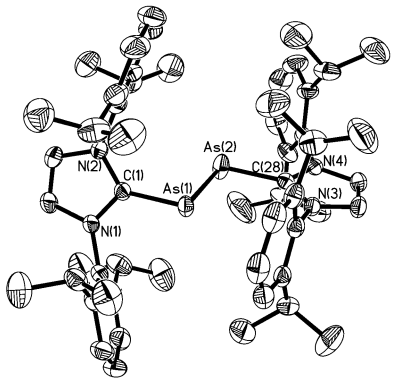

Figure 1. Molecular structure of **2**$^{\bullet+}$. Thermal ellipsoids represent 30% probability. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): As(1)–As(2) 2.332(3), As(1)–C(1) 1.960(4), As(2)–C(28) 1.938(5), C(1)–N(1) 1.358(5), C(1)–N(2) 1.346(5), C(28)–N(3) 1.357(5), C(28)–N(4) 1.359(5); C(1)–As(1)–As(2) 92.10(14), C(28)–As(2)–As(1) 101.02(16), N(1)–C(1)–As(1) 123.9(3), N(2)–C(1)–As(1) 129.0(3), N(3)–C(28)–As(2) 135.3(3), N(4)–C(28)–As(2) 118.9(3).

As–As bond distance of 2.388 Å in the simplified model **2H**$^{\bullet+}$ [in which L: was replaced by :C(NHCH)$_2$; optimized in C_2 symmetry][16] is ~0.06 Å longer than that in **2**$^{\bullet+}$. The As$_2$-based localized molecular orbitals (LMOs) of the simplified **2H**$^{\bullet+}$ model (Figure 2) include one As–As σ bonding orbital (a), one lone-pair orbital on each As atom (b), one As–As π bonding orbital (c), and one As–As π* singly occupied molecular orbital (SOMO) (d), which is in accordance with the 1.218 As–As Wiberg bond index (WBI). Natural bond orbital (NBO) analysis[30] of **2H**$^{\bullet+}$ showed that the As$_2$ core bears a positive charge of +0.18, which compares to the charge of +0.16 on the P$_2$ unit in carbene-stabilized P$_2$$^{\bullet+}$ radical (**3**).[19] Similar to **3**, the spin density distribution of **2H**$^{\bullet+}$ indicates that the unpaired electron is largely localized at the As$_2$ core (0.41 at each As atom), consistent with the SOMO depicted in Figure 2.

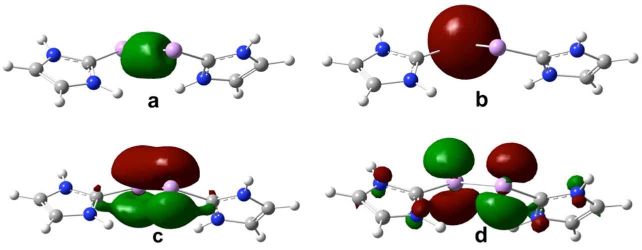

Figure 2. LMOs of **2H**$^{\bullet+}$ with C_2 symmetry: (a) As–As σ bonding orbital; (b) one of the two As lone-pair orbitals; (c) As–As π bonding orbital; (d) As–As π* antibonding SOMO.

The room-temperature EPR spectrum of **2**$^{\bullet+}$ in fluorobenzene displays a broadened septet ($g \approx 2.05$) with poorly resolved low- and high-field hyperfine components resulting from large hyperfine coupling with two equivalent ^{75}As ($I = {}^3/_2$) nuclei ($A \approx 68$ MHz) (Figure 3). Using the correlation time estimated from parallel NMR studies (10^{-5} s), the spectrum was well-simulated as that of a diarsenic radical involving equivalent As atoms (the simulation parameters are shown in the Figure 3 caption). Thus, the EPR data unambiguously support the radical nature of **2**$^{\bullet+}$.

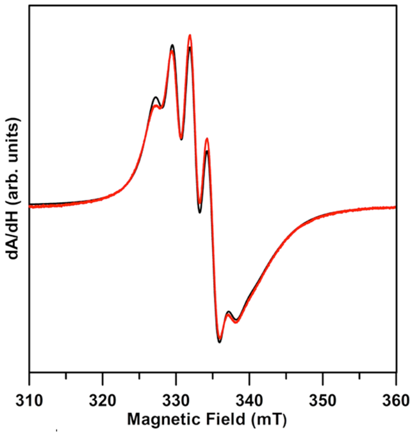

Figure 3. Room-temperature X-band EPR spectrum of **2**$^{\bullet+}$ in fluorobenzene (red line) recorded at 9.59 GHz with a modulation amplitude of 1 mT and a microwave power of 80 mW. Also shown is the almost perfectly superposed simulated spectrum (black line), which was generated with the EasySpin software package using a correlation time of 10^{-5} s; $g_{x,y,z}$ = 2.0458, 2.0457, and 2.0452; and two identical ^{75}As nuclei ($I = {}^3/_2$) with $A_{x,y,z}$ = 67.1, 68.0, and 67.8 MHz.

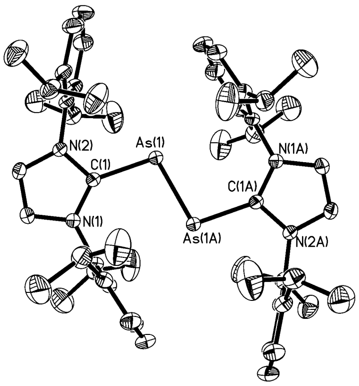

Figure 4. Molecular structure of **2**$^{2+}$. Thermal ellipsoids represent 30% probability. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): As(1)–As(1A) 2.2803(5), As(1)–C(1) 1.977(2), C(1)–N(1) 1.353(3), C(1)–N(2) 1.351(3); C(1)–As(1)–As(1A) 100.10(7), N(1)–C(1)–As(1) 135.61(17), N(2)–C(1)–As(1) 118.70(17).

The structural metrics of the present carbene-stabilized diarsene cations are particularly significant. Both **2**$^{2+}$ (Figure 4) and **1** possess C_i symmetry, and they exhibit similar trans-bent geometries with C(1)–As(1)–As(1A)–C(1A) torsion angles of 180.0° and C(1)–As(1)–As(1A) bond angles of ~100°.[9,15] The As–As bond distance in **2**$^{2+}$ [2.2803(5) Å] is ~0.16 Å shorter than that in **1** [2.442(1) Å] and only marginally shorter than that observed for **2**$^{\bullet+}$ (2.32 Å av). However, the As–As bond in **2**$^{2+}$ is 0.06 Å longer than the As=As double bond reported for RAs=AsR′ [2.224(2)].[29]

The As–C bond distances in **2**$^{2+}$ [1.977(2) Å] are slightly longer than those in **2**$^{\bullet+}$ (1.92–1.95 Å av) but 0.1 Å longer than those in **1** [1.881(2) Å]. The same trend has also been observed for the changes in the P–P and P–C bond distances in carbene-stabilized P$_2$[7] and its cationic derivatives P$_2$$^{\bullet+}$ and P$_2$$^{2+}$.[19] The computed As–As (2.296 Å) and As–C (1.979 Å) bond distances in the simplified model **2H**$^{2+}$ [in which L: was replaced by :C(NHCH)$_2$][16] are very similar to those in **2**$^{2+}$ [As–As, 2.2803(5) Å; As–C, 1.977(2) Å]. The LMOs of **2H**$^{2+}$ (Figure 5) indicate the presence of one As–As σ bond (a) and one As–As π bond (b) in **2**$^{2+}$. The WBI of 1.78 for **2H**$^{2+}$ is supportive of arsenic–arsenic double-bond character in **2**$^{2+}$.

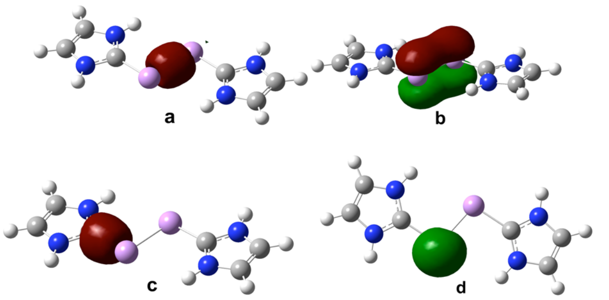

Figure 5. LMOs of $\mathbf{2H}^{2+}$ with C_i symmetry: (a) As−As σ bonding orbital; (b) As−As π bonding orbital; (c) one of the As−C σ bonding orbitals; (d) one of the As lone-pair orbitals.

The positive partial charge of +0.77 on the As_2 core in $\mathbf{2}^{2+}$ compares well with the charge of +0.73 on the P_2 unit in dicationic **3**.[19]

In summary, one- and two-electron oxidations of carbene-stabilized diarsenic using gallium chloride were achieved. Complex $\mathbf{2}^{\bullet+}$ is the first stable arsenic radical to be structurally characterized.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete refs 16a and 16b and full details of the syntheses, computations, and X-ray crystal structure determination, including CIFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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