

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

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S Supporting Information

ABSTRACT: Oxidation of carbene-stabilized diarsenic, L:As–As:L [L: = :C{N(2,6-*i*-Pr₂C₆H₃)CH}₂] (**1**), with gallium chloride in a 1:4 ratio in toluene affords the dicationic diarsene complex [L:As=As:L]²⁺([GaCl₄]⁻)₂ (2²⁺[GaCl₄]₂), while oxidation of **1** with GaCl₃ in a 1:2 ratio in Et₂O yields the monocationic diarsenic radical complex [L:AsAs:L]•⁺[GaCl₄]⁻ (2•⁺[GaCl₄]). 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.

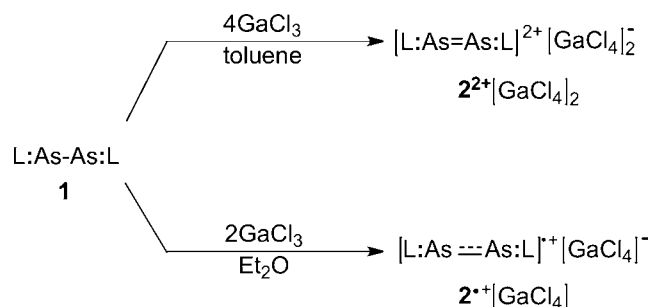
Carbene-stabilized diatomic main-group allotropes^{1–5} are intriguing, as they provide convenient “zero-oxidation-state” platforms from which further chemistry may be explored. While the first such complex, carbene-stabilized disilicon, L:Si=Si:L [L: = :C{N(2,6-*i*-Pr₂C₆H₃)CH}₂], was reported by this laboratory in 2008,⁶ subsequent examples of carbene-stabilized diatomic main-group allotropes include P₂,^{7,8} As₂,⁹ Ge₂,¹⁰ B₂,¹¹ and Sn₂.¹² 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 (:SiH₂)¹³ while L:P–P:L functioned as a bidentate ligand in chelating the BH₂⁺ cation.¹⁴ Might carbene-stabilized diarsenic, L:As–As:L (**1**), 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⁺([GaCl₄]⁻)₂ (2²⁺[GaCl₄]₂) and [L:AsAs:L]•⁺[GaCl₄]⁻ (2•⁺[GaCl₄]). Complex 2²⁺, 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, persistent¹⁸ and stable¹⁸ radicals have been experimentally realized only for phosphorus.^{19–24} Bertrand recently reported that carbene–P₂ complexes could be oxidized to the corresponding monocationic P₂•⁺ radicals and P₂²⁺ dications using Ph₃C⁺B(C₆F₅)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 diffraction²⁵ 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 GaCl₃ is significant.²⁸ In our laboratory, the reaction of **1** with GaCl₃ in a 1:4 ratio in toluene quantitatively resulted in the orange dicationic diarsene complex 2²⁺[GaCl₄]₂ (Scheme 1). However, the reaction of **1** with GaCl₃ in a 1:2 ratio in Et₂O

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



afforded the green monocationic diarsenic radical complex 2•⁺[GaCl₄] in 29.1% yield (Scheme 1). Similarly, AlCl₃ and InCl₃ were also shown to oxidize **1** to 2²⁺[ECl₄]₂ (E = Al, In). Our investigation suggested that the [ECl₄][–] (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 2²⁺[ECl₄]₂ (E = Al, Ga) were stable, orange 2²⁺[InCl₄]₂ gradually decomposed with the color changing to green.

The compound 2•⁺[GaCl₄] was isolated from the hexane/THF mixed solvent as dark-green crystals. X-ray structural analysis¹⁵ (Figure 1) showed that the As₂ 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-*i*Bu₃C₆H₂; R' = CH(SiMe₃)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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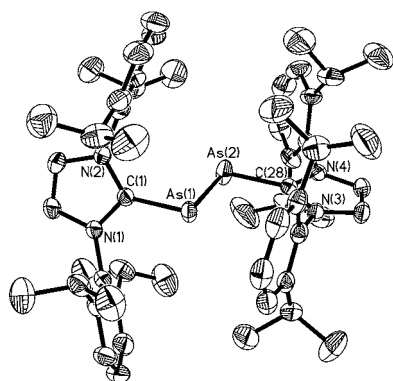


Figure 1. Molecular structure of 2^{2+} . Thermal ellipsoids represent 30% probability. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): As(1)–As(2) 2.332(3), As(1)–C(1) 1.960(4), As(2)–C(28) 1.938(5), C(1)–N(1) 1.358(5), C(1)–N(2) 1.346(5), C(28)–N(3) 1.357(5), C(28)–N(4) 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^{2+} [in which L: was replaced by :C(NHCH)₂; optimized in C₂ symmetry]¹⁶ is ~0.06 Å longer than that in 2^{*+} . The As₂-based localized molecular orbitals (LMOs) of the simplified 2H^{2+} model (Figure 2) include one As–As σ bonding orbital (a), one

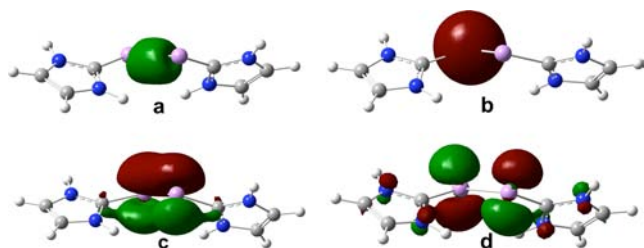


Figure 2. LMOs of 2H^{2+} with C₂ symmetry: (a) As–As σ bonding orbital; (b) one of the two As lone-pair orbitals; (c) As–As π bonding orbital; (d) As–As π* antibonding SOMO.

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) analysis³⁰ of 2H^{2+} showed that the As₂ core bears a positive charge of +0.18, which compares to the charge of +0.16 on the P₂ unit in carbene-stabilized P₂^{•+} radical (3).¹⁹ Similar to 3, the spin density distribution of 2H^{2+} indicates that the unpaired electron is largely localized at the As₂ core (0.41 at each As atom), consistent with the SOMO depicted in Figure 2.

The room-temperature EPR spectrum of 2^{2+} 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 ⁷⁵As ($I = 3/2$) 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^{2+} .

The structural metrics of the present carbene-stabilized diarsene cations are particularly significant. Both 2^{2+} (Figure 4)

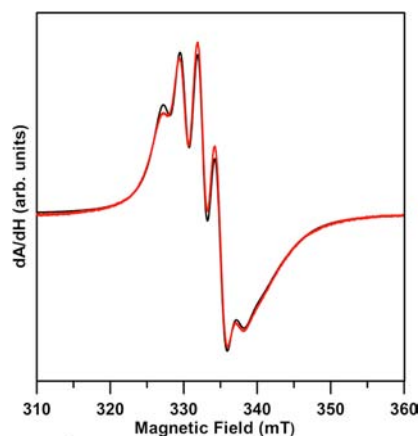


Figure 3. Room-temperature X-band EPR spectrum of 2^{2+} in fluorobenzene (red line) recorded at 9.59 GHz with a modulation amplitude of 1 mT and a microwave power of 80 mW. Also shown is the almost perfectly superposed simulated spectrum (black line), which was generated with the EasySpin software package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

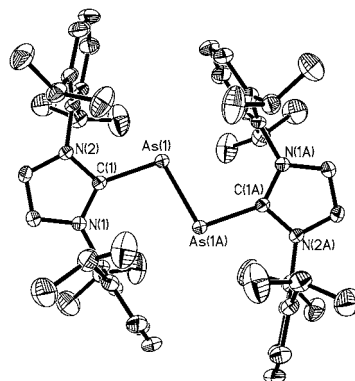


Figure 4. Molecular structure of 2^{2+} . Thermal ellipsoids represent 30% probability. H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): As(1)–As(1A) 2.2803(5), As(1)–C(1) 1.977(2), C(1)–N(1) 1.353(3), C(1)–N(2) 1.351(3); C(1)–As(1)–As(1A) 100.10(7), N(1)–C(1)–As(1)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

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°. 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^{*+} (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^{*+} (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 P₂⁷ and its cationic derivatives P₂^{•+} and P₂²⁺.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+} .

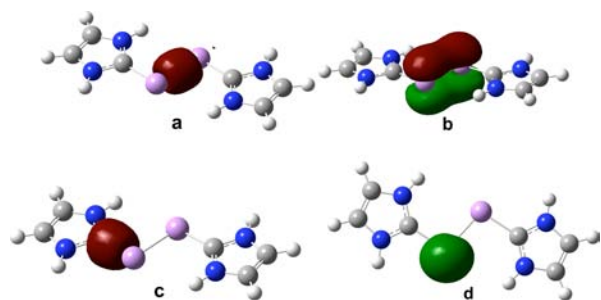


Figure 5. LMOs of 2H^{2+} with C_2 symmetry: (a) As–As σ bonding orbital; (b) As–As π bonding orbital; (c) one of the As–C σ bonding orbitals; (d) one of the As lone-pair orbitals.

The positive partial charge of +0.77 on the As_2 core in 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 2^{2+} 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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