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Syntheses, structures and theoretical calculations of stable triarylarsine radical cations†

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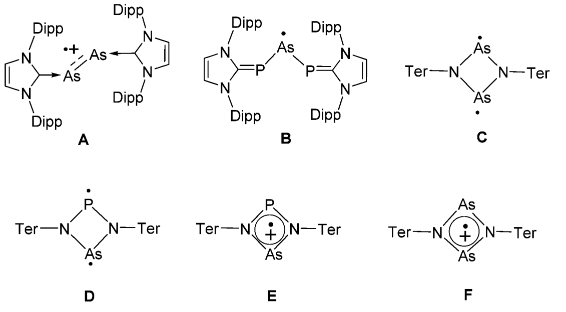
The first stable triarylarsine radical cation salts $1^{\bullet+}[BAr^F{}_4]^-$ and $2^{\bullet+}[BAr^F{}_4]^-$ were afforded by one-electron oxidation of triarylarsines $Trip_3As$ (1, Trip = 2,4,6-$iPr_3C_6H_2$) and $Dipp_3As$ (2, Dipp = 2,6-$iPr_2C_6H_3$) with $AgSbF_6$ and $NaBAr^F{}_4$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$), respectively. Their molecular and electronic structures were investigated by single-crystal X-ray diffraction, electron paramagnetic resonance (EPR) and UV-vis absorption spectroscopy, in conjunction with density functional theory (DFT) calculations. The EPR and computational results demonstrate that the spin density of $1^{\bullet+}$ and $2^{\bullet+}$ is mainly distributed on the As nuclei.

Radicals have attracted increasing attention in contemporary chemical research because of their essential roles in numerous chemical and biological processes, as well as their potential application as functional materials.[1] So far, many efforts have been made to access main group element-based radicals, and a variety of stable radicals have been synthesized and structurally characterized. However, the search for the heavier Group 15 element-based radicals remains a challenge, although several phosphorus-centered radicals have been reported.[2,3]

In comparison to its phosphorus analogue, radical chemistry based on the arsenic element is much less explored, and only a few stable arsenic-based radicals having been reported (Scheme 1). For instance, in 2013, Robinson and coworkers reported the first example of structurally characterized diarsenic radical cation **A** through one-electron oxidation of N-heterocyclic carbene (NHC) stabilized diarsenic with $GaCl_3$.[4] In 2014, Grützmacher and coworkers successfully obtained the phosphinidene stabilized neutral arsenic radical **B**.[2f] Schulz *et al.* reported the 6π-electron four-membered heterocyclic biradicaloids $[As(\mu\text{-}NTer)]_2$ (**C**)[5] and $[AsP(\mu\text{-}NTer)]_2$ (**D**),[3k] which underwent one-electron oxidation to give the radical cations **E** and **F**, respectively.[3i] Recently, we have successfully isolated the stable triarylphosphine[6] and triarylstibine[7] radical cations bearing sterically encumbered aryl groups, but the triarylarsine radical cations still escape from isolation. It is noteworthy that Sasaki *et al.*[8] and Boeré *et al.*[9] reported the synthesis and characterization of the persistent arsenic-centered radical cations $Trip_3As^{\bullet+}$ (Trip = 2,4,6-$iPr_3C_6H_2$) and $Dipp_3As^{\bullet+}$ (Dipp = 2,6-$iPr_2C_6H_3$) by EPR spectroscopy in solutions, respectively, the latter of which was also investigated by density functional theory (DFT) calculations. However, their crystal structures were not obtained. Considering the limited numbers of isolable arsenic-centered radicals, we were interested in obtaining triarylarsine radical cations. Herein, we report the one-electron oxidation of triarylarsines $Trip_3As$ (**1**) and $Dipp_3As$ (**2**) affording the first salts of the stable triarylarsine radical cations $1^{\bullet+}$ and $2^{\bullet+}$, respectively, which were characterized by single crystal X-ray crystallography, electron paramagnetic resonance (EPR) and UV-vis absorption spectroscopy, along with the DFT calculations.



Dipp = 2,6-$iPr_2C_6H_3$
Ter = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$

Scheme 1 Structurally characterized As-centered radicals.

The neutral triarylarsines **1** and **2** were synthesized according to the published procedures.[8,9] According to our (Fig. S1 in ESI†)

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and previously reported[8,9] electrochemical studies, the radical cations of **1** and **2** should be stable enough to be isolated. As reported, the chemical oxidations of **1** and **2** with $AgClO_4$[8] and $AgPF_6$,[9] respectively, afforded their radical cations, but the products could not be crystallized. Moreover, we found that the $[BAr^F{}_4]^-$ anion[10] was a suitable counterion in the isolation of the triarylstibine radical cations.[7] Therefore, we performed the one-electron chemical oxidation of **1** and **2** with a stoichiometric amount of $AgSbF_6$ and $NaBAr^F{}_4$ in CH_2Cl_2 at room temperature, and fortunately the radical salts of **1**$^{\bullet+}\cdot[BAr^F{}_4]^-$ and **2**$^{\bullet+}\cdot[BAr^F{}_4]^-$ were isolated in 78% and 80% yields as purple and red crystals, respectively (Scheme 2). The salts feature a high thermal stability under an inert atmosphere.

The EPR spectra of **1**$^{\bullet+}\cdot[BAr^F{}_4]^-$ and **2**$^{\bullet+}\cdot[BAr^F{}_4]^-$ were measured in CH_2Cl_2 solutions at 298 K and 86 K, and they were simulated using the SimFonia software package (Fig. S2, ESI†). The spectra are similar to the previously reported ones.[8,9] The obtained hyperfine coupling parameters for **1**$^{\bullet+}\cdot[BAr^F{}_4]^-$ and **2**$^{\bullet+}\cdot[BAr^F{}_4]^-$ are almost identical. The isotropic coupling constant is $a(^{75}As)$ = 264 G, while the anisotropic hyperfine coupling tensors are as follows: $g_\parallel$ = 2.002, $a_\parallel$ = 48.3 mT; $g_\perp$ = 2.020, $a_\perp$ = 19.5 mT. These parameters are similar to those reported previously.[9] The distribution of the electron in 4s and 4p orbitals of the As atom can be estimated from the obtained hyperfine coupling constants.[11] For both radical cations **1**$^{\bullet+}$ and **2**$^{\bullet+}$, the unpaired electron occupation numbers are 0.05 e and 0.81 e for 4s(As) and 4p(As) orbitals, respectively, which agree well with our calculated results (*vide infra*) and the one reported for the radical cation $Dipp_3As^{+\bullet}$.[9] Therefore, from the above EPR spectra and the estimated distribution of the spin density, it can be deduced that the unpaired electron is mainly localized on the arsenic atoms in both radical salts.

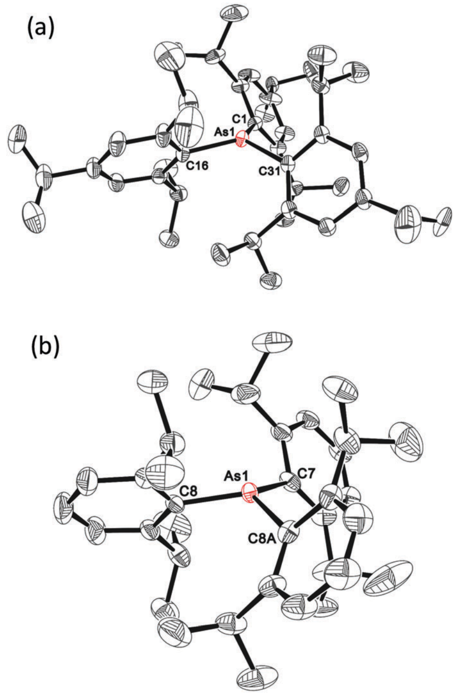
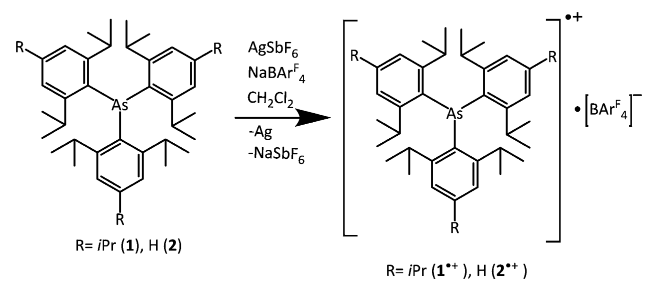


Fig. 1 The thermal ellipsoid drawings of **1**$^{\bullet+}$ (a) and **2**$^{\bullet+}$ (b) at 30% probability. Hydrogen atoms and disorders (iPr groups and As atoms) were omitted for the sake of clarity. Selected bond lengths (Å) and angles (°): **1**$^{\bullet+}$: As1–C1 1.915(3), As1–C31 1.915(3), As1–C16 1.920(3); C1–As1–C31 117.93(11), C1–As1–C16 117.09(12), C31–As1–C16 119.33(12). **2**$^{\bullet+}$: As1–C7 1.935(3), As1–C8 1.876(3), As1–C8A 1.961(3); C8–As1–C7 120.34(9), C8–As1–C8A 115.55(15), C7–As1–C8A 116.10(8).



Scheme 2 Synthesis of the triarylarsine radical cation salts.

Crystals of **1**$^{\bullet+}[BAr^F{}_4]^-$ and **2**$^{\bullet+}[BAr^F{}_4]^-$ suitable for X-ray diffraction analysis were grown from the CH_2Cl_2 solutions at −30 °C. **1**$^{\bullet+}[BAr^F{}_4]^-$ crystallizes in the triclinic space group $P\bar{1}$, while **2**$^{\bullet+}[BAr^F{}_4]^-$ belongs to the monoclinic space group $C2/c$. The structures of **1**$^{\bullet+}$ and **2**$^{\bullet+}$ are shown in Fig. 1 and the crystal packing diagrams are depicted in Fig. S3 and S4 (ESI†). They feature a similar structural configuration although only **2**$^{\bullet+}$ possesses C_{2v} symmetry, and the three aryl groups exhibit a propeller-like arrangement. The average As–C bond lengths (1.917(3) Å for **1**$^{\bullet+}$; 1.924(3) Å for **2**$^{\bullet+}$) are slightly shortened when compared to those in the neutral precursors (1.987(3) Å for **1**;[8] 1.9904(10) Å for **2**[9]). The sum of angles around the As center in **2**$^{\bullet+}$ (351.99°) is slightly smaller than that in **1**$^{\bullet+}$ (354.35°),[12] but is close to that predicted from the Coulson equation (351°).[9] They are much larger than those in the neutral compounds **1** (327.5°)[8] and **2** (329.17°),[9] suggesting a smaller degree of pyramidalization of the As centers in radical cations in comparison to the neutral compounds, which is in accordance with the reported prediction.[9] This is likely attributed to the loss of one electron from the lone electron pair located orbital of the As nucleus. The similar tendency of metric parameter changing has also been observed in our previously reported triarylphosphine[6] and triarylstibine[7] radical cations. Moreover, the sum of angles around the As center in **1**$^{\bullet+}$ (354.35°) is between those of $Trip_3P^{\bullet+}$ (359.99°)[6] and $Trip_3Sb^{\bullet+}$ (348.54°),[7] which is probably due to the medium C–As bond length when compared to those of C–P and C–Sb bonds.

To rationalize the experimental results, we carried out theoretical calculations for the neutral compounds **1** and **2** and the radical cations **1**$^{\bullet+}$ and **2**$^{\bullet+}$ using the Gaussian 09 program.[13] Complete geometry optimizations were performed at the (U)CAM-B3LYP/6-31G(d) level, and the obtained stationary points were characterized by frequency calculations. The optimized structures are in good agreement with those of the experimental data obtained by single crystal X-ray diffraction. Consistent with the experimental data, in comparison to the neutral precursors, the As–C distances in the radical cations become shorter, while the sum of the C–As–C bond angles becomes larger.

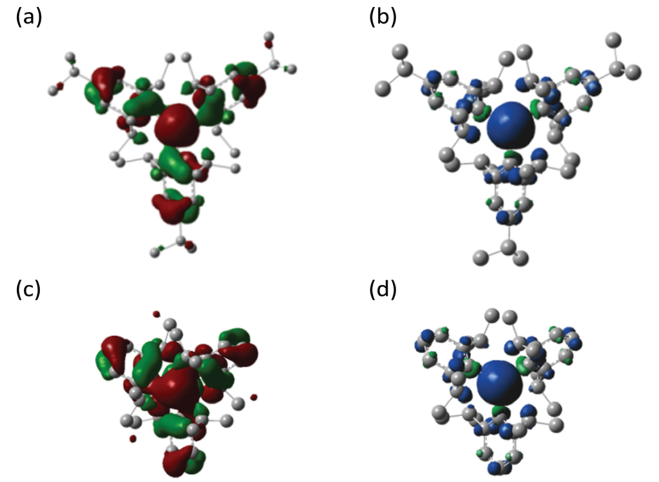


Fig. 2 Singly occupied molecular orbital (SOMO) of $1^{\bullet +}$ (a) and $2^{\bullet +}$ (c); and Mulliken spin density distribution of $1^{\bullet +}$ (b) and $2^{\bullet +}$ (d) calculated at the UCAM-B3LYP/6-31G(d) level.

Interestingly, the difference in the average C–As–C bond angle (9.61°) between $\mathbf{2}^{\bullet +}$ and **2** is larger than that of $\mathbf{1}^{\bullet +}$ and **1** (9.19°), which is most probably attributed to the higher spin density at the As atom of $\mathbf{2}^{\bullet +}$ (0.86) in comparison with that of $\mathbf{1}^{\bullet +}$ (0.84), as shown in Table S2 in the ESI† (Fig. 2). The calculated spin density is in accordance with that of the previously reported radical cation $Dipp_3As^{+\bullet}$ (0.787) at the UB3LYP/6-31G(d,p) level of theory.[9] Moreover, the spin density at the pnictogen centers of the isolable radical cations $Ar_3E^{\bullet +}$ (E = P,[6] As, Sb[7]) is similar. What is more, from Table S2 and SOMOs, it can be found that the total spin density at the arsine atom is mainly distributed on the 4p(As) orbital.

The UV-vis absorption spectra of the studied neutral compounds and the radical cation salts measured in CH_2Cl_2 solutions are shown in Fig. 3. The radicals $\mathbf{1}^{\bullet +}[BAr^F_4]^-$ and $\mathbf{2}^{\bullet +}[BAr^F_4]^-$ exhibit strong characteristic absorptions at 518 and 486 nm, respectively, and these absorption bands are red-shifted in comparison to that of the corresponding neutral compounds. Besides, the UV-vis absorption spectrum of $\mathbf{2}^{\bullet +}[BAr^F_4]^-$ is slightly blue-shifted than that of $\mathbf{1}^{\bullet +}[BAr^F_4]^-$, which might be caused by the decreased electron-donating ability of the substituents. To further figure out the nature of the absorption spectra, the calculations on the UV-vis absorption spectra were performed by the time-dependent (TD) DFT method at the UPBE1PBE/6-31G(d) level, which indicates that the maximum absorption peaks of the studied compounds are in reasonable agreement with the experimental values. The long wavelength absorptions are mainly attributed to the HOMO−3 (β) → LUMO (β) and HOMO−4 (β) → LUMO (β) electronic transitions (the energy levels of HOMO−3 (β) and HOMO−4 (β) are a set of quasi-degenerate orbitals for both $\mathbf{1}^{\bullet +}$ and $\mathbf{2}^{\bullet +}$, respectively), which are the distinct intramolecular charge transfer from the peripheral aromatic substituents to the central As centers (Fig. S5 in the ESI†).

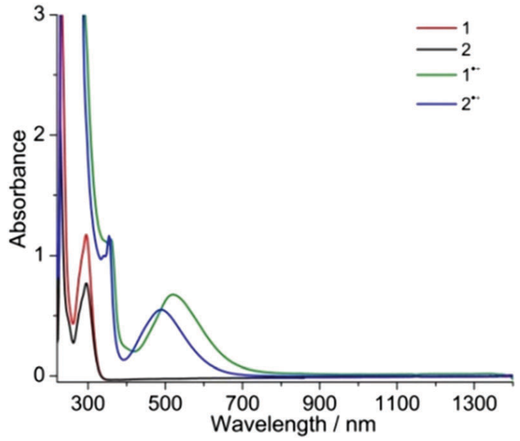


Fig. 3 The UV-vis absorption spectra of **1**, **2**, $\mathbf{1}^{\bullet +}[BAr^F_4]^-$ and $\mathbf{2}^{\bullet +}[BAr^F_4]^-$ in CH_2Cl_2 solutions at room temperature.

In summary, we have presented the structural characterization of the first stable triarylarsine radical salts $\mathbf{1}^{\bullet +}[BAr^F_4]^-$ and $\mathbf{2}^{\bullet +}[BAr^F_4]^-$. The two radical salts are thermally stable under anaerobic and anhydrous conditions at ambient temperatures, attributed to the steric protection from the aromatic ligands. The EPR spectroscopy and DFT calculations reveal that most of the spin density resides at the As atoms. The reactivity and property studies of these radical cations are underway in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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