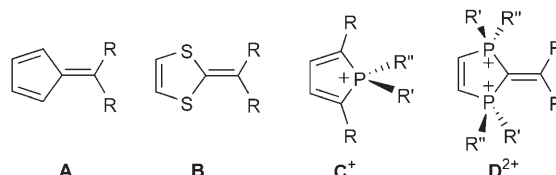


because these species often act as reaction intermediates and because their structure can determine the result of many chemical processes.^[3] Considerable efforts have been devoted to gaining a better knowledge of their electronic structure; unfortunately their high reactivity make their identification difficult, and reports on their crystal structures remain sparse.^[4] Renewed interest in the behavior of organic ion radicals has recently appeared owing to the practical applications predicted for some of these compounds in materials science and because of their potential use as electronic devices, organic magnets, and organic conductors.^[5,6] Fulvene derivatives (**A**, Scheme 1) play an important role in this field;



Scheme 1.

for example, dithiafulvene (**B**) constitutes one of the elementary units of conducting, semiconducting, and superconducting molecular solids. In this context, a crucial property of tetrathiafulvalene lies in its capacity to easily release one electron to give, reversibly, a rather persistent radical cation.^[7] The discovery of novel fulvene-centered systems that are able to reversibly stabilize a radical cation is of considerable interest. The results herein contribute to this project, and as will be seen further, phosphorus chemistry can open new and very attractive perspectives in this area.

On the basis of early reports on the chemistry of 1,4-diphosphoniacyclohexa-2,5-dienes,^[8] as well as our recent EPR study on the reduction processes of monophosphonium cations **C**⁺,^[9] we postulated that pentavalent phosphorus atoms could behave as strong electron acceptors and thus allow the synthesis and stabilization of persistent radical cations through reduction processes. We validate this hypothesis herein in the case of a diphosphafulvenium dication **D**²⁺ whose reduction leads to a stable radical cation. To the best of our knowledge, diphosphafulvenium cations have never been reported so far.^[10]

The *trans*-tetraphenyldiphosphafulvene derivative **1**, whose synthesis was recently reported, was chosen as the starting precursor.^[11] Reaction of **1** with excess methyl triflate (MeOTf) at 25 °C cleanly afforded dication **2**²⁺, which was isolated as a very stable white solid. The structure of **2**²⁺ was confirmed by NMR data and elemental analyses. Unfortunately, despite many attempts, **2**²⁺ proved to be reluctant towards crystallization, thus precluding the recording of an X-ray crystal structure. As expected, dication **2**²⁺ can be easily reduced, as indicated by cyclic voltammetry (CH₃CN, room temperature), which revealed four waves at −0.54 V (reversible), −1.10 V (irreversible), −1.37 V (partially reversible), and −1.72 V (irreversible) versus SCE. Importantly, the first reduction process was found to be reversible even at low scan rates (50 mV s^{−1}), thereby suggesting that it would be possible to isolate a persistent radical cation. Reduction of **2**²⁺ was

Persistent Radical Cations

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Formation and Structure of a Stable Monoradical Cation by Reduction of a Diphosphafulvenium Salt**

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The attention paid by physical chemists to organic radical ions has never ceased to increase over the last 20 years,^[1,2] mainly

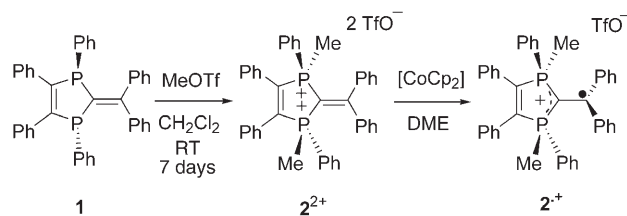
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carried out at low temperature by adding 1,2-dimethoxyethane (DME) to a solid mixture of $\mathbf{2}^{2+}$ and $[\text{CoCp}_2]$. The solution immediately turned deep purple, and after warming to 25°C, *n*-hexane was added to crystallize the radical monocation $\mathbf{2}^+$, which was then easily separated from cobaltocenium triflate (Scheme 2).



Scheme 2. Synthesis of compounds $\mathbf{2}^{2+}(\text{TfO}^-)_2$ and $\mathbf{2}^+\text{TfO}^-$.

The structure of $\mathbf{2}^+$ was confirmed by an X-ray crystallographic study.^[12] A view of one molecule of $\mathbf{2}^+$ is presented in Figure 1. The most significant piece of data concerns the two

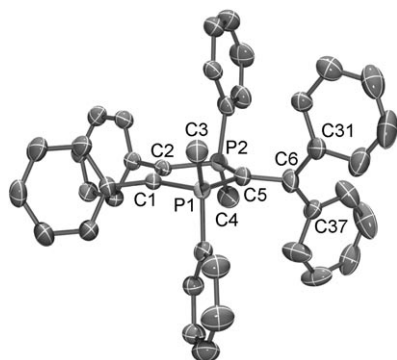


Figure 1. ORTEP plot of $\mathbf{2}^+$ (ellipsoids set at 50% probability). The cocrystallized triflate anion is omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C5 1.713(3), P2–C5 1.718(3), C5–C6 1.473(4); P2–C5–C6 123.2(2), P1–C5–P2 109.6(2), P1–C5–C6 127.0(3), C5–C6–C31 121.2(2), C5–C6–C37 118.4(3), C31–C6–C37 119.2(3).

P1–C5 (1.713(3) Å) and P2–C5 (1.718(3) Å) bond lengths, which are very short compared to the P1–C1 and P2–C2 bond lengths (1.809(3) Å). On the other hand, the C5–C6 bond (1.473(4) Å) is also very long and has clearly lost its double-bond character. The geometry at C6 is planar ($\Sigma\text{angles} = 358.8^\circ$). Furthermore, the CPh_2 group is twisted from the plane that is defined by the ring ($\zeta(\text{P1–C5–C6–C31}) = -70.5^\circ$) and participates in stabilizing the extra electron, as attested to by the short C6–C31 and C6–C37 bond lengths (av. 1.46 Å).^[13] All these data suggest that reduction has taken place at the P1–P2–C5–C6 segment. This observation is confirmed by the fact that the C1–C2 bond length remains close to what is expected for a classical carbon–carbon double bond (1.34 Å).

EPR experiments and DFT calculations were carried out to determine the precise electronic structure of $\mathbf{2}^+$. Electrolysis in the EPR cavity at a potential corresponding to the first reduction wave leads to the spectrum shown in Figure 2a.

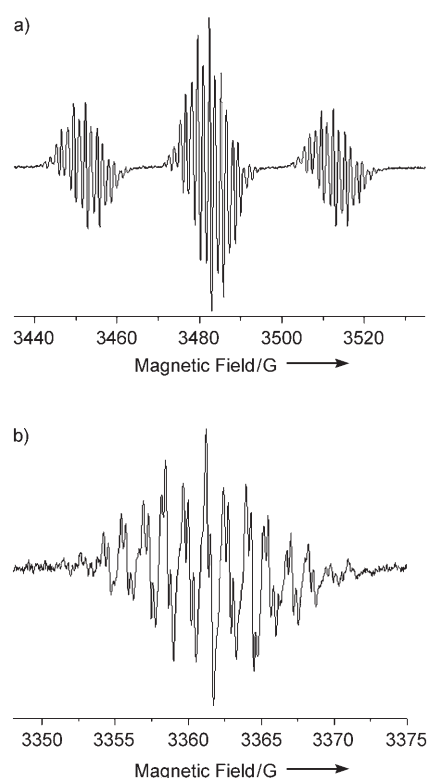


Figure 2. a) Liquid-solution EPR spectrum obtained at 300 K after reduction of a solution of $\mathbf{2}^{2+}(\text{TfO}^-)_2$ in THF. b) Expansion of the central part of the spectrum.

This spectrum, measured at 300 K, is characterized by a *g* value equal to 2.0029 and by a hyperfine interaction of about 30 G with two equivalent ^{31}P nuclei. Additional structure resulting from coupling with several protons of two phenyl rings is clearly visible (Figure 2b). It is interesting to note that these couplings are quite similar to those measured by ENDOR on $\text{Ph}_3\text{C}^\bullet$.^[14] A simulation was performed by using the following coupling constants (expressed in Gauss): ^{31}P 30.1, H_a 3.00, H_b 2.83, H_c 2.82, H_d 1.35, H_e 1.11. Note that the spectrum of $\mathbf{2}^+$, which was also recorded at 100 K, clearly shows that the *g* and ^{31}P coupling tensors do not exhibit any anisotropy.^[15] The reduced species is rather persistent, and its spectrum could be observed for several hours without voltage under a nitrogen atmosphere. The same spectrum was obtained by reducing a solution of $\mathbf{2}^+$ in THF with one equivalent of $\text{C}_{10}\text{H}_8\text{Na}$.

To get further insights into the electronic structure of $\mathbf{2}^+$, DFT calculations were carried out on the actual molecules $\mathbf{2}^{2+}$ and $\mathbf{2}^+$ at the quantum level.^[15] A good agreement was found between the experimental and theoretical structures of $\mathbf{2}^+$. Only the dihedral angle of the CPh_2 group differs.^[16] An examination of the molecular orbitals of the two species furnishes important information. In $\mathbf{2}^{2+}$ the LUMO is antibonding between C5 and C6 and bonding between the phosphorus atoms and C5 (Figure 3), thus explaining why the P–C5 bonds are shortened^[17] upon reduction and why the C5–C6 bond is significantly elongated.^[18] Upon reduction, one electron is added into the LUMO of $\mathbf{2}^{2+}$ as shown in the SOMO of $\mathbf{2}^+$ (Figure 3). Calculations of Wiberg bond indices

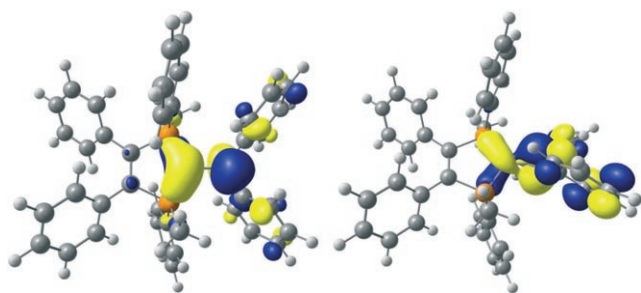
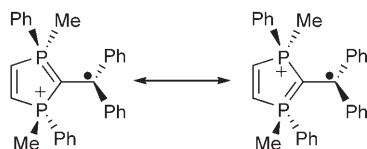


Figure 3. LUMO of 2^{2+} (left) and SOMO of 2^{+} (right) as given by DFT calculations (P orange, C dark gray, H light gray).

confirm that the order of the C5–C6 bond has been reduced on going from 2^{2+} to 2^{+} (1.58 to 1.11).

Isotropic and anisotropic hyperfine interactions with ^1H ($A_{\text{iso}} = -2.63$ and -2.84 G for H_{ortho} , 1.16 and 1.43 G for H_{meta} , and -3.05 G for H_{para}) and ^{31}P nuclei ($A_{\text{iso}} = 32.9$ and 33.2 G; $\tau_{\text{aniso}} = -4$, -3 , and $+7$) were obtained from the DFT calculations and agree with the experimental values. In accord with frozen-solution spectra, the anisotropy of the ^{31}P coupling was also found to be rather small. All these data suggest that in diphosphafulvenium systems the two pentavalent phosphorus atoms behave as strong acceptors and prevent delocalization over the ring. Such systems are therefore different from their sulfur or carbon counterparts. The excess of electron density gained upon reduction mainly resides on the exocyclic double bond and is strongly stabilized by negative hyperconjugation with the two pentavalent phosphorus atoms. Therefore, two ylidic forms can be proposed to rationalize the electronic structure of 2^{+} (Scheme 3).



Scheme 3. Ylidic forms involved in 2^{+} .

From this study we can conclude that 1,1-bis(phosphonium) olefins can act as suitable precursors for the synthesis of persistent monoradical cations upon reduction at low potential. Further studies aimed at expanding this simple idea to the elaboration of highly conjugated paramagnetic structures are currently underway in our laboratories.

Experimental Section

All experiments were carried out in a dry argon or nitrogen atmosphere by using distilled and degassed solvents. For the synthesis of $2^{2+}(\text{TfO}^-)_2$, see the Supporting Information.

2^{+}TfO^- : DME (25 mL) was condensed onto a mixture of $2^{2+}(\text{TfO}^-)_2$ (0.24 g, 0.27 mmol) and $[\text{CoCp}_2]$ (51 mg, 0.27 mmol) at -78°C . The solution was warmed to room temperature and stirred for two hours. A mixture of hexanes was then condensed onto the crude mixture at -78°C , which resulted in the formation of deep purple crystals of 2^{+}TfO^- within 12 h. The resulting crystals were isolated

and washed with diethyl ether (3×5 mL) to afford 2^{+}TfO^- in 93% yield (0.19 g, 0.25 mmol). No NMR spectrum is available for this compound owing to its paramagnetic nature.

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free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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