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EPR and DFT studies of the one-electron reduction product of phospholium cations

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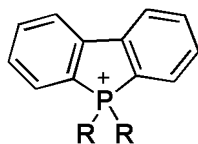
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Cyclic voltammetry and EPR spectroscopy show that cationic phospholium groups are good electron acceptors whose reduction leads to a neutral radical where the unpaired electron is mainly delocalized on the carbon atoms of the five-membered ring. DFT calculations together with the crystal structure of phospholiums indicate that the electron addition causes a drastic diminution of the exocyclic CPC angle. The SOMO of reduced phospholium is compared to the SOMO of the phosphole radical anion.

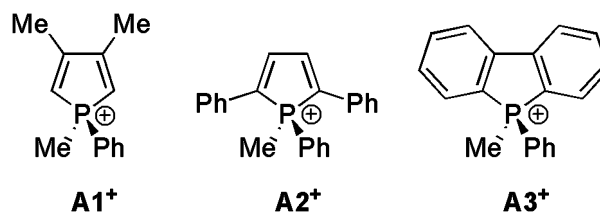
1. Introduction

Intense efforts are currently underway to find new chemical groups able to accept an additional electron and to transmit it to another part of the molecular assembly. This implies that this group must possess at least three properties: (1) has an accessible reduction potential; (2) has delocalized frontier orbitals; (3) is reasonably stable in both states. Unsaturated systems with a low coordinated phosphorus atom possess some of these properties.¹ Their low energy π^* orbital can easily accommodate an extra electron and can conjugate with neighbouring multiple bonds. However, the resulting radical anion often tends to capture a proton (*e.g.* from solvent) and to irreversibly lead to secondary reaction products.² Another possibility is to start from a molecule containing a positively charged tetracoordinated phosphorus atom. Such systems are robust and are expected to easily accept an extra electron to give a neutral reduction product: a phosphoranyl radical. This radical, however, presents two disadvantages: (1) its stability is still rather modest; (2) it strongly localizes the unpaired electron in a non-bonding equatorial orbital of the phosphorus atom which adopts a trigonal bipyramid coordination.³ In an attempt to find a way to overcome these difficulties we have investigated the redox behaviour of phospholiums, prompted by early results obtained by Buck *et al.* in 1970 with 2,2'-biphenylenediphenyl phosphoniums (I^+).⁴



These authors reported that the reduction of 2,2'-biphenylenediphenyl phosphoniums led to radicals that were localized on the benzene rings of the biphenyl ligand; this effect was attributed to the high electron affinity of the biphenylene system. The role of this ligand seemed to be confirmed by the failure to detect any EPR signal with a phospholium containing no benzo groups.⁵ It is possible, however, that this spin delocalisation results rather from the incorporation of the positively charged phosphorus atom inside an unsaturated five-membered ring whose constraints prevent the phosphoranyl radical from adopting its trigonal bipyramid structure (Scheme 1). If this is the case, most phospholium systems should, after reduction, delocalize their unpaired electron in the butadienyl moiety, giving rise to a stabilized radical as suggested by several mesomeric structures.

In the present study, in order to check the pertinence of this hypothesis, we first investigate the one-electron reduction of $A1^+$ and $A2^+$ —two phospholiums whose stability of the reduction compounds cannot result from the presence of the biphenylene ligand.

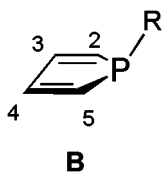


Geometrical parameters of these molecules, obtained by solving their crystal structures, have been used to verify the relevance of the DFT predictions. The objective of this EPR/DFT study is three-fold: (1) determination of the electronic configuration of neutral radicals derived from phospholium systems; (2) evaluation of the structural changes provoked by this one-electron reduction process; (3) assessment of the role played by the aromatic substituents linked to the carbon atoms of the phospholium ring. Attention is also paid to the differences in the reduction behaviour

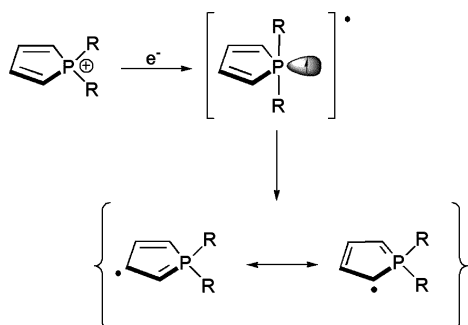
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of phospholes (**B**) and phospholiums.⁶



In particular, the participation of the phosphorus orbitals to the SOMO of the neutral radical formed from phospholium is compared to the contribution of these orbitals to the SOMO of the corresponding phosphole radical anion.



Scheme 1

2. Results

2.1. Crystal structures

Crystal structures have been determined for **A1**⁺ and **A2**⁺. For the sake of comparison with a system containing the biphenylene ligand, the crystal structure of **A3**⁺ has also been measured. Views of these structures are shown in Fig. 1 together with some geometrical parameters.

2.2. Electrochemistry

The voltammogram of **A1**⁺ exhibits a reversible reduction wave at -1397 mV, while **A2**⁺ undergoes two reversible reductions at -745 and -1420 mV vs. SCE (Fig. 2). For **A3**⁺ a reversible reduction wave is observed at -1500 mV.

Reductions of phospholes are more difficult, a reversible wave is observed at -1835 mV for **B1**, at -1915 mV for **B2** and at -2250 mV for **B3**. For this latter compound two small irreversible waves—probably due to impurities—were also detected at -1250 and -1750 mV.

2.3. EPR experiments

Electrochemical reduction of a solution of **A1**⁺ in CH_2Cl_2 at room temperature or at 200 K led to a well-resolved EPR spectrum centred at $g = 2.0037$ (Fig. 3). The hyperfine structure results from a coupling of 5.5 G with eight equivalent protons and from a coupling of 21.0 G attributed to ³¹P. No colour change was observed upon reduction.

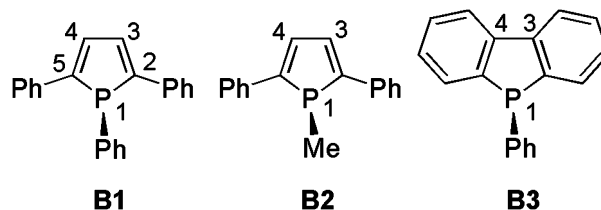
Electrochemical reduction of a solution of **A2**⁺ in THF at room temperature or at 200 K led to an EPR spectrum ($g = 2.0036$) whose hyperfine structure is due to a coupling of 4.6 G with two equivalent protons and to a coupling of 22.7 G with a

³¹P nucleus. During the reduction process, the colour of the solution turns from orange to red.

A colorless solution of **A3**⁺ in THF became yellow during electrochemical reduction. Although no EPR signal was observed at 300 K, a doublet ($A_{\text{iso}}(^{31}\text{P}) = 13.9$ G) of triplets ($A_{\text{iso}}(^1\text{H}) = 3.6$ G), centred at $g = 2.0038$, was clearly detected at 200 K. The line shape of the triplet reveals the presence of unresolved additional couplings. This spectrum is consistent with the ³¹P hyperfine splitting reported in ref. 4 after reaction of **A3**⁺ with potassium, although, the triplet remained unresolved in this early work.

With the three phospholiums **A1**⁺, **A2**⁺, **A3**⁺ we could record good quality spectra by reduction with Na naphthalenide or by contact of the solution with a potassium mirror at 200 K. The resulting spectra were identical to those produced by electrochemical reduction. These spectra could also be detected at 300 K, but their intensity rapidly decreased at this temperature. The EPR parameters measured for the three phospholiums are reported in Table 1.

In order to assess to what extent the electron acceptor properties of these phospholiums differ from those of phospholes, measurements and calculations were also performed on the three compounds **B1**, **B2**, and **B3** although their EPR spectra have already been reported after reduction with potassium.^{6,7}



Electrochemical reduction of **B1** and **B2** lead to parameters (Table 1) which are similar to those reported in ref. 6. For **B3**, the earlier study, carried out by reduction with potassium, mentioned couplings of 2.4 G with two equivalent protons and a ³¹P coupling of 8.5 G.⁷ As shown below, these couplings do not agree with the DFT predictions for **B3**⁻. We could record a spectrum similar to the one reported in ref. 7 by adjusting the potential just above the small irreversible reduction wave ($E = -1750$ mV) (*vide supra*). However, by fixing the potential just above the intense reversible reduction wave (-2250 V), the spectrum described in Table 1, characterized by a larger ³¹P splitting, was immediately observed.

In contrast with phospholiums, we did not obtain a clear EPR response by electrochemical or chemical reduction of phospholes at room temperature; at 200 K, however, spectra were readily observed. Electrochemical reduction caused a change in the colour of the solutions, which turned from yellow to violet.

2.4. DFT calculations

2.4.1. Phospholiums. Geometry optimizations have first been carried out on the phospholium model **1**⁺, which bears no substituent, and on the corresponding one-electron

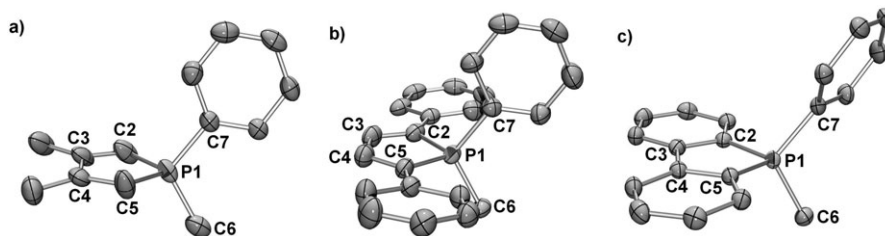
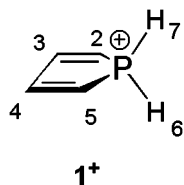


Fig. 1 View of one molecule of $\mathbf{A1}^+$ (a), $\mathbf{A2}^+$ (b) and $\mathbf{A3}^+$ (c) (ellipsoids set as 50% probability). The hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: a) for $\mathbf{A1}^+$: P1–C2 1.775(4), C2–C3 1.355(6), C3–C4 1.487(6), C4–C5 1.380(6), C5–P1 1.782(4), P1–C6 1.787(5), P1–C7 1.791(3), C2–P1–C5 94.5(2), C6–P1–C7 110.1(2); b) for $\mathbf{A2}^+$: P1–C2 1.800(4), C2–C3 1.348(6), C3–C4 1.462(6), C4–C5 1.348(5), C5–P1 1.798(4), P1–C6 1.775(3), P1–C7 1.786(4), C2–P1–C5 95.5(2), C6–P1–C7 112.5(2); c) for $\mathbf{A3}^+$: P1–C2 1.789(2), C2–C3 1.398(3), C3–C4 1.483(3), C4–C5 1.404(3), C5–P1 1.795(2), P1–C6 1.785(2), P1–C7 1.788(2), C2–P1–C5 94.0(1), C6–P1–C7 109.2(1).

reduction product $\mathbf{1}^*$.



For both systems the ring is planar. Addition of an electron hardly modifies the intracyclic C2PC5 angle, but affects the value of the exocyclic H6PH7 angle that decreases from 106.1 to 96.6°.

For the three phospholiums— $\mathbf{A1}^+$, $\mathbf{A2}^+$ and $\mathbf{A3}^+$ —the optimized geometries and the crystal structures present the same features (Table 2): the five-membered rings are practically planar, the intracyclic bond angle C2PC5, close to 95°, are quite smaller than the exocyclic bond angle C6PC7 close to 110°. Two additional angles are useful to describe the geometries of these systems (Fig. 4): (1) the ζ_1 angle formed by the normal \mathbf{n}_1 to the C2PC5 plane and the normal \mathbf{n}_2 to the $C_{Me}PC7$ plane, (2) the ζ_2 angle formed by the phenyl ring linked to the phosphorus atom and the normal \mathbf{n}_2 to the $C_{Me}PC7$ plane.

For the four optimized structures ($\mathbf{1}^+$, $\mathbf{A(1-3)}^+$), the ζ_1 angle which characterizes the coordination geometry of the phosphorus atom, is close to 90° and the $C_{Me}PC7$ plane practically lies in the bisector of the C2PC5 angle.⁹ The values of ζ_2 , close to 0° for the four optimized structures, indicate that the phenyl

ring bound to the phosphorus atom also lies in the bisector of the C2PC5 angle. Probably due to strong matrix effects, this property is not observed in the crystal structure of $\mathbf{A3}^+$ ($\zeta_2 = 52^\circ$). One-electron reduction affects neither the value of the C2PC5 angle nor the planarity of the phosphorus-containing ring. Moreover, for the four neutral radicals, the ζ_1 angles remain close to 90°, as for the cationic precursor. However, appreciable modifications are observed for the ζ_2 angle and the $C_{Me}PC7$ angle. As indicated by the Mulliken charges analysis, in the reduced phospholiums the partial positive charge borne by the phosphorus atom is balanced by a negative charge delocalized on the “butadienyl” system.

The ^{31}P and ^1H isotropic coupling constants predicted by DFT for the three radicals $\mathbf{A1}^*$, $\mathbf{A2}^*$, $\mathbf{A3}^*$ are shown in Table 3. They lead to an excellent simulation of the EPR spectra.

2.4.2. Phospholes. As shown by the optimized parameters reported in Table 4—for $\mathbf{B1}$, $\mathbf{B2}$, $\mathbf{B3}$ —the phosphole ring slightly deviates from planarity ($C4C3C2P \approx 6^\circ$) and the phosphorus coordination is pyramidal (sum of the phosphorus bond angles smaller than 360°). For $\mathbf{B1}$ and $\mathbf{B3}$ the phenyl ring linked to the phosphorus atom lies in the bisector of the C2PC5 angle. Although the C2PC5 angle is not affected by the addition of an electron, the pyramidalicity of the phosphorus is more pronounced in the radical anion than in the neutral species. Moreover, the reduction is accompanied by an increase in the C2–C3 (and C4–C5) bond lengths and a decrease in the C3–C4 bond length.

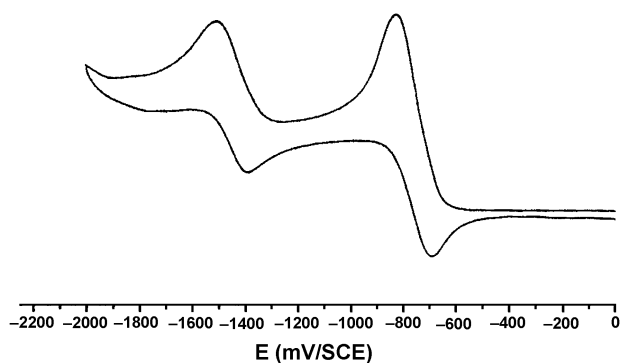


Fig. 2 Voltammogram obtained at room temperature with a solution of $\mathbf{A2}^+$ in THF.

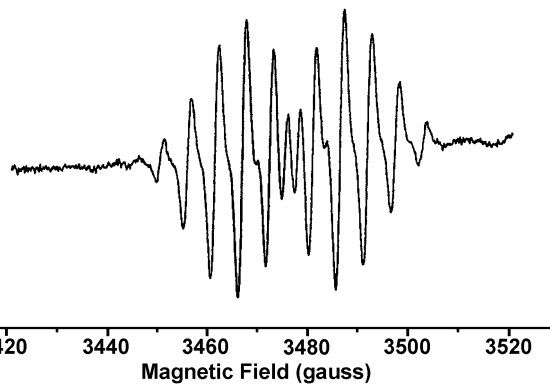


Fig. 3 EPR spectrum obtained by electrochemical reduction of a solution of $\mathbf{A1}^+$ in CH_2Cl_2 , at 200 K.

Table 1 Experimental EPR parameters⁸

Precursor	<i>g</i> -value	<i>A</i> _{iso} (³¹ P) ^a	<i>A</i> _{iso} (¹ H) ^b
A1 ⁺	2.0037	21.0	5.5 (×8)
A2 ⁺	2.0036	22.7	4.6 (×2), 1.5 (×6)
A3 ⁺	2.0038	13.9	3.6 (×2), 1.20 (×2), 0.90 (×2)
B1	2.0027	28.5	2.8 (×2), 2.3 (×2), 2.0 (×2), 1.8 (×2), 0.8 (×2)
B2	2.0024	18.0	2.0 (×2), 1.8 (×2), 1.7 (×2), 0.5 (×2)
B3	2.0025	19.6	4.5 (×2), 2.0 (×2), 1.4 (×2)

^aSome of the ¹H couplings were not resolved but were used to fit the line shape.^a Values in Gauss; only the absolute values of the coupling constants are known. ^b Values in Gauss; in parentheses: number of equivalent protons.

Table 2 Geometrical parameters^a for phospholiums and corresponding radicals

		C3–C4	C2–C3	C2–P	C2PC5	C6PC7	C4C3C2P	ξ ₁ ^b	ξ ₂ ^c
1 ⁺		1.487	1.347	1.796	95.7	106.1	0.0	90.0	
1 [•]		1.421	1.398	1.751	96.6	96.6	0.0	90.0	
A1 ⁺	Crystal	1.487	1.367 ^d	1.778 ^e	94.5	110.1	3.8	92.3	1.7
	DFT	1.514	1.351	1.796	93.6	110.8	0.2	90.1	1.8
A1 [•]	DFT	1.435	1.400	1.755	95.0	102.5	1.1	92.2	41.7
A2 ⁺	Crystal	1.462	1.348 ^d	1.800 ^e	95.5	112.5	0.7	92.2	6.8
	DFT	1.461	1.362	1.825	95.6	111.4	0.2	90.1	0.1
A2 [•]	DFT	1.407	1.408	1.785	96.5	105.6	0.3	92.5	15.0
A3 ⁺	Crystal	1.483	1.401 ^d	1.792 ^e	94.0	109.2	3.0	91.6	52.4
	DFT	1.481	1.414	1.802	93.7	110.3	1.2	90.0	0.0
A3 [•]	DFT	1.440	1.446	1.763	94.3	103.5	0.8	90.0	0.2

^a Bond lengths in Å, angles in degrees. ^b ξ₁: angle between the normal to the C2PC5 plane and the normal to the C6PC7 plane. ^c ξ₂: angle between the normal to the C6PC7 plane and the normal to the plane of the phenyl ring bound to the phosphorus atom. ^d Average value (C2–C3), (C4–C5). ^e Average value (C2–P), (C5–P).

The calculated isotropic coupling constants for the three phosphole anions (**B1**^{•−}, **B2**^{•−}, **B3**^{•−}) are reported in Table 3; they are in good accordance with the experimental values. They also indicate that **B3**^{•−} is indeed sufficiently stable to be detected by EPR, and that its spectrum is different from the spectrum previously observed after reduction with alkali metal.⁷

3. Discussion

Although the data given in Table 1 and 3 indicate that the absolute values of the ³¹P couplings for the one-electron reduction products of phospholiums and phospholes are all comprised in the 14–28 G range, the stabilities of the two types of radicals clearly differentiate the nature of these two species. The phospholium derivative could be observed at room tem-

perature whereas no signal could be detected with the phosphole radical anion above 240 K. Moreover, as shown by cyclic voltammetry, the reduction of phospholium is quite easier than that of phospholes. There is therefore no doubt that the EPR signals observed by reduction of (**A1-3**)⁺ are due to the corresponding neutral molecule and do not result from the reduction of a phosphole associated to a degradation of the phospholiums.

We will first examine the structural modifications induced by reduction of the phospholiums. As shown by DFT calculations, addition of an electron to (**A1-3**)⁺ leads to an elongation of the C2–C3 (and C4–C5) bond lengths and to a shortening of the C3–C4 bond. The most drastic effect concerns the C6PC7 angle whose value appreciably decreases during the reduction process (variation angle Δ = −8.3°, −5.8°, and −6.8° for **A1**, **A2**, **A3**, respectively). These modifications are consistent with the SOMO shown in Fig. 5.

In contrast with classical phosphoranyl radicals, the unpaired electron is not centered on the phosphorus atom but is delocalized in a π* molecular orbital which is bonding between C3 and C4 and between C2, P and C5. The decrease in the C6PC7 angle improves the spin delocalization by allowing an overlap of the C2PC5 π system with a combination of the s orbitals of the C6 and C7 atoms.¹⁰ However, as shown by the ξ₂ angle, this sharpening of the C6PC7 angle causes steric interaction between the methyl and phenyl groups and leads the phenyl plane to deviate from the C2PC5 bisector. The less encumbered and flexible the phospholium system, the more pronounced is this geometry change: ξ₂ increases from 1.8 to 41.7° for **A1** (no substituent in *ortho* position), from 0.1 to

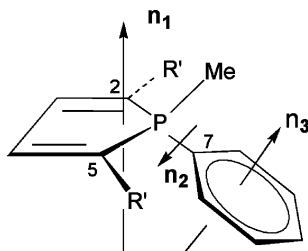


Fig. 4 Geometrical characteristics for the phospholium system: **n**₁: normal to the C2PC5 plane, **n**₂: normal to the C_{Me}PC7 plane, **n**₃: normal to the phenyl ring. ξ₁ = angle formed by **n**₁ and **n**₂, ξ₂ = angle formed by **n**₂ and **n**₃.

Table 3 DFT predictions of the isotropic hyperfine coupling constants (Gauss)

	$A_{\text{iso}} (^{31}\text{P})$	$A_{\text{iso}} (^1\text{H})/\text{Gauss}$
A1[•]	-19.7 ^a -21.7 ^b	(5.8 [Me-C4] ^c , 5.3 [Me-C3] ^c , -5.5 [C2-H], -5.3 [C5-H]) ^a (5.6 [Me-C4] ^c , 5.4 [Me-C3] ^c , -4.5 [C2-H], -4.4 [C5-H]) ^b
A2[•]	-19.5 ^a -22.7 ^b	(-4.4[C3-H], -4.5 [C4-H], -1.8[<i>para</i> ,2×] ^d , -1.6[<i>ortho</i> ,2×] ^d , -1.8 [ortho,2×] ^d) ^a (-4.6[C3-H], -4.6 [C4-H], -1.7[<i>para</i> ,2×] ^d , -1.5[<i>ortho</i> ,2×] ^d , -1.6 [ortho,2×] ^d) ^b
A3[•]	-13.1 ^a -14.3 ^b	(-3.6 [<i>para</i> to C2 or C5], -1.2 [<i>para</i> to C3 or C4], -1.1 [<i>ortho</i> to C2 or C5]) ^{ea} (-3.4 [<i>para</i> to C2 or C5], -0.8 [<i>para</i> to C3 or C4], -1.5 [<i>ortho</i> to C2 or C5]) ^{eb}
B1^{•-}	24.5 ^a	(-2.6 [C4-H, C3-H], -2.4 [<i>ortho</i> ,2×] ^f , -2.2 [<i>ortho</i> ,2×] ^f , -3.2 [<i>para</i> ,2×] ^f) ^a
B2^{•-}	18.6 ^a	(-2.3 [C3-H, C4-H], -2.5 [<i>ortho</i> ,2×] ^f , -2.2 [<i>ortho</i> ,2×] ^f , -3.4 [<i>para</i> ,2×] ^f , -1.0 [<i>methyl</i>]) ^a
B3^{•-}	22.4 ^a	(-5.5 [<i>para</i> to C4 or C3], 1.3 [<i>ortho</i> to C2 or C5], -1.7 [<i>ortho</i> to C3 or C4]) ^{ga}

^a 6-31G* for neutral species, 6-31+G* for radical anions. ^b IGLO-III. ^c Average value for the methyl protons. ^d Phenyl rings bound to C2 and C5. ^e Protons of the benzo rings; the coupling with protons in *ortho* position to C3 or C4 is less than 1 G. ^f Phenyl rings bound to carbons C2 and C5, couplings for protons in *meta* are less than 1 G. ^g Protons of the benzo rings.

Table 4 Optimized structures^a of neutral phospholes and phosphole radical anions

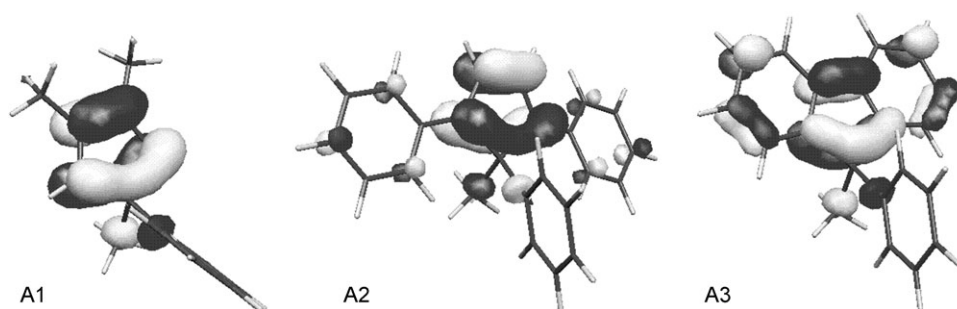
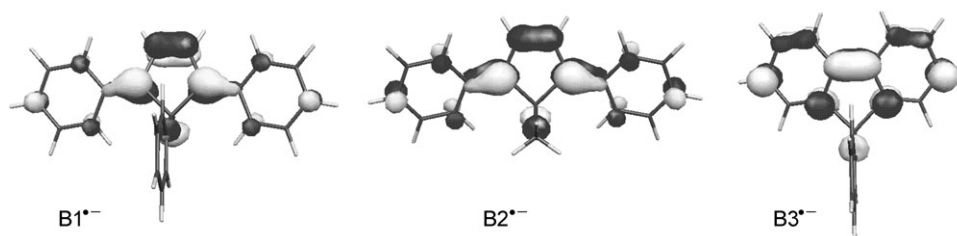
	C3-C4	C2-C3	C2-P	C2PC5	C2PR	C4C3C2P	$\Sigma C_iPC_j^b$
B1	1.444	1.367	1.832	91.2	105.1	6.4	301.4
B1^{•-}	1.403	1.408	1.840	91.5	102.6	2.3	296.6
B2	1.444	1.368	1.829	91.2	103.6	6.0	301.5
B2^{•-}	1.402	1.407	1.839	91.5	101.3	1.3	294.1
B3	1.472	1.414	1.841	89.1	103.4	4.4	295.9
B3^{•-}	1.424	1.451	1.832	89.2	102.3	2.1	293.8

^a Bond lengths in Å, angles in degrees. ^b Sum of the phosphorus bond angles.

15.0° for **A2** (phenyl groups in *ortho* position) and remains practically equal to zero in **A3** (benzo groups). This effect explains, at least in part, why, despite the high electron affinity of the diphenylene ligand, **A3⁺** ($E_{1/2} = -1500$ mV) is more difficult to reduce than **A1⁺** ($E_{1/2} = -1397$ mV): the rigidity of the dibenzo moieties hinders reorientation of the phenyl ring by preventing its rotation around the P-C7 bond. In **A2**, this reorientation is less hindered since the phenyl rings in *ortho* position can rotate around the C_{ortho}-C_{phenyl} bond.

It is interesting to compare the electronic configuration of the neutral radical formed from phospholiums with that of phosphole radical anions. The SOMO of these latter species are shown in Fig. 6.

The spin is mainly delocalized on the five-membered ring. As for the reduced phospholium **A2[•]** the orbital is bonding between C3 and C4; for **B1^{•-}** and **B2^{•-}**, however, a bonding interaction occurs between C2 (or C5) and the carbon of the adjacent phenyl and not between C2 (or C5) and the

**Fig. 5** SOMO of the neutral radicals resulting from reduction of phospholiums.**Fig. 6** SOMO of phosphole radical anions.

phosphorus atom. For $\mathbf{B3}^{\bullet-}$, the orbitals of the dibenzo noticeably contribute to the SOMO. These properties are in accordance with the bond-length changes provoked by the electron addition (*vide supra*, DFT results).

4. Concluding remark

The phospholium system is an efficient electron acceptor, its reduction leads to a neutral radical delocalized on the five-membered ring with a modest spin density on the phosphorus. In contrast with the rather unstable phosphole radical anion, this neutral radical is observed at room temperature. Investigations are currently in progress for incorporating phospholiums as a reduction site inside an unsaturated system able to delocalize the spin.

5. Experimental

5.1. Syntheses

Phospholiums and phospholes were prepared according to reported procedures. For $\mathbf{A1}^+$, $\mathbf{A2}^+$, $\mathbf{A3}^+$ see ref. 11–13, respectively; for $\mathbf{B1}$, $\mathbf{B2}$ and $\mathbf{B3}$ see ref. 14–16, respectively.

5.2. Crystal structures

Crystals of $\mathbf{A1}^+$ were obtained by diffusing hexanes in a solution of the compound in dichloromethane. Crystal data for $\mathbf{A1}^+$: $\text{C}_{13}\text{H}_{16}\text{P}, \text{I}, \text{H}_2\text{O}$; $M_r = 348.14$; orthorhombic; $a = 14.3540(10)$, $b = 11.2070(10)$, $c = 17.5480(10)$ Å; $V = 2822.9(4)$ Å³; $T = 150.0(1)$ K; space group $Pbca$; $Z = 8$; $\mu = 2.362$ cm⁻¹; 6621 reflections measured, 3641 unique, 2698 used reflections, criterion $I > 2\sigma(I)$; $R_{\text{int}} = 0.0199$; $wR2 = 0.1421$. Crystals of $\mathbf{A2}^+$ were obtained by diffusing hexanes in a solution of the compound in dichloromethane. Crystal data for $\mathbf{A2}^+$: $3(\text{C}_{23}\text{H}_{20}\text{P}), \text{CH}_2\text{Cl}_2, 3(\text{I}), \text{H}_2\text{O}$; $M_r = 488.57$; monoclinic; $a = 10.6360(10)$, $b = 17.2400(10)$, $c = 34.9150(10)$ Å; $\beta = 96.6600(10)^\circ$; $V = 6359.0(7)$ Å³; $T = 150.0(1)$ K; space group $P2_1/n$; $Z = 12$; $\mu = 1.677$ cm⁻¹; 25 001 reflections measured, 16 138 unique, 11 615 used reflections, criterion $I > 2\sigma(I)$; $R_{\text{int}} = 0.0240$; $wR2 = 0.1188$. Crystals of $\mathbf{A3}^+$ were obtained by diffusing hexanes in a solution of the compound in dichloromethane. Crystal data for $\mathbf{A3}^+$: $\text{C}_{19}\text{H}_{16}\text{P}, \text{CH}_2\text{Cl}_2, \text{I}$; $M_r = 487.11$; monoclinic; $a = 19.0070(10)$, $b = 10.6970(10)$, $c = 20.4380(10)$ Å; $\beta = 104.5700(10)^\circ$; $V = 4021.8(5)$ Å³; $T = 150.0(1)$ K; space group $P2_1/n$; $Z = 8$; $\mu = 1.937$ cm⁻¹; 20481 reflections measured, 11 713 unique, 8815 used reflections, criterion $I > 2\sigma(I)$; $R_{\text{int}} = 0.0212$; $wR2 = 0.0750$. CCDC reference numbers 276879 ($\mathbf{A1}^+$), 276878 ($\mathbf{A2}^+$) and 276880 ($\mathbf{A3}^+$). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513736p

5.3. Electrochemistry, EPR

Cyclic voltammograms have been obtained with a BAS station model CV-50W. Carefully dried CH_2Cl_2 or THF were used as solvents, tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. Measurements were carried out using a 1 mm diameter platinum wire as working electrode and counter electrode, and a SCE reference electrode.

EPR spectra were recorded on a Bruker 300 and a Bruker 200 spectrometer (X-band, 100 kHz field modulation) equipped with a variable temperature attachment. Electrochemical reductions were performed *in situ* in the EPR cavity using a three-electrode cell with a 0.1 mm Ag wire treated with HCl/HNO₃ as pseudo reference.

5.4. DFT

DFT calculations were performed using the Gaussian 98 package.¹⁷ The hybrid functional B3LYP and the 6-31G* basis set were used for the geometry optimizations.^{18,19} Hyperfine coupling constants for neutral radicals were calculated with both the 6-31G* and the IGLO-III basis sets;²⁰ for radical anions the 6-31+G* basis set was used.

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- 8 Some of the ¹H couplings were not resolved but were used to fit the line shape.
- 9 For all structures the value of the C2PC6 angle is very close to the value of the C5PC6 angle.
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