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Characterization of transient radicals in the reduction product of the –P=C=C=P– system: EPR and theoretical studies

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The EPR spectrum obtained at room temperature after electrochemical or chemical reduction of a solution of Ar–P=C=C=P–Ar in THF exhibits hyperfine interaction (165 MHz) with two equivalent ^{31}P nuclei. Additional couplings with two equivalent ^{13}C are observed with Ar–P=^{13}C=^{13}C=P–Ar. The ^{31}P anisotropic coupling constants could be obtained from spectra recorded at low temperature. They indicate that the unpaired electron is mainly localized (78%) on the two phosphorus atoms. Quantum chemical calculations (DFT and *ab initio* SCI) were performed on the various isomers of the two radical anions: [H–P=C=C=P–H]$^{\bullet-}$ and [H–P=CH–CH=P–H]$^{\bullet-}$. Although the optimized geometries of these two species are clearly different, neither of them leads to ^{13}C/^{31}P hyperfine tensors in conflict with the experimental results. The absence of any ^{1}H splitting on the EPR spectrum together with the quasi-reversibility of the reduction wave make the identification of [Ar–P=C=C=P–Ar]$^{\bullet-}$ more probable.

Introduction

Low-coordinated phosphorus atoms at the extremity of delocalized systems have been shown to give interesting properties to these molecules. It is mainly related to the presence of low-lying empty orbitals suitable for electronic transfer. How these properties are modified when the number of delocalized bonds between the extremities increases has not yet been considered. It has been found that moderately persistent radical anions are formed when an electron is added to the antibonding level of a P=C[1] or a P=P[2] double bond by means of chemical or electrochemical reduction. When the phosphorus atoms are separated by a carbon (P=C=P) or part of 3-atom system (P=C=C) as in phosphaallenes[3] the addition of an electron leads to a drastic structural change revealed by EPR studies. The spectrum observed is not, as originally thought,[4] that expected of an allenic anion but rather that of an allylic neutral radical.[5–7] The reason is that the primary anion formed is so basic that it is neutralized by a proton. This interpretation is based on a complementary study using both EPR spectroscopy and quantum chemical calculations. On the EPR side, it relies only upon the analysis of the ^{31}P and ^{13}C hyperfine couplings since the additional proton has a very weak coupling and the line-width of the EPR signal is large due to the presence of tri-*tert*-butyl phenyl (Ar) groups necessary to protect the low-coordinated phosphorus.[8] Theoretically the assignment to the allylic species is supported by DFT and configuration interaction (CI) calculations on appropriate model compounds.

The present study is centered on diphosphabutatrienic compounds,[9,10] *i.e.*, compounds in which the phosphorus atoms are incorporated at the extremities of a 4-atom delocalized fragment. The objective is to determine if the presence of a third adjacent double bond will lead to the formation of an observable negative ion by direct addition of an electron to the neutral system or induce a reduction–protonation process forming a phosphabutadienic anion after fixation of two hydrogen atoms on the C=C bond (the equivalence of the two ^{31}P couplings rules out a single addition). Such an addition on an unsaturated carbon–carbon bond would be reminiscent of a recent observation on 1,2-bis(3-pyridyl)acetylene.[11] Information about the reduction product of diphosphabutatriene is obtained from liquid/frozen EPR spectra recorded after reduction of Ar–P=C=C=P–Ar and Ar–P=^{13}C=^{13}C=PAr. These experimental results are interpreted in the light of *ab initio*/DFT calculations on representative model systems [H–P=C=C=P–H]$^{\bullet-}$ and [H–P=CH–CH=P–H]$^{\bullet-}$.

Materials and methods

Compounds

Ar–P=C=C=P–Ar was synthesized by following the method reported by Yoshifuji *et al.*:[12] ArP=CCl$_2$[13] was allowed to react with n-BuLi in THF in presence of anhydrous CuCl$_2$. The compound was purified by chromatography on a SiO$_2$ column using pentane as an eluant. (mp: 230 °C, ^{31}P{^{1}H} NMR (CDCl$_3$), $\delta = 179.5$ ppm (isomer *E*) and $\delta = 171.8$ ppm (isomer *Z*).

The ^{13}C enrichment of the two central atoms of ArP=C=C=P–Ar was performed by using ArP=^{13}CCl$_2$ as a reactant. This ^{13}C-enriched compound was obtained by reacting ArPCl$_2$ with ^{13}C(H)Cl$_3$ in the presence of n-BuLi as described by Goede and Bickelhaupt.[13]

Measurements

Voltammograms were recorded on a BAS station using a platinum electrode and an SCE reference electrode. Freshly distilled THF was used as a solvent and Bu$_4$NPF$_6$ (0.2 M) as an electrolyte.

EPR spectra were recorded on a Bruker 200-D EPR spectrometer (100 kHz field modulation) equipped with a variable

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temperature attachment. Electrochemical reductions of solutions of Ar–P=C=C=P–Ar in THF (Bu_4NPF_6 as an electrolyte) were carried out *in situ* in the EPR cavity by using a quartz cell and platinum electrodes. Chemical reductions were performed in sealed tubes, under high vacuum, by reacting degassed THF solutions of Ar–P=C=C=P–Ar at the surface of a potassium mirror.

Calculations

The DFT calculations were performed with GAUSSIAN98;[14] CI treatments were carried out with the MELDF package.[15] Representations of the molecular structures and spin density distributions were obtained with the Molekel program.[16]

As indicated by crystal structures, in ArP=C moieties, where Ar is a bulky protective group (Ar = tri-*tert*-butylphenyl), the Ar plane is oriented almost perpendicular to the CP=C plane.[17–19] The spin delocalisation on the Ar group is therefore small, and previous calculations on phosphorus compounds containing allenic fragments have shown that replacement of bulky aryl groups by hydrogens retains the essential characteristics of the actual system. Density functional theory (DFT) and *ab initio* post Hartree–Fock calculations were therefore performed on the neutral molecule H–P=C=C=P–H and on the model radicals $[\text{H–P=C=C=P–H}]^{\bullet-}$ and $[\text{H–P=CH–CH=P–H}]^{\bullet-}$. The actual systems are far beyond the possibility of present methods if quantitative information is needed.

The optimizations of the various structures were performed with the DFT method. We used hybrid B3LYP as functionals (Becke's three-parameter nonlocal exchange potential[20] coupled to the nonlocal correlation functional of Lee, Yang and Parr[21]). The basis set employed for the neutral closed-shell phosphabutatriene H–P=C=C=P–H is standard 6-311G**; it was extended with diffuse functions to 6-311++G** in the negative ions $[\text{H–P=C=C=P–H}]^{\bullet-}$ and $[\text{H–P=CH–CH=P–H}]^{\bullet-}$ to better describe the region, far from the nuclei, covered by the unpaired electron. Vibrational frequencies have been calculated (and scaled by 0.975 following Bauschlicher and Langhoff[22]) for characterization of the energy minima. The CI calculations were used for the determination of the isotropic coupling constants. In order to avoid spin contamination artefacts which, if marginal for the anisotropic parameters, may severely affect the determination of the isotropic values, these calculations employed a basis of spin-adapted configurations that lead to a pure doublet wave function. The single-CI treatment which was employed is known to give reliable results for magnetic properties governed by spin-polarization effects; it was used with the well-balanced aug-cc-pVDZ atomic basis set.[23]

Results

Experimental results

As shown by cyclic voltammetry, the reduction potential of Ar–P=C=C=P–Ar is equal to −1.23 V *vs.* SCE reference (ΔE_p = 90 mV, scan rate = 10 mV s^{-1}) and corresponds to a quasi-reversible process. Under electrolysis, the yellow solution of Ar–P=C=C=P–Ar in THF turns orange and leads to the EPR spectrum shown in Fig. 1(a).

At room temperature, the maximum of intensity is reached after 5 min of electrolysis; the signal disappears 5 min after having cut the voltage. A similar spectrum is obtained after reaction of a THF solution of Ar–P=C=C=P–Ar on a potassium mirror; the line-widths are nevertheless smaller than by electrolysis and the signals are stable for 4 h. Increasing the temperature causes a narrowing of the signals and an appreciable augmentation of the intensity of the lateral signals. These temperature effects are reversible. This broadening of the sidebands is probably due to the presence of the bulky Ar groups which precludes a rapid reorientation of the radical and, therefore, a total averaging of the *g* and hyperfine anisotropy and a 1-2-1 distribution of the intensities cannot be observed. These spectra are consistent with a large hyperfine coupling of 165 MHz with two equivalent ^{31}P nuclei and a *g* value equal to 2.006. The spectrum obtained after chemical reduction is clearly modified when the reduction is carried out with a solution of the ^{13}C-enriched compound: the central band is split into three lines as a result of a small hyperfine interaction (6 MHz) with two equivalent spin $\frac{1}{2}$ nuclei (Fig. 1(b)); certainly due to the larger line-width of the phosphorus-$M_I = \pm 1$ transitions, this additional splitting is not resolved on the external lines. With the electrochemically reduced solution, the ^{13}C enrichment leads only to an increase of the line-widths. Freezing the solutions of Ar–P=C=C=P–Ar or Ar–P=^{13}C=^{13}C=P–Ar after electrochemical or chemical reductions leads to similar spectra, an example of which is given in Fig. 2. This spectrum exhibits very large anisotropic couplings with two ^{31}P nuclei, and indicates that the corresponding two hyperfine tensors are axial and parallel. The absence of any additional splitting with the ^{13}C-enriched compound indicates that the ^{13}C couplings are smaller than the line-widths. The *g* and hyperfine parameters are given in Table 1.

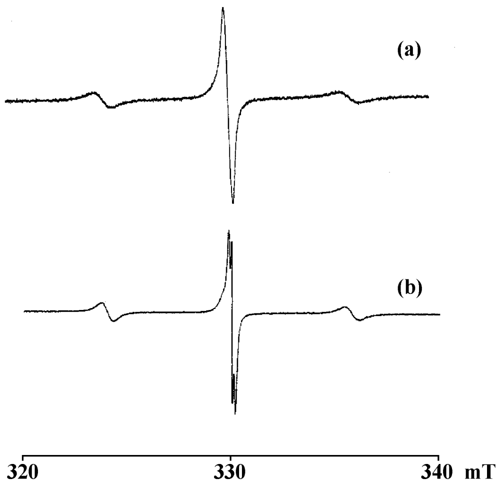

Fig. 1 EPR spectrum obtained at room temperature after electrochemical reduction of a solution of (a) Ar–P=C=C=P–Ar in THF; (b) Ar–P=^{13}C=^{13}C=P–Ar in THF.

Calculations

Optimized structures*HP=C=C=PH.* Two different minima, hereafter referred to as *cis* and *trans*, are found for H–P=C=C=P–H whose parameters are given in Table 2. Both have a planar geometry; they belong to C_{2v} and C_{2h} symmetry

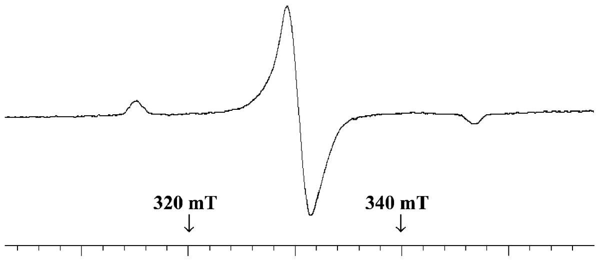

Fig. 2 Frozen solution EPR spectrum obtained after reduction of Ar–P=C=C=P–Ar.

Table 1 EPR parameters measured after reduction of a solution of ArP=^{13}C=^{13}C=PAr in THF

	g		^{31}P hyperfine coupling^a/MHz			^{13}C-hyperfine coupling^a/MHz	
	Liquid solution	Frozen solution	Liquid solution	Frozen solution	Anisotropic constants^d	Liquid solution	Frozen solution
ArP=^{13}C=^{13}C=PAr	2.006(3)	$g_\perp{}^b = 2.008$ $g_\parallel = 2.003$	$A_{iso} = 165$	$T_\perp{}^b = 26$ $T_\parallel = 444$	$\tau_\perp = -139$ $\tau_\parallel = 279$	6	^{c} ^{c}

[a] Only the absolute value of the hyperfine coupling is determined from the EPR spectra. [b] The perpendicular component was deduced from the isotropic (liquid solution) and the "parallel" (frozen solution) values. [c] Not observed; taking the line-width of the lateral and central signals into account, $|T_\perp(^{13}C)|$ and $|T_\parallel(^{13}C)|$ are less than 17 and 10 MHz respectively. [d] $\tau_i = T_i - A_{iso}$.

Table 2 Selected optimized parameters of diamagnetic diphosphabutatrienes (B3LYP/6-311G**)

	cis H–P=C=C=P–H	*trans* H–P=C=C=P–H
P=C/Å	1.663	1.663
C=C/Å	1.263	1.264
P–H/Å	1.432	1.432
∠PCC/°	174.29	171.48
∠HPC/°	96.42	96.45
Di-HPPH/°	0.00	180.00
ΔE/kcal mol^{-1}	0.16	0.00

Table 3 Selected optimized parameters of paramagnetic diphosphabutatrienes (B3LYP/6-311++G**)

	[*cis* H–P=C=C=P–H]$^{\bullet-}$	[*trans* H–P=C=C=P–H]$^{\bullet-}$
P=C/Å	1.723	1.723
C=C/Å	1.246	1.246
P–H/Å	1.437	1.436
∠PCC/°	174.94	172.44
∠HPC/°	96.63	96.63
Di-HPPH/°	0.00	180.00
ΔE/kcal mol^{-1}	0.12	0.00

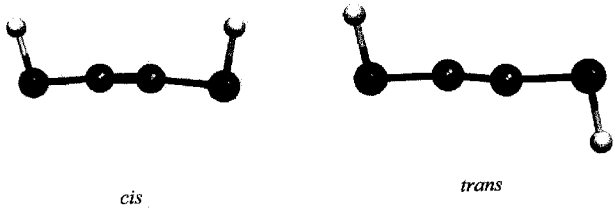

Fig. 3 The *cis* and *trans* conformers of diphosphabutatriene.

respectively (Fig. 3) and are very close in energy with a slight preference for the *trans* isomer.

Comparison of the cumulene chain in P=C=C=P and P=C=P[4] shows very little structural difference: both systems are quasi-linear. The central C=C bond is intermediate between a double and a triple bond: the ∠PCC angles are larger than the value of 170.73°[24] of the P=C=P backbone. The fundamental difference between these compounds is found in the orientation of the end groups; due to the parity of the number of bonds, the substituents of the phosphorus atoms are in the same plane in the butatrienic structure (odd number of bonds) whereas they are in perpendicular planes for the allenic compounds (even number of bonds).

[HP=C=C=PH]$^{\bullet-}$. In [H–P=C=C=P–H]$^{\bullet-}$ the electron is added to the antibonding π* orbital of a butatrienic system. This anion shows two planar isomers, *cis* and *trans*, as close in energy as the parent compounds. The stability order is the same with *trans* (C_{2h} symmetry) more stable than *cis* (C_{2v}). The structural parameters are reported in Table 3.

With respect to the neutral parents, one can note the increase in the P=C bond lengths coupled to the shortening of the central C=C bond consecutive to the addition of the electron in the lowest unoccupied molecular orbital (LUMO). This is consistent with the very structure of the π* level which is antibonding between the phosphorus and carbon atoms but has a bonding character between the central carbons (see discussion below).

[H–P=CH–CH=P–H]$^{\bullet-}$. In this radical anion the unpaired electron lies in the antibonding π* of a butadienic system perpendicular to the molecular plane. Six different isomers can be identified which are represented on Fig. 4. They belong to symmetry C_{2v} (**a** and **c**), C_2 (**e** and **f**) and C_s (**b** and **d**). The structural parameters of these ions are given in Table 4.

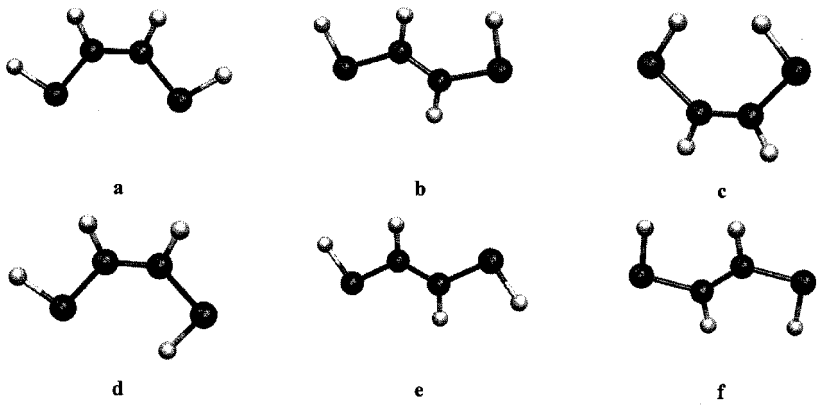

Fig. 4 The six isomers of the diphosphabutadiene anion.

Table 4 Selected optimized parameters of paramagnetic diphosphabutadienes (B3LYP/6-311++G**)

	a	**b**	**c**	**d**	**e**	**f**
$P{=}C_1/\text{Å}$	1.768	1.772	1.759	1.768	1.771	1.766
$P{=}C_2/\text{Å}$	1.768	1.765	1.759	1.760	1.771	1.766
$C_1\text{–}C_2/\text{Å}$	1.396	1.387	1.399	1.397	1.386	1.387
$\angle PC_1C_2/°$	128.73	125.20	134.99	133.52	125.24	130.81
$\angle PC_2C_1/°$	128.73	130.87	134.99	128.73	125.24	130.81
$\Delta E/\text{kcal mol}^{-1}$	5.21	0.45	3.37	3.98	0.83	0.00

Compared to [H–P=C=C=P–H]$^{\bullet -}$, all the bonds of the PCCP backbone are longer, which is consistent with the addition of the hydrogen atoms breaking any possibility of in-plane conjugation. The differences between PCC angles reflect steric repulsion.

Vibration frequencies. The infrared frequencies related to the P–C–C–P skeleton of the neutral compound and corresponding negative ions are listed in Table 5. The sym-PC and asym-PC stretching vibrations are shifted by 50 and 130 cm^{-1} to lower frequencies (10%) which is a measure of the weakness introduced in the P=C bond by addition of the extra electron. At the same time the CC stretching frequency increases by 50–60 cm^{-1} in agreement with the shortening of the CC bond in the negative ion. Concerning the protonated species, the rupture of the in-plane conjugation appears mainly in the CC frequency which is shifted by 500 cm^{-1} to lower wavenumbers. It is an illustration of the fact that a valence bond structure such as [H–P$^{\bullet}$–C≡C–P^{-}–H] is no longer possible with the protonated ion which behaves like an ethylenic compound.

Hyperfine interactions. The isotropic and anisotropic hyperfine constants, as obtained in the SCI/aug-cc-pVDZ treatments, are presented in Tables 6 and 7 for [H–P=C=C=P–H]$^{\bullet -}$ and [H–P=CH–CH=P–H]$^{\bullet -}$ respectively.

For [H–P=C=C=P–H]$^{\bullet -}$, the calculated anisotropic values τ show that the unpaired electron belongs to a π^* system, antisymmetric to the molecular plane. The difference in the $\tau_\perp$ values is of the order of 10 MHz, which means that the atoms linked to phosphorus have little influence. The isotropic couplings are due to spin polarization of the inner shells by the π^* spin distribution that is essentially the same for both *cis* and *trans* isomers.

Table 5 Vibrational analysis of minimum energy structures of H–P=C=C=P–H,[a] of its radical anion [H–P=C=C=P–H]$^{\bullet -}$ [b] and the radical anion [H–P=CH–CH=P–H]$^{\bullet -}$ [b]

	Sym-PC stretch ν/cm^{-1} ($I/\text{km mol}^{-1}$)	Asym-PC stretch ν/cm^{-1} ($I/\text{km mol}^{-1}$)	CC stretch ν/cm^{-1} ($I/\text{km mol}^{-1}$)
Molecule H–P=C=C=P–H[a]			
cis	488 (0)	1034 (8)	1910 (3)
trans	494 (0)	1034 (9)	1907 (0)
Anion [H–P=C=C=P–H]$^{-}$ [b]			
cis	436 (0)	900 (47)	1965 (3)
trans	446 (0)	902 (59)	1963 (0)
Anion [HP=CH–CH=PH]$^{-}$ [b]			
a	655 (2)	800 (25)	1362 (36)
b	705 (0)	805 (48)	1415 (2)
c	621 (1)	767 (12)	1368 (4)
d	643 (1)	778 (15)	1370 (13)
e	920 (0)	802 (48)	1412 (0)
f	687 (0)	797 (28)	1416 (0)

[a] B3LYP/6-311G**. [b] B3LYP/6-311++G**.

For [H–P=CH–CH=P–H]$^{\bullet -}$, the calculated anisotropic values show the same localisation of the unpaired electron in a π^* system, antisymmetric to the molecular plane as in the non-hydrogenated anion. In the same way, the difference in the $\tau_\perp$ values is small (in the order of 10 MHz).

Discussion

A preliminary description of the molecular orbital containing the unpaired electron in the reduction product of Ar–P=C=C=P–Ar can be obtained by decomposing the experimental ^{31}P hyperfine tensors into their Fermi contact and dipolar interactions. The resulting values are reported in Table 1; they lead, after comparison with the atomic coupling constants[25] ^{31}P-A^*_{iso} (13 360 MHz), and ^{31}P-$2B_{\text{o}}$ (733 MHz), to the s and p characters of the phosphorus orbitals participating in the SOMO. It is clear from the experimental spin densities that 78% of the total spin is equally delocalized in two phosphorus p-orbitals. As indicated by the relative orientations of the g and ^{31}P coupling tensors, the two phosphorus p orbitals are parallel and aligned along the g eigenvector associated to the g value close to that of the free electron. These properties are indicative of a π molecular orbital with a large contribution of the two phosphorus atoms; this is in agreement with the very small phosphorus s spin densities ($\rho_{\text{s}} = 0.01$) which are probably due to inner shell polarization. The participation of the central carbon atoms to this SOMO appears to be very small: the dipolar ^{13}C couplings are too weak to be resolved on the frozen solution spectra and are therefore less than *ca.* 20 MHz; nevertheless, their presence is revealed by their small isotropic coupling constant (6 MHz).

This description of the SOMO derived from experiment is entirely consistent with the DFT results obtained for [H–P=C=C=P–H]$^{\bullet -}$. As shown in Fig. 5, the spatial distribution of the spin density belongs to a π^* orbital with a strong participation of the phosphorus p-orbitals, and the calculated coupling constants reported in Table 6 reasonably agree with the experimental values.

It is worthwhile remarking, however, that the ^{31}P and ^{13}C coupling constants calculated for [H–P=CH–CH=P–H]$^{\bullet -}$ are not in conflict with the experimental values. Although [H–P=C=C=P–H]$^{\bullet -}$ and [H–P=CH–CH=P–H]$^{\bullet -}$ are obviously different, one being quasi linear, the other with a planar

Table 6 EPR parameters of paramagnetic diphosphabutatriene radical anions (MHz)

	[*cis* H–P=C=C=P–H]$^{\bullet -}$	[*trans* H–P=C=C=P–H]$^{\bullet -}$
A_{iso} ^{31}P	100	100
A_{iso} ^{13}C	−3	−4
τ^{31}P	−121	−121
	−110	−110
	231	231
τ^{13}C	−12	−12
	−8	−8
	20	20

Table 7 EPR parameters of paramagnetic diphosphabutadiene radical anions (MHz)

	[H–P=CH–CH=P–H]$^{\bullet-}$					
	a	**b**[a]	**c**	**d**[a]	**e**	**f**
A_{iso} ^{31}P	79	91	88	83	93	88
A_{iso} ^{13}C	3	4	2	3	5	4
A_{iso} ^{1}H	−11	−10	−11	−11	−10	−10
τ^{31}P	−106	−114	−116	−111	−118	−109
	−117	−113	−106	−112	−108	−119
	223	227	222	223	226	228
τ^{13}C	−8	−10	−8	−9	−10	−10
	−8	−9	−8	−9	−9	−9
	16	19	16	18	19	19
τ^{1}H	−2	−4	−2	−2	−3	−4
	−5	−3	−4	−5	−4	−3
	7	7	6	7	7	7

[a] Average value for non symmetric compounds.

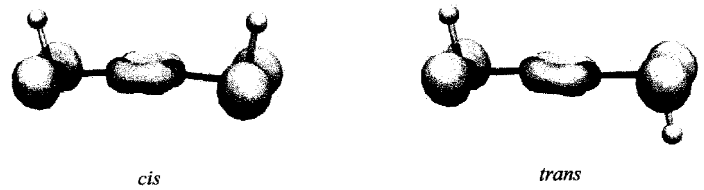

Fig. 5 Three-dimensional view of calculated spin density distribution in [H–P=C=C=P–H]$^{\bullet-}$ radical anion (isosurface value: 0.08 au).

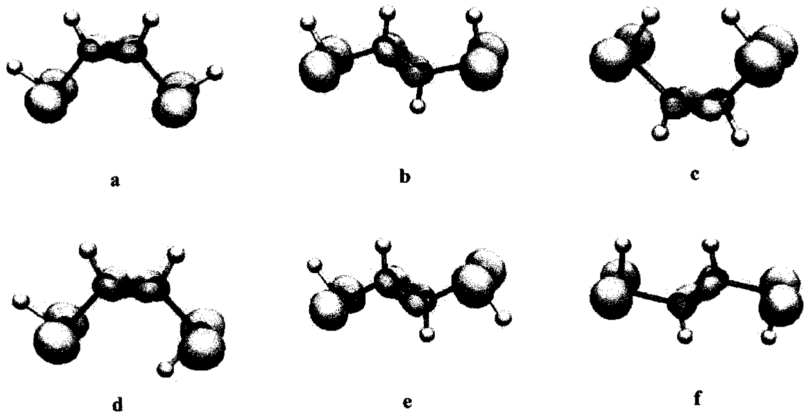

Fig. 6 Three-dimensional view of calculated spin density distribution in [H–P=CH–CH=P–H]$^{\bullet-}$ radical anion (isosurface value: 0.08 au).

arrangement governed by the geometry of sp^2 carbons, their spin distributions (Figs. 5 and 6) present the same relative contributions of the phosphorus and carbon p-orbitals and lead therefore to similar couplings (Table 7). No difference can be found in the phosphorus or carbon anisotropic tensors which can help in discriminating between the hydrogenated and non-hydrogenated anions. The isotropic couplings which are here also due to spin polarization of the inner shells by the π^* spin distribution are slightly lower in [H–P=CH–CH=P–H]$^{\bullet-}$, but the difference is too small to be decisive in regards of the simplifications inherent to the model radicals.

The difference between the EPR signatures of the two radicals has to be found in the additional proton couplings present for [H–P=CH–CH=P–H]$^{\bullet-}$. The calculated values show that the isotropic ^{1}H coupling is larger than the ^{13}C coupling; under these conditions, the proton splittings would probably be resolved on the EPR spectrum of [Ar–P=CH–CH=P–Ar]$^{\bullet-}$. The fact that this coupling is not observed, either after electrolysis of a solution of Ar–P=C=C=P–Ar or after reaction on a potassium mirror, suggests that the secondary product Ar–P=CH–CH=P–Ar has not been formed in the reduction process. In contrast with Ar–P=C=CPh$_2$[5] or Ar–P=C=P–Ar,[7] the life time of the radical anion is sufficiently long to be observed by EPR. This is consistent with the quasi-reversibility of the reduction wave observed for Ar–P=C=C=P–Ar whereas cyclic voltammetry had showed that reduction of Ar–P=C=CPh$_2$[5] or of fulvenephosphaallene[26] was irreversible as a consequence of the formation of the stable protonated species.

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