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Phosphaalkene radical anions: Electrochemical generation, ab initio predictions, and ESR study

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Compounds. Compound I was synthesized by the method of Yoshifuji et al.⁴ $\text{ArP}=\text{}^{13}\text{C}(\text{H})(\text{C}_6\text{H}_5)$ ($\text{Ar} = 2,4,6\text{-tri-}i\text{-tert-butylphenyl}$) was synthesized by using $\text{C}_6\text{H}_5\text{}^{13}\text{C}(\text{H})\text{O}$ (Cambridge Isotope Laboratories) as a reagent. $\text{C}_6\text{D}_5\text{C}(\text{H})\text{O}$ (Glaser AG, Basel, Switzerland) was used for the synthesis of $\text{ArP}=\text{C}(\text{H})\text{C}_6\text{D}_5$. $(\text{C}_6\text{D}_5)_2\text{CD}_2$, used for the subsequent syntheses of $\text{C}_6\text{D}_5\text{C}(\text{D})\text{O}$ and $\text{ArP}=\text{C}(\text{D})\text{C}_6\text{D}_5$, was obtained from Glaser AG. All the isotopic substitutions were controlled by ^1H or ^{13}C NMR. The *E* and

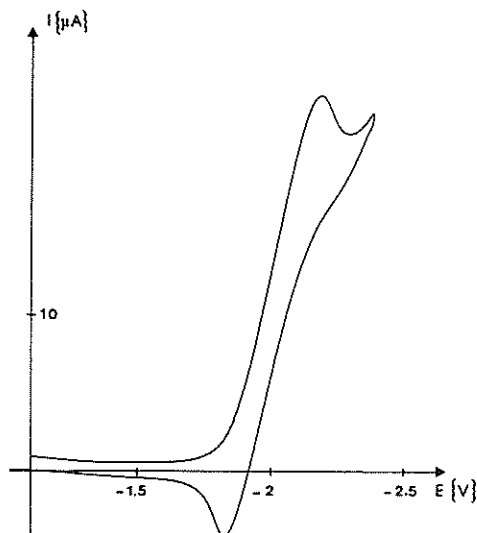


Figure 1. Cyclic voltammogram (100 mV/s) of ArP=CHC₆H₅, at a platinum electrode, in THF with 0.10 M *n*-Bu₄NPF₆ electrolyte.

Z-isomers of I were separated by silica gel column chromatography. The Z-isomer was considerably less abundant than the E-isomer and a small amount of this isomer could be obtained only for the compound containing neither ¹³C nor ²D.

Electrochemistry and Electron Spin Resonance. The redox behavior of the phosphalkene (I) was investigated by cyclic voltammetry at a platinum electrode using *n*-Bu₄NPF₆ (0.1 M) as the supporting electrolyte in THF. The solvent was distilled from Na/benzophenone and degassed with argon. The measurements were carried out with a Princeton Applied Research scanning potentiostat (Model 362).

The ESR spectra were obtained on a Bruker-200D spectrometer (X-band, 100-kHz magnetic field modulation). A home-made electrolytic cell (Pt electrodes) was used to generate radical ions directly in the ESR cavity at room temperature. The solvent and supporting electrolyte were the same as those used for cyclic voltammetry. In order to measure the anisotropic hyperfine constants, the electrolyzed solution was rapidly frozen at 100 K by using the Bruker variable-temperature unit. All the spectral assignments were supported by simulation. The frozen solution spectra were simulated by using a second-order perturbation⁶ program which sums the spectra calculated for 120 000 random orientations of the magnetic field.

Calculations. The calculations were performed on a Silicon Graphics workstation (Iris 4D) with Gaussian 90⁷ and the 6-31G* basis set. The equilibrium structure, spin densities, and hyperfine couplings for [HP=PH]⁻ and [HP=CH₂]⁻ were calculated by using the UHF formalism and by performing spin annihilation of the quartet contamination.⁸ The final ⟨S²⟩ value for [HP=CH-CH=CH₂]⁻ and [HP=C(H)C₆H₅]⁻ was found to be higher than 0.75, and calculations on these radical ions were therefore performed by using the ROHF method. For the sake of comparison, ROHF results have also been obtained for all the other radical anions investigated in the present study.

Results

Electrochemistry. As shown in Figure 1, the phosphalkene I showed a quasi-reversible one electron reduction at the platinum electrode. The anodic and cathodic peak potential values are *E*_p(a) = -1.82 V vs SCE and *E*_p(c) = -2.15 V vs SCE, respectively (*E*_{1/2} = -1.98 V vs SCE, *I*_p(a) = *I*_p(c)). The same results were obtained when mercury or carbon-glass electrode was used.

Electron Spin Resonance. Electroreduction of the phosphalkene I was performed directly in the ESR cavity. The orange radical anion was formed at -2.25 V vs SCE.

Liquid Solution Spectra. The ESR spectrum obtained at room temperature during the electrolysis of a solution of I in THF is shown in Figure 2a. It is composed of two groups of lines exhibiting unresolved structure; the difference in the intensities of

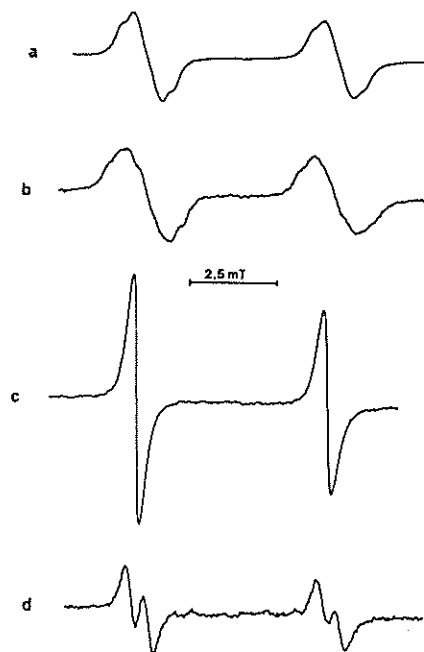


Figure 2. EPR spectra obtained at room temperature by electrochemical reduction of a solution of (a) ArP=CHC₆H₅, (b) ArP=¹³CHC₆H₅, (c) ArP=CDC₆D₅, and (d) ArP=CHC₆D₅.

TABLE I: Experimental EPR Parameters Obtained with Phosphalkene and Diphenylphosphine Radical Anions

anion	liquid solution <i>g</i>	solid solution <i>g</i> ₁	nucleus	hyperfine couplings (MHz)		
				liquid solution <i>A</i> _{iso}	solid solution <i>T</i> ₁	solid solution <i>T</i> ₂
ArP=C(D) ₂ C ₆ D ₅	2.006	2.002	³¹ P	152	455	0.5
ArP=C(H)C ₆ D ₅	2.007	2.002	³¹ P	152	455	0.5
			¹ H	13		
ArP= ¹³ C(H)C ₆ H ₅	2.005	2.003	³¹ P	151	455	1
			¹³ C	16	47	0.5
ArP=C(H)C ₆ H ₅	2.005	2.003	³¹ P	152	455	0.5
			¹ H	13		
			¹ H	11		
			¹ H	7		
			¹ H	7		
ArP=PAr	2.009	2.002	³¹ P	158	458	10

these two signals probably reflects some motional effects. The main splitting is without any doubt due to hyperfine interaction with ³¹P and corresponds to *A*_{iso}(³¹P) = 152 MHz. The same results were obtained with the Z-isomer. When the same experiment was performed with ArP=¹³C(H)C₆H₅, the line shape was modified by an additional unresolved splitting (Figure 2b). Insofar as the electronic relaxation time was not significantly changed by isotopic substitution, the increase in the peak-to-peak line width revealed a ¹³C-isotropic coupling of 16 MHz. The spectrum obtained with the deuterated compound ArP=C(D)₂C₆D₅ is characterized by a strong narrowing of the two groups (Figure 2c). The main splitting (152 MHz) is practically not affected by the isotopic substitutions. The coupling constant with the proton of the P=CH moiety (*A*_{iso} = 13 MHz) was directly measured on the spectrum obtained with ArP=C(H)C₆D₅ (Figure 2d). All the isotropic constants are reported in Table I and have been obtained after successive simulations of the experimental spectra.

Frozen Solution Spectra. The ESR spectrum obtained at 100 K with a solution of ArP=C(H)C₆H₅ which has been electrochemically reduced is shown in Figure 3a. The intensity of the central signal, marked A, was found to be very sensitive to the microwave power and to the experimental conditions (e.g., time used for cooling the solution, nitrogen bubbling), and it appeared that this line was due to an additional species. All the other signals of the spectrum could be simulated by using an axial ³¹P tensor

TABLE II: Experimental Isotropic and Anisotropic ^{31}P Coupling Constants for I^- and II^- and Calculated Isotropic and Anisotropic ^{31}P Coupling Constants for $[\text{HP}=\text{CH}_2]^-$, $[\text{HP}=\text{PH}]^-$, and $[\text{CH}_3\text{P}=\text{PCH}_3]^-$ (C_s Symmetries, UHF Calculations)

radical ion	$A_{\text{iso}}(^{31}\text{P})$ (MHz)	^{31}P anisotropic coupling const (MHz)		
		$\tau_x = \tau_{\parallel}$	$\tau_{\perp 1}$	$\tau_{\perp 2}$
I^- (exptl)	152	303	-152	-152
II^- (exptl)	158	300	-148	-148
$[\text{HP}=\text{CH}_2]^-$ (calcd)	25	130	-60	-70
$[\text{HP}=\text{PH}]^-$ (calcd)	70	279	-136	-142
$[\text{CH}_3\text{P}=\text{PCH}_3]^-$ (calcd)	75	275	-134	-141

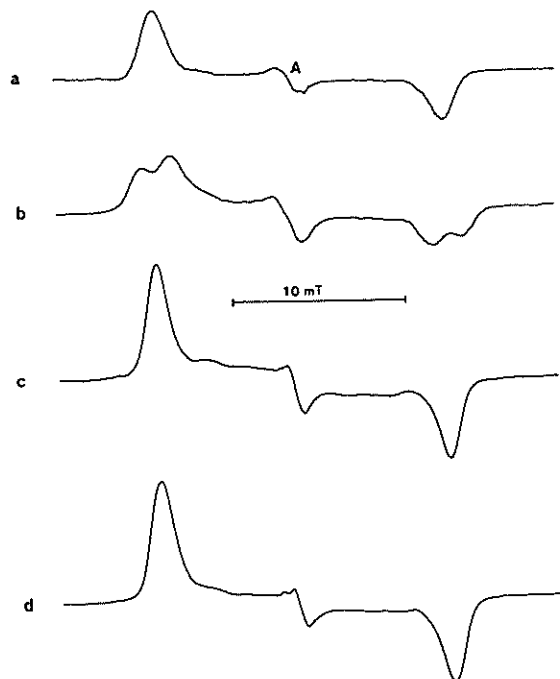


Figure 3. EPR spectra recorded at 100 K with electrolyzed solutions of (a) $\text{ArP}=\text{CHC}_6\text{H}_5$, (b) $\text{ArP}=\text{CHC}_6\text{H}_5$, (c) $\text{ArP}=\text{CDC}_6\text{D}_5$, and (d) $\text{ArP}=\text{CHC}_6\text{D}_5$.

having a "perpendicular" eigenvalue almost equal to zero and a "parallel" eigenvalue equal to 455 MHz (total line width equal to 16 G). The same spectrum was obtained with the Z-isomer. A similar experiment, performed with $\text{ArP}=\text{C(D)}\text{C}_6\text{D}_5$, led to the same hyperfine constants (Figure 3c) but to a narrower line width (14 G); a similar spectrum is obtained with $\text{ArP}=\text{C(H)}\text{C}_6\text{D}_5$ (Figure 3d). Finally, the spectrum obtained with $\text{ArP}=\text{CHC}_6\text{H}_5$ (Figure 3b) is characterized by the same ^{31}P tensor and by an additional splitting (16.8 G) of the parallel transitions; this splitting certainly corresponds to the parallel component of the ^{13}C coupling, and the perpendicular eigenvalue can be deduced from the isotropic constant (16 MHz) measured with the liquid solution: $T_{\perp}(^{13}\text{C}) = (3A_{\text{iso}} - T_{\parallel})/2 \sim 0$ MHz.

The hyperfine eigenvalues are reported in Table I; they were obtained on the hypothesis of aligned axial ^{13}C and ^{31}P tensors. The resulting isotropic and anisotropic hyperfine coupling constants are given in Table II.

Although the liquid solution spectrum of $[\text{ArP}=\text{PAr}]^-$ has been previously observed,⁵ the anisotropic coupling constants are not known for this radical anion. We have therefore generated this

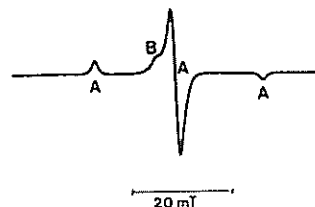
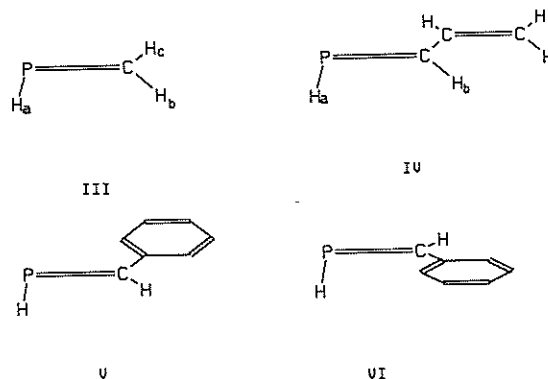


Figure 4. EPR spectrum obtained at 100 K after electrochemical reduction of a solution of $\text{ArP}=\text{PAr}$.

anion by electrolyzing a solution of $\text{ArP}=\text{PAr}$ in THF at -20°C and by rapidly freezing the sample at 100 K. The resulting spectrum, shown in Figure 4, exhibits signals marked A and B. A careful examination of the temperature dependence of the spectrum showed that the line marked B was due to an additional species. The simulation of the spectrum A indicates that two equivalent phosphorus nuclei are present and that the corresponding tensors are aligned and exhibit axial symmetry: $T_{\parallel}(^{31}\text{P}) = 458$ MHz and $T_{\perp}(^{31}\text{P}) = 10$ MHz. At -20°C , the liquid solution gives rise to an ESR spectrum characterized by an interaction with two ^{31}P nuclei whose coupling is indeed equal to $(T_{\parallel} + 2T_{\perp})/3$ and is in accordance with previous liquid-phase results.⁵ The experimental ^{31}P coupling tensors (Table I) lead to the anisotropic coupling constants shown in Table II.

Calculations.



$[\text{HP}=\text{CH}_2]^-$ and $[\text{HP}=\text{CH}-\text{CH}=\text{CH}_2]^-$. The UHF calculations for $(\text{HP}=\text{CH}_2)^-$ were performed by assuming both a C_1 and a C_s symmetry. The $\langle S^2 \rangle$ value, total energy, geometry parameters, and spin densities obtained for each optimized structure are reported in Table III and IV. The C_1 structure, which corresponds to a pyramidal carbon, is found to be more stable than the planar structure. However, the energy difference between the two conformations is very low ($\Delta E = 0.132$ kcal/mol),⁹ and it can be expected that substitution of a proton by an aromatic ring will lead to a planar molecule. The isotropic and anisotropic ^{31}P hyperfine coupling constants resulting from the UHF calculations (C_s structure, the x-axis perpendicular to the molecular plane) are given in Table II. The ROHF calculations lead to the optimized structures shown in Table III. They are very similar to those obtained from UHF calculations and also indicate that the C_1 and C_s structures have practically the same energy; the ROHF spin densities calculated for the C_s structure are given in Table IV.

We have optimized the geometry of $[\text{HP}=\text{CHCH}=\text{CH}_2]^-$ with the hypothesis of a planar structure by using the ROHF method: the resulting equilibrium geometry and spin densities are given in Tables V and IV, respectively.

TABLE III: Optimized Geometries for $[\text{HP}=\text{CH}_2]^-$

symmetry	energy (hartrees)	P-C (Å)	H _a -P (Å)	C-H _b (Å)	C-H _c (Å)	$\angle\text{HPC}$ (deg)	$\angle\text{H}_a\text{PCH}_c$ (deg)	$\angle\text{H}_b\text{CPH}_c$ (deg)	$\angle\text{H}_b\text{CPH}_a$ (deg)
C_1 (UHF)	-380.2507407 ($\langle S^2 \rangle_{\text{aa}} = 0.750$)	1.793	1.429	1.083	1.083	97.5	175.8	155.4	20.3
C_s (UHF)	-380.2505305 ($\langle S^2 \rangle_{\text{aa}} = 0.750$)	1.791	1.428	1.081	1.082	97.4	180.0	(180.0)	(0.0)
C_1 (ROHF)	-380.2452385	1.796	1.429	1.083	1.083	97.3	173.9	151.8	22.0
C_s (ROHF)	-380.2448384	1.792	1.428	1.079	1.080	97.3	180.0	(180.0)	(0.0)

TABLE IV: Calculated Spin Densities for the Optimized Structures of Some Phosphaalkene Radical Anions (C_s Symmetry) and Experimental Spin Densities for I^- and II^-

atom	spin density	III ⁻		IV ⁻	V ⁻	VI ⁻	HPPH ⁻		I ⁻ (expt)	II ⁻ (expt)
		UHF	ROHF	ROHF	ROHF	ROHF	UHF	ROHF		
P	ρ_s	0.011	0.000	0.000	0.000	0.000	0.021	0.000	0.01	0.01
	ρ_{p_x}	0.236	0.223	0.351	0.437	0.411	0.496	0.497	0.41	0.41
C1	ρ_s	0.044	0.000	0.000	0.000	0.000			0.004	
	ρ_{p_x}	0.752	0.768	0.414	0.326	0.344			0.18	
C2	ρ_s			0.000	0.000	0.000				
	ρ_{p_x}			0.040	0.052	0.052				
C3	ρ_s			0.000	0.000	0.000			0.10	
	ρ_{p_x}			0.178	0.044	0.045				
C4	ρ_s				0.000	0.000				
	ρ_{p_x}				0.006	0.006				
C5	ρ_s				0.000	0.000				
	ρ_{p_x}				0.058	0.061			0.16	
C6	ρ_s				0.000	0.000				
	ρ_{p_x}				0.002	0.002				
C7	ρ_s				0.000	0.000				
	ρ_{p_x}				0.059	0.062			0.10	

TABLE V: Optimized Structure for $[HP=C1(H)C2(H)=C3H_2)]^-$ (C_s Symmetry, IV⁻)

method	energy (hartrees)	P=C1 (Å)	H ₁ -P (Å)	C1-C2 (Å)	C2-C3 (Å)	∠HPC1 (deg)	∠PC1C2 (deg)	∠C1C2C3 (deg)
ROHF	-457.1515950	1.772	1.422	1.418	1.353	97.2	123.8	128.7

TABLE VI: Optimized Geometries for $[HP=C(H)C_6H_5]^-$ (ROHF, C_s Symmetry)

isomer	energy (hartrees)	P=C1 (Å)	H ₁ -P (Å)	C1-H _b (Å)	C1-C (Å)	∠HPC (deg)	∠PCH (deg)	∠PCC (deg)
V ⁻	-609.820 262 8	1.761	1.420	1.078	1.423	96.6	119.9	126.2
VI ⁻	-609.817 631 2	1.757	1.414	1.080	1.433	99.8	112.3	130.9

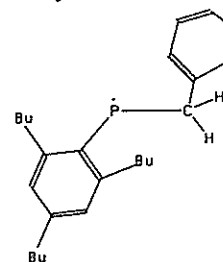
$[HP=C(H)C_6H_5]^-$. A partial optimization of the isomer V⁻ was performed by fixing the geometry of the benzene ring and by varying all the other parameters. The very high value found for $\langle S^2 \rangle$ precluded us from using UHF results, and the optimized geometry and spin densities reported in Table VI were obtained from ROHF calculations on the hypothesis of a C_s symmetry. When the geometry optimization was carried out by assuming a C_1 symmetry, the resulting structure was found to be practically the same as the planar structure. A partial optimization of the isomer VI⁻ was performed by using the same method as for the isomer V⁻; the corresponding geometry is given in Table VI and the spin densities are shown in Table IV.

$[RP=PR]^-$. The optimized structure (UHF calculations) for HPPH⁻ (P-P = 2.133 Å, ∠HPP = 95.8°) is in accord with that calculated by Nguyen.¹⁰ Substitution of the H atoms by methyl groups does not modify this structure (for $[CH_3P=PCH_3]^-$; we found the following parameters: P-P = 2.123 Å, C-P = 1.892 Å, ∠CPP = 98.9°, see ref 11). After spin annihilation of the quartet contamination, $\langle S^2 \rangle$ is equal to 0.750. The reference frame is similar to the frame used for III⁻ and the various spin densities are given in Table IV. The quasi totality of the unpaired electron is located in the two phosphorus 3p_x orbitals oriented perpendicular to the molecular plane and the isotropic and anisotropic ³¹P coupling constants are given in Table II. The calculated isotropic and anisotropic ³¹P coupling constants for $(CH_3P=PCH_3)^-$ are respectively $A_{iso} = 75$ MHz, $T_{||} = 275$ MHz (aligned along the x-axis), $T_{\perp 1} = -134$ MHz, $T_{\perp 2} = -141$ MHz. ROHF calculations lead to very similar results for the optimized geometries ($[HPPH]^-$: P-P = 2.131 Å, ∠HPP = 95.8°) as well as for the corresponding spin densities (Table IV).

Interpretation and Discussion

By assuming the sign combination shown in Table I for the phosphorus hyperfine eigenvalues, the spectra 2a-d and 3a-d lead to the isotropic and anisotropic ³¹P coupling constants shown in Table II. Comparison of these values with those respectively associated with a 3s and a 3p phosphorus electron¹² indicates that the phosphorus spin densities are equal to $\rho_s = 0.01$ and $\rho_p = 0.41$. Such spin densities are not inconsistent with a phosphinyl radical¹³

and could be attributed to a neutral species VII resulting from the capture of a proton by the anion.



VII

However, two observations make this interpretation very dubious: (i) The incorporation in the solution of traces of D₂O, expected to generate ArPC(D)HAr', decreased the intensity of the spectrum but did not modify the line width of the signals. (ii) Deuterating the C(H)C₆H₅ moiety considerably decreased the line width (suppression of the unresolved hyperfine structure) and did not reveal the ¹H splitting expected for ArPC(H)(D)C₆D₅. We therefore concluded that the studied spectra were due to the phosphaalkene anion and tried to determine its structure.

We first observed that both the isotropic and anisotropic experimental ³¹P coupling constants were practically identical for the phosphaalkene anion and the diphosphene anion (Table I). For this last species, comparison of the hyperfine coupling constants with the ³¹P atomic constants shows that the spin density in the phosphorus s orbitals is very low ($\rho_s = 0.01$) whereas each phosphorus 3p_x orbital contains 41% of the spin. These results are in excellent accordance with the ab initio calculations reported in Table IV, which, as expected, predict a π^* structure for $[HP=PH]^-$ or $[CH_3P=PCH_3]^-$ and a spin density of 0.48 in each 3p_x orbital.¹¹ This accordance also appears in the calculated Fermi and dipolar coupling constants which reasonably agree with the experimental results (Table II). For the phosphaalkene radical anion, however, the spin density on the unsaturated carbon seems to be considerably lower since the values given in Table I correspond to very small carbon spin densities $\rho_p(C) = 0.15$ when estimated from the anisotropic ¹³C coupling, and $\rho(C) = 0.18$ when

estimated from the adjacent proton coupling). A large amount of the total spin density is therefore delocalized on another part of the molecule and the drastic effect of the ring deuteration on the line width indicates that this delocalization occurs on the phenyl ring bound to the carbon atom. In fact, it was possible to obtain a satisfactory simulation of the spectrum of $[\text{ArP}=\text{C}(\text{H})\text{C}_6\text{H}_5]^-$ recorded in liquid solution by adding three proton coupling constants (7, 11, and 7 MHz) to the measured ^{31}P and ^1H coupling constants measured with $[\text{ArP}=\text{C}(\text{D})\text{C}_6\text{D}_5]$ and $[\text{ArP}=\text{C}(\text{H})\text{C}_6\text{D}_5]$, respectively. It is worthwhile remarking that for $[\text{ArP}=\text{PAr}]^-$ as well as for $[\text{ArP}=\text{C}(\text{H})\text{C}_6\text{H}_5]^-$ no spin delocalization occurs on the aromatic ring bound to the phosphorus atom. This indicates that the orientation of this ring, which is known⁴ not to be coplanar with the CPP moiety in the neutral diphosphene (or with the CPC moiety in the neutral phosphaalkene¹⁴), is maintained for the radical anions. Similarly, the spin delocalization that is observed on the phenyl ring bound to the carbon atom is consistent with the fact that this ring is almost located in the same plane as the PCC fragment in the neutral phosphaalkene.¹⁴

We will now examine to what extent the EPR results agree with the predictions of ab initio calculations on phosphaalkene anions. The ROHF calculations performed on $(\text{HP}=\text{CH}_2)^-$ show that, for this radical anion, the energy of the C_s structure is very close to the energy minimum and that, near this optimized planar structure, the spin is strongly localized on the carbon (gross spin densities: $\rho_{\text{carbon}} = 0.76$, $\rho_{\text{phosphorus}} = 0.22$) in contrast with the experimental results obtained for Γ^- . Substituting a hydrogen bonded to the carbon by an ethylenic moiety slightly increases the phosphorus spin density ($\rho_{\text{phosphorus}} = 0.35$) and appreciably delocalizes the unpaired electron on the terminal carbon ($\rho_{\text{carbon}} = 0.18$). Finally, when a phenyl group is bound to the phosphaalkene carbon, the highest spin density is found on the phosphorus atom ($\rho_{\text{phosphorus}} = 0.43$) and the spin density on the adjacent carbon is only 0.32; the remaining part of the spin is essentially delocalized on the benzene ring ($\rho_{\text{total,benzene}} = 0.22$) and is very similar to the spin delocalization found on the ethylenic group in $(\text{HP}=\text{CHCH}=\text{CH}_2)^-$. These spin densities are qualitatively in accord with the EPR results, and the main difference lies in the experimental carbon spin density which is only 0.17; such a discrepancy could be due to structural modifications induced in Γ^- by the presence of a tri-*tert*-butylphenyl ring bound to the phosphorus atom. A slight difference of the geometry of V^- can indeed induce an appreciable change in the spin densities; for example, a single-point calculation shows that for the following new parameters, $\text{P}-\text{C} = 1.612 \text{ \AA}$ and $\angle\text{PCC} = 115^\circ$, the spin delocalization becomes $\rho(\text{P}) = 0.57$, $\rho(\text{C}) = 0.18$.

The fact that the same ESR spectra were obtained with the *E*- and *Z*-isomers of $\text{ArP}=\text{C}(\text{H})\text{Ar}'$ is quite in accord with the structures calculated for the two isomers of $[\text{HP}=\text{C}(\text{H})\text{C}_6\text{H}_5]^-$; as seen in Table IV, these two isomers have very similar spin densities and it can be remarked that the energy of VI^- lies only

1.65 kcal above the energy of V^- .

It is interesting to compare the results found for Γ^- with those reported in the literature¹⁵ for the styrene radical anion. For this last radical, more than half the total spin density (0.577) is delocalized on the phenyl group; the terminal vinyl carbon bears 37% of the spin while the spin density on the second vinyl carbon is only 0.06. It seems therefore that the presence of the phosphorus atom draws a part of the spin from the phenyl ring toward the double bond.

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Supplementary Material Available: Simulations of the EPR spectra and a table containing the geometry and spin densities obtained with the 6-31+G basis set (4 pages). Ordering information is given on any current masterhead page.

References and Notes

- (1) (a) Thomson, C. J. *Chem. Soc., Chem. Commun.* 1977, 322. (b) Fuchs, F.; Breit, B.; Heydt, H.; Schoeller, W.; Busch, T.; Kruger, C.; Betz, P.; Regitz, M. *Chem. Ber.* 1991, 124, 2843. (c) Yoshifuji, M.; Toyota, K.; Inamoto, N. *Tetrahedron. Lett.* 1985, 26, 1727. (d) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* 1981, 20, 731. (e) Schoeller, W. W.; Niek, E. J. *Chem. Soc., Chem. Commun.* 1982, 569.
- (2) (a) Van der Knaap, T. A.; Bickelhaupt, F.; Kraaykamp, J. G.; Van Koten, G.; Bernards, J. P. C.; Edzes, H. T.; Veeman, W. S.; De Boer, E.; Baerends, E. J. *Organometallics* 1984, 3, 1804. (b) Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. J. *Chem. Soc., Chem. Commun.* 1992, 155. (c) Eshtiaq-Hosseini, H.; Kroto, H. W.; Nixon, J. F.; Maah, M. J.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* 1981, 199.
- (3) Schoeller, W. W.; Niemann, J.; Thiele, R.; Hang, W. *Chem. Ber.* 1991, 124, 417.
- (4) Yoshifuji, M.; Shima, I.; Inamoto, N. *J. Am. Chem. Soc.* 1981, 103, 4587.
- (5) Cetinkaya, B.; Hudson, A.; Lappert, M.; Goldwhit, H. J. *Chem. Soc., Chem. Commun.* 1982, 609. (b) For bis[tris(trimethylsilyl)methyl]diphosphene radical anion see also: Culcasi, M.; Gronchi, G.; Escudé, J.; Couret, C.; Pujol, L.; Tordo, P. *J. Am. Chem. Soc.* 1986, 108, 3130.
- (6) Iwasaki, M. *J. Magn. Reson.* 1974, 16, 417.
- (7) GAUSSIAN 90, Revision F. Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1990.
- (8) Amos, T.; Snyder, L. C. *J. Chem. Phys.* 1964, 41, 1773.
- (9) With the 6-31+G basis set (which incorporates diffuse functions) the optimized structure for $[\text{HP}=\text{CH}_2]^-$ is planar, and the geometry and spin densities are very similar to those found for the C_s structure optimized with the 6-31G* basis set.
- (10) Nguyen, M. T. *J. Phys. Chem.* 1987, 91, 2679.
- (11) For $[\text{CH}_3\text{P}=\text{PCH}_3]^-$ the calculated phosphorus spin densities are $\rho_s = 0.02$, $\rho_{\text{px}} = 0.48$.
- (12) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* 1978, 30, 577.
- (13) (a) Geoffroy, M.; Lucken, E. A. C.; Mazeline, C. *Mol. Phys.* 1974, 28, 839. (b) Tordo, P. *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; J. Wiley and Sons: New York, 1990; Vol. 1, p 187.
- (14) Appel, R.; Menzel, J.; Knoch, F.; Volz, P. *Z. Anorg. Allg. Chem.* 1986, 534, 100.
- (15) Buick, A. R.; Kemp, T. J.; Stone, T. J. *J. Phys. Chem.* 1970, 74, 19.