Acknowledgment. We heartily thank Dr. M. Akiyama of Rikkyo University for the use of his computer program for determining force constants. Thanks are also due to Professor E. Miki of Rikkyo University for the use of the Oxford Instrument Model DN70 cryostat.

**Registry No.** CH<sub>3</sub>COCOONa, 113-24-6; CH<sub>3</sub>CO<sup>13</sup>COONa, 87976-71-4; CH<sub>3</sub><sup>13</sup>COCOONa, 87976-70-3; <sup>13</sup>CH<sub>3</sub><sup>13</sup>COCOONa, 89196-78-1; CH<sub>3</sub>C<sup>18</sup>OCOONa, 89196-79-2.

# Electron Paramagnetic Resonance Study of $Ph_2P(O)CH_2CI^-$ Trapped in X-ray Irradiated (Chloromethyl)diphenylphosphine Oxide Crystals at 3 K and $Ph_2P(O)\dot{C}H_2$ at 77 K<sup>†</sup>

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The radical Ph<sub>2</sub>P(O)CH<sub>2</sub>Cl<sup>-</sup> is observed in 3 K X-ray irradiated crystals of (chloromethyl)diphenylphosphine oxide. The X-ray irradiation was carried out in the dark. The hyperfine coupling tensors were found to be  $A(^{35}Cl) = (40.4, 17.9, 16.1 \text{ G})$ ,  $A_1(^1\text{H}) = (24.0, 17.2, 13.1 \text{ G})$ ,  $A_2(^1\text{H}) = (25.0, 16.4, 9.0 \text{ G})$ , and  $A(^{31}\text{P}) = (42.1, 33.6, 23.8 \text{ G})$ . The g-tensor components are equal to 2.0021, 2.0040, and 2.0046. The maximium <sup>35</sup>Cl coupling and the minimum g value are located within 5° of the parent C-Cl bond direction. Upon thermal annealing to ~170 K, the anion decays and the Ph<sub>2</sub>P(O)CH<sub>2</sub> radical appears. UV photolysis of the anion at 3 K results in the disappearance of the anion and the formation of Ph<sub>2</sub>P(O)CH<sub>2</sub>. Ph<sub>2</sub>P(O)CH<sub>2</sub> decays above 230 K, giving rise to a room-temperature-stable species.

#### Introduction

Organic molecules containing heteroatoms are very sensitive to ionizing radiation. It is however difficult, in general, to propose a reaction mechanism when more than one site for electron capture is possible because not enough is yet known about the identification and structure of the primary radicals and the associated thermal and photolytic stability. Some mechanistic studies of electroncapture processes and subsequent radiation aspects have been reported for some phosphorus compounds.<sup>1</sup> Unfortunately, the corresponding experiments were carried out at 77 K with frozen glasses and powders, so comparison of principal directions to crystallographically derived directions was not possible. In the present work we study the radiolytic behavior of a molecule in which three sites can give rise—a priori—to competitive addition: (1) the benzene ring, (2) the phosphine oxide moiety, and (3) the C-Cl bond. To carry out this study, we have irradiated (chloromethyl)diphenylphosphine oxide crystals at 3 K in the dark. Electron capture in the P=O group to form a phosphoranyl radical is not detected. In addition, no clear evidence exists for electron capture in the phenyl ring to form a  $\pi^*$  anion although an unassigned EPR (line width equals 11 G) line is detected at g =2. Rather, the primary radical formed by the radiation is shown to be the radical anion  $Ph_2P(O)CH_2Cl^-$ . As the present study was performed with single crystals, direct information about the structure of this anion was obtained: (i) the directions of the hyperfine coupling tensors were compared with the bond directions of the parent molecule; (ii) the magnitude of these couplings was compared with calculated INDO spin densities. It is found that the unpaired electron is confined to an orbital aligned along the parent C-Cl bond. The INDO results indicate a lengthening of this bond during the anion formation. EPR spectra modifications induced by annealing or photolytic treatments allow us to identify two intermediates following the decay of the Ph<sub>2</sub>P(O)CH<sub>2</sub>Cl<sup>-</sup> radical.

#### Experimental Section

Crystalline plates of (chloromethyl)diphenylphosphine oxide were grown from an acetone solution by evaporation at room temperature. A recent crystal structure determination<sup>2</sup> shows that they are monoclinic and are elongated along the b axis with  $c^*$ located perpendicular to the plate. The crystal was mounted on a rotatable gear attached to the side of a  $TE_{111}$  X-band cavity. The X-ray irradiation and EPR measurement were performed in the dark with a Janis Supervaritemp Dewar. Rotation of the magnet about the tail of the Dewar, plus rotation of the gear, permitted complete rotation over all Eulerian angles. The EPR spectra were recorded on a Varian E-12 spectrometer using 270-Hz field modulation with the applied magnetic field in each of the crystallographic planes ab,  $bc^*$ , and  $c^*a$ . The magnetic field was measured with a NMR gaussmeter and the microwave frequency was measured with a Hewlett-Packard frequency counter Model 5246 L. Bleaching experiments were carried out with a Kratos variable-wavelength (200-700 nm), 1-kW (Hg/Xe lamp) illumination system.

## Results

Radical A. The EPR spectrum of (chloromethyl)diphenylphosphine oxide (Ph<sub>2</sub>P(O)CH<sub>2</sub>Cl) after irradiation in the dark at 3 K with H||(0,0,1) is given in Figure 1. The same spectrum is also observed when the irradiation and the measurement are performed at 77 K, but with less resolution of the high- and low-field lines. The stick spectrum in Figure 1a identifies one of the radicals (A) as consisting of three nonequivalent I = 1/2nuclei in the (0,0,1) direction with couplings of 35.4, 29.0, and 18.6 G, respectively, and one I = 3/2 nucleus with a coupling of 35.4 G. The largest coupling for one of the I = 1/2 nuclei accidentally equals that for I = 3/2 and thus the spectrum simplifies in this direction. The assignment of the three I = 1/2 couplings is made possible by examining the EPR spectrum of an X-ray

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TABLE I: Hyperfine Couplings and g Values for Ph<sub>2</sub>P(O)CH<sub>2</sub>Cl<sup>-a,b</sup>

	principal	direction cos <sup>d</sup>					
coupli	ngs values, <sup>c</sup> G	<i>a</i> .	b	с*	bond directions	$\Delta \Psi$ , deg	
<sup>35</sup> C	16.1 17.9 40.4	-0.8048 -0.2249 -0.5493	-0.2285 0.9715 -0.0630	$0.5478 \\ 0.0748 \\ -0.8332$	C <sub>1</sub> -Cl (-0.4890, -0.1210, -0.8639)	5.1	
'H,	-13.1 -17.2 -24.0	0.0033 0.4025 0.9154	0.9699 0.2217 -0.1010	0.2436 0.8882 0.3896	C <sub>1</sub> -H (0.1878, 0.9717, 0.1431)	12.1	
<sup>1</sup> H <sub>2</sub>	-9.0 -16.4 -25.0	$-0.7334 \\ 0.6774 \\ -0.0566$	$-0.6789 \\ -0.7341 \\ -0.0118$	$0.0335 \\ -0.0471 \\ 0.9983$	C <sub>1</sub> -H (0.8626, -0.5050, -0.0303)	13.0	
<sup>31</sup> P	23.8 33.6 42.1	-0.0505 0.7884 -0.6131	-0.9925 -0.1083 -0.0574	-0.1116 0.6056 0.7879	C <sub>1</sub> -P (-0.5620, -0.3461, 0.7513)	17.0	
g	2.0021 2.0040 2.0046	-0.5407 -0.8384 -0.0688	-0.1555 0.0192 0.9877	-0.8267 0.5447 -0.1407	C <sub>1</sub> Cl (-0.4890, -0.1210, -0.8639)	4.1	

<sup>a</sup> Radical A. <sup>b</sup> C<sub>1</sub>-O plane (-0.8269,0.1974,-0.5266), angle between this plane and  $a_p^{\text{int}} = 172.8^{\circ}$  (7.2°).



<sup>c</sup> All hyperfine couplings are accurate to  $\pm 0.3$  G and the g values are accurate to  $\pm 0.0001$ . <sup>d</sup> The direction cosines are given to four decimal places to retain orthogonality; however, due to mounting errors, the accuracy is  $\pm 5^{\circ}$ .

irradiated single crystal of  $Ph_2P(O)CD_2Cl$  at 3 K when H||(0,0,1). The four lines due to two resolved doublet couplings of 29.0 and 18.6 G for irradiated  $Ph_2P(O)CH_2Cl$  are replaced by a broadline in irradiated  $Ph_2P(O)CD_2Cl$  with unresolved structure suggesting couplings of 3-4 G. Such a change in the observed couplings is expected when protons are replaced by deuteriums. Thus, the two couplings of 29.0 and 18.6 G are due to two protons on the CH<sub>2</sub>Cl group. The remaining doublet is due to a phosphorus-31 coupling as deduced from the angular dependence observed in the *ab*, *bc*<sup>\*</sup>, and *c*<sup>\*</sup>*a* plane.

The coupling of 35.4 G when H || (0,0,1) for the  $I = \frac{3}{2}$  nucleus is due to a <sup>35</sup>Cl nucleus as additional lines due to <sup>37</sup>Cl are observed. The high- and low-field <sup>37</sup>Cl line positions calculated from a 35.4-G <sup>35</sup>Cl coupling are indicated by arrows in Figure 1a. The intensity ratio of the two lowest field lines in Figure 1a does not equal exactly 3:1, the ratio of the natural isotopic abundance of <sup>35</sup>Cl to <sup>37</sup>Cl, as accidental overlap of the <sup>37</sup>Cl line occurs with the spectral line of another radical. The presence of an additional radical is shown by bleaching radical A with 300-nm light and observing the underlying spectrum of a second radical with similar spectral width and angular dependence that does not decay upon exposure to 300-nm light. A complete study of this second radical was not carried out and its identity is unknown. At selected crystal orientations, where spectral overlap with this unknown radical does not occur, the intensity ratio of the low or the high two EPR lines for radical A equals the expected 3:1 ratio. The two proton tensors were deduced from a least-squares fit of the proton couplings measured in the ab,  $bc^*$ , and  $c^*a$  planes of the irradiated  $Ph_2P(O)CH_2Cl$  crystals. The principal values of one proton tensor equaled -13.1, -17.2, and -24.0 G while those for the second tensor equaled -9.0, -16.4, and -25.0 G. The observed anisotropy is that normally observed for  $\alpha$ -protons and thus the sign of each principal value is negative. The direction cosines for each proton tensor are given in Table I.

The chlorine and phosphorus hyperfine coupling could be measured directly in a few orientations for which the spectra were well resolved as in Figure 1. At other crystal orientations, the phosphorus coupling was measured from the spectra of irradiated  $Ph_2P(O)CD_2Cl$ . Where spectral resolution permitted, the <sup>35</sup>Cl coupling was derived from a measure of the separation between the highest field <sup>35</sup>Cl and <sup>37</sup>Cl spectral lines and equals 0.251*a*-(<sup>35</sup>Cl). When this was not possible, the chlorine coupling was estimated from the width of the spectra for irradiated Ph<sub>2</sub>P-



**Figure 1.** First derivative EPR spectrum of 3 K X-ray irradiated (chloromethyl)diphenylphosphine oxide single crystals with  $H||c^*$ : (a) at 3 K, (b) warmed to 77 K and bleached with 300-nm light, and (c) crystal under conditions in b warmed to 300 K and recooled to 77 K. The radical observed in b can also be formed by warming the sample from condition a to 170 K and then recooling to 77 K. The spectrum observed in part a is essentially unchanged if the sample is warmed to 77 K in the dark. The stick spectrum in part a denotes the spectrum of radical A as due to three nonequivalent  $I = \frac{1}{2}$  couplings and one  $I = \frac{3}{2}$  coupling with the largest  $I = \frac{1}{2}$  coupling equal to the  $I = \frac{3}{2}$  coupling. The stick spectrum in b is due to two equivalent  $I = \frac{1}{2}$  couplings and one equivalent  $I = \frac{1}{2}$  coupling. A downfield shift is observed for the spectrum in c due to a higher g value. The magnetic field scan is the same for all spectra.

(O)CH<sub>2</sub>Cl by using the following algebraic relation:  $a_{\rm H}(1) + a_{\rm H}(2) + a(^{31}P) + 3a(^{35}Cl)$  equals the spectral width.

Unfortunately, it was not possible to deduce the hyperfine coupling at all angles in the three planes for which spectra were recorded; however, at least 10 or more values for each nucleus in each plane were deduced so that a least-squares fit to the

TABLE II:	Hyperfine Couplings and g	Values for Ph <sub>2</sub> P(O)CH	<sup>2</sup> a Formed upon	Bleaching Ph <sub>2</sub> P(O)	CH <sub>2</sub> Cl <sup>-</sup> at 77 K
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	principal	direction cos <sup>d</sup>					
couplings	values, <sup>c</sup> G	a	b	c*	ref direction $\Delta V$	$\Delta \Psi$ , deg	
<sup>31</sup> P	36.3 38.1 40.4	$0.1891 \\ 0.7452 \\ -0.6395$	$\begin{array}{r} 0.8718 \\ -0.4271 \\ -0.2399 \end{array}$	0.4519 0.5121 0.7304	<i>n</i> (C, <b>-P</b> -O) (-0.8269, 0.1974, -0.5266) C <sub>1</sub> -P (-0.5620, -0.3461, 0.7513)	14.0 7.6	
<sup>1</sup> H(2) <sup>b</sup>	-16.9 -21.8 -27.8	-0.2989 -0.7564 -0.5864	-0.8377 + 0.4968 - 0.2268	-0.4629 -0.4255 0.7776	С <sub>1</sub> -Р (-0.5620, -0.3461, 0.7513)	7.1	
g	2.0023 2.0026 2.0031	$-0.6802 \\ 0.1787 \\ 0.7109$	0.1166 0.9839 -0.1358	-0.7237 -0.0095 -0.6900	<i>n</i> (C <sub>1</sub> -P-O)	14.9	

<sup>a</sup> Radical B. <sup>b</sup> Within the EPR line width, both protons appear equivalent at all crystal angles at 77 K. <sup>c</sup> All hyperfine couplings are accurate to  $\pm 0.3$  G and the g values are accurate to  $\pm 0.0001$ . <sup>d</sup> The direction cosines are given to four decimal places to retain orthogonality; however, due to mounting errors, the accuracy is  $\pm 5^{\circ}$ .

angular data could be made, resulting in the calculated tensors (A and g) listed in Table I. The signs of the chlorine hyperfine couplings have not been deduced experimentally. However, they all have been assigned a positive sign based on the following argument. If the signs of the two smaller chlorine hyperfine couplings are assumed negative, then an unusually small isotropic coupling and an unusually large anisotropic coupling are expected but are not observed. Furthermore, at some angles, the chlorine hyperfine coupling would be zero and forbidden lines would be observed and in addition the high- and low-field first-order chlorine lines would disappear at some angles. These effects are not observed.

The principal values and direction cosines of the <sup>31</sup>P tensor are given in Table I. The principal values of the <sup>31</sup>P tensor equal 42.1, 33.6, and 23.8 G and are in reasonable agreement with the  $^{31}P$ couplings reported<sup>3,4</sup> for  $Ph_3P^+CH_2$  if the signs of the couplings are assigned as all positive. The minimum g value equals 2.0021 and lies parallel to the direction of the maximum value of the chlorine tensor and within 4° of the CCl bond direction. The magnitude of the phosphorus, chlorine, and proton couplings and the direction of the maximum chlorine coupling and the minimum g value suggest that radical A is  $Ph_2P(O)CH_2Cl^-$ .

The decay characteristics of radical A were observed in two different ways: first by thermally annealing, while keeping the sample in the dark, and secondly by bleaching the sample with UV/visible light at either 3 or 77 K.

Radicals B and C. If the sample is thermally annealed to approximately 170 K, radical A decays and simultaneously a six-line spectrum due to radical B grows in. The same six-line spectrum (see Figure 1b) due to radical B appears if the sample is warmed to 77 K, where radical A is still stable, and then bleached with 300-nm light. The six-line spectrum due to radical B will also appear if radical A is bleached at 3 K with 300-nm light. Exposure of the sample to intense light at 3 K from an unfiltered Hg arc lamp not only causes the decay of radical A and the formation of radical B but also caused decay of the unidentified radical that was found underlying radical A at 3 K. The weaker EPR lines at magnetic fields higher and lower than those of the six-line pattern in Figure 1b are due largely to this unknown radical. Some residual lines due to radical A are also observed.

Angular rotation at 77 K in three orthogonal planes shows the spectrum of radical B to be due to a coupling of two equivalent protons at all angles and to a phosphorus atom. The principal hyperfine tensor components for  ${}^{31}P$ , two equivalent protons, and the g values are given in Table II. Comparison to couplings of other phosphorus-containing organic radicals<sup>3,4</sup> suggests the radical to be due to  $Ph_2P(O)CH_2$ . Warming the sample to room temperature results in the decay of radical B and the formation of radical C (Figure 1c). The spectrum of radical C is shifted

downfield from the spectra of radical A and B when  $H \parallel (0,0,1)$ because g = 2.008. Radical C has been identified as due to  $Ph_2P(O)$ ČHCl. Unfortunately the spectra are very complex and complete analysis by ENDOR techniques is required. Such a study is currently under way.

## Discussion

The crystal structure of (chloromethyl)diphenylphosphine oxide has been determined.<sup>2</sup> The compound crystallizes in monoclinic space group  $P2_1/c$  with four molecules per unit cell. Except for one intermolecular van der Walls H.HI contact distance of 2.39 Å, the crystal structure is loosely packed. The chloromethyl group is located in nearly a staggered conformation with respect to the diphenylphosphinyl moiety. The phenyl groups make quite different dihedral angles with respect to the Cl-C(1)-P plane; the P-O bond and the plane of one phenyl ring occur in nearly an eclipsed position.

A comparison is given in Table I between the crystallographic  $C_1$ -Cl,  $C_1$ - $H_1$ ,  $C_1$ - $H_2$ , and  $C_1$ -P bond directions and the directions of principal hyperfine couplings and the g tensors for  $Ph_2P(O)$ - $CH_2CI^-$ . It is to be noted that the  $C_1$ -Cl bond direction makes an angle of 5.1° to the direction of the largest chlorine coupling and the minimum g value makes an angle of 4.1° to this direction. The presence of both the minimum g values and the largest chlorine coupling occurring in the same direction would suggest the orientation of the orbital containing the unpaired electron. This direction lies very nearly parallel to the  $C_1$ -Cl bond. The  $C_1-H_1$  and  $C_1-H_2$  bond directions lie only 12.1° and 13.0° from the minimum direction coupling for protons 1 and 2 while the angle between the largest phosphorus coupling direction and the direction of the  $C_1$ -P bond equals 17.0°. The intermediate phosphorus coupling lies nearly in the C<sub>1</sub>-P-O plane.

An INDO calculation was carried out to determine the structure of  $Ph_2P(O)CH_2Cl^-$ . The recent success reported for halogensubstituted radicals using the RHF/CI method within the INDO framework described by Oloff and Huttermann<sup>5</sup> suggested it to be the method of choice.

The crystallographic bond lengths and angles were used in the starting geometry. To reduce the amount of computer time, protons were substituted for the phenyl rings since measurable unpaired spin density was not observed on the phenyl rings. Only s,  $p_x$ ,  $p_y$ , and  $p_z$  basis functions were used. Incorporation of d-orbital basis functions placed unacceptably too much spin density on chlorine and phosphorus and in general made poor agreement with experimental spin density. To permit faster SCF convergence, the starting wave function was computed for a neutralized and closed-shell system, and after converging an electron was added to form the radical, a procedure suggested by Oloff and Hutterman.5

The spin densities as a function of the C-Cl bond length are shown in Table III. The best overall fit appears when the C-Cl bond has been lengthened from 1.79 Å (crystallographic distance)

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TABLE III: Calculated INDO Spin Densities as a Function of the C-Cl Bond Length for H<sub>2</sub>P(O)CH<sub>2</sub>Cl<sup>-</sup>

			C-Cl distanc	e	
		1.79 Å	2.05 Å	2.20 Å	exptl value
C ,	2s <sup>a</sup>	0.049	0.098	0.099	0.73 <sup>c</sup>
	$2p^a$	0.091	0.248	0.327	
C1	3 s	0.025	0.026	0.018	0.015
	3p	0.189	0.349	0.413	0.16
Р	3s	0.030	0.019	0.009	0.009
	3p	0.362	0.111	0.028	0.043
0	2s	0.001	0.001	0.004	
	2p	0.075	0.039	0.025	
$H_{x}$	$1s^b$	0.012	-0.001	-0.001	
3 <sup>2</sup>	$1s^b$	0.174	0.117	0.087	

<sup>a</sup> The 2p and 3p spin density is given as a sum of the calculated unpaired spin density in the  $2p_x$ ,  $2p_y$ , and  $2p_z$  or  $3P_x$ ,  $3P_y$ , and  $3p_z$  orbitals, respectively. <sup>b</sup> Total spin densities for the two proton  $(H_x, H_y)$  substituted for the phenyl ring. The spin density is largest on  $\dot{H}_{\rm y}$  because the phenyl ring which it replaces lies nearly in the CPO plane. <sup>c</sup> Deduced from the  $\alpha$ -proton couplings using  $a_{\rm H} = -22.8\rho_{\rm c}$ . Remaining experimental values deduced from couplings given in ref 6.

TABLE IV: Hyperfine Couplings for Selected Radical Ions

 	halogen coupling, <sup>a</sup> G					
radical ion	halogen	$T_{\perp}$	$T_{\parallel}$	ref		
 CF,CI	<sup>35</sup> Cl	17.7	43.2	7		
CF₄Γ	127	178	373	7		
(CF,),CI⁻	<sup>127</sup> I	174	458	8		
RC≡CI	<sup>127</sup> I	263	639	12		
H <sub>3</sub> SiCl <sup>-</sup>	35Cl	27	50	11		

<sup>a</sup> All these anions were studied in frozen solutions.

to 2.2 Å. It appears that, as the C-Cl bond is elongated, the 2s and 2p densities on  $C_1$  increase, the densities on phosphorus decrease, and the total spin density on chlorine increases. The relation between spin density and hyperfine coupling was obtained from ref 6. It is to be noted that the chlorine and phosphorus 3s spin densities are in very good agreement with those found experimentally. The phosphorus 3p spin density is in fair agreement with that found for <sup>31</sup>P and the calculated spin density on  $C_1$  differs by nearly a factor of 2 from that deduced from the observed proton couplings. In addition, the 3p density on chlorine is too large by nearly a factor of 2.

A number of articles have appeared, in the past, attempting to differentiate between  $\sigma^*$  radicals<sup>7-12</sup> and adducts.<sup>13-15</sup> The chlorine hyperfine couplings in Ph<sub>2</sub>P(O)CH<sub>2</sub>Cl<sup>-</sup> are similar to those reported for CF<sub>3</sub>Cl<sup>-</sup> (ref 7) and H<sub>3</sub>SiCl<sup>-</sup> (ref 11) (Table IV). The experimental EPR tensors together with the INDO

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TABLE V: Isotropic Coupling Constants<sup>a</sup> for Some R, R'CH, Radicals

	$(HO)_2 P(O)\dot{CH}_2$	Ph <sub>3</sub> P <sup>+</sup> CH <sub>2</sub>	$\dot{Ph_2P(O)CH_2}$
<sup>1</sup> H	21.5	21.6	22.1
31 P	41.5	40.3	38.2
<sup>a</sup> In gauss.			

calculations show that radical A is not an adduct such as observed for  $CH_3$ ---Br<sup>13</sup> but rather a  $\sigma$  type radical with the C-Cl bond length increased by approximately 0.4 Å. Except for a shift in the C-H bond direction from that in the parent molecule, little rearrangement of the bond directions appears to have occurred upon electron addition.

The phosphorus couplings exhibit a slightly smaller isotropic and a slightly larger anisotropic value than those observed for  $(HO)_2P(O)CH_2^3$  and  $Ph_3P^+CH_2^4$ . However, the INDO calculation shows that, if the C-Cl bond does not lengthen upon electron addition, larger isotropic and anisotropic phosphorus coupling would be observed than found for  $R_2P(O)CH_2$ . Thus, the similarity between the <sup>31</sup>P coupling for  $Ph_2P(O)CH_2Cl^-$  and  $R_2P_ (O)CH_2$  is purely coincidental.

Comparison of the directions of the prinicipal hyperfine couplings of Ph<sub>2</sub>P(O)CH<sub>2</sub> suggests that some reorientation has occurred upon loss of Cl<sup>-</sup>. The minimum g value lies  $14.9^{\circ}$  from the perpendicular to the  $C_1$ -P-O plane, while the maximum phosphorus coupling lies only 7.6° from the C–P bond direction. From the tensors given in Table II, it appears that even at 77 K  $Ph_2P(O)CH_2$  undergoes rapid reorientation about a twofold axis. These data show that the rotation axis, given by the eigenvector corresponding to the maximum <sup>1</sup>H eigenvalue, is almost aligned with the C-P bond. This result agrees with our identification and we can compare the isotropic <sup>31</sup>P and <sup>1</sup>H coupling constants with those obtained for  $(OH)_2P(O)\dot{C}H_2^3$  and  $Ph_3P^+\dot{C}H_2^4$  A comparison of the isotropic couplings is given in Table V and indicates that the three radicals have the same structure. It was previously shown from the <sup>13</sup>C coupling in Ph<sub>3</sub>P<sup>+13</sup>CH<sub>2</sub> that the unpaired electron is localized in a  $2p_z$  orbital of an sp<sup>2</sup> hybridized carbon. It is therefore certain that  $Ph_2P(O)CH_2$  is a planar carbon-centered radical.

From a radiation chemistry point of view Ph<sub>2</sub>P(O)CH<sub>2</sub>Cl is a particularly interesting molecule because three sites are present for an electron capture. Moreover, phosphine oxide moieties are expected to play an important role when irradiating biological compounds: electron capture leads to the phosphoranyl radical  $R_2P(O^-)R'$ , which has been proposed as the primary damage in nucleic acids.<sup>16</sup> In the case of  $Ph_2P(O)CH_2Cl$ , the present results show that electron capture occurs to give  $Ph_2P(O)CH_2Cl^-$  and does not lead to the formation of Ph2P(O<sup>-</sup>)CH2Cl (which would be characterized by a large <sup>31</sup>P coupling). As the Ph<sub>2</sub>P(O) $\dot{C}H_2$ radical is shown to be planar, the formation of the present anion illustrates the fact that the change in the structure of R (planar or pyramidal) by passing from RX to R. is not the only factor to consider when predicting the formation and stability of the anion RX<sup>-.9,10</sup>

Acknowledgment. This work was supported by the U.S. Department of Energy (Office of Basic Energy Sciences).

Registry No. A, 89302-49-8; B, 89302-50-1; C, 89302-51-2; (HO)<sub>2</sub>P(O)CH<sub>2</sub>, 54888-97-0; Ph<sub>3</sub>P<sup>+</sup>CH<sub>2</sub>, 56898-80-7; Ph<sub>2</sub>P(O)CH<sub>2</sub>Cl, 1806-49-1.

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