of the distances in **1** with crystallographic data for complexes with other coordination numbers[7] establishes an average increase in the Hg–S distance of 0.1 Å in the series of mononuclear $Hg(SR)_n$ complexes where $n = 2, 3, 4$, underscoring the interpretation of the Hg–MerR EXAFS studies.[4] In combination, these data indicate that **1** is the closest model for the metal-receptor site in Hg–MerR to date and strongly support the tridentate $Hg(S\text{-}Cys)_3$ center proposed for this biosensor.

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Note Added in Proof. The structure of an additional tricoordinate Hg(II) complex with aromatic thiolates has recently been reported: Gruff, E. S.; Koch, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 1245.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and thermal parameters for **1** (5 pages); table of structure factors for **1** (24 pages). Ordering information is given on any current masthead page.

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(19) $Hg(SEt)_2$ and $Hg(SPr^i)_2$ were prepared by a modification of the method of Wertheim, E. (*J. Am. Chem. Soc.* **1929**, *51*, 3661). A methanol solution of the appropriate thiol was added to a solution of $Hg(NO_3)_2{\cdot}H_2O$ in methanol. The precipitated product was then collected, washed with methanol, and dried in vacuo. $Hg(SEt)_2$: mp 73–75 °C (lit. mp 72–73 °C); ^1H NMR (DMSO) δ 1.29 (t, 3 H), 2.93 (q, 2 H). $Hg(S^iPr)_2$: mp 61–62 °C (lit. mp 62–63 °C); ^1H NMR (DMSO) δ 1.32 (d, 6 H), 3.59 (m, 1 H).

Trapping and ESR Study of an Allylic Radical Involving the Participation of a Phosphoranyl Moiety: $(R_3P\overset{\cdots}{-}CH\overset{\cdots}{-}CR_2)^{\bullet}$

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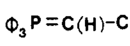
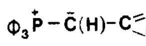
Allyl radicals play a fundamental role in both theoretical and experimental chemistry:[1] they are the simplest example of a species exhibiting negative spin density on a carbon atom, and their stability, which depends upon the nature of the substituents, has been the subject of considerable work in radical chemistry (e.g., captodative effects[2]). In this context, the electronic structure of allylic radicals containing a heteroatom has been intensively investigated, and species like $[CH_2N(H)CH_2]^{\bullet+}$,[3] $(CH_2OCH_2)^{\bullet+}$,[4] and $(R_2CNCR_2)^{\bullet}$[5] have been trapped recently. An allyl radical containing a phosphorus atom has, however, never been observed. Previous experiments[6] have led to the conclusion that, for $(R_3PCHCH_2)^{\bullet}$, the unpaired electron is mainly localized on the terminal carbon and the real structure of this radical is in fact $R_3P^+C^-(H)CH_2^{\bullet}$.

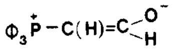
In order to produce a phosphorus-containing radical having a true allylic structure, we have tried to stabilize the contribution of the phosphoranyl radical form $R_3P^{\bullet}{-}CH{=}C(R')H$ by using a precursor bearing a strong electron-donating substituent R′. The (triphenylphosphoranylidene)acetaldehyde molecule (I), a well-known Wittig reagent, has been selected because its mesomeric form (Ic) suggests that an electron-capture process could yield the desired species (II).


$\Phi_3P{=}C(H){-}C^{\,=O}_{\,-H}$

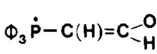
Ia


$\Phi_3\overset{+}{P}{-}\overset{-}{C}(H){-}C^{\,=O}_{\,-H}$

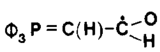
Ib


$\Phi_3\overset{+}{P}{-}C(H){=}C^{\,-O^-}_{\,-H}$

Ic


$\Phi_3\dot{P}{-}C(H){=}C^{\,-O^-}_{\,-H}$

IIa


$\Phi_3P{=}C(H){-}\dot{C}^{\,-O^-}_{\,-H}$

IIb

We have determined the crystal structure[7,8] of I; in accordance with a phosphoranylidene structure,[9] we find that P–C = 1.709 Å, C–C = 1.384 Å, C–O = 1.248 Å, the four CPC angles are close to the tetrahedral angle, and the PCCO atoms are coplanar. After X-ray irradiation at room temperature, performed to cause the electron-capture process, a single crystal of I has been studied by ESR. One day after irradiation, the spectrum is composed of signals A, which decrease slowly with time and exhibit coupling with a ^{31}P (large splitting) and a ^1H (small splitting) nucleus, and stable central lines C. The angular dependence of signals A leads to the ESR tensors given in Table I. The eigenvalues and eigenvectors of the magnetic hyperfine tensors will be denoted by T and $\vec{T}$, respectively.

The coupling tensors are decomposed into isotropic (A_{iso}) and anisotropic coupling constants (τ) (Table I) by assuming that all ^{31}P hyperfine eigenvalues are positive and that all ^1H hyperfine eigenvalues are negative. The phosphorus spin densities (Table I) are estimated by comparing ^{31}P-A_{iso} and ^{31}P-τ_{max} with the atomic constant respectively associated with a phosphorus 3s electron (A_{iso} = 13 300 MHz) and a phosphorus 3p electron ($2B_0$ = 733 MHz).[10] The ^{31}P hyperfine interaction for a σ^* phosphoranyl radical is known to be very large (for Ph_3PCl,[11] ^{31}P-A_{iso} = 1690 MHz, ^{31}P-τ_{max} = 325 MHz) and is not consistent with the experimental values given in Table I. On the other hand, this experimental ^{31}P hyperfine interaction is too large to be due to $R_3P^+C(R)H^{\bullet}$ [for $(C_6H_5)_3P^+CH_2^{\bullet}$, ^{31}P-A_{iso} = 110 MHz, ^{31}P-τ_{max} = 9 MHz[12]] and is also considerably larger than that reported for $(MeO)_2(Me)P^+C^-(H)CH_2^{\bullet}$ (A_{iso} = 50 MHz).[6] It is well-known[13] that, in an $R_2CH^{\bullet}$ radical, the ^1H anisotropic coupling constants are expected to be near τ_{max} = 43 MHz, $\tau_{intermediate}$ = −5 MHz, and τ_{min} = −38 MHz and that the ^1H-T_2 eigenvector (associated with $\tau_{intermediate}$) is aligned along the carbon p_π orbital. The experimental ^1H anisotropic coupling constants shown in Table I are quite consistent with such an $R_2CH^{\bullet}$ fragment containing 35% of the total spin density. Moreover, this spin population is also in accordance with the value derived from the isotropic coupling

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(8) I crystallizes in the monoclinic space group $C2/c$ with a = 18.418 (2) Å, b = 9.8254 (14) Å, c = 18.555 (4) Å, β = 93.64 (1)°, V = 3351.0 (9) Å^3, Z = 8, and λ(Mo Kα) = 0.71069 Å; a Philips PW100 diffractometer was used to collect 2628 reflections in the range 2° > 2θ > 46°. Refinement of 181 parameters, R_w = 0.056. The quality of fit index is 1.9.

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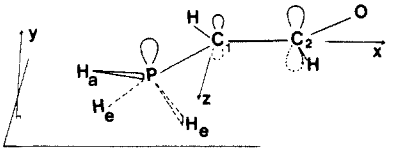
Table I. ESR Tensors (MHz) Measured for Signals A and Calculated Couplings for $[H_3PCHC(O)H]^{\bullet -}$

tensor	eigenvalues	eigenvectors[a]	anisotropic couplings	spin densities	calcd couplings[c]
$\bar{g}$	2.0023	0.035, −0.9612, 0.2736			
	2.0051	0.3810, +0.2659, 0.8855			
	2.0065	−0.9239, +0.0733, 0.3755			
$^{31}P\text{-}\bar{T}$	(+)879	−0.3346, −0.7923, 0.5102	τ_1, = (+)225	$\rho_p = 0.30$	$\tau_1' = 167$
	(+)538		τ_2 = (−)116		$\tau_2' = -92$
	(+)546		τ_3 = (−)108		$\tau_3' = -74$
	A_{iso} = (+)654			$\rho_s = 0.045$	$A_{iso} = 225$
$^{1}H\text{-}\bar{T}$	(−)4	0.7684, 0.2557, 0.5867	τ_1 = (+)16.3		$\tau_1' = 11.4$
	(−)22	−0.1582, −0.8124, 0.5613	τ_2 = (−)1.7		$\tau_2' = -3.0$
	(−)35	−0.6201, 0.5241, 0.5838	τ_3 = (−)14.7		$\tau_3' = -8.4$
	A_{iso} = (−)20.3			$\rho_c = 0.31$[b]	$A_{iso} = -16.5$

[a] ESR reference frame: $-0x//c, -0y//b, -0z//a^*$. [b] Estimated spin density on the carbon bound to the proton. [c] Hyperfine couplings calculated for structure III.

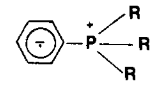
constant [$\rho_c = A_{iso}/A(^{\bullet}CH_3) = 0.31$]. The orientation of the phosphorus p orbital which participates in the SOMO is given by the eigenvector associated with the maximum phosphorus anisotropic coupling, $^{31}P\text{-}\vec{T}_{max}$. This direction is found to be rather close to that of the radical carbon p_π orbital since the angle ($^1H\text{-}\vec{T}_2$, $^{31}P\text{-}\vec{T}_{max}$) is equal to only 10°. These properties agree with those expected for a $(R_3P\overset{..}{-}CH\overset{..}{-}C(O^-)H)^{\bullet}$ radical, but the π direction does not coincide with the direction perpendicular to the CCP plane in the crystal. We have therefore used ab initio calculations[14,15] in order to get information about the spin densities and hyperfine coupling tensors for some selected geometries of $(H_3PCHC(O)H)^{\bullet -}$. We could not find any acceptable agreement between experimental and calculated results when the tetrahedral coordination of the phosphorus, observed in the crystal structure, was maintained. A good accord was found, however, by imposing a trigonal-bipyramidal structure on the phosphoranyl moiety (structure III): $\angle C(1)PH_a = 150°$, $\angle C(1)PH_e = 100°$, and $\angle PC(1)C(2) = 119°$.



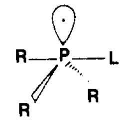
III

The calculated spin densities and hyperfine tensors are very sensitive to the P–C and C–C lengths; we give, in Table I, the coupling parameters calculated for C(1)–C(2) = 1.48 Å, P–C(1) = 1.7 Å, and C–O = 1.46 Å. The unpaired electron is mainly delocalized in atomic p_y orbitals [$\rho_y(P) = 0.36$, $\rho_y(C1) = -0.10$, $\rho_y(C2) = 0.26$, $\rho_y(O) = 0.12$] and in a phosphorus s orbital [$\rho_s(P) = 0.07$]. A small spin density ($\rho_z = 0.09$) is also found in the phosphorus p_z orbital. The calculated tensors lead to a ($^{31}P\text{-}\vec{T}_{\parallel}$, $^1H\text{-}\vec{\tau}_2$) angle equal to 14°. The small negative spin density on the central carbon explains why a second ^1H coupling is not observed on the ESR spectrum (line width ~ 4 G), and the reorganization of the ligands around the phosphorus atom is certainly the cause of the reorientation of the normal to the PCC plane.

The role of the R′ group in the stabilization of the allylic structure, $(R_3P\overset{..}{-}C(H)\overset{..}{-}C(H)R')^{\bullet}$, lies therefore in its ability to destabilize a phosphonium moiety. When R′ is an electrodonor group, it makes more difficult the transfer of an electron from the phosphorus toward the ethylenic system [which would yield the analogue of the previously reported structure IVa for the phosphoranyl radical $(C_6H_5)PR_3$[16]] and so allows conjugation of the equatorial phosphoranyl orbital (TBP structure, IVb) with the π system of the olefin moiety L.[17]



IVa



IVb

Acknowledgment. We thank the Swiss National Research Fund for their support.

Supplementary Material Available: ESR spectrum and angular variation of the signals and a listing of crystallographic data including atomic coordinates and bond lengths and angles for $Ph_3P{=}CHC(O)H$ (8 pages). Ordering information is given on any current masthead page.

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[17] Studies are underway to detect other delocalized radicals derived from phosphoranes and to optimize the structure of some phosphoallyl radicals.

Cloth-like Aggregates of Micellar Fibers Made of *N*-Dodecyltartaric Acid Monoamides

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Amphiphiles with an electroneutral glyconamide head group and *N*-alkyl chains ranging from C-7 to C-12 form micellar fibers of bimolecular thickness in aqueous solution that are stabilized by amide hydrogen-bond chains.[1] At elevated temperatures and/or in the presence of detergents, such fibers are long-lived,[2] but at room temperature, the pure amphiphiles usually precipitate within a few hours. From anionic polymer fibers it is known that the repulsive interaction of negatively charged surfaces, e.g., in tobacco mosaic virus (TMV),[3,4] keeps fibers apart from each other. We therefore investigated several chiral and anionic amphiphiles, for example, the tartaric amide monocarboxylates **1a,b**,[5] for their

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