ethyl ether is less than 15 ps and is at the limit of our instrumental resolution.[13] Nanosecond transient absorption measurements[14] on excited **1** show the characteristic absorption maximum at 700 nm for the anthracene radical anion.[15] The decay time of the 700-nm transient absorption feature agrees very well with the decay time of the exciplex-like luminescence in **1**, Table I. Thus, we suggest that the exciplex-like luminescence from excited **1** is radiative ion-pair recombination. A parallel mode of decay of the ion pair of **1** is also observed by monitoring the rise of the lowest excited triplet state of anthracene at 430 nm. This rise time parallels the decay time of the transient absorption at 700 nm.

These results suggest that intramolecular electron transfer in **1** occurs with a rate constant $>7 \times 10^{10}$ s^{-1} to yield a species that exhibits properties commonly attributed to both a radical ion pair and an exciplex without the large changes in molecular geometry normally requisite for exciplex formation. The efficient formation of the ion pair in **1** is presumably due to significant electronic coupling of the chromophores across the single saturated carbon atom bridges joining the chromophores. Further investigations on this and related molecules are underway in our laboratories to ascertain the conditions under which radical ion pairs decay radiatively to the ground state.

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Supplementary Material Available: Scheme outlining the synthesis of **1** and listing of physical data for **1** including HRMS, (electron impact), 500-MHz ^{1}H NMR data, and a graph of emission frequency of **1** vs solent polarity factor (3 pages). Ordering information is given on any current masthead page.

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Trigonal Mercuric Complex of an Aliphatic Thiolate: A Spectroscopic and Structural Model for the Receptor Site in the Hg(II) Biosensor MerR

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As the heavy metal receptor component of an Hg(II)-responsive genetic switch, the MerR metalloregulatory protein[1,2] has been shown to possess nanomolar mercuric ion sensitivity and a 10^2–10^3-fold selectivity for Hg(II) over other soft metals such as Cd(II), Zn(II), and Au(I).[3] Results from X-ray absorption,[4] chemical protection studies, and mutagenesis studies on Hg–MerR have been interpreted in terms of models with two,[5a,b] three,[4,5c] or four[5,6] cysteines coordinating to Hg(II) in the metal-receptor site. Further elucidation of the coordination number and chemistry underlying mercuric ion recognition by MerR has been hampered by the absence of spectroscopic probes and appropriate three- and four-coordinate mercuric thiolate model complexes.[7] We report evidence from spectroscopic and structural studies of a trigonal mercuric complex of an aliphatic thiolate, $[Et_4N][Hg(SBu^t)_3]$ (**1**), and from spectroscopic studies of Hg–MerR that Hg(II) is coordinated to *three* cysteines in the latter. Distorted four-coordinate

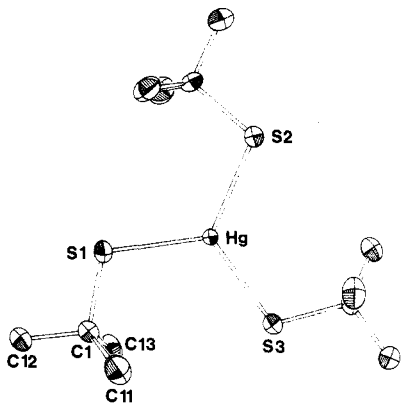

Figure 1. ORTEP drawing of $[Hg(SBu^t)_3]^{1-}$ (**1**), showing 50% thermal probability ellipsoids. Selected bond distances (Å) and angles (deg): Hg-S1, 2.438 (1); Hg-S2, 2.451 (1); Hg-S3, 2.436 (1); S1-Hg-S2, 121.24 (4); S1-Hg-S3, 120.85 (4); S2-Hg-S3, 117.90 (4). Mean Hg displacement from the S1-S2-S3 plane: 0.0185 Å.

Table I. Principal Electronic Transitions in Hg(II)–Thiolate Complexes

Hg complex	λ_{max}, nm	$\Delta\epsilon$,[a] M^{-1} cm^{-1}	ϵ, M^{-1} cm^{-1}	ref
Neurospora Hg_3–MT[b]	283	8800		8
Hg_7–MT	304	NR[f]		9
Hg–plastocyanin	247	9800		10
	280 (sh)[b]	2130		
Hg–MerR[c]	240	16620		this work
	260 (sh)	11150		
	290 (sh)	4120		
$[Et_4N][Hg(SBu^t)_3]$[d]	235		24000	this work
	260 (sh)		17700	
$Hg(SEt)_2$[e]	228 (sh)		4700	this work
	282 (sh)		740	
$Hg(SPr^i)_2$	228 (sh)		3400	this work
	262 (sh)		650	

[a] $\Delta\epsilon = \epsilon_{Hg\text{-}protein} - \epsilon_{protein}$. [b] MT = metallothionein; sh = shoulder. [c] See Figure 2 for experimental details; mean value of five separate titrations. Largest deviation from mean <3%. [d] Data obtained from Beer's law plot in concentration range $(2-5) \times 10^{-3}$ M. ϵ_{235} for $[Et_4N][SBu^t]$ = 500 M^{-1} cm^{-1}. [e] 5×10^{-3} M in acetonitrile. Single measurement; see ref 19 for preparation of compounds. [f] NR = not reported.

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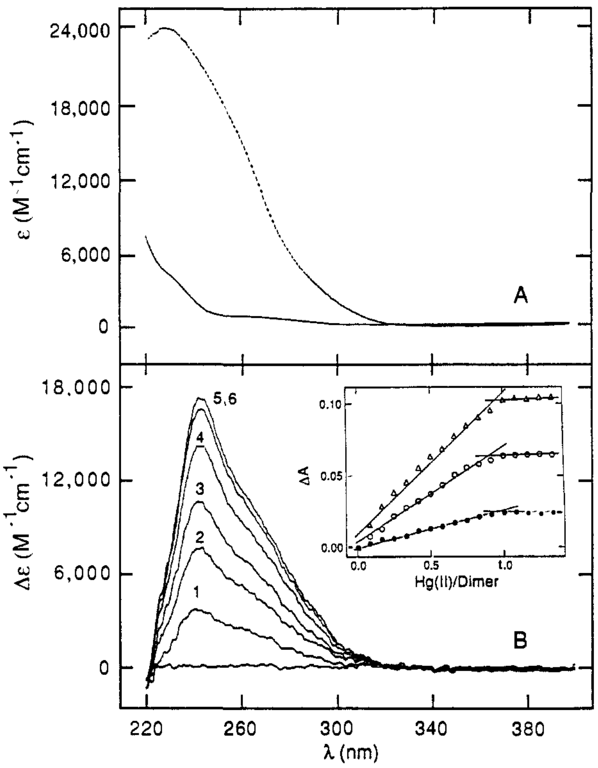

Figure 2. (A) UV spectra of model complexes: solid line, 0.005 M $Hg(SEt)_2$ in acetonitrile; dashed line, 0.005 M $[Et_4N][Hg(SBu^t)_3]$ in acetonitrile. (B) UV difference spectra of Hg–MerR complex. Spectra were obtained under anaerobic conditions by addition of an $HgCl_2$ solution to a 6×10^{-6} M solution of the protein dimer in 0.01 M sodium phosphate pH 7.00, 1 M NaCl, 0.001 M 2-mercaptoethanol, and 0.1% w/v β-*n*-octylglucopyranoside. Spectra 1–6 represent addition of 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 equiv of Hg(II)/MerR dimer, respectively. Inset: plot of absorbance change vs ratio of Hg(II) to MerR dimer, demonstrating 1:1 stoichiometry of complex (●, −290 nm; ○, −260 nm; △, −240 nm). MerR was purified as previously described.[2]

environments have been postulated for several other Hg-substituted proteins based on the presence of low-energy UV transitions,[8-10] but such assignments have not been verified in either of the structurally characterized $Hg(SR)_n$ (n = 3,4)[11,12] mononuclear complexes because both contain aromatic ligands that obscure the metal–ligand charge-transfer transitions. We now show that similar transitions are observed in solutions of **1**, and we find a close correlation between ligand-to-metal charge-transfer (LMCT) transitions in the UV spectra of Hg–MerR and of **1**. This trigonal model, the first crystallographically characterized example of a mononuclear Hg(II) *aliphatic* thiolate complex with a primary coordination number greater than 2, also shows a close structural correspondence to the mercuric environment in Hg–MerR. Hg–S bond distances determined for **1** are shown to be the same within experimental error as those reported in EXAFS studies of Hg–MerR,[4] providing further support for a primary mercuric thiolate coordination number of 3.

Using a combination of X-ray crystallography and solution and solid-state ^{199}Hg NMR, we demonstrate that **1** is a trigonal-planar anion in the solid state and in acetonitrile solution. Single crystals of **1**, synthesized by the method of Bowmaker et al.,[13] were obtained by slow evaporation from an ethanol/water mixture. The structure[14] consists of regular trigonal-planar anions, with S–Hg–S bond angles close to 120° (Figure 1). UV absorbance spectra for **1** and analogous bis(alkylthiolate) complexes are shown in Figure 2A and summarized in Table I. Direct correspondence of the ^{199}Hg chemical shifts for **1** in the solid state and in acetonitrile indicates that the major species in solution is the trigonal-planar anion under conditions used for UV spectral measurement.[15] Bands arising from **1** in the region between 230 and 280 nm are assigned as S → Hg LMCT bands on the basis of intensity and solvent dependence[16] and are not found in solutions of bis complexes such as $Hg(SEt)_2$ (Figure 2A). Similar bands of lower intensity, observed in Hg-plastocyanin[10] and two types of Hg-metallothionein,[8,9] were attributed to LMCT transitions arising from distorted tetrahedral Hg(S-Cys) centers. We thus find that intense electronic transitions previously assigned to distorted tetrahedral coordination environments in Hg-proteins can arise from trigonal planar $Hg(SR)_3$ complexes of alkylthiolates, but are absent in spectra of linear bis(thiolates).

Difference spectra for the Hg–MerR complex over a range of mercury concentrations are shown in Figure 2B. The maxima at 240 nm, like the shoulders at 260 and 290 nm, increase as a function of added mercuric ion until an endpoint is observed at metal ion:MerR dimer ratios of ca. 1:1 (Figure 2B, inset). The 1:1 ratio is consistent with the stoichiometry previously determined by gel filtration and dialysis experiments[1c,2] and thus confirms that the chromophore corresponds to specific Hg(II) receptor interactions. The magnitudes of the extinction coefficients ($\Delta\epsilon_{240}$ = 16620 M^{-1} cm^{-1} and $\Delta\epsilon_{290}$ = 4120 M^{-1} cm^{-1}) support assignment of these bands as charge-transfer transitions. As shown in Figure 2A, these bands are absent in the spectra of linear two-coordinate thiolate complexes, ruling out this mode of coordination for the Hg–MerR complex. Extinction coefficients for Hg–MerR and **1** are much larger than those found for the structurally characterized Hg–plastocyanin,[10] where the ligands include one cysteine thiolate, two histidines, and a weakly bound methionine,[17] suggesting that the coordination environments in these two Hg-proteins are different. The direct correlation of low-energy UV transitions in **1** and Hg–MerR rules out linear bis coordination and indicates either three- or four-coordination in this protein. In the absence of spectroscopic data on additional model compounds, primary coordination environments corresponding to HgS_2N_n (n = 1,2) cannot be ruled out.

Strong support for a three-coordinate environment comes from the observation that the average Hg–S bond distance in **1** (2.442 (10) Å) is the same within experimental error as that determined from recent EXAFS data for Hg–MerR (2.43 (2) Å).[4] The average Hg–S bond length in **1** is also comparable to that observed in the only other crystallographically characterized three-coordinate mercury thiolate complex, $[(Bu^n)_4N][Hg(SPh)_3]$[11] (2.448 Å) and to the Hg–S distance determined from solution X-ray scattering studies of mercuric thiolate complexes.[18] Comparison

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(14) $[(C_2H_5)_4N][Hg(SC_4H_9)_3]$, *Mr* = 598.37; monoclinic space group $P2_1/n$ (No. 14); a = 11.539 (1) Å, b = 11.046 (1) Å, c = 21.027 (2) Å, β = 90.65 (1)°, V = 2679.9(7) $Å^3$; Z = 4; D_{calcd} = 1.48 g cm^{-3}; μ (Mo Kα) 59.70 cm^{-1}. The structure was solved by the heavy-atom method and refined with Texsan 4.0. Full-matrix least-squares refinement yielded $R(F)$ = 0.025 and $R_w(F)$ = 0.032 for 3548 reflections with $I > 3\sigma(I)$ measured on an Enraf-Nonius CAD4 diffractometer, 2θ = 4–50° at −120 °C.

(15) Because ligand dissociation was observed at low concentration, the composition of solutions used in UV experiments was confirmed by using ^{199}Hg NMR spectroscopy. The chemical shift of a 7.5 mM CH_3CN solution of **1** gives δ = −160 ppm (relative to $HgMe_2$). This is in close agreement with the chemical shift obtained by solid-state CPMAS NMR (δ = −158 ppm). Further details may be found in the following: Natan, M. J.; Millikan, C. F.; Wright, J. G.; O'Halloran, T. V. *J. Am. Chem. Soc.* In press.

(16) UV spectra were obtained by using a 0.205 mm path length quartz cell, calibrated by using $K_3Fe(CN)_6$ (ϵ_{418} = 1030 M^{-1} cm^{-1}). Spectra obtained in ethanol display similar characteristics to the acetonitrile spectra, but the positions of the absorption bands are blue-shifted by approximately 10 nm.

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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.

Acknowledgment. This work was supported by NIH Grant GM 38784 to T.V.O. Additional support was provided by the Searle Scholars Program of the Chicago Community Trust, an NSF Presidential Young Investigator Award (CHE-8657704), and grants from the Exxon Educational Foundation and the Gillette Company to T.V.O. We thank C. Millikan for crystallization of **1** and discussion of solid-state NMR measurements and S. Johnson, M. J. Natan, and D. Ralston for helpful discussions.

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: $(R_3P\overset{\cdots}{-}CH\overset{\cdots}{-}CR_2)^{\cdot}$

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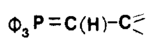
Allyl radicals play a fundamental role in both theoretical and experimental chemistry:[1] they are the simplest example of a species exhibiting negative spin density on a carbon atom, and their stability, which depends upon the nature of the substituents, has been the subject of considerable work in 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 $[CH_2N(H)CH_2]^{\cdot+}$,[3] $(CH_2OCH_2)^{\cdot+}$,[4] and $(R_2CNCR_2)^{\cdot}$[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 $(R_3PCHCH_2)^{\cdot}$, the unpaired electron is mainly localized on the terminal carbon and the real structure of this radical is in fact $R_3P^+C^-(H)CH_2^{\cdot}$.

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 $R_3P^{\cdot}{-}CH{=}C(R')H$ 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).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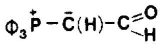
Ia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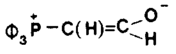
Ib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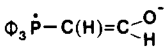
Ic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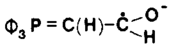
IIa


$\Phi_3\mathrm{P}{=}\mathrm{C(H)}{-}\dot{\mathrm{C}}\genfrac{}{}{0pt}{}{-\mathrm{O}^-}{-\mathrm{H}}$

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 $^{31}P\text{-}A_{iso}$ and $^{31}P\text{-}\tau_{max}$ 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] $^{31}P\text{-}A_{iso}$ = 1690 MHz, $^{31}P\text{-}\tau_{max}$ = 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 $R_3P^+C(R)H^{\cdot}$ [for $(C_6H_5)_3P^+CH_2^{\cdot}$, $^{31}P\text{-}A_{iso}$ = 110 MHz, $^{31}P\text{-}\tau_{max}$ = 9 MHz[12]] and is also considerably larger than that reported for $(MeO)_2(Me)P^+C^-(H)CH_2^{\cdot}$ (A_{iso} = 50 MHz).[6] It is well-known[13] that, in an $R_2CH^{\cdot}$ 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 $^1H\text{-}\vec{T}_2$ 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 $R_2CH^{\cdot}$ 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) = 0.710 69 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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