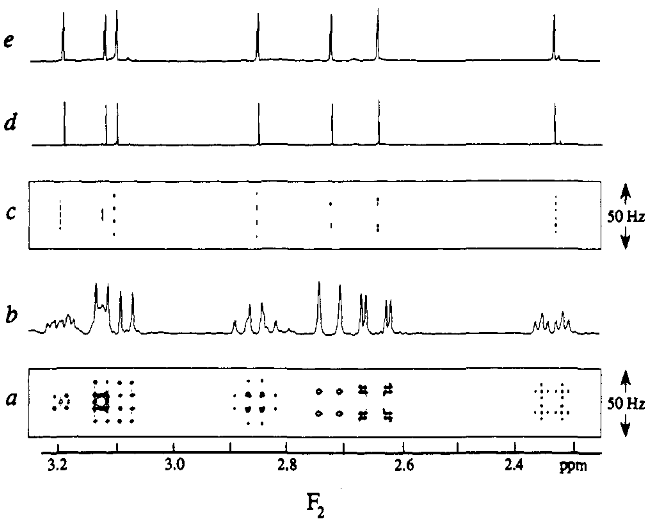

Figure 1. (a) Part of the two-dimensional *J*-spectrum of strychnine recorded by the new method; (b) projection onto the F_2 axis; (c) after symmetrization and suppression of the splittings in the F_2 dimension; (d) projection onto the F_2 axis; (e) after reimposition of the instrumental line width. Note the uniformity of the intensities.

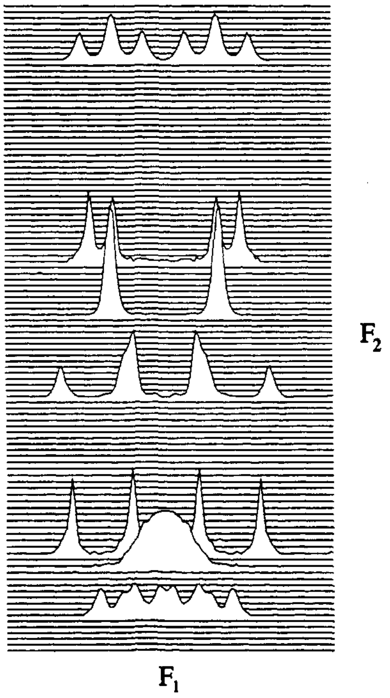

Figure 2. Stacked trace display of the spectrum shown in Figure 1c. For clarity of reproduction only every tenth trace is shown.

the lower intensity at both locations.[12] This operation is carried out on a 50-Hz square data matrix centered on the coordinates $F_1 = 0$, $F_2 = x$ Hz, where x is incremented to scan through all data points along the F_2 axis. After symmetrization, the total integrated signal intensity within the 50-Hz test square remains at a low value unless x has reached a center of C_4 symmetry. Once this center has been identified, all signals within the test region are projected onto a single F_1 trace passing through the center of symmetry, giving the spin multiplet pattern for that particular chemical site. Overlap between adjacent multiplets is handled by subtracting the symmetrized multiplet patterns from the raw experimental data one at a time, if necessary by a gradual iterative procedure.[4]

Projection of each separated multiplet trace onto the F_2 axis gives a single sharp peak at the chemical shift frequency. The height represents the integrated intensity from the chemical site in question; ideally, all intensities would be equal for single-proton sites. The symmetrization operation is very sensitive to the F_2 frequency, so these lines are artifically narrow, essentially only one data point wide. This does not imply a comparably high resolving power for overlapping responses, and to emphasize this point, a Gaussian line width has been imposed (by repeated 1:2:1 convolution) on the final chemical shift spectrum. Although the symmetry filter works well for first-order coupling, strong coupling distorts the intensities and slightly displaces the apparent chemical shifts.

Experimental tests were carried out on the 400-MHz proton spectrum of strychnine recorded on a Varian VXR-400 spectrometer; a region between 2.3 and 3.2 ppm is examined in Figure 1. Each chemically distinct site has *J*-splittings in both dimensions (Figure 1a) with local C_4 symmetry. Figure 1b shows the projection on the F_2 axis, giving a trace essentially identical with the conventional (coupled) high-resolution spectrum. The spin-spin splitting in the F_2 dimension may be suppressed (Figure 1c) once the symmetry centers (Figure 1d) have been located. Note the uniformity of the intensities. Figure 1e shows the chemical shift spectrum with a 1.2 Hz instrumental line width reimposed. The information is perhaps most effectively displayed as a stacked-trace plot (Figure 2) with the individual spin multiplets in the F_1 dimension and the chemical shifts in the F_2 dimension.

Acknowledgment. We thank James Keeler for illuminating discussions and for information about the adiabatic pulse scheme[9] prior to publication.

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Synthesis and Structural Characterization of a Novel Cluster with a Ga-P Framework

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Recent investigations in this laboratory concerning the formation of novel quasi-aromatic rings such as $(RBPR')_3$,[1] $(RAlNR')_3$,[2] and $(GeNR)_3$,[3] (R and R' = variety of bulky alkyl or aryl groups) have suggested that similar rings comprising exclusively heavier main-group elements could be isolated as stable entities. This goal has been partially realized through the synthesis of the zinc-sulfur ring systems $(RZnSR')_3$[4,5] which possess almost planar Zn_3S_3 arrays.[4,5] In addition, the synthesis of an organogallium-arsenic cluster $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ (R = CH_2SiMe_3) has given grounds for confidence that the proposed unsaturated rings can be synthesized if the appropriate substituents were selected.[6] As part of an experimental program designed to attain this objective, we report here on the synthesis and characterization of the novel gallium phosphide cluster species $[Ga_4(Trip)_3\{P(1\text{-}Ad)_4\}P(H)(1\text{-}Ad)]$, **1** [1-Ad = 1-adamantyl, Trip = 2,4,6-$(i\text{-}Pr)_3C_6H_2$].

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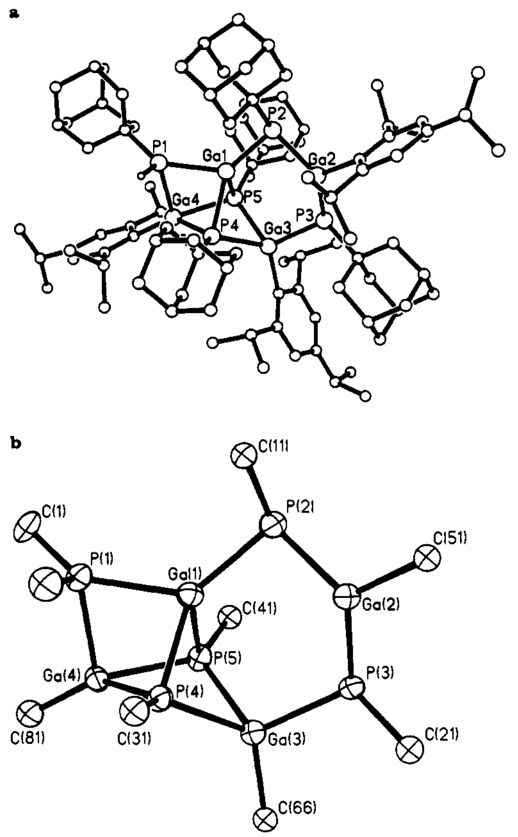

Figure 1. Schematic drawings of (a) $[Ga_4(Trip)_3\{P(1\text{-}Ad)\}_4P(H)(1\text{-}Ad)]$ and (b) core atoms and substituent carbons. Important bond distances (Å) and angles (deg): Ga(1)–P(1) = 2.443 (3), Ga(1)–P(2) = 2.295 (4), Ga(1)–P(4) = 2.400 (4), Ga(1)–P(5) = 2.374 (4), Ga(2)–P(2) = 2.320 (4), Ga(2)–P(3) = 2.290 (4), Ga(3)–P(3) = 2.370 (3), Ga(3)–P(4) = 2.475 (4), Ga(4)–P(4) = 2.434 (4), Ga(4)–P(5) = 2.432 (3), Ga(2)–C(51) = 1.985 (11), Ga(3)–C(66) = 2.061 (13), Ga(4)–C(81) = 1.985 (10), P(1)–C(1) = 1.871 (15), P(2)–C(11) = 1.875 (12), P(3)–C(21) = 1.891 (14), P(4)–C(31) = 1.898 (13), P(5)–C(41) = 1.882 (14), P(1)–H = 1.4, P(2)Ga(1)P(5) = 117.0 (1), P(2)Ga(1)P(4) = 136.1 (1), P(2)Ga(2)P(3) = 113.5 (1), P(3)Ga(3)P(4) = 114.5 (1), P(3)Ga(3)P(5) = 106.4 (1), P(1)Ga(1)P(4) = 86.2 (1), P(1)Ga(1)P(5) = 93.6 (1), P(1)Ga(4)P(4) = 86.4 (1), P(1)Ga(4)P(5) = 93.3 (1), Ga(1)P(2)Ga(2) = 96.4 (2), Ga(2)P(3)Ga(3) = 114.0 (1), Ga(1)P(4)Ga(3) = 86.1 (1), Ga(1)P(5)Ga(3) = 87.7 (1), Ga(1)P(1)Ga(4) = 76.8, Ga(1)P(2)C(11) = 107.1 (3), Ga(2)P(2)C(11) = 113.5 (4), Ga(2)P(3)C(21) = 109.7 (4), Ga(3)P(3)C(21) = 110.3 (4), P(2)Ga(2)C(51) = 116.8 (4), P(3)Ga(2)C(51) = 123.6 (4).

The synthesis[7] of compound **1** was accomplished by the reaction of $Li_2P(1\text{-}Ad)$[8] with 1 equiv of $Cl_2GaTrip(THF)$.[9] This reaction consistently afforded a mixture of two main products. One, the title compound, was isolated as colorless crystals, mp = dec >300 °C. The other product, which was obtained as yellow crystals, has not yet been identified owing to crystal twinning. The structure of **1** was determined by X-ray crystallography and is illustrated in Figure 1.[10] The core framework is composed of the atoms Ga_4P_5. Its structure may be described as consisting of a bifurcated six-membered ring involving the atoms Ga(1), P(2), Ga(2), P(3), Ga(3), and either P(4) or P(5), which has common edges with three four-membered rings [Ga(1), P(1), Ga(4), and P(4); Ga(1), P(1), Ga(4), and P(5), and Ga(3), P(4), Ga(4), and P(5)], which are themselves fused at the Ga(4) P(4) and Ga(4) P(5) edges. With the exception of Ga(1), the core atoms are also bound to one organic substituent. Stripping of the organo group from Ga(1) apparently occurs during the course of the reaction. In addition, the P(1) center bears a hydrogen as well as a 1-Ad substituent.

The structure of **1** possesses several features of interest. First, the overall ratio of substituents to the main-group elements is unity, and **1** appears to be among the first[11] examples of a main group 3–5 cluster for which this type of structure and stoichiometry has been observed. Second, the cluster contains a gallium center, Ga(2), and two phosphorus centers, P(2) and P(3), that are three-coordinate. Although compounds that involve bonds between three-coordinate heavier main group 3 and 5 elements are known,[12-17] **1** appears to be the first instance in which they are incorporated in more highly associated species. It is tempting to view the six-membered-ring system Ga(1), P(2), Ga(2), P(3), Ga(3), and either P(4) (to give the boat conformation) or P(5) (to give a chair conformation) as a progenitor of an $(RGaPR')_3$ quasi-aromatic ring. It is notable, however, that these rings are puckered and show little tendency to become planar. The P(2) and P(3) centers are pyramidal although P(3) ($\Sigma° = 334.2°$) is somewhat flattened. The Ga(2) center is, not surprisingly, nearly planar, and the Ga(2)–P(2) and Ga(2)–P(3) bond lengths (~2.3 Å) are short, but some shortening is to be expected on the basis of the lower coordination. It is of course possible that, if the bridging to Ga(1), Ga(3), P(4), and P(5) were absent, the achievement of a six-π-electron system similar to that in the corresponding $(RBPR')_3$ ring might have resulted in a planar Ga_3P_3 array and shorter Ga–P bonds. The atoms Ga(1), Ga(3), Ga(4), P(1), P(4), and P(5) are all four-coordinate, and they have angles that exhibit severe distortion from regular tetrahedral values. The Ga–P distances involving these atoms are generally longer, ranging from 2.370 (3) Å to 2.475 (4) Å, and average ~2.4 Å, which is near to what is expected on the basis of the sum of the covalent radii. The longer P(1)–Ga distances, in comparison to those involving P(2) and P(3), are also consistent with a hydrogen bound to P(1) and also with the distances observed in a number of structures that involve these coordination numbers.[18,19]

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(7) Under anaerobic and anhydrous conditions, 1.4 mL of a 1.6 M hexane solution of *n*-BuLi was added dropwise to an Et_2O solution (20 mL) of $H_2P(1\text{-}Ad)$[8] (0.2 g, 1.1 mmol) with cooling in an ice bath. Stirring was continued for 30 min at ambient temperature, and the volume was reduced to ca. 5 mL. Tetrahydrofuran (20 mL) was added to redissolve the precipitated $Li_2P(1\text{-}Ad)$. This solution was then added, via a double-tipped stainless steel needle, to $Cl_2GaTrip(THF)$[9] (0.47 g, 1.1. mmol) in THF (20 mL) and stirred for 20 h. All the volatile material was removed under reduced pressure. Addition of hexane (25 mL) resulted in a clear yellow solution and a white precipitate. Filtration followed by concentration to ca. 2 mL afforded **1** as colorless crystals in about 20% yield (0.08 g). Anal. Calcd for $C_{101}H_{159}Ga_4P_5$: C, 67.1; H, 8.57. Found: C, 66.9; H, 8.6. IR: $\nu(P\text{–}H) = 2320\ cm^{-1}$ (w). ^1H NMR (C_6D_6): δ 7.1 (br s, *m*-H, 6 H), 3.55 (m, *o*-C*H*Me$_2$, 6 H) 2.79 (m, *p*-C*H*Me$_2$, 3 H), 1.33 (d, J = 8 Hz, *o*-CHMe$_2$, 36 H), 1.02 (d, J = 8 Hz, *p*-CHMe$_2$, 18 H), 1-Ad partially obscured by *i*-Pr resonances between δ 2.7 and 1.2.

(8) The precursor $H_2P(1\text{-}Ad)$ for $Li_2P(1\text{-}Ad)$ was synthesized by the LAH reduction of $Cl_2(O)P(1\text{-}Ad)$: Stetter, H.; Last, W. *Chem. Ber.* **1969**, *102*, 3364.

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(10) Crystal data for **1** at 130 K with Cu Kα (λ = 1.541 78 Å) radiation: **1**, $C_{101}H_{159}Ga_4P_5$, a = 14.489 (2) Å, b = 18.484 (8) Å, c = 19.339 (8) Å, α = 85.02 (3)°, β = 88.95 (3)°, γ = 70.20 (3)°, Z = 2, triclinic, space group $P\bar{1}$, d_{calcd} = 1.236 g cm^{-3}, V = 4854 (3) Å^3, 5908 unique observed ($I > 2\sigma I$) data, R = 0.070. Data were obtained on a Siemens P3R diffractometer equipped with a locally modified Siemens LT-2 low-temperature device and a rotating anode. The structure contains a molecule of solvent hexane in its lattice.

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Further confirmation of the presence of H at P(1) comes from the presence of an absorption at 2320 cm^{-1} in the IR spectrum (Nujol mull).

The $^{31}P\{^1H\}$ NMR spectrum of **1** displays two somewhat broad peaks centered at 31.4 and 46 ppm and further peaks at −67.8 and −80.3 ppm. The structure of **1** shows that there are four different types of phosphorus centers, although the P(2) and P(3) environments resemble each other quite closely. It is not possible at present to assign a particular phosphorus resonance to its position in the structure, but the downfield peaks are probably due to the four-coordinate phosphorus centers, and the upfield peaks are probably due to the three-coordinate P(2) and P(3). It is notable, however, that some of the values seen here are in the same range (but with broader peaks) as those observed in other gallium–phosphorus compounds.[19] The ^1H NMR spectrum of **1** confirms the presence of 2,4,6-$(i\text{-}Pr)_3C_6H_2$ and 1-Ad groups in the ratio seen in the structure.

Acknowledgment. We thank the National Science Foundation for financial support through instrumentation Grant No. CHE-8602721 and Grant No. CHE-8618739 (P.P.P.).

Supplementary Material Available: Tables of atom coordinates, bond distances, bond angles, H coordinates, and thermal parameters for **1** (14 pages); listing of observed and calculated structure factors for **1** (43 pages). Ordering information is given on any current masthead page.

Chromophore-Assisted Peroxy Bond Breakage: Laser Flash Spectroscopic Studies of a Benzophenone Perester

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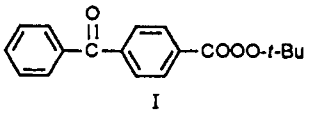
Benzoyl peroxide and, to a lesser extent, *tert*-butyl perbenzoate are widely used as thermal initiators for free radical chain reactions.[3] Like simpler peroxides such as hydrogen peroxide, these compounds do not absorb above 300 nm and are neither useful[4] nor problematic[5] sources of radicals from photolytic routes.[6] There have been a number of reports of systems that combine a long wavelength absorbing chromophore with the weak –O–O– bond of a peroxide in a single molecule. These putative unimolecular peroxide photoinitiators are said to combine the characteristics of known excited states with easily dissociated functions.[7] Our thought was that conjugation of the long-lived triplet of benzophenone with a peroxide unit susceptible to dissociation would provide an efficient source of carboxy and *tert*-butoxy radicals by combining the absorption maximum of the aromatic ketone with the function susceptible to homolysis (I). Inherent flexibility in synthesis led us to conceive of the so-called phototunable perester,[6,8] a concept that has led to substantial patent activity as well as related publications.[9-11]



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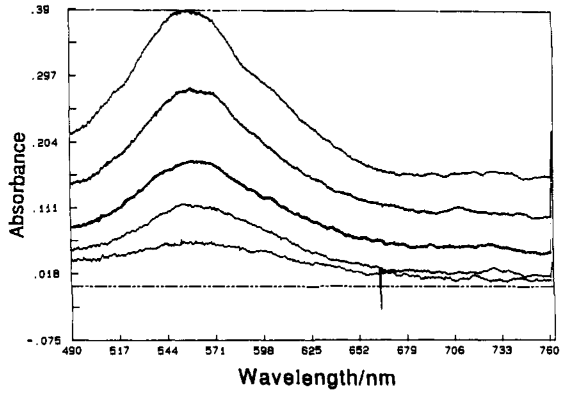

Figure 1. Transient absorption spectra resulting from absorption of a 25-ps pulse of 355-nm light in a deaerated perester I solution (7 mM) in CCl_4. Reading from top to bottom, the delay settings are 30, 462, 792, 1122, and 2442 ps.

Recently, *tert*-butyl peresters derived from fluorenone, benzophenone, and 9-methylfluorene have been investigated by laser flash photolysis experiments.[12,13] On the few hundred nanosecond time scale, the fluorenone perester entities showed transient absorptions that were assigned[12] to T_1 states of the chromophores; however, no T–T absorption in the benzophenone perester I case was found[12] in that time scale. Falvey and Schuster[13] employed picosecond laser flash techniques to investigate the 9-methylfluorene perester system. They observed growth of the 9-methylfluorenyl radical with a 55-ps time constant and inferred that energy translocation from the chromophore and fission of the peroxy bond occur within their experimental time resolution (ca. 25 ps). These limited examples show that chromophore-linked peroxides exhibit a wide range of excited-state stability prior to peroxy bond breakage. This has led us to inquire into what factors govern the dynamics of energy dissipation in chromophore-linked peresters. Our inquiry reflects, to a limited extent, the earlier work of Scaiano and Wubbels,[14] who studied the photosensitized intermolecular dissociation of di-*tert*-butyl peroxide. They concluded that energy transfer occurs to a repulsive state of the peroxide. Here we introduce our findings on the ultrafast processes that follow population of the T_1 state of a benzophenone perester.

Deaerated solutions of *tert*-butyl *p*-benzoylperbenzoate (benzophenone perester I) in CCl_4 with absorbance of unity at 355

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(1) National Science Foundation Undergraduate Research Participant (REU 8900563).

(2) Publication No. 93 from the Center for Photochemical Sciences.

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