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 artificially 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 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 VX-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.

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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")$_3$, (RAINR")$_3$ (and (GeNR")$_3$ (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 (RZNRS)"$_3$ which possess almost planar Zn$_3$S$_3$ arrays. In addition, the synthesis of an organogallium-arsenic cluster [(PhAsH)(R,Ga)(PhAs)$_3$(RGa)$_3$ (R = CH$_3$SiMe$_3$)] has given grounds for confidence that the proposed unsaturated rings can be synthesized if the appropriate substituents were selected. 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)$_2$]$_2$[(1-Ad)$_4$]$_2$[H(1-Ad)$_4$]$_2$. [1-Ad = 1-adamantyl, Trip = 2,4,6-(i-Pr)$_3$C$_6$H$_2$]$

The synthesis of compound 1 was accomplished by the reaction of Li$_2$P$_4$ with 1 equiv of c$_1$Tri$_2$Mg(THF)$_2$. This reaction consistently afforded a mixture of two main products. One, the title compound, was isolated as colorless crystals, mp 135-139°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. The core framework is composed of the atoms Ga$_4$P$_5$. 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(2), Ga(2), and P(5)], and (b) core atoms and substituent carbons. Important bond distances and angles that exhibit severe distortion from regular tetrahedral and P$_4$ centers are pyramidal although P(3) and P(4) are three-coordinate. Although compounds that involve bonds between three-coordinate heavier main group 3 and 5 elements are known, 1-7 it 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), and Ga(3), and either P(4) (to give the boat conformation) or P(5) (to give a chair conformation) as a progenitor of an (RGaP)$_3$ 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) (2$^\#$ = 334.2$^\circ$) 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-electron system similar to that in the corresponding (RP$_3$)$_3$ ring might have resulted in a planar Ga$_4$P$_5$ 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 observed 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. 8,9

Figure 1. Schematic drawings of (a) [Ga$_4$(Trip)$_3$P$_4$(1-Ad)$_8$]$_2$ and (b) core atoms and substituent carbons. Important bond distances and angles (Å) and (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(2)-P(4) = 2.475 (4), Ga(4)-P(4) = 2.434 (4), Ga(4)-P(5) = 2.523 (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) = 1.170 (1), P(2)Ga(1)P(4) = 1.361 (1), P(2)Ga(2)P(3) = 1.135 (1), P(3)Ga(3)P(4) = 1.145 (1), P(3)Ga(3)P(5) = 1.064 (1), P(1)Ga(1)P(4) = 1.862 (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(4) = 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) = 113.4 (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 of compound 1 was accomplished by the reaction of Li$_2$P$_4$(1-Ad)$^+$ with 1 equiv of Cl$_2$Ga(Trip)(THF)$^+$. This reaction consistently afforded a mixture of two main products. One, the title compound, was isolated as colorless crystals, mp = dec >300°C.
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 31P[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 current masthead page.

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. The 1H NMR spectrum of 1 confirms the presence of 2,4,6-(i-Pr)3C₆H₂ and 1-Ad groups in the ratio seen in the structure.

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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 Benzenophene Perester

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Benzy1 peroxide and, to a lesser extent, tert-butyl perbenzoate are widely used as thermal initiators for free radical chain reactions. Like simpler compounds such as hydrogen peroxide, these compounds do not absorb above 300 nm and are neither useful nor problematic sources of radicals from photolytic routes. There have been a number of reports of systems that combine a chromophore with the function susceptible to homolysis in CCl₄. Reading from top to bottom, the delay settings are 100, 150, 200, and 250 ps.

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 CCl₄. Reading from top to bottom, the delay settings are 30, 462, 792, 1122, and 2442 ps.

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, a concept that has led to substantial patent activity as well as related publications.

Recently, tert-butyl peresters derived from fluorenone, benzenophene, and 9-methylfluorenyle have been investigated by laser flash photolysis experiments. On the few hundred nanosecond time scale, the fluorenone perester entities showed transient absorptions that were assigned to T states of the chromophores; however, no T → T absorption in the benzenophene perester I case was found in that time scale. Falvey and Schuster employed picosecond laser flash techniques to investigate the 9-methylfluorenyle 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 peresters exhibit a wide range of excited-state stability prior to the 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, who studied the photosensitized intermolecular dissociation of di-tert-buty1 peroxy. They concluded that energy transfer occurs to a repulsive state of the peroxy. Here we introduce our findings on the ultrafast processes that follow population of the T₁ state of a benzenophene perester. Deaerated solutions of tert-butyl p-benzoypbenzoate (benzenophene perester I) in CCl₄ with absorbance of unity at 355

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(8) The phototunable perester is based on tert-butyl p-(bromomethyl)-perbenzoate and related aromatic molecules. The idea is that one can synthesize a series of related photodissociable peresters merely by virtue of a nucleophilic displacement of bromide by the appropriate chromophore-containing molecule.