4908 *Organometallics* 1993, *12*, 4908-4916

# Reactivity of Organogallium Peroxides: Oxidation of Phosphines, Phosphites, and Triphenylarsine. X-ray Crystal Structures of $(^tBu)_2Ga(O^tBu)(O{=}AsPh_3)$, $(^tBu)_2Ga(\mu\text{-}O^tBu)(\mu\text{-}OO^tBu)Ga(^tBu)_2$, and $(^tBu)_2Ga[(O)P(Ph)_2CH(O)P(Ph)_2]$

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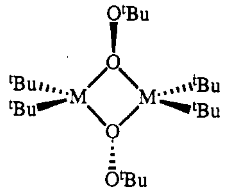
*Received January 29, 1993*®

The interaction of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ with 2 molar equiv of alkyl- and arylphosphines, $PR_3$, and triphenylarsine, $AsPh_3$, leads to the formation of the Lewis acid–base complexes $(^tBu)_2Ga(O^tBu)(O{=}PR_3)$ (1, 3–6) and $(^tBu)_2Ga(O^tBu)(O{=}AsPh_3)$ (2), respectively. The triphenylphosphine oxide complex (1) is also isolated from the reaction of $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ with $O{=}PPh_3$. In a similar reaction, the terminal peroxide complex $(^tBu)_2Ga(OO^tBu)(O{=}PPh_3)$ (7) is formed by the cleavage of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$. No adduct formation is observed for the reaction of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ with the phosphites $P(OPh)_3$ and $P(OMe)_3$. Instead, $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ and the appropriate phosphate are formed in quantitative yield. In contrast to the oxidation of $PR_3$ and $P(OR)_3$, the oxidation of the diphosphine, dppe ($Ph_2PC_2H_4PPh_2$), requires 2 molar equiv of the gallium peroxide dimer, and the phosphine oxide adduct is not isolated. Instead, the free phosphine oxide, $dppeO_2$, is formed along with the asymmetric dimer $(^tBu)_2Ga(\mu\text{-}O^tBu)(\mu\text{-}OO^tBu)Ga(^tBu)_2$ (8). Compound 8 is also formed as one of the gallium containing products in the oxidation of dppm ($Ph_2PCH_2PPh_2$). However, $dppmO_2$ reacts further to yield the heterocyclic compound $(^tBu)_2Ga[(O)P(Ph)_2CH(O)P(Ph)_2]$ (9), which may be prepared independently by the thermolysis of $Ga(^tBu)_3(dppmO_2)$ (10). Although the $dppmO_2$ acts as a monodentate ligand in the Lewis acid–base complex (10), NMR spectra indicate it to be fluxional at ambient temperatures. The exchange in 10 is compared to that of the monodentate donor complex $Ga(^tBu)_3(O{=}PPh_3)$ (11). The molecular structures of $(^tBu)_2Ga(O^tBu)(O{=}AsPh_3)$ (2), $(^tBu)_2Ga(\mu\text{-}O^tBu)(\mu\text{-}OO^tBu)Ga(^tBu)_2$ (8) and $(^tBu)_2Ga[(O)P(Ph)_2CH(O)P(Ph)_2]$ (9) have been determined by X-ray crystallography. Crystal data for 2: monoclinic, $C2/c$, $a = 24.092(7)$ Å, $b = 17.200(7)$ Å, $c = 17.724(8)$ Å, $\beta = 126.10(2)°$, $Z = 8$, $R = 0.059$, $R_w = 0.085$. Crystal data for 8: monoclinic, $C2/m$, $a = 16.642(1)$ Å, $b = 11.167(1)$ Å, $c = 8.7415(8)$ Å, $\beta = 118.475(8)°$, $Z = 2$, $R = 0.062$, $R_w = 0.072$. Crystal data for 9: triclinic, $P\bar{1}$, $a = 11.724(1)$ Å, $b = 14.917(1)$ Å, $c = 18.070(1)$ Å, $\alpha = 100.341(6)°$, $\beta = 93.989(8)°$, $\gamma = 99.318(8)°$, $Z = 4$, $R = 0.037$, $R_w = 0.046$.

## Introduction

Although isolable alkyl peroxide compounds of aluminum have been known since the early 1960s,[2] it is only recently that gallium and indium peroxides have been reported.[3] This seminal work by Alexandrov and coworkers has led to a detailed study of their preparation, thermal decomposition, and reactivity with alcohols, esters, and aldehydes. A review of their work has recently appeared.[4]

As part of our ongoing investigations into the reactivity of the heavier group 13 elements, we have isolated and crystallographically characterized the alkyl peroxides (I)



M = Ga, In

(I)

derived from the oxidation of tri-*tert*-butylgallium[5] and indium.[6] In order to demonstrate the oxidative ability of these isolable alkyl peroxide compounds we have reported[5] that the reaction of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ with 2 equiv of triphenylphosphine yields, after hydrolysis, a stoichio-

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® Abstract published in *Advance ACS Abstracts*, November 1, 1993.

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[2] See for example: (a) Razuvaev, G. A.; Mitrofan, E. V.; Petukhov, G. G. *Zh. Obshch. Khim.* **1961**, *31*, 2343. (b) Razuvaev, G. A.; Graevskii, A. I. *Zh. Obshch. Khim.* **1962**, *32*, 1006. (c) Razuvaev, G. A.; Graevskii, A. I.; Minsker, K. S.; Zakharova, V. N. *Izv. Akad. Nauk. SSSR, Otdel. Khim. Nauk* **1962**, 1555.

[3] (a) Alexandrov, Y. A.; Chikinova, N. V.; Makin, G. J.; Kornilova, N. V.; Bregadze, V. J. *Zh. Obshch. Khim.* **1978**, *48*, 467. (b) Alexandrov, Y. A.; Vyshinskii, N. N.; Kokorev, N. V.; Alferov, V. A.; Chikinova, N. V.; Makin, G. J. *J. Organomet. Chem.* **1987**, *32*, 259.

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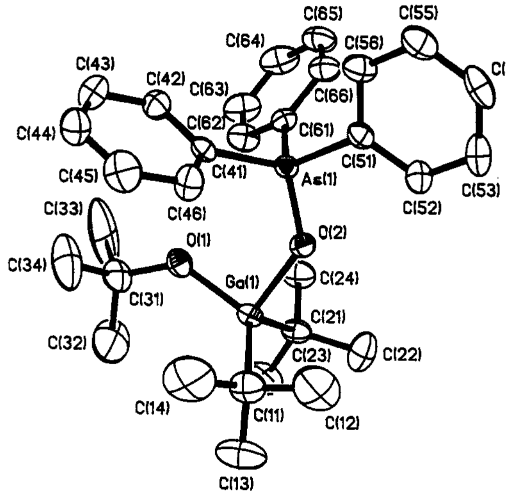


**Figure 1.** Structure of $(^tBu)_2Ga(O^tBu)(O{=}AsPh_3)$ (2). Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms are omitted for clarity.

metric quantity of the phosphine oxide. However, at that time no attempt was made to isolate any intermediates in the reaction. We have now more fully investigated the reaction of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ with phosphines, phosphites, and triphenylarsine, and the results of this study are presented herein.

## Results and Discussion

**Phosphines and Triphenylarsine.** The interaction of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ with 2 molar equiv of $PPh_3$ (in the absence of water) results in the formation of the Lewis acid–base adduct $(^tBu)_2Ga(O^tBu)(O{=}PPh_3)$ (1) in near quantitative yield (eq 1). Hydrolysis of 1 yields, as determined by $^{31}P$ NMR spectroscopy, uncomplexed $O{=}PPh_3$ as the only phosphorus containing species

$$[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2 + 2ER_3 \xrightarrow[\text{pentane}]{25\,^\circ C} 2(^tBu)_2Ga(O^tBu)(O{=}ER_3) \quad (1)$$

$$E = P, As$$

Similar phosphine and arsine oxide complexes $(^tBu)_2Ga(O^tBu)(O{=}ER_2R')$ [E = As, R = R′ = Ph (2), and E = P, R = Ph, R′ = Me (3), R = R′ = Et (4), R = R′ = $^n$Bu (5), R = R′ = $^i$Pr (6)] are obtained from the reaction of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ with $AsPh_3$ or the appropriate phosphine; *cf.*, eq 1.

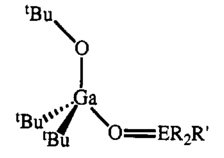
Although it is only for the triphenylarsine oxide complex that a parent ion is observed in the mass spectrum, all of the isolated complexes appear to be monomeric, showing peaks due to $M^+ - {}^tBu$ and $M^+ - O^tBu$ (see Experimental Section). It is interesting to note that there is a lack of peaks due to $M^+ - O{=}ER_3$; however, peaks due to $Ga(O{=}ER_3)$ and $GaPR_3$ are observed. Since we have no spectroscopic evidence for the presence of unoxidized phosphine in the isolated compounds, this latter observation implies that reduction of the phosphine oxide has occurred within the mass spectrometer.

The $\nu(P{=}O)$ frequency of $(^tBu)_2Ga(O^tBu)(O{=}PR_3)$ (1100–1200 cm$^{-1}$) and the $\nu(As{=}O)$ frequency of $(^tBu)_2Ga(O^tBu)(O{=}AsPh_3)$ (880 cm$^{-1}$) are lowered from the free ligand values,[7] indicative of coordination.[8]

**Table I. Selected Bond Lengths (Å) and Bond Angles (deg) in $(^tBu)_2Ga(O^tBu)(O{=}AsPh_3)$ (2)**

| | | | |
|---|---|---|---|
| Ga(1)–O(1) | 1.860(6) | Ga(1)–O(2) | 1.980(3) |
| Ga(1)–C(11) | 2.026(7) | Ga(1)–C(21) | 2.004(8) |
| O(1)–C(31) | 1.423(9) | O(2)–As(1) | 1.659(5) |
| As(1)–C(41) | 1.899(7) | As(1)–C(51) | 1.900(5) |
| As(1)–C(61) | 1.901(5) | | |
| O(1)–Ga(1)–O(2) | 93.5(2) | O(1)–Ga(1)–C(11) | 119.8(3) |
| O(1)–Ga(1)–C(21) | 112.8(3) | O(2)–Ga(1)–C(11) | 102.7(2) |
| O(2)–Ga(1)–C(21) | 102.4(2) | C(11)–Ga(1)–C(21) | 119.2(4) |
| Ga(1)–O(1)–C(31) | 132.3(4) | Ga(1)–O(2)–As(1) | 132.8(3) |
| O(2)–As(1)–C(41) | 114.4(2) | O(2)–As(1)–C(51) | 104.2(3) |
| O(2)–As(1)–C(61) | 112.6(3) | C(41)–As(1)–C(51) | 107.8(3) |
| C(41)–As–C(61) | 107.7(3) | C(51)–As(1)–C(61) | 110.1(2) |

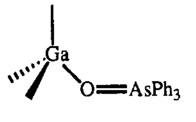
The $^1H$ NMR spectra of 1–6 are consistent with terminal as opposed to bridging butoxide groups.[5] The $^{31}P$ NMR chemical shifts for the complexes are shifted downfield with respect to the respective free phosphine oxides,[9] indicative of complexation of phosphine oxides to a group 13 metal center.[10] Spectroscopic data for 1–6 are therefore consistent with monomeric Lewis acid–base complexes of the $(^tBu)_2Ga(O^tBu)$ moiety (**II**). This structure has been confirmed for 2 by X-ray crystallography.



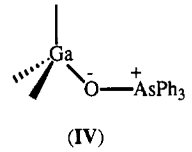
E = P, As

(II)

The molecular structure of 2 is shown in Figure 1; selected bond lengths and angles are given in Table I. The As—O bond in 2 [1.659(5) Å] is within the range of distances reported for As=O bonds (1.64–1.67 Å),[11] and the Ga(1)—O(2)—As(1) angle [123.8(3)°] is consistent with *ca.* sp$^2$ hybridization at oxygen. Both of these observations indicate that the mode of arsine oxide coordination is best described as depicted in **III**, without significant contribution of the resonance form **IV**.



(III)



(IV)

The geometry about the four-coordinate gallium is highly distorted from tetrahedral, with the smallest angle being between the two oxygen donors [O(1)–Ga(1)–O(2) = 93.5(2)°]; however, the large O(1)···O(2) distance (2.79 Å) clearly precludes any O–O bond contribution. While the gallium–carbon bond distances are within the range

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previously observed (1.96–2.16 Å),[12] the difference between the two gallium oxygen interactions is worthy of note. The Ga(1)–O(2) bond associated with the arsine oxide [1.980(3) Å] is within the 3$\sigma$ condition of those found in $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ [1.990(2) and 1.989(2) Å].[5] In contrast, the terminal butoxide Ga(1)–O(1) bond distance is significantly shorter than found for alkoxide bridging two gallium centers.[5] From a consideration of the extent of M–O bond shortening, i.e., $\Delta_{o,c}$ (eq 2),[13] it can be seen that while the

$$\Delta_{o,c} = d(\text{M-O}) - d(\text{M-C}) \qquad (2)$$

$\Delta_{o,c}$ value for the *tert*-butoxide in 2 (−0.155 Å) is significantly larger than those for either the arsine oxide Ga–O bond distance in 2 (−0.035 Å) or the bridging alkoxy and peroxy ligands in $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ (−0.057 Å) and $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ (−0.02 Å), respectively, it is smaller than observed for the aluminum aryl oxide complexes (−0.22 Å < $\Delta_{o,c}$ < −0.28 Å). We propose, therefore, that while some hyperconjugative interaction between the alkoxide oxygen lone pairs and the gallium center may account for the significant geometrical distortion around both the gallium and the arsenic centers in 2, its effect, as would be predicted from relative orbital energy considerations, is much weaker than observed for aluminum. It should be noted, however, that the *tert*-butoxy group, the Ga, and As–O bond are close to coplanar, consistent with the presence of hyperconjugation.

While phosphine and arsine oxide complexes of group 13 Lewis acids have been known for many years,[17] few examples have been crystallographically characterized.[18,19] Burford and co-workers have undertaken an extensive study of phosphine oxide—group 13 complexes, including $GaCl_3(O{=}PPh_3)$,[19] in which the Ga—O—P angle is crystallographically linear (180°) and the Ga—O distance is 1.81 Å. These values are consistent with the gallium in $GaCl_3(O{=}PPh_3)$ being a highly Lewis acidic center in comparison to that in 2.

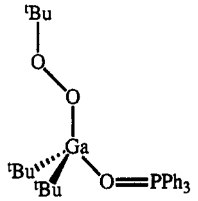
Compound 1 may be prepared by an independent synthesis (see Experimental Section) involving the phosphine oxide cleavage of the $Ga_2O_2$ unit in $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ (eq 3). This reaction is indicative of the strongly

$$^1/_2[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2 + O{=}PPh_3 \rightarrow (^tBu)_2Ga(O^tBu)(O{=}PPh_3) \qquad (3)$$

Lewis basic nature of $O{=}PPh_3$ since the dimeric alkoxide is not cleaved by THF or pyridine. Triphenylphosphine oxide also cleaves the Ga—O—Ga bridges in $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ (eq 4) to give the Lewis acid–base complex, $(^tBu)_2Ga(OO^tBu)(O{=}PPh_3)$(7). Unfortunately, difficulties in isolating 7 preclude its structural characterization

$$^1/_2[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2 + O{=}PPh_3 \rightarrow \underset{\mathbf{7}}{(^tBu)_2Ga(OO^tBu)(O{=}PPh_3)} \qquad (4)$$

by X-ray crystallography. However, the $^1$H, $^{13}$C, and $^{31}$P NMR spectra (see Experimental Section) are consistent with the empirical formula given. The $^{31}$P NMR shift for 7 ($\delta$ 37.2) is similar to that observed for 1 ($\delta$ 36.6) indicative of a coordinated $O{=}PPh_3$ moiety. In addition, we have previously shown that the $^1$H and $^{13}$C NMR shifts of alkyl substituents on group 13 metals are highly dependent on the coordination geometry around the metal center.[20] Thus, in the case of 7 the *tert*-butyl NMR chemical shifts are close to those for 1 and 3–6 (see Experimental Section), indicating that the gallium is four-coordinate tetrahedral. We propose, therefore, that 7 exists as a four-coordinate monomer (V) and is the first example of a terminal alkyl peroxide of gallium.



(V)

**Phosphites.** In contrast to the interaction of phosphines with $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$, the oxidation of phosphites, $P(OR)_3$ (R = Ph, Me) does not result in adduct formation, but a quantitative yield (based on $^1$H and $^{31}$P NMR) of $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ and the appropriate phosphate (eq 5). This lack of adduct formation is in accord with the weaker donor ability of phosphates as compared to phosphine oxides.

$$^1/_2[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2 + P(OR)_3 \rightarrow {}^1/_2[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2 + O{=}P(OR)_3 \qquad (5)$$

**Diphosphines.** Whereas $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ reacts under ambient conditions quantitatively with 2 molar equiv of either $PR_3$ or $P(OR)_3$, under corresponding conditions only partial reaction occurs with dppe ($Ph_2PC_2H_4PPh_2$). Interaction of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ with 1 equiv of dppe, in pentane or benzene, results in the oxidation of 0.5 equiv of the dppe and the formation of an organogallium compound, 8. When the reaction is carried out with 2 equiv of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$, 8 and $dppeO_2$ are the only products isolated (eq 6).

$$2[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2 + \text{dppe} \rightarrow 2\ \mathbf{8} + \text{dppeO}_2 \qquad (6)$$

The $^1$H NMR spectrum of 8 shows the presence of four chemically equivalent *tert*-butyl groups ($\delta$ 1.36), which from the $^{13}$C NMR spectrum may be assigned as being bound to gallium due to the upfield shift of the quaternary carbon resonance ($\delta$ 27.6), as compared to those found for *tert*-butyl groups bound to oxygen ($\delta$ 70–90). In addition to the resonances due to the gallium bound *tert*-butyl groups, the $^1$H NMR spectrum of 8 indicates the presence of two oxygen bound $^t$Bu groups ($\delta$ 1.26 and 1.17). While the former is closer to the alkoxy–$^t$Bu resonance in

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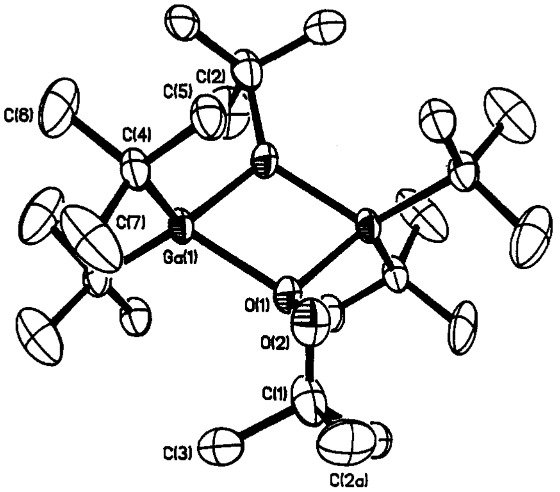

**Figure 2.** Structure of $(^tBu)_2Ga(\mu\text{-}O^tBu)(\mu\text{-}OO^tBu)Ga(^tBu)_2$ (8). Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are omitted for clarity.

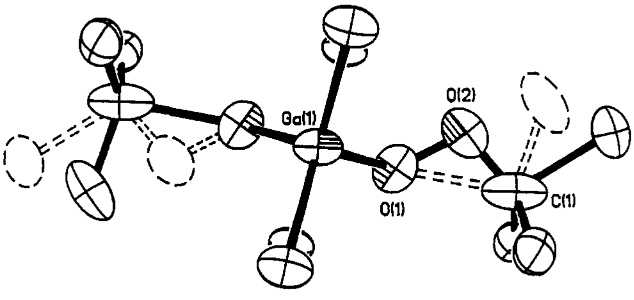

**Figure 3.** Partial coordination sphere of the $Ga_2O_2$ core in $(^tBu)_2Ga(\mu\text{-}O^tBu)(\mu\text{-}OO^tBu)Ga(^tBu)_2$ (8) viewed down the Ga···Ga vector, showing the disorder between the alkyl and alkyl peroxide ligands. The *tert*-butyl methyl groups have been omitted for clarity.

**Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in $(^tBu)_2Ga(\mu\text{-}O^tBu)(\mu\text{-}OO^tBu)Ga(^tBu)_2$ (8)**

| | | | |
|---|---|---|---|
| Ga(1)–O(1) | 2.001(2) | Ga(1)–O(1a) | 2.001(2) |
| Ga(1)–C(4) | 2.028(6) | O(1)–O(2) | 1.21(1) |
| O(2)–C(1) | 1.890(9) | O(2)–C(1) | 1.19(1) |
| | | | |
| O(1)–Ga(1)–O(1a) | 77.0(2) | O(1)–Ga(1)–C(4) | 114.1(2) |
| O(1a)–Ga(1)–C(4) | 113.7(2) | C(4)–Ga(1)–C(4a) | 117.7(3) |
| Ga(1)–O(1)–O(2) | 117.2(4) | Ga(1)–O(1)–C(1) | 128.3(1) |
| O(1)–O(2)–C(1) | 103(1) | Ga(1)–O(1)–Ga(1a) | 103.0(2) |

$[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ ($\delta$ 1.32), the latter shift is similar to that found for $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ ($\delta$ 1.14), i.e., that of a *tert*-butyl peroxide. The elemental composition $C_{24}H_{54}Ga_2O_3$ was established by elemental analysis (see Experimental Section), while the medium resolution mass spectral fragmentation pattern revealed peaks at $m/z$ 473 and 457, corresponding to $M^+ - {}^tBu$ and $M^+ - O^tBu$, respectively. Thus, the analytical and spectroscopic characterization of 8 is consistent with a unique dimeric structure containing both alkoxy and alkylperoxy bridges, i.e., $(^tBu)_2Ga(\mu\text{-}O^tBu)(\mu\text{-}OO^tBu)Ga(^tBu)_2$. This proposed structure has been confirmed by X-ray crystallography.

The structure of 8 is shown in Figure 2; selected bond lengths and angles are given in Table II. The molecule consists of two $(^tBu)_2Ga$ fragments bridged by one $\mu_2$-*tert*-butylperoxo and one $\mu_2$-*tert*-butoxo group. The molecule is located on a site of $2/m$ symmetry, and as a consequence the peroxide and alkoxide ligands are disordered (see Experimental Section). Figure 3 shows a composite structure.

The Ga–O distances and Ga–O–Ga angles in 8 are similar to those found for other $Ga_2O_2$ cores[5,21] while the Ga–C bond lengths are within the region expected (see above). The peroxo O–O bond distance is shorter than that found for free alkyl hydrogen peroxides,[22] $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$,[5] and alkyl peroxides coordinated to transition metals.[23] However, given the disorder within the ligand we do not attach any chemical significance to the shortening. The *tert*-butylperoxo ligand is oriented in an eclipsed-staggered conformation, presumably so as to minimize lone pair repulsion on the oxygen atoms.

If the reaction of dppe with $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ is carried out in an NMR tube, a small quantity of transient species can be observed by $^{31}P$ NMR. The chemical shift is in the region expected for a Lewis acid–base adduct of $dppeO_2$, and we therefore tentatively assign this to $[(^tBu)_2Ga(O^tBu)]_x dppeO_2$ ($x$ = 1 or 2). We were unable, however, to derive identifiable peaks in the $^1H$ NMR due to such a species, although at the end of the reaction trace quantities of $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$ are observed by $^1H$ NMR (see Experimental Section).

We cannot, at present, rationalize the reasons for the formation of 8 as opposed to $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$, since the remaining peroxide in the former reacts readily with $PPh_3$ to yield 1 and 0.5 equiv of $[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2$. We note that the sulfur analog to 8, $(^tBu)_2Ga(\mu\text{-}S^tBu)(\mu\text{-}SS^tBu)Ga(^tBu)_2$ is formed as the thermodynamic product from the reaction of $Ga(^tBu)_3$ with elemental sulfur, $S_8$.[24]

In contrast to the results observed for dppe, the reaction of 2 equiv of $[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2$ with dppm ($Ph_2PCH_2PPh_2$) does not yield the free phosphine oxide but, as determined by $^1H$ NMR, a mixture of four products (eq 7) of which only 9 contains phosphorus. Compound 9

$$2[(^tBu)_2Ga(\mu\text{-}OO^tBu)]_2 + \text{dppm} \rightarrow$$
$$9 + 8 + {}^1/_2[(^tBu)_2Ga(\mu\text{-}O^tBu)]_2 + {}^tBuOOH \quad (7)$$

may readily be separated from the other products by fractional crystallization and its structure determined by X-ray crystallographic analysis (see below) to be $(^tBu)_2Ga[(O)P(Ph)_2CH(O)P(Ph)_2]$. All spectroscopic characterization is entirely consistent with this structure.

The molecular structure of one of the two independent molecules of 9 present in the asymmetric unit is shown in Figure 4. Selected bond lengths and angles for both molecules are given in Table III. Compound 9 consists of a planar six-membered $GaO_2P_2C$ heterocycle in which the deprotonated $dppmO_2$, acts as a chelating ligand to a $(^tBu)_2Ga$ unit. The P=O bonds distances in 9 [1.530(2)–1.534(2) Å] are toward the high end of the range observed for phosphine oxide complexes (1.49–1.56 Å),[18] consistent with delocalization within the ligand. In addition, the ring P–C bonds [P(1)–C(33) = 1.700(3) Å and P(2)–C(33) = 1.698(3) Å] are significantly shorter than those to the phenyl substituent [1.806(2)–1.813(2) Å].

The Ga–O distances [1.935(2)–1.948(2) Å] are not significantly shorter than that observed for the arsine oxide ligand in 2 and are within the range expected for a normal

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(24) Power, M. B.; Ziller, J. W.; Tyler, A. N.; Barron, A. R. *Organometallics* **1992**, *11*, 1055.

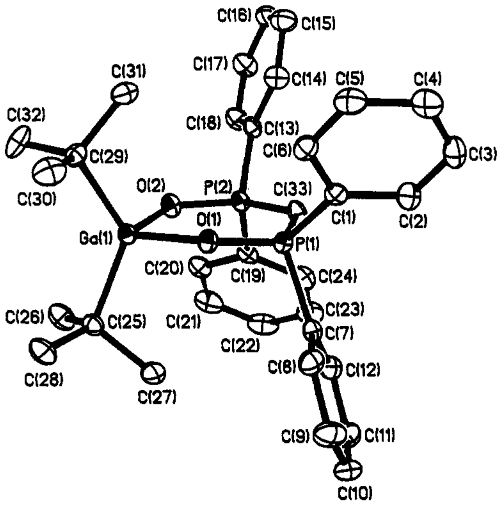
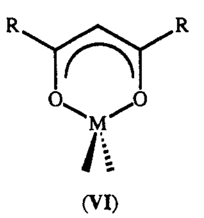


**Figure 4.** Structure of one of the independent molecules of ($^t$Bu)$_2$Ga[(O)P(Ph)$_2$CH(O)P(Ph)$_2$] (9). Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms are omitted for clarity.

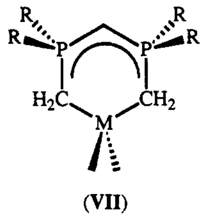
**Table III. Selected Bond Lengths (Å) and Bond Angles (deg) in ($^t$Bu)$_2$Ga[(O)PPh$_2$CH(O)PPh$_2$] (9)**

| | | | |
|---|---|---|---|
| Molecule 1 | | | |
| Ga(1)–O(1) | 1.948(2) | Ga(1)–O(2) | 1.935(2) |
| Ga(1)–C(25) | 1.998(2) | Ga(1)–C(29) | 1.984(3) |
| P(1)–O(1) | 1.530(2) | P(1)–C(1) | 1.809(3) |
| P(1)–C(7) | 1.813(2) | P(1)–C(33) | 1.700(3) |
| P(2)–O(2) | 1.531(2) | P(2)–C(13) | 1.806(2) |
| P(2)–C(19) | 1.812(3) | P(2)–C(33) | 1.698(3) |
| O(1)–Ga(1)–O(2) | 97.7(1) | O(1)–Ga(1)–C(25) | 110.0(1) |
| O(2)–Ga(1)–C(25) | 104.6(1) | O(1)–Ga(1)–C(29) | 104.1(1) |
| O(2)–Ga(1)–C(29) | 107.7(1) | C(25)–Ga(1)–C(29) | 128.6(1) |
| O(1)–P(1)–C(1) | 109.8(1) | O(1)–P(1)–C(7) | 106.3(1) |
| C(1)–P(1)–C(7) | 103.4(1) | O(1)–P(1)–C(33) | 114.5(1) |
| C(1)–P(1)–C(33) | 107.7(1) | C(7)–P(1)–C(33) | 114.5(1) |
| O(2)–P(2)–C(13) | 109.6(1) | O(2)–P(2)–C(19) | 106.4(1) |
| C(13)–P(2)–C(19) | 104.0(1) | O(2)–P(2)–C(33) | 115.1(1) |
| C(13)–P(2)–C(33) | 108.3(1) | C(19)–P(2)–C(33) | 112.9(1) |
| Ga(1)–O(1)–P(1) | 131.7(1) | Ga(1)–O(2)–P(2) | 132.6(1) |
| P(1)–C(33)–P(2) | 125.3(2) | | |
| Molecule 2 | | | |
| Ga(2)–O(3) | 1.936(2) | Ga(2)–O(4) | 1.937(2) |
| Ga(2)–C(58) | 1.986(3) | Ga(2)–C(62) | 1.989(3) |
| P(3)–O(3) | 1.534(2) | P(3)–C(34) | 1.809(3) |
| P(3)–C(40) | 1.805(3) | P(3)–C(66) | 1.704(3) |
| P(4)–O(4) | 1.534(2) | P(4)–C(46) | 1.804(3) |
| P(4)–C(52) | 1.805(2) | P(4)–C(66) | 1.703(3) |
| O(3)–Ga(2)–O(4) | 97.4(1) | O(3)–Ga(2)–C(58) | 101.6(1) |
| O(4)–Ga(2)–C(58) | 109.5(1) | O(3)–Ga(2)–C(62) | 109.2(1) |
| O(4)–Ga(2)–C(62) | 107.8(1) | C(58)–Ga(2)–C(62) | 127.2(1) |
| O(3)–P(3)–C(34) | 108.1(1) | O(3)–P(3)–C(40) | 105.7(1) |
| C(34)–P(3)–C(40) | 104.3(1) | O(3)–P(3)–C(66) | 115.2(1) |
| C(34)–P(3)–C(66) | 108.2(1) | C(40)–P(3)–C(66) | 114.7(1) |
| O(4)–P(4)–C(46) | 110.0(1) | O(4)–P(4)–C(52) | 104.8(1) |
| C(46)–P(4)–C(52) | 103.5(1) | O(4)–P(4)–C(66) | 115.6(1) |
| C(46)–P(4)–C(66) | 106.8(1) | C(52)–P(4)–C(66) | 115.4(1) |
| Ga(2)–O(3)–P(3) | 129.9(1) | Ga(2)–O(4)–P(4) | 129.2(1) |
| P(3)–C(66)–P(4) | 122.0(2) | | |

Ga–O bond without any $\pi$-interaction. Thus, the cycle is not pseudoaromatic in character but is analogous to a metal–acetylacetonate complex (VI). In addition, we note the similarity between **9** and its bis(ylide) analogue (VII).[25]



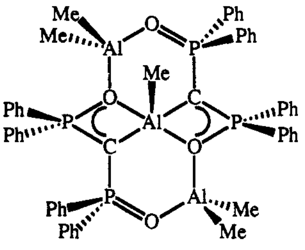
(VI)



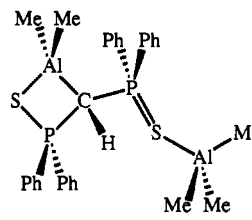
(VII)

**Reaction of Ga($^t$Bu)$_3$ with dppmO$_2$.** Since group 1 and 2 complexes have previously been formed by the deprotonation of dppmO$_2$ with the appropriate metal hydride or alkyls, it is expected that the group 13 complexes analogous to **9** should be attainable by the reaction of dppmO$_2$ with the trialkyl, MR$_3$ (eq 8). However, Robinson *et al* have reported[26] that the reaction of dppmO$_2$ with AlR$_3$ (R = Me, Et) results in cleavage of both of the central methylene C–H bonds and the formation of a trialuminum complex (**VIII**). In contrast, only one of the methylene C–H bonds is cleaved in the reaction of AlMe$_3$ with dppmS$_2$, *cf.*, **IX**.[27]

$$\mathrm{MR_3 + dppmO_2 \rightarrow R_2M(dppmO_2\text{-}H) + RH} \quad (8)$$

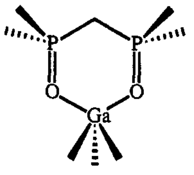


(VIII)

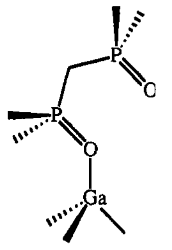


(IX)

Interaction of Ga($^t$Bu)$_3$ with dppmO$_2$ at ambient temperatures results in the formation of the Lewis acid–base complex Ga($^t$Bu)$_3$(dppmO$_2$) (**10**). The $^1$H and $^{31}$C NMR spectra of **10** both show the presence of a single set of resonances for the phenyl rings, while the $^{31}$P NMR spectrum at room temperature consists of a single broad resonance ($\delta$ 27.5). This suggests that the dppmO$_2$ is coordinated to gallium *via* both oxygens (**X**) or has unidentate coordination (**XI**) and is fluxional. The former would result in a five-coordinate gallium which, although previous examples have been reported,[28] are rare. The latter would be analogous to the fluxionality present in the bidentate amine complexes of alane and AlMe$_3$.[29]



(X)



(XI)

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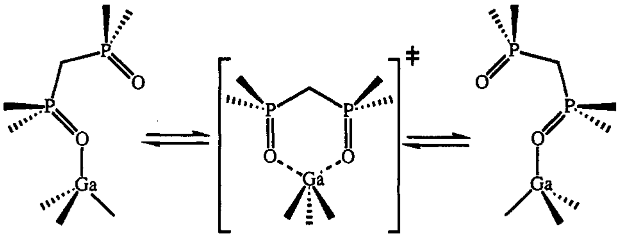
Cooling a toluene-$d_8$ solution of **10** results in the broadening and eventual decoalescence ($T_c$ = 296 K) of the $^{31}$P NMR resonance, to give two peaks of equal intensity which in comparison to the shift of free dppmO$_2$ ($\delta$ 23.0) are consistent with one coordinated ($\delta$ 29.4) and one uncomplexed ($\delta$ 25.6) phosphinoyl group (i.e., **XI**).

The mechanism by which the dppmO$_2$ ligand isomerizes may either involve ligand dissociation (eq 9) or an associative process *via* a five-coordinate transition state similar to **X** (eq 10). Unfortunately, although the activation barrier for the dppmO$_2$ isomerization can be calculated from the $^{31}$P NMR data[30] ($\Delta G^* = 50.7$ kJ mol$^{-1}$), it does not allow for the differentiation of the two mechanisms. On the basis of the activation energies of the two degenerate exchange reactions of Ga($^t$Bu)$_3$(O=PPh$_3$) (**11**) (see Experimental Section for synthesis and characterization), i.e., eqs 11 and 12, $\Delta G^* = 58.9$ kJ mol$^{-1}$ and $\Delta G^* = 59.4$ kJ mol$^{-1}$ respectively, we believe that the exchange shown in eq 10 is probable.

$$\mathrm{Ga(^tBu)_3(dppmO_2)} \rightleftharpoons \mathrm{Ga(^tBu)_3} + \mathrm{(dppmO_2)} \qquad (9)$$



(10)

$$\mathrm{Ga(^tBu)_3(O{=}PPh_3) + Ga^*(^tBu)_3} \rightleftharpoons \mathrm{Ga^*(^tBu)_3(O{=}PPh_3) + Ga(^tBu)_3} \qquad (11)$$

$$\mathrm{Ga(^tBu)_3(O{=}PPh_3) + O{=}P^*Ph_3} \rightleftharpoons \mathrm{Ga(^tBu)_3(O{=}P^*Ph_3) + O{=}PPh_3} \qquad (12)$$

Although compound **10** is indefinitely stable at ambient temperatures under an inert atmosphere, it is converted quantitatively to **9** and isobutane (HCMe$_3$) on thermolysis (>40 °C) in solution (see Figure 5). However, no evidence is found for cleavage of the second methylene C–H bond, even upon extended periods of thermolysis.

## Experimental Section

Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. Thermogravimetric analyses and melting points were obtained on a Seiko 200 TG/DTA instrument using an argon carrier gas. Mass spectra were obtained by using a JEOL AX-505H mass spectrometer and associated data system. An electron beam energy of 70 eV was used for EI mass spectra, with a mass resolution of 1500. Ammonia was used as a reagent gas for CI mass spectra. Reported *m/z* values are for the predominant ion within the isotope pattern for each signal. IR spectra (4000–400 cm$^{-1}$) were recorded on a Nicolet 5ZDX FTIR as Nujol or Fluorolube mulls on KBr plates. $^1$H and $^{13}$C NMR spectra were obtained on a Bruker AM-500 spectrometer and chemical shifts are reported relative to SiMe$_4$, and in C$_6$D$_6$, unless otherwise stated. $^{31}$P NMR spectra were recorded on a Bruker AM-500 spectrometer and chemical shifts are reported versus 85% H$_3$PO$_4$.

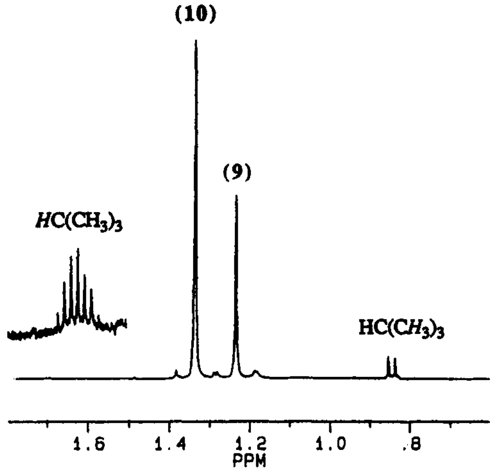


**Figure 5.** $^1$H NMR showing the formation of ($^t$Bu)$_2$Ga[(O)P(Ph$_2$)CH(O)P(Ph)$_2$] (**9**) and HC(CH$_3$)$_3$ as the only products from the thermolysis of Ga($^t$Bu)$_3$(dppmO$_2$) (**10**).

[($^t$Bu)$_2$Ga($\mu$-OO$^t$Bu)]$_2$ was prepared according to our previously reported procedure.[5] All phosphines, phosphites, and triphenylarsine were used as supplied, while solvents were dried, distilled, and degassed prior to use.

**($^t$Bu)$_2$Ga(O$^t$Bu)(O=PPh$_3$) (1). Method 1.** To [($^t$Bu)$_2$Ga($\mu$-OO$^t$Bu)]$_2$ (1.0 g, 2.11 mmol) and PPh$_3$ (1.10 g, 4.19 mmol) at room temperature under nitrogen was added pentane (*ca.* 40 mL). The resulting colorless solution was stirred overnight during which time some colorless white crystals, determined to be OPPh$_3$ [$^{31}$P (C$_6$D$_6$): $\delta$ 25.45], were deposited. The solution was filtered and the filtrate set aside in the freezer overnight (–25 °C), to yield large needlelike crystals. These were filtered and dried under vacuum. Yield = 85%.

**Method 2.** [($^t$Bu)$_2$Ga(O$^t$Bu)]$_2$ (1.0 g, 1.94 mmol) and Ph$_3$PO (1.08 g, 3.89 mmol) were dissolved together in benzene (*ca.* 20 mL), and the resulting mixture was warmed to reflux for 1 h. After cooling, the solvent was removed under vacuum to leave a white solid. Yield: *ca.* 98%. Mp: 110–112 °C. Anal. Calcd for C$_{30}$H$_{42}$GaO$_2$P: C, 67.30; H, 7.90; P, 5.78. Found: C, 67.13; H, 8.01; P, 5.94. MS (*m/z*, CI, isobutane): 463 (M$^+$ – $^t$Bu, 10%), 419 (M$^+$ – 2 $^t$Bu, 5%), 401 [$^t$BuGa(O=PPh$_3$), 5%], 385 ($^t$BuGaPPh$_3$, 30%), 345 (GaOPPh$_3$, 35%), 279 (O=PPh$_3$, 100%), 263 (PPh$_3$, 100%), 201 (O=PPh$_2$, 20%), 185 (PPh$_2$, 65%). IR (cm$^{-1}$): 1591 (m), 1571 (w), 1310 (w), 1205 (s), 1185 (s), 1170 (sh), 1150 [s, $\nu$(P=O)], 1120 (s), 1087 (s), 1071 (m), 1025 (m), 1005 (m), 995 (sh), 979 (s), 940 (w), 920 (w), 895 (w), 860 (s), 767 (m), 755 (s), 745 (s), 724 (s), 690 (s), 616 (w), 566 (m), 542 (s), 512 (m), 463 (m), 440 (w). $^1$H NMR: $\delta$ 7.85 (6H, *m*, *o*-C*H*), 7.04 (9H, m, *m* + *p*-C*H*), 1.50 [9H, s, OC(C*H*$_3$)$_3$], 1.37 [18H, s, GaC(C*H*$_3$)$_3$]. $^{13}$C NMR: 133.43, 132.69 (br, *m* + *p*-CH), 128.55 [d, *J*(C—P) = 11.12 Hz, *o*-CH], 68.00 [O*C*(CH$_3$)$_3$], 35.00 [OC(*C*H$_3$)$_3$], 31.75 [GaC(*C*H$_3$)$_3$], 23.25 [Ga*C*(CH$_3$)$_3$]. $^{31}$P NMR: $\delta$ 36.6.

**($^t$Bu)$_2$Ga(O$^t$Bu)(O=AsPh$_3$) (2)** was prepared in a manner analogous to that for 1. Yield: 80%. Mp: 115–120 °C. Anal. Calcd for C$_{30}$H$_{42}$AsGaO$_2$: C, 62.20; H, 7.30. Found: C, 61.89; H, 7.24. MS (*m/z*, EI): 578 (M$^+$, 3%), 521 (M$^+$ – $^t$Bu, 100%), 505 (M$^+$ – O$^t$Bu, 20%), 463 (M$^+$ – 2$^t$Bu, 10%), 447 [$^t$BuGa(O=AsPh$_3$), 28%], 391 [Ga(O=AsPh$_3$), 62%], 321 (O=AsPh$_3$, 100%), 306 (AsPh$_3$, 20%), 227 (AsPh$_2$, 100%), 183 ($^t$Bu$_2$Ga, 28%), 152 (AsPh, 60%). IR (cm$^{-1}$): 1485 (m), 1310 (w), 1215 (sh), 1200 (s), 1190 (m), 1090 (s), 1070 (w), 1025 (w), 1010 (w), 1000 (m), 970 (s), 940 (w), 880 [s, $\nu$(As=O)], 815 (s), 760 (w), 750 (s), 740 (s), 725 (w), 695 (s), 620 (w), 570 (m), 480 (s), 460 (s), 415 (s), 350 (s), 340 (s). $^1$H NMR: $\delta$ 7.83 [6H, d, *J*(H—H) = 7.5 Hz, *o*-C*H*], 7.04 [9H, m, *m* + *p*-C*H*], 1.42 [18H, s, C(C*H*$_3$)$_3$], 1.41 [9H, s, OC(C*H*$_3$)$_3$]. $^{13}$C NMR: $\delta$ 132.87, 132.59, 130.89, 129.23 (*C*$_6$H$_5$), 68.02 [O*C*(CH$_3$)$_3$], 34.90 [OC(*C*H$_3$)$_3$], 32.20 [C(*C*H$_3$)$_3$], 23.44 [*C*(CH$_3$)$_3$].

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[30] (a) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; p 223. (b) Shanan-Atidi, H.; BarEli, K. H. *J. Phys. Chem.* **1970**, *74*, 961.

**$({}^{t}Bu)_2Ga(O^{t}Bu)(O{=}PPh_2Me)$ (3)** was prepared in a manner analogous to that of 1. Yield: 70%. Mp: 59–61 °C. Anal. Calcd for $C_{25}H_{40}GaO_2P$: C, 63.44; H, 8.51; P, 6.54. Found: C, 63.30; H, 8.51; P, 6.27. MS (*m/z*, EI): 401 ($M^+ - O^{t}Bu$, 55%), 343 [${}^{t}BuGa(O{=}PPh_2Me)$, 65%], 285 [$Ga(O{=}PPh_2Me)$, 25%], 271 ($GaPPh_2Me$, 30%), 216 ($O{=}PPh_2Me$, 80%), 200 ($PPh_2Me$, 80%), 183 (${}^{t}Bu_2Ga$, 70%), 108 (PPh, 12%), 77 (Ph, 50%). IR ($cm^{-1}$): 1970 (w), 1900 (w), 1831 (w), 1821 (w), 1777 (w), 1592 (m), 1313 (m), 1293 (s), 1200–1100 [s, $\nu(P{=}O)$], 1071 (s), 1029 (s), 1009 (s), 977 (s), 938 (s), 894 (s), 882 (s), 812 (s), 778 (s), 740 (s), 718 (s). ${}^{1}H$ NMR: $\delta$ 7.62 [4H, m, *o*-C*H*], 7.03 [6H, m, *m* + *p*-C*H*], 2.01 [3H, d, $J(H{-}P)$ = 13.94 Hz, $CH_3$], 1.53 [9H, s, $OC(CH_3)_3$], 1.36 [18H, s, $C(CH_3)_3$]. ${}^{13}C$ NMR: $\delta$ 132.51 (*p*-CH), 131.64 [d, $J(C{-}P)$ = 10.31 Hz, *m*-CH], 128.65 [d, $J(C{-}P)$ = 12.82 Hz *o*-CH], 68.15 [$OC(CH_3)_3$], 35.09 [$OC(CH_3)_3$], 31.97 [$PCH_3$], 31.60 [$C(CH_3)_3$], 23.05 [$C(CH_3)_3$]. ${}^{31}P$ NMR: $\delta$ 42.2.

**$({}^{t}Bu)_2Ga(O^{t}Bu)(O{=}PEt_3)$ (4)** was prepared in a manner analogous to that of 1. MS (*m/z*, EI): 317 ($M^+ - O^{t}Bu$, 75%), 203 [$Ga(O{=}PEt_3)$, 50%], 183 (${}^{t}Bu_2Ga$, 75%), 135 ($O{=}PEt_3$, 100%), 69 (Ga, 45%), 57 (${}^{t}Bu$, 100%). ${}^{1}H$ NMR: $\delta$ 1.44 [9H, s, $OC(CH_3)_3$], 1.36 [18H, s, $C(CH_3)_3$], 1.38 [6H, m, $PCH_2$], 0.69 [9H, dt, $J(H{-}H)$ = 7.7 Hz, $J(H{-}P)$ = 17.23 Hz, $PCH_2CH_3$]. ${}^{13}C$ NMR: $\delta$ 67.81 [$OC(CH_3)_3$], 35.11 [$OC(CH_3)_3$], 31.75 [$C(CH_3)_3$], 22.76 [$C(CH_3)_3$], 18.35 [d, $J(C{-}P)$ = 65.82 Hz, $PCH_2$], 5.65 [d, $J(C{-}P)$ = 4.27 Hz, $PCH_2CH_3$]. ${}^{31}P$ NMR: $\delta$ 66.6.

**$({}^{t}Bu)_2Ga(O^{t}Bu)(O{=}P^{n}Bu_3)$ (5)** was prepared in a manner analogous to that of 1. ${}^{1}H$ NMR: $\delta$ 1.71 [6H, m, $PCH_2$], 1.39 [9H, s, $OC(CH_3)_3$], 1.32 [12H, m, $PCH_2CH_2CH_2$], 1.28 [18H, s, $C(CH_3)_3$], 0.82 [9H, t, $J(H{-}H)$ = 7.16 Hz, $CH_3$]. ${}^{13}C$ NMR: $\delta$ 67.83 [$OC(CH_3)_3$], 35.10 [$OC(CH_3)_3$], 31.69 [$GaC(CH_3)_3$], 26.25 [d, $J(P{-}C)$ = 64.13 Hz, $PCH_2$], 24.46 [d, $J(P{-}C)$ = 14.83 Hz, $PCH_2CH_2$], 23.87 [d, $J(P{-}C)$ = 4.15 Hz, $CH_2CH_3$], 23.62 [$GaC(CH_3)_3$], 13.70 (s, $CH_3$). ${}^{31}P$ NMR: $\delta$ 62.9.

**$({}^{t}Bu)_2Ga(O^{t}Bu)(O{=}P^{i}Pr_3)$ (6)** was prepared in a manner analogous to that of 1. ${}^{1}H$ NMR: $\delta$ 1.74 [3H, d sep, $J(P{-}H)$ = 67 Hz, $J(H{-}H)$ = 6.29 Hz, $PCH$], 1.46 [9H, s, $OC(CH_3)_3$], 1.35 [18H, s, $C(CH_3)_3$], 0.95 [18H, dd, $J(H{-}H)$ = 6.94 Hz, $J(P{-}H)$ = 14.7 Hz), $CH_3$]. ${}^{13}C$ NMR: $\delta$ 67.78 [$OC(CH_3)_3$], 35.07 [$OC(CH_3)_3$], 31.94 [$C(CH_3)_3$], 25.14 [d, $J(C{-}P)$ = 60.86 Hz, $PCH$], 16.52 [d, $J(P{-}C)$ = 17.1 Hz, $PCCH_3$]. ${}^{31}P$ NMR: $\delta$ 69.3.

**$({}^{t}Bu)_2Ga(OO^{t}Bu)(O{=}PPh_3)$ (7).** To a benzene-$d_6$ (2.0 mL) solution of $[({}^{t}Bu)_2Ga(\mu\text{-}OO^{t}Bu)]_2$ (0.010 g, 0.0183 mmol) was added $O{=}PPh_3$ (0.010 g, 0.0366 mmol). ${}^{1}H$ NMR: $\delta$ 7.78 [6H, s, br, *o*-C*H*, Ph], 7.04 [9H, m, *m* + *p*-C*H*], 1.44 [9H, s, $OOC(CH_3)_3$], 1.41 [18H, s, $GaC(CH_3)_3$]. ${}^{13}C$ NMR: 133.22, 132.85, 128.69, 128.60 ($PC_6H_5$), 77.24 [$OOC(CH_3)_3$], 31.45 [$GaC(CH_3)_3$], 27.05 [$OOC(CH_3)_3$], 23.88 [$GaC(CH_3)_3$]. ${}^{31}P$ NMR: $\delta$ 37.2.

**Reaction of $[({}^{t}Bu)_2Ga(\mu\text{-}OO^{t}Bu)]_2$ with $P(OPh)_3$ and $P(OMe)_3$.** To a pentane (30 mL) solution of $[({}^{t}Bu)_2Ga(\mu\text{-}OO^{t}Bu)]_2$ (1.0 g, 2.11 mmol) was added $P(OPh)_3$ (0.96 mL, 4.22 mmol). The reaction was stirred at room temperature overnight, after which the solvent was removed under vacuum and the residues were determined by ${}^{1}H$ and ${}^{31}P$ NMR to be $[({}^{t}Bu)_2Ga(\mu\text{-}O^{t}Bu)]_2$ {${}^{1}H$ NMR: $\delta$ 1.32 [9H, s, $OC(CH_3)_3$], 1.31 [18H, s, $GaC(CH_3)_3$]}, and $O{=}P(OPh)_3$ (${}^{31}P$ NMR: $\delta$ −16.47). Similar results were obtained for the analogous reaction with $P(OMe_3)$ {${}^{31}P$ NMR: 2.2 [$O{=}P(OMe)_3$]}.

**$({}^{t}Bu)_2Ga(\mu\text{-}O^{t}Bu)(\mu\text{-}OO^{t}Bu)Ga({}^{t}Bu)_2$ (8).** A pentane (*ca.* 70 mL) solution of $[({}^{t}Bu)_2Ga(\mu\text{-}OO^{t}Bu)]_2$ (4.0 g, 7.32 mmol) and dppe (1.45 g, 3.66 mmol) were stirred together at room temperature overnight. The next day a clear solution had resulted. The volume of solvent was reduced under vacuum, and a small quantity of a white precipitate formed which was filtered out and dried under vacuum. From ${}^{1}H$, ${}^{13}C$, and ${}^{31}P$ NMR this was determined to consist of mainly $dppeO_2$ (${}^{31}P$ NMR: $\delta$ 29.2 ppm) and $[({}^{t}Bu)_2Ga(\mu\text{-}O^{t}Bu)]_2$. The filtrate was set aside in the freezer (−20 °C). More crystalline material was obtained which was filtered out and dried under vacuum. Yield: 60%. Mp: 87 °C (explodes). Anal. Calcd for $C_{24}H_{54}Ga_2O_3$: C, 54.37; H, 10.26. Found: C, 55.09; H, 10.38. MS (*m/z*, CI, Isobutane): 473 ($M^+ - {}^{t}Bu$, 90%), 457 ($M^+ - O^{t}Bu$, 60%), 441 ($M^+ - OO^{t}Bu$, 10%), 417 ($M^+ - 2\,{}^{t}Bu$, 100%), 401 ($M^+ - {}^{t}Bu - O^{t}Bu$, 100%), 385 ($M^+ - 2\,O^{t}Bu$, 15%). IR ($cm^{-1}$): 1244 (s), 1174 (s), 1046 (w), 1027 (m), 1009 (s), 937 (s), 917 (s), 894 (s), 835 (s), 812 (s), 765 (s), 750 (s), 722 (m), 583 (s), 556 (s), 542 (s), 481 (s), 454 (sh), 438 (s), 403 (s), 365 (s). ${}^{1}H$ NMR: $\delta$ 1.36 [36H, s, $GaC(CH_3)_3$], 1.26 [9H, s, $OC(CH_3)_3$], 1.17 [9H, s, $OOC(CH_3)_3$]. ${}^{13}C$ NMR: $\delta$ 81.94 [$OOC(CH_3)_3$], 71.76 [$OC(CH_3)_3$], 33.05 [$OC(CH_3)_3$], 32.55 [$GaC(CH_3)_3$], 27.60 [$GaC(CH_3)_3$], 26.83 [$OOC(CH_3)_3$].

**Reaction of $({}^{t}Bu)_2Ga(\mu\text{-}O^{t}Bu)(\mu\text{-}OO^{t}Bu)Ga({}^{t}Bu)_2$ with $O{=}PPh_3$.** $({}^{t}Bu)_2Ga(\mu\text{-}O^{t}Bu)(\mu\text{-}OO^{t}Bu)Ga({}^{t}Bu)_2$ (0.01 g, 0.0188 mmol) and $O{=}PPh_3$ (0.010 g, 0.0377 mmol) were heated at *ca.* 50 °C in benzene-$d_6$ in an NMR tube. Analysis of the resulting reaction mixture indicated the presence of an equimolar mixture of 1 and 7.

**$({}^{t}Bu)_2\overline{Ga[(O)P(Ph)_2CH(O}})P(Ph)_2]$ (9). Method 1.** A pentane solution (60 mL) of $[({}^{t}Bu)_2Ga(\mu\text{-}OO^{t}Bu)]_2$ (4.0 g, 7.324 mmol) and dppm (1.4 g, 3.66 mmol) were stirred at room temperature overnight. The volume of the resulting clear solution was reduced (40 mL) under vacuum and set aside in the freezer (−25 °C) to yield several batches of crystalline material. Yield: *ca.* 60%.

**Method 2.** $Ga({}^{t}Bu)_3(dppmO_2)$ (1.0 g, 1.52 mmol) was refluxed in hexane (50 mL) overnight. Upon cooling, large colorless crystals formed. These were filtered out and dried under vacuum. The filtrate was evaporated to dryness under vacuum to yield more crude product. Yield: *ca.* 90%. Mp: 140–141 °C. Anal. Calcd for $C_{33}H_{39}GaO_2P_2$: C, 66.13; H, 6.55; P, 11.63. Found: C, 66.04; H, 6.48; P, 11.68. MS (*m/z*, CI, Isobutane): 599 ($M^+ + 1$, 45%), 541 ($M^+ - {}^{t}Bu$, 100%). IR ($cm^{-1}$): 1305 (w), 1195 (s), 1185 (sh), 1165 (s), 1110 (s), 1076 (s), 1060 (s), 1022 (m), 1010 (m), 994 (m), 953 (s), 843 (w), 811 (s), 776 (sh), 749 (s), 739 (s), 716 (s), 693 (s), 618 (w), 594 (w), 530 (s), 515 (sh), 505 (sh), 460 (w), 425 (m), 400 (m). ${}^{1}H$ NMR: $\delta$ 7.82 [8H, m, *o*-C*H*, Ph], 7.00 [12H, m, *m*-C*H*, and *p*-C*H*, Ph], 2.07 [1H, t, $J(P{-}H)$ = 3.53 Hz, $P_2CH$], 1.38 [18H, s, $C(CH_3)_3$]. ${}^{13}C$ NMR: $\delta$ 137.92 [d, $J(P{-}C)$ = 113.02 Hz, P–*C*, Ph], 131.26 [m, *o*-CH and *m*-CH, Ph], 130.91 (*p*-CH, Ph), 30.70 [$C(CH_3)_3$], 23.54 [$C(CH_3)_3$], 14.67 [t, $J(P{-}C)$ = 121.94 Hz, $P_2CH$]. ${}^{31}P$ NMR: $\delta$ 44.7.

**$Ga({}^{t}Bu)_3(dppmO_2)$ (10).** To a suspension of $dppmO_2$ (2.0 g, 4.8 mmol) in pentane (30 mL) was added a solution of $Ga({}^{t}Bu)_3$ (1.15 g, 4.77 mmol) in pentane (20 mL) dropwise. After stirring for 1 h, the precipitate was filtered out and dried under vacuum. Yield: *ca.* 90%. Mp: 153–155 °C. Anal. Calcd for $C_{37}H_{49}GaO_2P_2$: C, 67.59; H, 7.51; P, 9.42. Found: C, 67.24; H, 6.86; P, 9.34. IR ($cm^{-1}$): 1993 (w), 1976 (w), 1956 (w), 1927 (w), 1908 (w), 1887 (w), 1830 (w), 1808 (w), 1590 (m), 1311 (w), 1283 (w), 1210 (s), 1187 (s), 1170 (s), 1158 (sh), 1129 (sh), 1121 (s), 1100 (s), 1075 (m), 1028 (m), 1008 (m), 998 (m), 969 (w), 934 (w), 811 (s), 776 (s), 759 (s), 746 (s), 727 (m), 697 (s), 670 (s), 553 (s), 526 (sh), 512 (s), 500 (s), 487 (s), 474 (m), 463 (m), 427 (m). ${}^{1}H$ NMR: $\delta$ 7.81 [8H, m, *o*-C*H*, Ph], 6.89 [12H, m, *m* and *p*-C*H*, Ph], 3.81 [2H, t, $J(H{-}P)$ = 15.41 Hz, $P{-}CH_2$], 1.46 [27H, s, $GaC(CH_3)_3$]. ${}^{13}C$ NMR: $\delta$ 132.23 (*o*-*C*, Ph), 128.69 (*m*-*C*, Ph), 128.59 (*p*-*C*, Ph), 34.52 [t, $J(C{-}P)$ = 56.95 Hz, $P_2CH_2$], 32.92 [$GaC(CH_3)_3$], 24.45 [$GaC(CH_3)_3$]. ${}^{31}P$ NMR: $\delta$ 27.5 (br).

**$Ga({}^{t}Bu)_3(O{=}PPh_3)$ (11).** To a suspension of $O{=}PPh_3$ (1.15 g, 4.14 mmol) in pentane (40 mL) was added $Ga({}^{t}Bu)_3$ (1.0 g, 4.14 mmol) dropwise at room temperature. After stirring for 1 h, the solvent was removed to leave a white powder. Yield: *ca.* 90%. Mp: 142–144 °C. Anal. Calcd for $C_{30}H_{42}OGaP$: C, 69.38; H, 8.15; P, 5.96. Found: C, 69.38; H, 8.26; P, 5.99. IR ($cm^{-1}$): 1590 (w), 1335 (w), 1310 (w), 1263 (w), 1183 (sh), 1166 (s), 1119 (s), 1095 (m), 1070 (m), 1027 (m), 1003 (m), 974 (w), 933 (m), 808 (s), 755 (m), 724 (s), 724 (s), 693 (s), 538 (s), 461 (w), 443 (w), 400 (m). ${}^{1}H$ NMR: $\delta$ 7.63 (6H, m, *o*-C*H*), 6.98 (9H, m, *m* + *p*-C*H*), 1.44 [27H, s, $C(CH_3)_3$]. ${}^{13}C$ NMR: $\delta$ 132.85, 132.77, 128.81, 128.71 ($C_6H_5$), 32.85 [$C(CH_3)_3$], 24.63 [$C(CH_3)_3$]. ${}^{31}P$ NMR: $\delta$ 34.2 (s).

**X-ray Crystallographic Studies.** A crystal data summary is given in Table IV; fractional atomic coordinates are listed in Tables V–VII.

A crystal of compound 2 was mounted directly onto the goniometer with silicon grease. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,

**Table IV. Summary of X-ray Diffraction Data**

| compd | $(^t\mathrm{Bu})_2\mathrm{Ga}(\mathrm{O}^t\mathrm{Bu})(\mathrm{O{=}AsPh_3})$ | $(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{O}^t\mathrm{Bu})(\mu\text{-}\mathrm{OO}^t\mathrm{Bu})\mathrm{Ga}(^t\mathrm{Bu})_2$ | $(^t\mathrm{Bu})_2\mathrm{Ga}[(\mathrm{O})\mathrm{P(Ph)_2CH(O)P(Ph)_2}]$ |
|---|---|---|---|
| formula | $C_{30}H_{42}AsGaO_2$ | $C_{24}H_{54}Ga_2O_3$ | $C_{33}H_{39}GaO_2P$ |
| $F_w$ | 579.3 | 530.1 | 599.3 |
| cryst syst | monoclinic | monoclinic | triclinic |
| space group | $C2/c$ | $C2/m$ | $P\bar{1}$ |
| $a$, Å | 24.092(7) | 16.642(1) | 11.724(1) |
| $b$, Å | 17.200(7) | 11.167(1) | 14.917(1) |
| $c$, Å | 17.724(8) | 8.7415(8) | 18.070(1) |
| $\alpha$, Å | | | 100.341(6) |
| $\beta$, Å | 126.10(2) | 118.475(8) | 93.989(8) |
| $\gamma$, Å | | | 99.318(8) |
| $V$, Å$^3$ | 5934(4) | 1428.1(3) | 3052.2(5) |
| $Z$ | 8 | 2 | 4 |
| $D_{\mathrm{calcd}}$, g cm$^{-3}$ | 1.297 | 1.233 | 1.304 |
| cryst dimens, mm | 0.43 × 0.35 × 0.33 | 0.30 × 0.40 × 0.40 | 0.33 × 0.37 × 0.38 |
| radiation | | Mo K$\alpha$ ($\lambda$ = 0.710 73) graphite monochromator | |
| temp, K | 273 | 183 | 183 |
| $2\theta$ range, deg | 4.0–45.0 | 4.0–55.0 | 4.0–50.0 |
| scan type | $2\theta$–$\theta$ | $2\theta$–$\theta$ | $2\theta$–$\theta$ |
| no. of reflcns collcd | 4357 | 1801 | 11384 |
| no. of ind reflcns | 3850 | 1652 | 10169 |
| no. of obsd reflcns | 3301 ($\lvert F_o\rvert > 4.0\sigma(\lvert F_o\rvert)$) | 1625 ($\lvert F_o\rvert > 1.0\sigma(\lvert F_o\rvert)$) | 9559 ($\lvert F_o\rvert > 2.0\sigma(\lvert F_o\rvert)$) |
| final $R$ indices (obsd data) | $R$ = 0.059, $R_w$ = 0.085 | $R$ = 0.062, $R_w$ = 0.072 | $R$ = 0.037, $R_w$ = 0.046 |
| largest diff peak, e Å$^{-3}$ | 0.95 | 1.25 | 0.36 |

**Table V. Fractional Coordinates (×10$^4$) and Equivalent Isotopic Thermal Parameters (×10$^4$ Å$^2$) of the Non-Hydrogen Atoms in $(^t\mathrm{Bu})_2\mathrm{Ga}(\mathrm{O}^t\mathrm{Bu})(\mathrm{O{=}AsPh_3})$ (2)**

| | $x$ | $y$ | $z$ | $U$(eq)$^a$ |
|---|---|---|---|---|
| Ga(1) | 3264(1) | –424(1) | 7201(1) | 33(1) |
| C(11) | 3913(4) | 467(4) | 7942(5) | 56(4) |
| C(12) | 3782(6) | 1115(5) | 7264(7) | 108(7) |
| C(13) | 4658(4) | 221(6) | 8427(7) | 88(6) |
| C(14) | 3832(5) | 785(6) | 8659(8) | 109(8) |
| C(21) | 3468(3) | –1137(3) | 6498(4) | 43(3) |
| C(22) | 3583(5) | –664(5) | 5884(6) | 73(6) |
| C(23) | 4097(4) | –1653(5) | 7151(5) | 68(4) |
| C(24) | 2866(3) | –1687(4) | 5879(5) | 56(4) |
| O(1) | 2815(2) | –923(2) | 7631(3) | 48(2) |
| C(31) | 3061(3) | –1363(4) | 8452(5) | 54(4) |
| C(32) | 3805(6) | –1516(10) | 8986(9) | 164(10) |
| C(33) | 2657(9) | –2077(5) | 8187(8) | 161(12) |
| C(34) | 2933(6) | –946(6) | 9063(7) | 107(8) |
| O(2) | 2423(2) | 118(2) | 6182(3) | 37(2) |
| As(1) | 1623(1) | 136(1) | 5862(1) | 29(1) |
| C(41) | 1546(3) | 326(3) | 6853(3) | 31(3) |
| C(42) | 1161(3) | –152(3) | 7009(4) | 44(3) |
| C(43) | 1127(4) | 29(5) | 7754(5) | 64(5) |
| C(44) | 1483(4) | 642(5) | 8320(5) | 62(4) |
| C(45) | 1850(4) | 1102(4) | 8163(5) | 63(5) |
| C(46) | 1885(3) | 960(4) | 7426(4) | 49(4) |
| C(51) | 1212(3) | 986(3) | 5019(4) | 34(3) |
| C(52) | 1554(3) | 1312(4) | 4682(4) | 46(3) |
| C(53) | 1264(4) | 1946(4) | 4077(5) | 62(4) |
| C(54) | 635(4) | 2238(4) | 3803(4) | 58(4) |
| C(55) | 292(3) | 1908(4) | 4123(5) | 56(4) |
| C(56) | 577(3) | 1280(4) | 4733(4) | 46(3) |
| C(61) | 1135(3) | –796(3) | 5256(4) | 35(3) |
| C(62) | 1373(3) | –1493(3) | 5698(5) | 49(4) |
| C(63) | 1037(4) | –2171(4) | 5279(6) | 60(5) |
| C(64) | 438(4) | –2158(4) | 4383(6) | 64(5) |
| C(65) | 186(3) | –1478(4) | 3925(5) | 59(4) |
| C(66) | 532(3) | –784(4) | 4341(5) | 47(4) |

$^a$ Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathrm{U}_{ij}$ tensor.

**Table VI. Fractional Coordinates (×10$^4$) and Equivalent Isotropic Thermal Parameters (×10$^4$ Å$^2$) of the Non-Hydrogen Atoms in $(^t\mathrm{Bu})_2\mathrm{Ga}(\mu\text{-}\mathrm{O}^t\mathrm{Bu})(\mu\text{-}\mathrm{OO}^t\mathrm{Bu})\mathrm{Ga}(^t\mathrm{Bu})_2$ (8)**

| | $x$ | $y$ | $z$ | $U$(eq)$^a$ |
|---|---|---|---|---|
| Ga(1) | 0 | 3597(1) | 0 | 44(1) |
| O(1) | –774(3) | 5000 | –1296(6) | 56(2) |
| O(2) | –1093(8) | 5000 | –2871(13) | 69(6) |
| C(1) | –1899(7) | 5000 | –3379(13) | 76(5) |
| C(2) | –1536(18) | 5000 | –4611(23) | 105(12) |
| C(3) | –2350(5) | 3890(7) | –3159(10) | 63(3) |
| C(2A) | –2274(13) | 5000 | –5642(21) | 87(9) |
| C(3A) | –1788(11) | 3860(13) | –4238(20) | 66(7) |
| C(4) | 502(3) | 2658(14) | –1344(6) | 53(2) |
| C(5) | 938(4) | 3422(4) | –2165(7) | 59(2) |
| C(6) | 1161(5) | 1729(6) | –225(9) | 101(4) |
| C(7) | –241(5) | 1939(7) | –2771(10) | 123(5) |

$^a$ Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathrm{U}_{ij}$ tensor.

using a Nicolet R3m/V diffractometer operating in the $\theta$–$2\theta$ scan mode. Data collection was controlled by using the Nicolet P3 program.[31] Empirical absorption corrections were applied to the data using the program PSICOR. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)_2$ where $w^{-1} = \sigma_2(|F_o|) + 0.0092(|F_o|)^2$. Further experimental data are given in Table IV.

The structure was solved using the direct methods program XS,[32] which revealed the position of most of the heavy atoms. Most but not all of the hydrogens were visible in the final difference map. Hydrogens were included as fixed atom contributors in the final cycles $d$(C–H) = 0.96 Å and $U$(iso) = 0.08 Å$^2$. Details of the refinement are given in Table IV. Atomic scattering factors and anomalous scattering parameters were as given in ref 33.

X-ray data for compound 8 and 9 were collected on a Siemens P3 diffractometer equipped with a modified LT-2 low-temperature system. Laue symmetry determination, crystal class, unit-cell parameters, and the crystal's orientation matrix were carried out by previously described techniques.

All data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. The systematic extinctions for 8 were $hkl$ for $h + k = 2n + 1$; the diffraction symmetry was $2/m$. The three possible monoclinic space groups are $C2$ [$C^3{}_2$, No. 5], $Cm$ [$C^3{}_s$; No. 8], and $C2/m$ [$C^3{}_{2h}$; No. 12]. The centrosymmetric space group $C2/m$ was later determined to be the best choice (see below). There were no systematic absences nor any diffraction symmetry other than the Friedel conditions observed for 9. The two possible triclinic space groups are $P1$ [$C^1{}_1$; No. 1] and $P\bar{1}$ [$C^1{}_i$; No. 2]. The centrosymmetric space group $P\bar{1}$ was chosen and later proved to be correct by successful refinement of the model.

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(31) *P3/R3 Data Collection Manual*; Nicolet Instrument Corp.: Madison, WI, 1987.

(32) Sheldrick, G. M. *SHELXTL-PLUS*; Nicolet Corp.: Madison, WI, 1986.

(33) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

**Table VII. Fractional Coordinates (×10$^4$) and Equivalent Isotopic Thermal Parameters (×10$^4$ Å$^2$) of the Non-Hydrogen Atoms in $(^t\mathrm{Bu})_2\overline{\mathrm{Ga}[(\mathrm{O})\mathrm{P}(\mathrm{Ph})_2\mathrm{CHP}(\mathrm{O}})(\mathrm{Ph})_2]$ (9)**

| | *x* | *y* | *z* | *U*(eq)[a] | | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|---|---|---|---|---|
| Ga(1) | 5832(1) | 7471(1) | 2012(1) | 189(1) | Ga(2) | 13391(1) | 1328(1) | 2741(1) | 227(1) |
| P(1) | 6790(1) | 5666(1) | 2274(1) | 186(2) | P(3) | 10726(1) | 1326(1) | 2369(1) | 203(2) |
| P(2) | 4275(1) | 5753(1) | 2480(1) | 195(2) | P(4) | 11426(1) | −324(1) | 2865(1) | 200(2) |
| O(1) | 6875(1) | 6576(1) | 1986(1) | 209(5) | O(3) | 12013(1) | 1707(1) | 2333(1) | 248(6) |
| O(2) | 4467(1) | 6700(1) | 2248(1) | 240(6) | O(4) | 12690(1) | 69(1) | 2773(1) | 258(6) |
| C(1) | 7339(2) | 4821(2) | 1610(1) | 217(8) | C(34) | 10074(2) | 2252(2) | 2858(1) | 222(8) |
| C(2) | 7491(2) | 3984(2) | 1806(2) | 300(9) | C(35) | 10744(3) | 3128(2) | 3071(2) | 326(10) |
| C(3) | 7829(2) | 3306(2) | 1278(2) | 345(10) | C(36) | 10270(3) | 3857(2) | 3443(2) | 389(11) |
| C(4) | 8026(2) | 3452(2) | 569(2) | 342(10) | C(37) | 9127(3) | 3707(2) | 3599(2) | 369(11) |
| C(5) | 7899(3) | 4292(2) | 374(2) | 342(10) | C(38) | 8458(3) | 2845(2) | 3386(2) | 353(10) |
| C(6) | 7554(2) | 4972(2) | 894(2) | 271(9) | C(39) | 8915(2) | 2111(2) | 3012(2) | 288(9) |
| C(7) | 7838(2) | 5889(2) | 3101(1) | 211(8) | C(40) | 10059(2) | 1111(2) | 1408(1) | 237(8) |
| C(8) | 9005(2) | 6163(2) | 3018(2) | 329(10) | C(41) | 10633(3) | 1496(2) | 863(2) | 336(10) |
| C(9) | 9820(3) | 6393(2) | 3645(2) | 398(11) | C(42) | 10090(3) | 1382(2) | 138(2) | 442(12) |
| C(10) | 9483(3) | 6349(2) | 4350(2) | 369(10) | C(43) | 8969(3) | 907(2) | −44(2) | 432(11) |
| C(11) | 8331(3) | 6072(2) | 4440(2) | 338(10) | C(44) | 8396(3) | 521(3) | 497(2) | 476(12) |
| C(12) | 7501(2) | 5835(2) | 3818(2) | 274(9) | C(45) | 8942(3) | 622(2) | 1216(2) | 366(10) |
| C(13) | 3033(2) | 5014(2) | 1909(1) | 220(8) | C(46) | 11342(2) | −676(2) | 3766(1) | 246(8) |
| C(14) | 3195(2) | 4418(2) | 1254(2) | 304(9) | C(47) | 12354(3) | −655(2) | 4218(2) | 394(11) |
| C(15) | 2250(3) | 3876(2) | 791(2) | 379(10) | C(48) | 12291(4) | −880(3) | 4927(2) | 520(14) |
| C(16) | 1138(3) | 3932(2) | 965(2) | 350(10) | C(49) | 11243(4) | −1142(2) | 5183(2) | 524(15) |
| C(17) | 959(2) | 4520(2) | 1612(2) | 344(10) | C(50) | 10234(4) | −1183(2) | 4733(2) | 493(13) |
| C(18) | 1896(2) | 5054(2) | 2081(2) | 305(9) | C(51) | 10283(3) | −947(2) | 4026(2) | 372(11) |
| C(19) | 3815(2) | 5940(2) | 3424(1) | 220(8) | C(52) | 11088(2) | −1406(2) | 2192(1) | 210(8) |
| C(20) | 3210(2) | 6650(2) | 3676(2) | 292(9) | C(53) | 11956(2) | −1934(2) | 2035(2) | 290(9) |
| C(21) | 2820(2) | 6735(2) | 4390(2) | 392(11) | C(54) | 11692(3) | −2807(2) | 1577(2) | 327(10) |
| C(22) | 3027(3) | 6129(2) | 4847(2) | 417(11) | C(55) | 10564(3) | −3161(2) | 1274(2) | 307(9) |
| C(23) | 3639(3) | 5429(2) | 4607(2) | 396(11) | C(56) | 9705(3) | −2644(2) | 1420(2) | 305(9) |
| C(24) | 4037(2) | 5343(2) | 3900(2) | 301(9) | C(57) | 9967(2) | −1771(2) | 1874(2) | 259(9) |
| C(25) | 6284(2) | 8471(2) | 2931(1) | 246(8) | C(58) | 14364(2) | 1324(2) | 1884(2) | 299(9) |
| C(26) | 5213(3) | 8867(2) | 3158(2) | 374(11) | C(59) | 13755(3) | 608(2) | 1205(2) | 398(11) |
| C(27) | 6775(3) | 8087(2) | 3588(2) | 400(11) | C(60) | 14506(3) | 2281(2) | 1665(2) | 463(13) |
| C(28) | 7192(3) | 9244(2) | 2773(2) | 343(10) | C(61) | 15565(3) | 1111(3) | 2083(3) | 515(15) |
| C(29) | 5567(2) | 7595(2) | 942(1) | 247(8) | C(62) | 13827(3) | 2007(2) | 3801(2) | 389(10) |
| C(30) | 6717(3) | 8017(3) | 685(2) | 392(12) | C(63) | 14798(4) | 1609(3) | 4175(2) | 499(14) |
| C(31) | 5124(3) | 6646(2) | 444(2) | 372(11) | C(64) | 12796(4) | 1965(3) | 4268(2) | 507(14) |
| C(32) | 4686(3) | 8229(3) | 853(2) | 449(13) | C(65) | 14276(5) | 3019(2) | 3780(3) | 615(16) |
| C(33) | 5423(2) | 5191(2) | 2414(2) | 241(9) | C(66) | 10465(2) | 410(2) | 2815(2) | 233(8) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computer Package[34] or the SHELXTL-Plus[32] program set.[28] The analytical scattering factors for neutral atoms were used through the analysis; the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)_2$ where $w^{-1} = \sigma^2(|F_o|) + x(|F_o|)_2$, $x$ = 0.0003 (**8**), 0.00016 (**9**).

The structures were solved by direct methods and refined by full least-squares methods (SHELXTL-PLUS).[32] Hydrogen atoms were included by using a riding model with $d$(C–H) = 0.96 Å and $U$(iso) = 0.08 Å$^2$. Refinement of positional and anisotropic thermal parameters led to convergence (see Table IV).

The structure of **8** was solved in all three possible space groups. In the chosen solution ($C2/m$) the molecule is a dimer which is located on a site of $2/m$ symmetry (0, $^1/_2$, 0). The peroxide and alkoxide ligands are disordered (see Figure 3). Attempts to model the disorder in space groups $C2$ and $Cm$ proved less satisfactory. In $C2$, there is a 2-fold rotation axis along the Ga···Ga vector which results in a disordered model similar to the $C2/m$ model. In the $Cm$ model, there is a mirror plane perpendicular to the Ga···Ga vector. It was expected that this model might be ordered; however, peroxide alkoxide mixing was still observed. In the end, it was determined that the present model best described the observed disorder. While the structure is not good enough for a detailed comparison of structural parameters, the structure is sufficient to determine atom connectivity.

**Acknowledgment.** Financial support for this work at Harvard is provided by the National Science Foundation and the Petroleum Research Fund (administered by the American Chemical Society). Funds for the purchase of the Nicolet R3m/V diffractometer system were made available to UCI from the National Science Foundation under Grant CHE-85-14495.

**Supplementary Material Available:** Listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (13 pages). Ordering information is given on any current masthead page.

OM930052F

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(34) *UCLA Crystallographic Computing Package*; University of California; Los Angeles, 1981. Strouse, C. Personal communication.