# MELDOLA LECTURE*
# Reactions of Group 13 Alkyls with Dioxygen and Elemental Chalcogens: From Carelessness to Chemistry

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## 1 Introduction

Since the atmospheric oxidation of group 13 organometallics is usually uncontrollably fast, often resulting in spontaneous combustion, chemists handling alkyl derivatives of the group 13 metals aluminium, gallium, and indium have traditionally made every effort to limit oxidative decomposition by carrying out reactions under an inert atmosphere. If the supply of oxygen is restricted, however, alkoxide compounds are formed as a result of auto-oxidation *via* unstable alkylperoxide intermediates (equation 1).[1,2]

$$\text{M–R} \xrightarrow{O_2} [\text{M–OOR}] \longrightarrow \text{M–OR} \qquad (1)$$

The literature on auto-oxidation of organo-aluminium compounds is extensive, and has been thoroughly reviewed.[3] In contrast, studies on the auto-oxidation of organo-gallium and indium compounds has been a recent development, the majority of work having been conducted by Alexandrov and coworkers.[4] While these researchers have studied the reactivity of a variety of gallium and indium trialkyls with dioxygen and organic peroxides, have successfully isolated several examples of gallium and indium alkylperoxide compounds (*e.g.*, $Me_2MOOR$ M = Ga, In; R = Me, $Bu^t$), and have studied the reactions of gallium and indium alkylperoxides with a number of organic substrates,[4] no structural data have been available for a group 13 alkylperoxide compound.

Our interest in the reactivity of organo-gallium and indium compounds with dioxygen and consequently the elemental chalcogens arose as a result of experimental carelessness. Having investigated the photochemical decomposition of the hybrid organo-gallium compounds $GaMe_x(Bu^t)_{3-x}$ we were attempting to prepare the indium analogues for study.[5] However, our efforts to do so were severely hindered by difficulties in the preparation and handling of the alkyl precursor $In(Bu^t)_3$, a yellow crystalline solid which is extremely light sensitive, decomposing in seconds under ambient light.[6] The proven stability of the Lewis base complexes of group 13 trialkyl as compared to the parent compounds prompted us to synthesize the quinuclidene (quin) adduct of $In(Bu^t)_3$. The Lewis acid–base complex $In(Bu^t)_3$(quin) is a colourless crystalline solid which shows no propensity to photochemical decomposition. The accidental oxidation of a sample of $In(Bu^t)_3$(quin) stored in pentane solution for six months in an inadequately greased Schlenck flask, resulted in the deposition of large colourless crystals, that were determined by *X*-ray crystallography to be the dimeric indium alkylperoxo compound $[(Bu^t)_2In(\mu\text{-}OOBu^t)]_2$![7] The stability of $[(Bu^t)_2In(\mu\text{-}OOBu^t)]_2$, and its gallium analogue, towards both thermolysis and further oxidation prompted our investigation into the reactions of $M(Bu^t)_3$ with dioxygen and also (the related reactions) with the elemental chalcogens. A review of these studies as well as related results from other laboratories are presented below.

## 2 Reactions of $M(Bu^t)_3$ with Dioxygen

The interaction of $M(Bu^t)_3$ (M = Ga, In) with an excess (1 atm) of dry oxygen leads to the formation of the alkylperoxo compounds $[(Bu^t)_2M(\mu\text{-}OOBu^t)]_2$ in essentially quantitative yield (equation 2).[7,8]

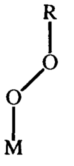
$$M(Bu^t)_3 + O_2 \xrightarrow[\text{pentane}]{-78\,^\circ C} \tfrac{1}{2}[(Bu^t)_2M(\mu\text{-}OOBu^t)]_2 \qquad (2)$$
$$M = Ga, In$$

Alexandrov *et al.* have reported[4,9] that the thermally sensitive alkyperoxo compounds $[Me_2M(\mu\text{-}OOR)]_2$ (M = Ga, In; R = Me, $Bu^t$) may be prepared by the reaction of $MMe_3$ and ROOH (equation 3). Attempts to synthesize $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ and $[(Bu^t)_2In(\mu\text{-}OOBu^t)]_2$ by an analogous route have, however, failed.

$$MMe_3 + ROOH \rightarrow \tfrac{1}{2}[Me_2M(\mu\text{-}OOR)]_2 + MeH \qquad (3)$$

The t-butyl substituted compounds $[(Bu^t)_2M(\mu\text{-}OOBu^t)]_2$ (M = Ga, In) are moisture sensitive, but are stable indefinitely under an atmosphere of dry oxygen at ambient conditions.[7,8] The enhanced stability of $[(Bu^t)_2M(\mu\text{-}OOBu^t)]_2$ as compared to the methyl derivatives is undoubtedly due to the steric hindrance provided by the group 13 t-butyl groups (see below).

Alkylperoxo moieties are known to act as monodentate ($\eta^1$) (1), bidentate ($\eta^2$) (2), and bridging ($\mu_2$) (3) ligands to transition metals.[10]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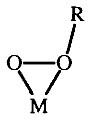
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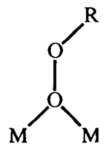
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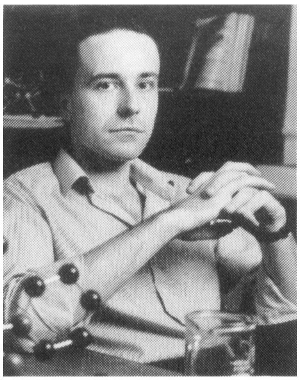
*Professor Andrew R. Barron received his B.Sc.(Hons) and A.R.C.S. degrees from Imperial College, University of London in 1983. He remained at Imperial to conduct his Ph.D and D.I.C. research under the supervision of Professor Sir Geoffrey Wilkinson, graduating in 1986. After a brief sojourn as a postdoctoral associate with Professor Alan H. Cowley at the University of Texas, Austin, in 1987 he joined the faculty at Harvard University, where he is currently an Associate Professor. In 1991 he received the Meldola medal and prize for his work with Group 13 organometallics, and is a recipient of a DuPont Young Faculty Fellowship and an Alcoa Prize Fellowship. His research interests span both the inorganic chemistry and materials science of aluminium, gallium, and indium.*



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Since the existence of dimers involving bridging alkoxides is a common feature in group 13 chemistry,[11] it would, therefore, be logical to expect the alkylperoxo group in $[(Bu^t)_2M(\mu\text{-}OOBu^t)]_2$ (M = Ga, In) to ligate in a similar fashion. The $\mu_2$-bridging mode of co-ordination of the t-butyl peroxide group and the dimeric nature in the solid state has been confirmed by *X*-ray crystallography, for both the gallium[8] and indium[7] compounds.

The molecular structure of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ is shown in Figure 1; the indium analogue is iso-structural. The molecules consist of two $(Bu^t)_2M$ fragments bridged by two $\mu_2$-t-butylperoxo groups, oriented in an eclipsed–staggered conformation, presumably so as to minimize lone-pair repulsion on the oxygen atoms. A similar t-butyl peroxide geometry was found in the *X*-ray structural study of the related complex $[(Cl_3CCO_2)Pd(\mu\text{-}OOBu^t)]_4$.[12]

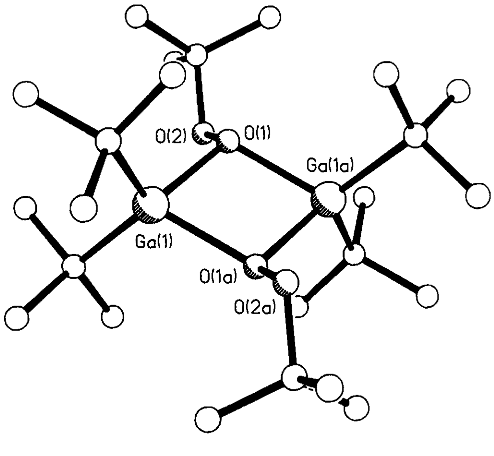


**Figure 1** The molecular structure of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$

Group 13 peroxides have previously been observed to undergo an auto-oxidation reaction in which one of the remaining alkyl groups is oxidized to an alkoxide by the peroxide ligand *via* either intra- (equation 4) or inter-molecular (equation 5) oxygen transfer.[4]

$$R_2MOOR \rightarrow RM(OR)_2 \qquad (4)$$

$$R_2MOOR + MR_3 \rightarrow 2R_2MOR \qquad (5)$$

A rapid inter-molecular oxygen transfer (*cf.* equation 5) appears to occur during the oxidation of $Al(Bu^t)_3$ since the mono-alkoxide $[(Bu^t)_2Al(\mu\text{-}OBu^t)]_2$ is the only product isolated.[13] However, no intra-molecular oxygen transfer reaction is observed for $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$, even at elevated temperatures. Instead, heating in benzene solution results in the formation of the mono-alkoxide dimer $[(Bu^t)_2Ga(\mu\text{-}OBu^t)]_2$ with the concomitant oxidation of benzene to phenol (equation 6).[8]

$$[(Bu^t)_2Ga(\mu\text{-}OO(Bu^t))_2 \xrightarrow[\text{benzene}]{\Delta} [(Bu^t)_2Ga(\mu\text{-}OBu^t)]_2 \qquad (6)$$

Since the dimeric structure of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ is undoubtedly similar to that of the less hindered methyl derivatives, the absence of significant auto-oxidation for $[(Bu^t)_2M(\mu\text{-}OOBu^t)]_2$ (M = Ga, In) suggests that the oxygen transfer for less sterically hindered alkyl peroxides is inter- and non intra-molecular. We presume, therefore, that this enhanced stability towards auto-oxidation is due to the steric bulk of t-butyl substituents on the metal, which preclude the close approach of the two molecules of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ required for inter-molecular oxygen transfer.

## 3 Reactivity of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$

While the reactivity of group 13 alkyl peroxides with aldehydes, alcohols, and esters has been investigated,[4] the isolation and crystallographic characterization of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$, and the observation that $[(Bu^t)_2Ga(\mu\text{-}OBu^t)]_2$ is the only gallium-containing side-product during the oxidation of benzene to phenol, provide an excellent system for gaining a better understanding of the reactivity of group 13 alkylperoxides with organic substrates. In order to demonstrate the oxidative ability of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ we have investigated the *model* oxidation of phosphines to phosphine oxides.[14]

### 3.1 Phosphines and Triphenylarsine

The interaction of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ with two molar equivalents of $PPh_3$ (in the absence of water) results in the formation of the Lewis acid–base adduct $[(Bu^t)_2Ga(\mu\text{-}OBu^t)(O{=}PPh_3)]$ in near quantitative yield (equation 7), hydrolysis of which gives uncomplexed $O{=}PPh_3$ as the only phosphorus-containing species, as determined by $^{31}P$ NMR spectroscopy.[14]

$$[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2 + 2ER_3 \xrightarrow[\text{Pentane}]{25\,^{\circ}C} 2[(Bu^t)_2Ga(OBu^t)(O{=}ER_3)] \qquad (7)$$
$$E = P, As$$

Similar phosphine and arsine oxide complexes $[(Bu^t)_2Ga(OBu^t)(O{=}ER_2R')]$ (E = As, R = R′ = Ph and E = P, R = Ph, R′ = Me; R = R′ = Et; R = R′ = Bu$^n$; R = R′ = Pr$^i$), are obtained from the reaction of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ with $AsPh_3$ or the appropriate phosphine (*cf.* equation 7).[14] Spectroscopic data for these compounds are consistent with monomeric Lewis acid–base complexes of the $(Bu^t)_2Ga(OBu^t)$ moiety (4). This structure has been confirmed for $[(Bu^t)_2Ga(OBu^t)(O{=}AsPh_3)]$ by *X*-ray crystallography (see Figure 2).[14]

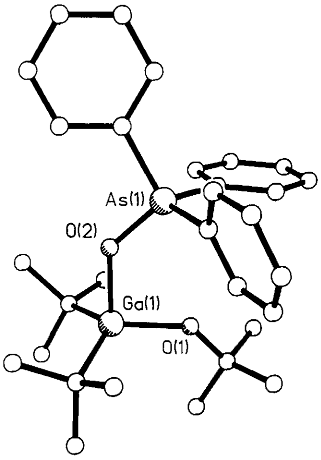
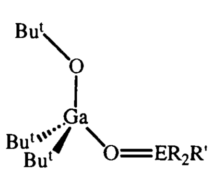


**Figure 2** The molecular structure of $[(Bu^t)_2Ga(OBu^t)(O{=}AsPh_3)]$.



E = P, As

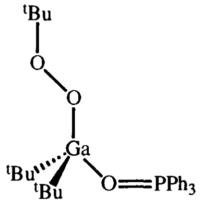
(4)

The triphenylphosphine oxide complex may be prepared by an independent synthesis involving the phosphine oxide cleavage of the $Ga_2O_2$ unit in $[(Bu^t)_2Ga(\mu\text{-}OBu^t)]_2$ (equation 8). This reaction is indicative of the strongly 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 $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ to give the Lewis acid–base complex $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)(O{=}PPh_3)]$ (equation 9).[14]

$$\tfrac{1}{2}[(Bu^t)_2Ga(\mu\text{-}OBu^t)]_2 + O{=}PPh_3 \rightarrow [(Bu^t)_2Ga(OBu^t)(O{=}PPh_3)] \quad (8)$$

$$\tfrac{1}{2}[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2 + O{=}PPh_3 \rightarrow [(Bu^t)_2Ga(OOBu^t)(O{=}PPh_3)] \quad (9)$$

Unfortunately difficulties in isolating $[(Bu^t)_2Ga(OOBu^t)(O{=}PPh_3)]$ precluded its structural characterization by $X$-ray crystallography However, based on spectroscopic characterization we propose that $[(Bu^t)_2Ga(OOBu^t)(O{=}PPh_3)]$ exists as a four-coordinate monomer (5), and is the first example of a terminal alkyl-peroxide of gallium



(5)

### 3.2 Phosphites

In contrast to the interaction of phosphines with $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$, the oxidation of phosphites, $P(OR)_3$ (R = Ph, Me), does not result in adduct formation, but a quantitative yield of $[(Bu^t)_2Ga(\mu\text{-}OBu^t)]_2$ and the appropriate phosphate [14]

$$\tfrac{1}{2}[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2 + P(OR)_3 \rightarrow \tfrac{1}{2}[(Bu^t)_2Ga(\mu\text{-}OBu^t)]_2 + (O{=}P(OR)_3 \quad (10)$$

This lack of adduct formation is in accord with the weaker donor ability of phosphates as compared to phosphine oxides

### 3.3 Diphosphines

Whereas $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ reacts under ambient conditions quantitatively with two molar equivalents of either $PR_3$ or $P(OR)_3$, under corresponding conditions only partial reaction occurs with 1,2-*bis*-(diphenylphosphino)ethane [dppe $Ph_2P(CH_2)_2PPh_2$] Interaction of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ with one equivalent of dppe, in pentane or benzene, results in the oxidation of half an equivalent of the dppe and the formation of the mixed alkoxide/alkylperoxide compound $[(Bu^t)_2Ga(\mu\text{-}OBu^t)(\mu\text{-}OOBu^t)Ga(Bu^t)_2]$ (equation 11) [14] When the reaction is carried out with two equivalents of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$, $[(Bu^t)_2Ga(\mu\text{-}OBu^t)(\mu\text{-}OOBu^t)Ga(Bu^t)_2]$ and the phosphine oxide ($dppeO_2$) are the only products isolated

$$\begin{array}{ccc} \tfrac{1}{2}[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2 & & [(Bu^t)_2Ga(\mu\text{-}OBu^t)(\mu\text{-}OOBu^t)Ga(Bu^t)_2] \\ + & \rightarrow & + \\ \text{dppe} & & \tfrac{1}{2}dppeO_2 + \tfrac{1}{2}dppe \end{array} \quad (11)$$

The structure of $[(Bu^t)_2Ga(\mu\text{-}OBu^t)(\mu\text{-}OOBu^t)Ga(Bu^t)_2]$ consists of two $(Bu^t)_2Ga$ fragments bridged by one $\mu_2$-t-butylperoxo and one $\mu_2$-t-butoxo group The geometries of which are analogous to those found in $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ and $[(Bu^t)_2Ga(\mu\text{-}OBu^t)]_2$ respectively [14]

In contrast to the results observed for dppe, the reaction of two equivalents of $[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2$ with 1,1-*bis*-(diphenylphosphino)methane (dppm, $Ph_2PCH_2PPh_2$) does not yield the free phosphine oxide, but a mixture of four products (equation 12), of which only one contains phosphorus This may readily be separated from the other products by fractional crystallization, and its structure has been determined by $X$-ray crystallographic analysis (Figure 3) to be $[(Bu^t)_2\overline{Ga\{(O)P(Ph)_2CHP(Ph)_2O\}}]$ This compound is also prepared by the direct reaction of $Ga(Bu^t)_3$ with $dppmO_2$

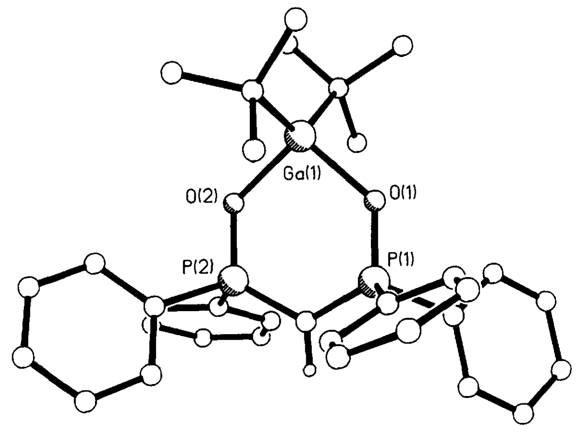


Figure 3 The molecular structure of $[(Bu^t)_2\overline{Ga\{(O)P(Ph)_2CHP(Ph)_2O\}}]$

$$\begin{array}{ccc} & & [(Bu^t)_2\overline{Ga\{(O)P(Ph)_2CHP(Ph)_2O\}}] \\ 2[(Bu^t)_2Ga(\mu\text{-}OOBu^t)]_2 & & + \\ + & \longrightarrow & [(Bu^t)_2Ga(\mu\text{-}OBu^t)(\mu\text{-}OOBu^t)Ga(Bu^t)_2] \\ \text{dppm} & & + \\ & & \tfrac{1}{2}[(Bu^t)_2Ga(\mu\text{-}OBu^t)]_2 + Bu^tOOH \end{array} \quad (12)$$

## 4 Reaction of $Ga(Bu^t)_3$ with Elemental Chalcogens

Whereas the often violent reaction of group 13 alkyls with dioxygen has, for obvious reasons, been a subject of both practical concern and academic interest for many years, few studies have dealt with their reactions with the elemental chalcogens The direct reaction of sulfur with trialkyl-aluminium compounds was first reported, in the patent literature,[15] to yield, after hydrolysis, small quantities of alkenethiols Further studies showed that, in contrast to the reactions with oxygen, elemental sulfur inserts into only one of the possible three aluminium–carbon bonds to afford good yields of dialkyl-aluminium thiolates [16]

$$AlR_3 + E \xrightarrow[E\,=\,S\ Se]{} R_2Al(ER) \quad (13)$$

Reactions under more forcing conditions led to the formation of RSR and RSSR,[17] but the aluminium-containing products were not isolated Similar results have been reported for the interaction of aluminium alkyls with powdered selenium metal (*cf* equation 13) [18]

Since the reaction of group 13 alkyls with dioxygen to give alkoxide products has been shown to occur *via* alkylperoxide intermediates, *e g* equation 1,[1 2 19] and the propensity for catenation is increased with the heavier group 16 elements, an interesting question may be posed *is it possible that alkyldichalcogenides are formed as transient intermediates in the reaction between group 13 alkyls and elemental chalcogens?* Given our isolation of the thermally robust alkylperoxides of gallium[8] and indium,[7] from the oxidation of the tri-t-butyl compounds (see above), this suggests that the use of sterically hindered alkyl substituents, such as t-butyl, should allow for the isolation of the chalcogenide analogues, *i e* , equation 14

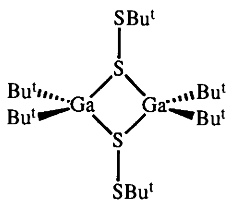
$$M(Bu^t)_3 + E(xs) \rightarrow \tfrac{1}{2}[(Bu^t)_2M(\mu\text{-}EEBu^t)]_2 \quad (14)$$

In addition, the presence of multiple allotropic forms of the chalcogenides raises a further question *does the identity of the products from the reaction of group 13 alkyls with the elemental chalcogens depend on the allotropic form of the chalcogen employed?*

In order to address these questions, and to further understand the reaction chemistry of group 13 alkyls with the group 16 elements, we investigated the reaction of Ga(Bu$^t$)$_3$ with elemental sulfur, selenium, and tellurium.[20]

### 4.1 Sulfur

The interaction of Ga(Bu$^t$)$_3$ with cycloocta-sulfur ($S_8$) at ambient temperatures results in the formation of a mixture of two colourless crystalline compounds, separable by fractional crystallization. They have been characterized by NMR spectroscopy and mass spectrometry as the bis-alkyldisulfido bridged compound [(Bu$^t$)$_2$Ga($\mu$-SSBu$^t$)]$_2$ (6) and the mixed bridge compound [(Bu$^t$)$_2$Ga($\mu$-SBu$^t$)($\mu$-SSBu$^t$)Ga(Bu$^t$)$_2$] (7).[20] In the absence of a large excess of sulfur, [(Bu$^t$)$_2$Ga($\mu$-SSBu$^t$)]$_2$ slowly decomposes at room temperature to give the mixed bridged species and elemental sulfur.



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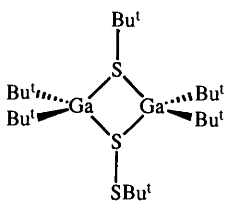


**(7)**

Thermolysis of [(Bu$^t$)$_2$Ga($\mu$-SSBu$^t$)]$_2$ in the presence of an excess of elemental sulfur yields the cubane compound [(Bu$^t$)Ga($\mu_3$-S)]$_4$ (equation 15),[20] which may also be prepared by the reaction of Ga(Bu$^t$)$_3$ with $H_2S$ *via* the hydrosulfido complex [(Bu$^t$)$_2$Ga($\mu$-SH)]$_2$ (equation 16).[21] The aluminium cubane compound [(Bu$^t$)Al($\mu_3$-S)]$_4$ has been prepared by analogous routes, however, the alkyldisulfide or the hydrosulfide compounds were not observed.[22]

$$\mathrm{Ga(Bu^t)_3 + S_8(xs) \rightarrow [(Bu^t)Ga(\mu_3\text{-}S)]_4 + Bu^tS(S)_nSBu^t} \quad (15)$$
$$n = 1, 2, 3, 4$$

$$\mathrm{Ga(Bu^t)_3 + H_2S \rightarrow [(Bu^t)_2Ga(\mu\text{-}SH)]_2 \rightarrow [(Bu^t)Ga(\mu_3\text{-}S)]_4 + Bu^tH} \quad (16)$$

The molecular structure of [(Bu$^t$)Ga($\mu_3$-S)]$_4$ has been determined by *X*-ray crystallography (Figure 4),[21] and consists of a distorted cubane core of four gallium atoms and four $\mu_3$-sulfido groups. Given the analogies observed for gallium and iron aqueous chemistry it is perhaps not surprising that the gallium homologue of the $Fe_4S_4$ cubes prepared as synthetic representations for ferrodoxins is isolable. What is notable, however, is that [(Bu$^t$)Ga($\mu_3$-S)]$_4$ [Ga–S = 2.359(3) Å] is structurally similar not to the isoelectronic [($\eta$-$C_5H_5$)Fe($\mu_3$-S)]$_4$ [Fe–S = 2.20(8)—2.26(4) Å],[23] but to the mixed valence (formally Fe$^{III}$Fe$^{II}$$_3$) trianions, [(X)Fe($\mu_3$-S)]$_4$$^{3-}$[Fe–S = 2.297(6)—2.351(9) Å].[24]

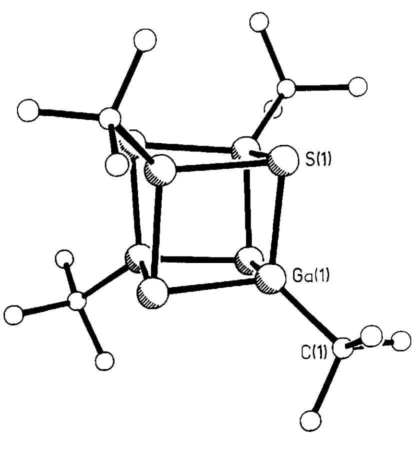
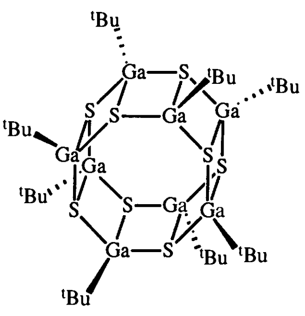


Figure 4 The molecular structure of [(Bu$^t$)Ga($\mu_3$-S)]$_4$.

Thermogravimetric analysis data indicate that [(Bu$^t$)Ga($\mu_3$-S]$_4$ sublimes completely above 225 °C, at atmospheric pressure, making it suitable as a single source precursor for gallium(II) sulfide.[25] However, repeated sublimation at atmospheric pressure results in its conversion from a tetramer into an octamer [(Bu$^t$)GaS]$_8$.[20] Although unable to obtain crystallographic structural data for the octamer, we proposed that, based on the chemistry of tin oxides,[26] it adopts a drum structure (8), consisting of two fused 8-membered $Ga_4S_4$ cycles.



**(8)**

Prolonged thermolysis of [(Bu$^t$)Ga($\mu_3$-S]$_4$ in refluxing hexane results in its near quantitative conversion to a single new species, [(Bu$^t$)Ga($\mu_3$-S)]$_7$ (Figure 5).[27] The heptamer may also be formed in excellent yield (>80%) by the solid state thermolysis of [(Bu$^t$)Ga($\mu_3$-S)]$_4$ in a sealed tube at 175 °C.[27] Dissolution of [(Bu$^t$)Ga($\mu_3$-S)]$_n$ ($n$ = 4, 7, 8) in pyridine results in the formation of [(Bu$^t$)Ga($\mu$-S)py]$_3$ (see Figure 6), which is converted to the tetramer by sublimation, but forms the hexamer (Figure 7) during solid-state thermolysis.[27] These topological rearrangements observed for [(Bu$^t$)Ga($\mu_3$-S)]$_x$ (as summarized in Scheme 1) are, if not unique in cluster chemistry (other rearrangements being accompanied by changes in speciation), certainly the most extensive and reversible for a single well-characterized species. It is likely that such cage transformations may be possible for a wider range of main group clusters, e.g. the iso-electronic aminoalanes, (RAlNR′)$_x$, and the alkyl alumoxanes, (RAlO)$_x$.

### 4.2 Selenium

In contrast to the results observed for $S_8$, the reaction of Ga(Bu$^t$)$_3$ with the analogous selenium allotrope, $Se_8$, does not yield a stable alkyl diselenide, but results in the direct formation of the $Ga_4Se_4$ cubane.[20] Thus, the reaction of Ga(Bu$^t$)$_3$ with red

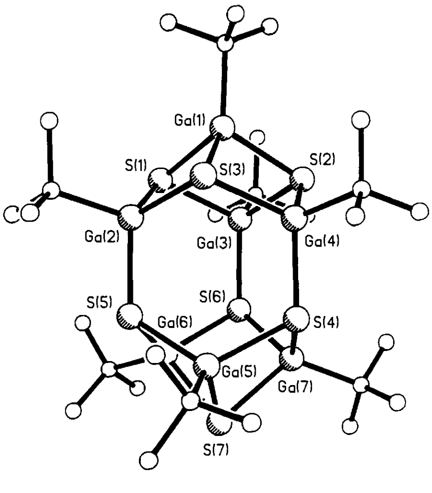


Figure 5 The molecular structure of [(Bu$^t$)Ga($\mu_3$-S)]$_7$.

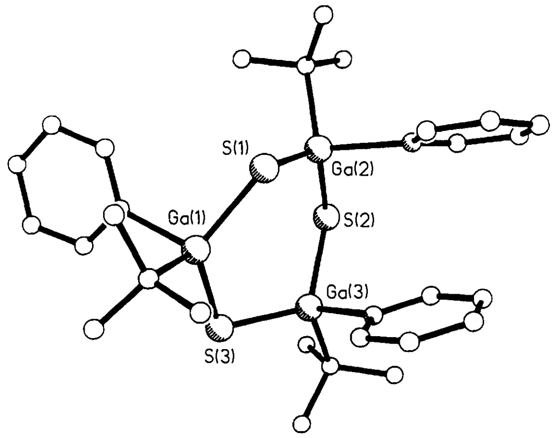


**Figure 6** The molecular structure of $[(Bu^t)Ga(\mu\text{-}S)py]_3$

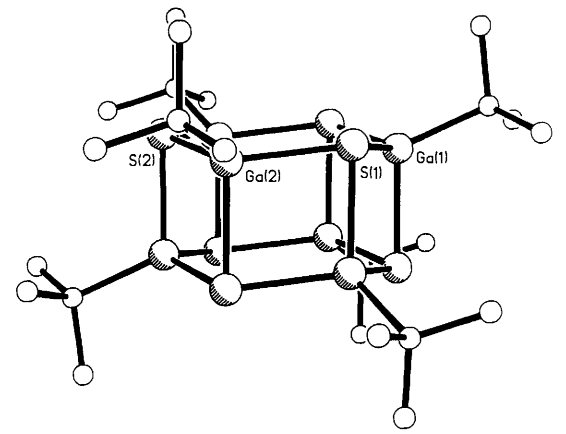
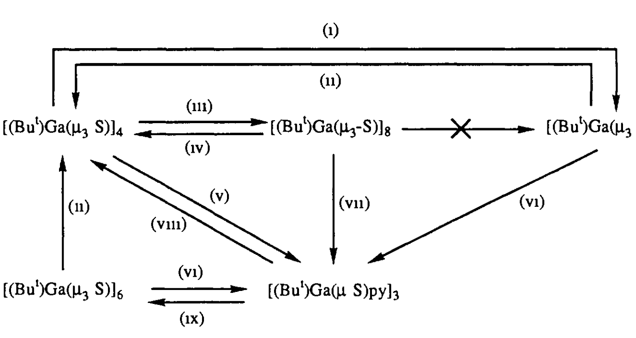


**Figure 7** The molecular structure of $[(Bu^t)Ga(\mu_3\text{-}S)]_6$



**Scheme 1** (i) Δ, hexane, 3—4 days, (ii) sublimation, 1 atm, (iii) Δ, pentane, 12h, (iv) Δ, pentane, (v) pyridine, mins, (vi) pyridine, 1—2 days, (vii) Δ, pyridine, (viii) vacuum sublimation, (ix) Δ, solid state

selenium ($Se_8$, α-cubic form), in pentane at room temperature, affords in essentially quantitative yield (based on $^{77}Se$ NMR) $Bu^tSeSeBu^t$, and $[(Bu^t)Ga(\mu_3\text{-}Se)]_4$ (equation 16) The cubane compound may also be prepared in near quantitative yield from the reaction of $Ga(Bu^t)_3$ with $H_2Se$ in pentane at ambient temperatures, presumably *via* a hydroselenolate intermediate (equation 18) [28]

$$Ga(Bu^t)_3 + Se_8 \rightarrow [(Bu^t)Ga(\mu_3\text{-}Se)]_4 + Bu^tSeSeBu^t \quad (17)$$

$$4Ga(Bu^t)_3 + 4H_2Se \xrightarrow[\text{Pentane}]{0\,°C} [(Bu^t)Ga(\mu_3\text{-}Se)]_4 + 8Bu^tH \quad (18)$$

It should be noted that the alkylgallium selenide $[(Et)GaSe]_x$ formed on the thermal decomposition of the triethylsilylselenolate (equation 19) was proposed to have a highly polymeric structure based on its high thermal stability (m p 360—410 °C, decomp ) and low solubility in non-coordinating solvents [29]

$$[(Et)_2Ga(\mu\text{-}SeSiEt_3)]_2 \xrightarrow{\Delta} [(Et)GaSe]_n + GaEt_3 + Se(SiEt_3)_2 \quad (19)$$

Treatment of $Ga(Bu^t)_3$ with metallic grey selenium ($Se_\infty$) in pentane results in the formation of the selenolate compound as the only gallium-containing product (equation 20) [20] Subsequent conversion of the selenolate into the cubane may be accomplished under more forcing conditions

$$M(Bu^t)_3 + E_\infty \rightarrow [(Bu^t)_2M(\mu\text{-}EBu^t)]_2 \quad (20)$$
$$M = Al\ Ga\quad E = Se\ Te$$

The cubane compounds $[(Bu^t)M(\mu_3\text{-}Se)]_4$ (M = Al, Ga) may also be prepared by the reaction of selenium metal directly with the liquid trialkyl [22]

### 4.3 Tellurium

Unlike either sulfur or selenium, tellurium exists as a single allotropic form, that of a silvery-white semi-metallic trigonal structure isomorphous with grey selenium Thus, as may be expected, the reaction of $M(Bu^t)_3$ (M = Al, Ga) with tellurium metal at room temperature proceeds in an analogous manner to that of grey selenium, resulting in the formation of the appropriate telluride dimer (*cf* equation 20) [20]

The first example of an organogallium compound containing a Ga—Te bond, recently reported by Beachley and coworkers,[30] was prepared by the reaction of $Ga(CH_2Bu^t)_2Cl$ with the appropriate lithium telluride

$$2Ga(CH_2Bu^t)_2Cl + 2LiTePh \xrightarrow{Et_2O} [(Bu^tCH_2)_2Ga(\mu\text{-}TePh)]_2 + 2LiCl \quad (21)$$

The reaction of either $M(Bu^t)_3$ or $[(Bu^t)_2M(\mu\text{-}TeBu^t)]_2$ (M = Al, Ga) with an excess of elemental tellurium in refluxing toluene proceeds in an analogous manner to that of its selenium counterparts yielding, in addition to a stoichiometric quantity of the organoditelluride, the telluride cubane (equation 22), which is spectroscopically similar to its sulfur and selenium analogues [20 22]

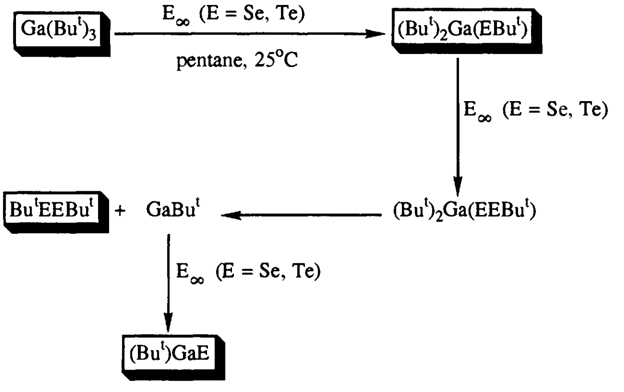
$$4M(Bu^t)_3 + Te(xs) \xrightarrow[\text{toluene}]{\Delta} [(Bu^t)M(\mu_3\text{-}Te)]_4 + 4Bu^tTeTeBu^t \quad (22)$$
$$M = Al\ Ga$$

## 5 A Possible Reaction Pathway of Group 13 Trialkyls with the Elemental Chalcogens

The homogeneous nature of the auto-oxidation reaction of group 13 alkyls has made it possible to obtain detailed mechanistic data concerning the reaction pathway Unlike organoaluminium compounds the oxidation of the second and the third M—C bonds is not typical for gallium and indium trialkyls Thus, as noted in the Introduction, the controlled auto-oxidation of $MR_3$ (M = Ga, In) yields the dialkyl mono-alkylperoxides, making any subsequent mechanistic study simpler Alexandrov has proposed that the auto-oxidation of gallium and indium trialkyls occurs by the following concurrent reaction [4]

$$MR_3 + O_2 \rightarrow [R_3M\,O_2] \rightarrow \begin{cases} R_2MOO^\bullet + R^\bullet \\ R_2MOOR \end{cases} \quad (23)$$

Unfortunately the heterogeneous nature of the reaction of $MR_3$ with the elemental chalcogens as well as the insolubility and uncharacterized nature of the products have precluded any equivalent study to those on the oxidation reaction However, as discussed above, use of the sterically hindered t-butyl group allows for the isolation of a number of the intermediates, which in turn allows for the postulation of the reaction pathways



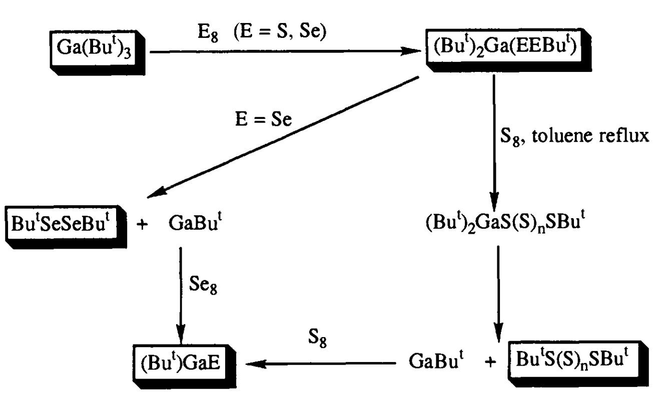
**Scheme 2** Isolated species are highlighted

### 5.1 Metallic Selenium and Tellurium (Scheme 2)

The initial reaction of $M(Bu^t)_3$ with metallic selenium (tellurium) results in the insertion of a single Se(Te) atom into one of the Ga–C bonds to yield the isolable selenolate (tellurolate) [20–22] At elevated temperature this product reacts further with the chalcogen to give an unstable transient alkyl diselenide (telluride), which decomposes to the di-t-butyl diselenide (telluride) and a reactive organogallium fragment [20] Dialkyl ditellurides have been shown to eliminate tellurium metal on thermolysis (equation 24)[31] but under the conditions employed for the synthesis of $[(Bu^t)Ga(\mu_3\text{-}Te)]_4$ the reverse reaction does not occur

$$RTeTeR \rightarrow RTeR + Te(metal) \qquad (24)$$

Thus, the di-t-butylditelluride (and selenide) must be formed as a direct reaction product and not *via* subsequent reactions with excess elemental chalcogen The organometallic fragment formed then reacts further to give the resulting selenide (telluride) It is highly unlikely that this gallium fragment will be as written, *i e* $Ga(Bu^t)$, but the formation of such a species on the chalcogen metal surface cannot be discounted, and we note that a number of examples of $(RM)_x$ have been isolated for aluminium [32]



**Scheme 3** Isolated species are highlighted

### 5.2 *Cyclo*-Octasulfur and *cyclo*-Octaselenium (Scheme 3)

The observation that $[(Bu^t)Ga(\mu\text{-}SSBu^t)]_2$ is the first detectable product in the reaction of $Ga(Bu^t)_3$ with $S_8$ poses the following question concerning the mechanism of sulfur atom insertion does the reaction proceed *via* the concerted insertion of two sulfur atoms to give the disulfide directly (equation 25), or a stepwise insertion of a single sulfur atom giving the thiolate which reacts further to give the disulfide (equation 26)?

$$Ga{-}R \xrightarrow{S_2} Ga{-}S{-}S{-}R \qquad (25)$$

$$Ga{-}R \xrightarrow{S} Ga{-}S{-}R \xrightarrow{S} Ga{-}S{-}S{-}R \qquad (26)$$

If the latter, *i e* equation 26, is the preferred pathway then it is reasonable to expect that the thiolate $[(Bu^t)_2Ga(\mu\text{-}SBu^t)]_2$ should react with excess sulfur to give both the disulfide compounds However, under analogous reaction conditions to those employed for the formation of the disulfides directly from $Ga(Bu^t)_3$, *i e* pentane and room temperature, no reaction is observed, even over an extended period of time Thus, unlike the case for the metallic elements, the reaction of $S_8(Se_8)$ results in the insertion of two sulfur (selenium) atoms In the case of selenium the resulting alkyl diselenide is unstable and undergoes further reaction as shown in Scheme 3 The alkyl disulfide compound is stable, undoubtedly due to the high stability of polysulfur species, and only reacts with excess sulfur under forcing conditions, to give unstable alkyl polysulfides whose decomposition yields the dialkyl polysulfide

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