Unclassified

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(2)

AD-A241 334

Unclassified

CUMENTATION PAGE

Form Approved OMB No. 0704-0188

1b. RESTRICTIVE MARKINGS

2a SECURITY CLASSIFICATION AUTHORITY

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approval for public release; distribution unlimited

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

4 PERFORMING ORGANIZATION REPORT NUMBER(S)
Technical Report No. DU/DC/TR-23

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Department of Chemistry
Duke University

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)
Durham, NC 27706

7b. ADDRESS (City, State, and ZIP Code)
300 North Quincy Street
Arlington, VA 22217-5000

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
N00014-89-J-1545; R&T Code 4135008

8c. ADDRESS (City, State, and ZIP Code)
800 North Quincy Street
Arlington, VA 22217-5000

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
NR	053	841	

11. TITLE (Include Security Classification)
SYNTHESIS AND CHARACTERIZATION OF COMPOUNDS CONTAINING THE $As(SiMe_3)_2$ BRIDGING GROUP: CRYSTAL STRUCTURES OF $[t\text{-}Bu_2GaAs(SiMe_3)_2]_2$, and $t\text{-}Bu_2GaAs(SiMe_3)_2Ga(t\text{-}Bu)_2Cl$

12. PERSONAL AUTHOR(S)
R.L. Wells, A.T. McPhail, and A. Alvanipour

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____	1991-10-03	18

16 SUPPLEMENTARY NOTATION
Accepted for publication in Polyhedron.

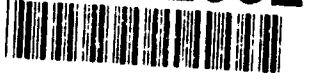
17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
gallium-arsenic, synthesis, crystal structure, ring compounds

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

See attached.

91-12662



20 DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Richard L. Wells	(919)660-1541	

DD Form 1473, JUN 86 Previous editions are obsolete SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

064

[19. ABSTRACT]

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Richard L. Wells*, Andrew T. McPhail, and Abbas Alvanipour

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(Received July .., 1991)

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OFFICE OF NAVAL RESEARCH

Grant NOOO14-89-J-1545

R&T Code 4135008

Technical Report No. DU/DC/TR-23

SYNTHESIS AND CHARACTERIZATION OF COMPOUNDS CONTAINING THE $As(SiMe_3)_2$ BRIDGING GROUP: CRYSTAL STRUCTURES OF $[t\text{-}Bu_2GaAs(SiMe_3)_2]_2$, and $t\text{-}Bu_2\overline{GaAs(SiMe_3)_2Ga(t\text{-}Bu)_2Cl}$

by

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Prepared for Publication in Polyhedron

Duke University
Department of Chemistry
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October 3, 1991

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[*Polyhedron* 1991, in press]

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It is generally accepted that much of the impetus for the rapid growth in the number of new organogallium arsenic compounds that have been reported since 1986 has been the quest for new gallium arsenide precursors.[1] As a result, considerable attention is being given to the search for new synthetic modes of forming the gallium-arsenic bond, and thus finding different pathways to new cyclic systems, clusters, and chains which may be studied further with respect to their reactivity, properties, and potential as precursors. To this end, we have been exploiting two synthetic routes, both first employed by us; namely, the metathetical elimination of (1) a silyl halide from a silylarsine and a gallium halide,[2] and (2) a salt from a metal arsenide and a gallium halide.[3] Among the compounds recently prepared and studied in our program are the cyclic mixed-bridge compounds $R_2\overline{GaAs(SiMe_3)_2Ga(R)_2Cl}$ [R = Me_3SiCH_2 (**III**)[4] and Me_3CCH_2 (**IV**)[5]] and the dimers $[R_2GaAs(SiMe_3)_2]_2$ [R = Me_3SiCH_2 (**V**)[4] and Me_3CCH_2 (**VI**)[5]]. Moreover, in an effort to extend these studies to other III-V combinations, we very recently reported the isolation of the indium-arsenic[6] and indium-phosphorus[7] analogs of **III** and **V**, $(Me_3SiCH_2)_2\overline{ME(SiMe_3)_2M(CH_2SiMe_3CH_2)_2Cl}$ and $[(Me_3SiCH_2)_2ME(SiMe_3)_2]_2$ (M = In, E = As and P).

As part of a continuing effort to expand the scope of the above gallium-arsenic series, it was deemed most appropriate for us to select *tert*-butyl as the alkyl substituent on the gallium atoms. Not only would this group add to the steric bulk around the gallium and thereby possibly influence the conformation of the ring(s) which may be formed, but any new compounds isolated should have certain desirable properties in common with the gallium arsenide *tert*-butyl containing single-source precursors recently reported by Cowley, Jones and co-workers[8], and by Higa and George[9]. We also sought to continue to address the interesting and important matters of the reactivity and interconvertibility of these types of compounds, and herein we report our results obtained with the *tert*-butyl ligand system.

EXPERIMENTAL

General information

All manipulations and reactions were performed under vacuum, under argon in a Vacuum/Atmospheres HE-493 Dri-Lab, or under N_2 in standard Schlenk apparatus. Solvents were distilled from sodium/benzophenone ketyl under dry N_2 and degassed by several freeze-pump-thaw cycles. *t*-Bu_2GaCl,[9] $(Me_3Si)_3As$,[10] and $LiAs(SiMe_3)_2 \cdot 2THF$[10] were prepared by literature procedures. ^1H (300 MHz) and $^{13}C\{^1H\}$ (75.4 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer at ambient temperatures using C_6D_6 solutions in 5 mm tubes which were flame-sealed under vacuum and were referenced to TMS using the residual protons or the carbons of deuterated benzene at δ 7.15 ppm or δ 128 ppm, respectively. Melting points (uncorrected) were obtained with a Thomas-Hoover Unimelt apparatus and capillaries were flame-sealed under argon. Crystals

used in the x-ray analyses were flame-sealed in 0.7 mm thin-walled glass capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, New York.

Syntheses

[t-Bu$_2$GaAs(SiMe$_3$)$_2$]$_2$ (I) by salt elimination *t*-Bu$_2$GaCl (0.14 g, 0.75 mmol) in C_6H_6 (20 mL) and LiAs(SiMe$_3$)$_2$•2THF (0.26 g, 0.75 mmol) in C_6H_6 (10 mL) were combined in a 100-mL one-necked round-bottomed flask equipped with a Teflon® valve and a magnetic stirbar. After one freeze-pump-thaw cycle of the solution, followed by stirring at room temperature for 48 h, the volatiles were removed *in vacuo* and pentane (20 mL) was added to the remaining solid. Filtration, followed by removal of the pentane from the filtrate, afforded a white solid which was subsequently recrystallized from pentane at -15 °C as colorless crystals of **I**, some of which were suitable for single-crystal X-ray analysis (0.27 g, 72% yield), mp 90-95 °C. Anal. Calcd (Found) for $C_{28}H_{72}As_2Ga_2Si_4$: C, 41.50 (41.66); H, 8.95 (8.96). ^{1}H NMR (C_6D_6): δ 0.45 (s, 18 H, Si*Me*$_3$), 1.25 (s, 18 H, C*Me*$_3$).

***t*-Bu$_2$GaAs(SiMe$_3$)$_2$Ga(*t*-Bu)$_2$Cl (II) by reaction of *t*-Bu$_2$GaCl with I (2:1 mole ratio).** Fifteen minutes after combining *t*-Bu$_2$GaCl (7.0 mg, 0.032 mmol) and **I** (13 mg, 16 mmol) in C_6D_6 (1 mL) in an NMR tube, the ^{1}H NMR spectrum of the resulting clear solution contained two resonances [δ 0.46 (s, 18 H, Si*Me*$_3$), 1.34 (s, 18 H, C*Me*$_3$)] indicative of **II** [subsequently obtained ^{13}C{^{1}H} NMR: δ 6.81 (s, Si*Me*$_3$), 30.95 (s, C*Me*$_3$)]. After opening the NMR tube in the Dri-Lab and transferring its contents to a glass vial, evaporation of the solvent afforded a white solid which was

dissolved in pentane. On cooling to -15 °C, colorless crystals of **II**, some of which were suitable for single-crystal X-ray analysis, were obtained in nearly quantitative yield, mp 85-100 °C (dec). Anal. Calcd (Found) for $C_{22}H_{54}AsClGa_2Si_2$: C, 42.30 (41.94); H, 8.71 (8.82).

Attempted Syntheses

[t-Bu$_2$GaAs(SiMe$_3$)$_2$]$_2$ (I) by dehalosilylation (reactants in a 1:1 mole ratio). *t*-Bu_2GaCl (0.22 g, 1.0 mmol) in C_6H_6 (35 mL) and $(Me_3Si)_3As$ (0.30 g, 1.0 mmol) in C_6H_6 (5 mL) were combined in a 100-mL one-necked round-bottomed flask equipped with a Teflon® valve and a magnetic stirbar. After one freeze-pump-thaw cycle of the solution, followed by stirring at room temperature for 6 days, the solvent was removed *in vacuo* leaving solid material, which on subsequent recrystallization from a pentane-ligroin mixture afforded large colorless crystals of *t*-Bu_2GaCl [mp 170-172 °C and ^1H NMR (C_6D_6): δ 1.26 (s) are comparable to lit values]. Most of this starting material was recovered on subsequent concentration and cooling of the pentane-ligroin solution. Repeating the reaction using the same stoichiometry, but with heating at 80 °C for 5 d, afforded only starting materials.

***t*-Bu$_2$GaAs(SiMe$_3$)$_2$Ga(*t*-Bu)$_2$Cl (II) by dehalosilylation (reactants in a 2:1 mole ratio).** In a manner similar to that described above, reaction of $(Me_3Si)_3As$ with 2 eq of t-Bu_2GaCl at room temperature and at 80 °C for 6 days did not afford **II**, and the latter starting material was recovered nearly quantitatively.

X-Ray Crystal Structure Analysis of I and II

All measurements were performed on an Enraf-Nonius CAD-4 diffractometer (Cu-K_α radiation, λ = 1.5418 Å; incident-beam graphite monochromator). Intensity data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections, based on the Φ-dependency of the intensities of several reflections measured at ψ ca. 90°, were also applied. Both crystal structures were solved by the heavy-atom approach. For compound I, the systematic absences, hkl when $h+k \neq 2n$, are consistent with space groups $C2$, Cm, and $C2/m$. Coordinates for the Ga and As atoms, derived from the Patterson map, were compatible with space group $C2/m$, and so all further calculations were performed using the equivalent positions of this space group. A weighted F_o Fourier synthesis phased by these two atoms yielded positions for the Si and C atoms and, moreover, identified the Ga and As atoms. For compound II, the systematic absences, hkl when $h + k \neq 2n$ and $h0l$ when $l \neq 2n$, are accommodated by the space groups Cc and $C2/c$. Interpretation of the vector peaks in the Patterson map yielded coordinates for the Ga and As atoms and established that the correct choice was the centrosymmetric space group $C2/c$ with the As and Cl atoms lying on a crystallographic C_2 symmetry axis. Coordinates for the other non-hydrogen atoms were derived from a weighted F_o Fourier synthesis phased by the Ga and As atoms. Non-hydrogen atom positional and thermal parameters (at first isotropic, then anisotropic) for both compounds were adjusted by means of several rounds of full-matrix least-squares calculations. In the later cycles, hydrogen atoms were included at their calculated positions (C-H = 1.05 Å) and an extinction correction was refined. A final difference Fourier

synthesis contained no unusual features. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP). For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from *International Tables for X-Ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham, U.K. In the least-squares iterations, $\Sigma w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized. Further details of data collection and refinement are in Table I. Selected bond lengths, bond angles and torsion angles are in Tables II and III. Supplementary material: atomic coordinates, thermal parameters, bond lengths and angles, and crystal data have been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

No reactions occurred at room temperature or at 80 °C in either the 1:1 or the 2:1 mole ratio mixture of *t*-Bu_2GaCl and $(Me_3Si)_3As$ in benzene. This is in contrast to results obtained by us when one or two equivalents of other dialkylgallium chlorides were allowed to react with one equivalent of the same silylarsine. For example, for the equimolar reaction using $(Me_3SiCH_2)_2GaCl$, mixed-bridge **III** and other uncharacterized products were produced;[4] whereas, in the case of $(Me_3CCH_2)_2GaCl$ the adduct $(Me_3CCH_2)_2Ga(Cl)\cdot As(SiMe_3)_3$ was isolated.[5] Furthermore, the 2:1 mole ratio reactions afforded the mixed-bridge species **III** and **IV**, respectively.

Nevertheless, by taking advantage of the metathetical salt elimination-bridge redistribution route, the desired *tert*-butyl containing compounds were accessible. Thus, as illustrated by equations 1 and 2, the reaction of

$$2t\text{-}Bu_2GaCl + 2LiAs(SiMe_3)_2{\bullet}2THF \longrightarrow \underset{\mathbf{I}}{[t\text{-}Bu_2GaAs(SiMe_3)_2]_2} + 2LiCl + 4THF \quad (1)$$

$$2t\text{-}Bu_2GaCl + [t\text{-}Bu_2GaAs(SiMe_3)_2]_2 \longrightarrow \underset{\mathbf{II}}{2t\text{-}Bu_2\overline{GaAs(SiMe_3)_2Ga(t\text{-}Bu)_2Cl}} \quad (2)$$

t-Bu_2GaCl with $LiAs(SiMe_3)_2{\bullet}2THF$ in benzene at room temperature yields dimer **I** in 72% yield, and redistribution of the latter with *t*-Bu_2GaCl affords mixed-bridge **II**, quantitatively. Obviously, the bulk of the *tert*-butyl group is such that interaction between *t*-Bu_2GaCl and $(Me_3Si)_3As$ can not be realized and thus result in chalosilylation. On the other hand, the bulk of this particular alkyl group is not so great that it prohibits dimer and mixed-bridge formation, when the appropriate pathways to these species are found.

Crystals of **I** and **II** suitable for X-ray diffraction studies were grown from pentane. Crystallographic data are provided in Table 1. ORTEP diagrams showing the atom numbering schemes and the solid-state conformations of **I** and **II** are presented in Figure 1 and 2, respectively. Tables 2 and 3 list selected bond lengths and angles for I and II, respectively.

Dimer **I** crystallizes in the monoclinic system, space group $C2/m$, with only two formula units per unit cell. The As atoms lie on a crystallographic C_2 axis and a mirror plane of symmetry bisects the Ga atoms, the central carbons of the *t*-Bu groups and one of their Me groups. The molecule has overall C_{2h} symmetry and thus the $(GaAs)_2$ ring is constrained to be perfectly flat. Comparison of the bond distances and angles of **I** with those of **V** and **VI** is very informative and reflects the greater amount of

steric crowding present in **I** where bond length extension is evident in all bonds involving the ring atoms. Thus, the Ga-As bond length of 2.630(1) Å in **I** is significantly longer than the means in **V** (2.567 Å) and **VI** (2.587 Å), the As-Si bond length in **I** [2.400(2) Å] is longer than the approximately equal mean values of 2.357 Å in **V** and 2.363 Å in **VI**, and the mean Ga-C bond length at 2.031 Å in **I** is also greater than the corresponding values of 1.990 Å in **V** and 1.997 Å in **VI**. In common with **V** and **VI**, the Ga-As-Ga angle [94.85(3)°] is greater that the As-Ga-As angle [85.14(3)°]; in **V** the Ga-As-Ga angle is 93.91(2)° and the mean As-Ga-As angle is 86.09°, while in **VI** the mean Ga-As-Ga angle is 94.97° and the As-Ga-As angle is 85.02(3)°. The exocyclic C-Ga-C and Si-As-Si bond angles at 114.3(3)° and 95.67(6)° in **I** are both considerably smaller that the corresponding angles in **V** [mean 123.9° and 103.66(6)°] and **VI** [135.2(3)° and 102.32(7)°] .

Compound **II** crystallizes in the monoclinic system, space group *C*2/*c* with only four formula units per unit cell. The molecule lies on a crystallographic C_2 symmetry axis which passes through the As and Cl atoms, and, accordingly, the Ga-As-Ga-Cl is planar. As with dimer **I**, comparison of distances and angles in **II** with corresponding values in **III** and **IV** provides an indication of the effects of the increased steric crowding associated with the presence of the bulky *t*-Bu substituents. The As-Ga distance of 2.577(1) Å in **II** is considerably greater than the means of 2.504 Å in **III** and 2.521 Å in **IV**, the As-Si length of 2.393(2) Å is longer than the means of 2.348 Å and 2.358 Å in **III** and **IV**, respectively, and the mean Ga-C distance of 2.017 Å is slightly longer than the mean of 1.990 Å in **III** and much longer than the mean of 1.966 Å in **IV**. In contrast to these differences, the Ga-Cl bond length of 2.426(1) Å in planar

II is similar to the means of 2.432 Å in puckered **III** and 2.425 Å in planar **IV**, and thus it remains fairly constant. Closure of the exocyclic bond angles subtended at Ga and As reflects steric compression at these centers. The Si-As-Si angle in **II** at 97.32(5)° in considerably smaller than the corresponding angles in **III** [108.64(6)°] and IV [105.39(5)°], and the C-Ga-C angle of 120.8(3)° in **II** is also less than the means of 123.6° and 127.7° in **III** and **IV**, respectively.

More severe bond strain in group 13-group 15 dimers vs. their chloro-bridged analogs is manifested in the consistently greater values of the Ga-As distances in dimeric **I**, **V**, and **VI** where they exceed those in **II**, **III**, and **IV** by 0.053 Å, 0.063 Å, and 0.066 Å, respectively. In addition, the increased steric compression present in the dimers is reflected in the fact that their Si-As-Si angles are smaller: Δ = 1.7° in I vs. **II**, Δ = 5.0° in **V** vs. **III**, and Δ = 3.0° in **VI** vs. **IV**. These appear to be general features of this class of compounds as like differences between corresponding lengths (Δ 0.051 Å, 0.052 Å) and angles (Δ 3.3°, 5.4) have recently been found in pairs of In-As and In-P analogues $[(Me_3SiCH_2)_2InM(SiMe_3)_2]_2$ and $(Me_3SiCH_2)_2InM(SiMe_3)_2In(CH_2SiMe_3)_2Cl$, M = As,[6] P.[7]

Acknowledgment. The financial support for this work by the Office of Naval Research is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and complete lists of interatomic distances and angles for **I** and **II**, (9 pages); a listing of observed and calculated structure amplitudes for **I** and **II** (31 pages).

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Captions to Figures

Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure of $[t\text{-}Bu_2GaAs(SiMe_3)_2]_2$ (I); hydrogen atoms have been omitted for clarity.

Figure 2. ORTEP diagram (40% probability ellipsoids) showing the solid-state structure of $t\text{-}Bu_2\overline{GaAs(SiMe_3)_2Ga(t\text{-}Bu)_2}Cl$ (II); hydrogen atoms have been omitted for clarity.

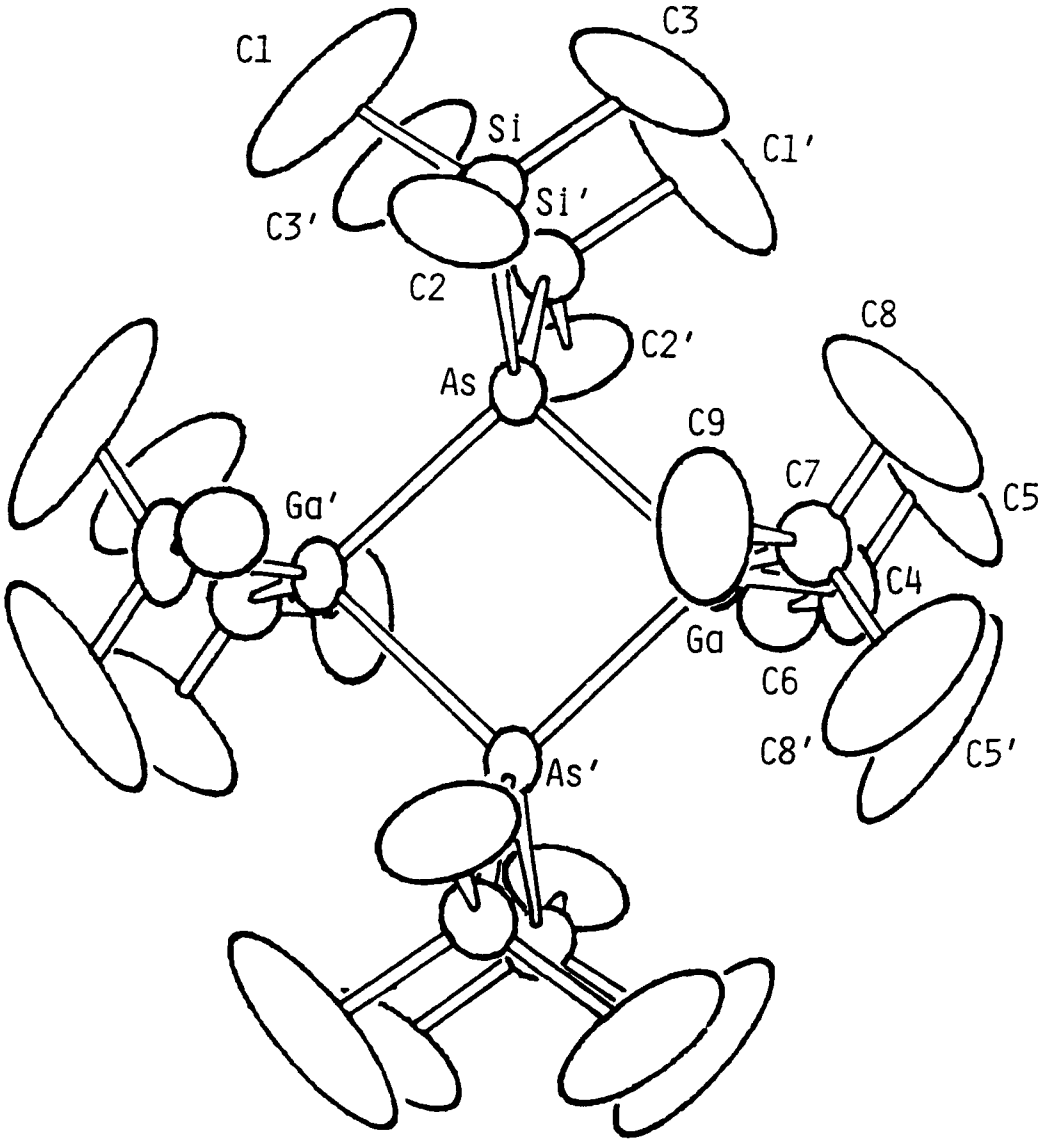
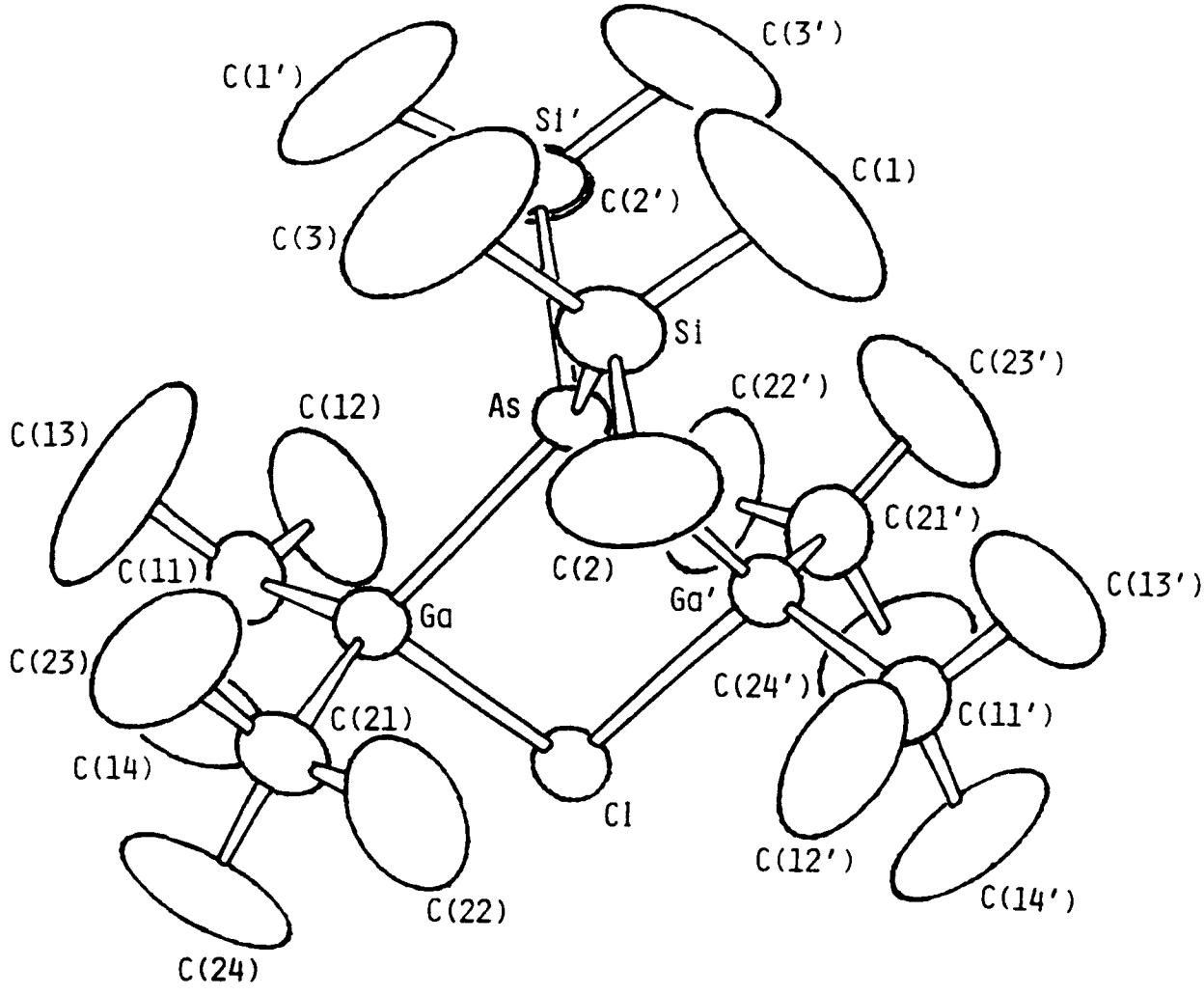


Figure 1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C(3')
Si'
C(2')
C(1)
C(3)
Si
C(23')
C(22')
C(12)
As
C(13)
C(21')
C(11)
C(2)
Ga'
C(13')
Ga
C(23)
C(24')
C(11')
C(21)
C(14)
Cl
C(12')
C(14')
C(22)
C(24)

Figure 2

Table 1. Crystallographic Data and Measurements[a] for [*t*-$Bu_2GaAs(SiMe_3)_2]_2$ (I) and *t*-$Bu_2\overline{GaAs(SiMe_3)_2Ga(t\text{-}Bu)_2Cl}$ (II)

	I	II
Formula	$C_{28}H_{72}As_2Ga_2Si_4$	$C_{22}H_{54}AsClGa_2Si_2$
Formula weight	810.51	624.66
Crystal system	monoclinic	monoclinic
Space group	$C2/m(C^3_{2h})$	$C2/c(C^6_{2h})$
a (Å)	18.188(2)	20.872(4)
b (Å)	13.017(1)	9.798(1)
c (Å)	9.916(1)	19.397(4)
β (°)	118.54(1)	124.13(2)
No. of orient. refls; θ (°) range	25; 42-48	25; 42-47
V (Å^3)	20624(8)	3284(2)
Z	2	4
D_{calcd} (g cm^{-3})	1.305	1.264
μ(Cu-*K*α rad., λ = 1.5418 Å)	46.4	46.5
Temp. (°C)	25	25
Crystal dimensions (mm)	0.18x0.24x0.28	0.50x0.50x0.50
T_{max}:T_{min}	1.00:0.72	1.00:0.90
Scan type	ω-2θ	ω-2θ
Scan width (°)	1.15 + 0.14tanθ	1.00 + 0.14tanθ
$\theta_{max.}$ (°)	75	75
Intensity control refls.	331, 22$\bar{3}$, 2$\bar{2}\bar{3}$, 3$\bar{3}$1	53$\bar{2}$, 242, 5$\bar{3}\bar{2}$, 2$\bar{4}$2

Table 1 (continued)

Variation; repeat time (h)	<2%; 2	<1%; 2
No. of rfls. ($+h,+k.\pm l$) recded	2279	3489
No. of non-equiv. refls. recded	2210	3380
R_{merge} (on I)	0.016	0.020
No. of refls. retained [$I>3.0\sigma(I)$]	1798	2812
No. of parameters refined	91	129
Extinction correction	$7.7(2)\times10^{-6}$	$1.8(1)\times10^{-6}$
R (R_w)[a]	0.057(0.079)	0.055 (0.081)
Goodness-of-fit[b]	2.77	2.70
Max. shift:esd in final least-sq. cycle	0.03	0.02
Final $\Delta\rho$(e/Å^3) max; min	0.90; -0.86	0.32; -0.41

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w\ (|F_o| - |F_c|)^2/\Sigma w\ |F_o|^2]^{1/2}$; $\Sigma w\Delta^2[w = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|)]$ was minimized.

[b] Goodness-of-fit = $[\Sigma w\Delta^2 / (N_{observations} - N_{parameters})]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [*t*-$Bu_2GaAs(SiMe_3)_2]_2$ (I), with Estimated Standard Deviations in Parentheses.

(a) Bond lengths			
As-Ga	2.630(1)	Ga-C(4)	2.025(9)
As-Si	2.400(2)	Ga-C(7)	2.036(6)
(b) Bond angles			
Ga-As-Si	116.65(3)	As-Si-C(1)	110.8(4)
Ga-As-Si'	117.36(5)	As-Si-C(2)	117.3(3)
Ga-As-Ga'	94.85(3)	As-Si-C(3)	110.3(4)
Si-As-Si'	95.67(6)	C(1)-Si-C(2)	102.8(6)
As-Ga-As'	85.15(3)	C(1)-Si-C(3)	110.6(6)
As-Ga-C(4)	113.2(1)	C(2)-Si-C(3)	104.6(4)
As-Ga-C(7)	113.9(2)		
C(4)-Ga-C(7)	114.3(3)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for t-Bu$_2$GaAs(SiMe$_3$)$_2$Ga(t-Bu)$_2$Cl (II), with Estimated Standard Deviations in Parentheses.

(a) Bond lengths					
As-Ga	2.577(1)	Ga-Cl	2.426(1)	Ga-C(21)	2.025(4)
As-Si	2.393(2)	Ga-C(11)	2.009(4)		
(b) Bond angles					
Ga-As-Si	118.12(2)		C(11)-Ga-C(21)	120.8(3)	
Ga-As-Ga'	89.49(2)		Ga-Cl-Ga'	96.81(7)	
Ga-As-Si'	117.84(2)		As-Si-C(1)	108.5(3)	
Si-As-Si'	97.32(5)		As-Si-C(2)	117.4(3)	
As-Ga-Cl	86.85(4)		As-Si-C(3)	110.0(3)	
As-Ga-C(11)	115.4(2)		C(1)-Si-C(2)	107.3(6)	
As-Ga-C(21)	116.9(2)		C(1)-Si-C(3)	109.2(5)	
Cl-Ga-C(11)	103.7(2)		C(2)-Si-C(3)	104.2(4)	
Cl-Ga-C(21)	105.0(2)				
(c) Torsion angles[a]					
Si-As-Ga-Cl	-121.65(5)		Si'-As-Ga-Cl	121.89(5)	
Si-As-Ga-C(11)	134.7(2)		Si'-As-Ga-C(11)	18.3(2)	
Si-As-Ga-C(21)	-16.4(2)		Si'-As-Ga-C(21)	-132.9(2)	
Ga'-As-Ga-Cl	0.0(-)		As-Ga-Cl-Ga'	0.0(-)	
Ga'As-Ga-C(11)	-103.6(2)		C(11)-Ga-Cl-Ga'	115.4(2)	
Ga'-As-Ga-C(21)	105.2(2)		C(21)-Ga-Cl-Ga'	-117.0(2)	

[a]The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

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