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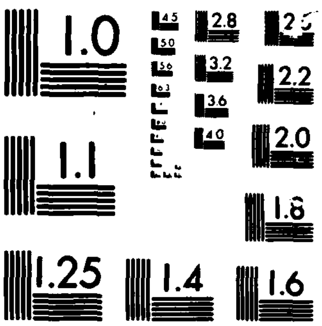

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Synthesis of Some Arsinogallanes and the Novel Rearrangement of a Dimeric Bisarsinogallane, Bis{bis[bis(trimethylsilylmethyl)arsino]chlorogallane}

by

C. G. Pitt, A. P. Purdy, K. T. Higa, and R. L. Wells

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Synthesis of Some Arsinogallanes and the Novel Rearrangement of a Dimeric Bisarsinogallane, Bis{bis[bis(trimethylsilylmethyl)arsino]chlorogallane}

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Abstract: Silylarsines have been used to synthesize arsinogallanes according to the following equations.

$$R_2AsSiMe_3 + GaCl_3 \longrightarrow 1/n(R_2AsGaCl_2)_n + Me_3SiCl$$
$$R = Me_3SiCH_2;\ n = 3$$
$$R = Mes = \text{Mesityl};\ n = ?$$

$$2R_2AsSiMe_3 + GaCl_3 \longrightarrow 1/n[(R_2As)_2GaCl]_n + 2Me_3SiCl$$
$$R = Me_3SiCH_2;\ n = 2$$
$$R = Mes;\ n = ?$$

$$R_2AsSiMe_3 + 1/n[(R_2As)_2GaCl]_n \longrightarrow (R_2As)_3Ga + Me_3SiCl$$
$$R = Mes$$

Dynamic NMR spectroscopy studies of one of these, $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$, show it has novel fluxional properties. Changes of the ^1H and ^{13}C NMR spectra were reconciled by rapid exchange of the endo- and exocyclic

+thermal conductivity (Delta G) +01-

bis(trimethylsilylmethyl)arsino groups, and spectra simulated on this basis were in excellent agreement with the experimental data. $\Delta G^{\ddagger}$ of 17.0 ± 0.0 kcal/mol for the ^{13}C exchange was obtained by line shape analysis, and was in agreement with the estimate derived from the coalescence temperature. The ^{1}H exchange process between 22 and 57 °C could be simulated using the same kinetic parameters, without invoking pyramidal inversion of the exocyclic arsenics.

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Synthesis of Some Arsinogallanes and the Novel Rearrangement of a Dimeric Bisarsinogallane, Bis{bis[bis(trimethylsilylmethyl)arsino]chlorogallane}

Colin G. Pitt*, Andrew P. Purdy, Kelvin T. Higa, and Richard L. Wells*

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Summary: Silylarsines, $R_2AsSiMe_3$ (R = Me_3SiCH_2 and Mesityl), have been used to synthesize arsinogallanes. Dynamic NMR spectroscopy studies of one of these, $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$, show it has novel fluxional properties.

Despite the importance of gallium arsenide in emerging semiconductor technology[1], the chemistry of this elemental combination had, until recently[2], been restricted to the studies of Coates *et al.*[3] in the 1960's. They prepared two monoarsinogallanes by cleavage of one Ga-C bond in Me_3Ga with secondary arsines, resulting in the elimination of methane (Eq. 1). In our hands, this

$$R_2AsH + Me_3Ga \longrightarrow 1/n(R_2AsGaMe_2)_n + CH_4 \quad (1)$$

$$R = Me;\ n = 3$$

$$R = Ph;\ n = 2$$

method became impractical, and eventually failed, as the steric bulk of the substituents was increased;[4] it was also found to be limited to the cleavage of a single Ga-C bond, and bis- and trisarsinogallanes, $[(R_2As)_{3-x}GaR_x]_n$

(x = 0, 1), were inaccessible by this route[5]. A number of reports of the synthesis of main group compounds by metathetical elimination of trimethylchlorosilane[6] prompted us to evaluate this route to arsinogallanes. Here we report its successful application (Eqs. 2-4), as well as the novel fluxional properties of a dimeric bisarsinogallane.

$$R_2AsSiMe_3 + GaCl_3 \longrightarrow 1/n(R_2AsGaCl_2)_n + Me_3SiCl \qquad (2)$$

$R = Me_3SiCH_2$; $n = 3$

$R = Mes = Mesityl$; $n = ?$

$$2R_2AsSiMe_3 \quad GaCl_3 \longrightarrow 1/n[(R_2As)_2GaCl]_n + 2Me_3SiCl \qquad (3)$$

$R = Me_3SiCH_2$; $n = 2$

$R = Mes$; $n = ?$

$$R_2AsSiMe_3 + 1/n[(R_2As)_2GaCl]_n \longrightarrow (R_2As)_3Ga + Me_3SiCl \qquad (4)$$

$R = Mes$

Silylarsines[7] are readily available from lithium arsenides and trimethylchlorosilane, and their reaction with trichlorogallane proceeds stepwise in hydrocarbon solvents[8]. The only by-product, trimethylchlorosilane, is easily removed in vacuo, a considerable advantage when handling these air and moisture sensitive materials. This method did not yield $[(Me_3SiCH_2)_2As]_3Ga$; however, it did afford the sterically hindered trisarsinogallane $(Mes_2As)_3Ga$ (Eq. 4) which was first prepared by us from lithium dimesitylarsenide and trichlorogallane and shown to be monomeric by single-crystal x-ray analysis[2d]. Lack of suitable crystals and the very low solubility of the mono- and bisarsinogallanes containing mesityl groups (Eqs. 2 and 3), also prepared from lithium dimesitylarsenide and trichlorogallane)[2d], prohibited determination of their degree of oligomerization.

The bisarsinogallane $[(Me_3SiCH_2)_2As]_2GaCl$ was shown by cryoscopic measurements to exist predominantly as the dimer (Eq. 3) in benzene. Its ^1H (300 MHz) NMR spectrum in toluene at 22 °C, reproduced in Figure 1a, consisted of singlets at δ 0.25 and 0.27 (72H, Me_3Si), and 1.65 (8H, <u>endo</u>-CH_2As), and doublets (AB quartet, $^2\underline{J}_{HH}$ = 13.5 Hz) at 0.94 and 1.76 (8H, <u>exo</u>-CH_2As). The ^{13}C NMR spectrum at 21 °C consisted of four singlets at δ 0.05 and 1.15 (Me_3Si), 7.87 and 8.78 ($SiCH_2As$). Only a single isomer was detected, assigned the <u>trans</u> structure on steric grounds. The ^1H NMR spectrum was measured using a range of concentrations (5.9-111 mmolar) in an attempt to detect equilibria with monomeric or other oligomeric species; no significant changes in peak intensities of the dimer were observed. However, the relative intensities of the peaks due to trace impurities, $(Me_3SiCH_2)_2AsH$ and $(Me_3SiCH_2)_2AsAs(CH_2SiMe_3)_2$, resulting from slight hydrolysis and decomposition of the dimer, respectively[9], increased somewhat with decreasing concentrations.

On raising the temperature from 22 °C to 97 °C, the ^1H AB quartet collapsed to a broadened doublet which then approached coalescence with the singlet. Likewise, the ^{13}C methyl peaks broadened and coalesced at 78 °C (Fig. 1b). This spectroscopic behavior was reversible, with the exception of the formation of a small amount of the above diarsine. These changes of ^1H and ^{13}C spectra, when coupled with the dimeric molecular weight and the absence of other species in the spectra, can only be reconciled by rapid exchange of the endo- and exocyclic bis(trimethylsilylmethyl)arsino groups. Spectra simulated on this basis were in excellent agreement with the experimental data. A $\Delta G^{\ddagger}$ of 17.0 ± 0.0 kcal/mol for the ^{13}C exchange was obtained by line shape analysis[10], and was in agreement with the estimate derived from the coalescence temperature[11]. The ^{1}H exchange process between 22 and 57 °C could be simulated using the same kinetic parameters, without invoking pyramidal inversion of the exocyclic arsenics. Evidently, the latter is not a significant process in this temperature range, despite the fact that the electropositive gallium might be expected to reduce the inversion barrier.

The equivalency of the bis(trimethylsilylmethyl)arsino groups can be achieved by associative or dissociative mechanisms. The associative mechanism is intuitively more attractive, involving an intermediate in which one or both gallium atoms assume a five-coordinate square pyramidal configuration (Fig. 2). There is ample precedent for five-coordinate gallium.[12] The dissociative mechanism requires cleavage of one endocyclic Ga-As bond, then reclosure of the ring, in a trans-cis-trans equilibrium process. Dissociation into two monomers is considered energetically improbable.

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(3) (a) Coates, G.E.; Graham, J.J. J. Chem. Soc. 1963, 233. (b) Beachley, O.T.; Coates, G.E. J. Chem. Soc. 1965, 3241.

(4) For example, $[(Me_3SiCH_2)_2AsGaPh_2]_2$ was prepared by this method (ref. 2c); however, heating Ph_2AsH and $(Me_3SiCH_2)_3Ga$ (1:1 molar ratio) at 60 °C for 2 days, afforded impure $[(Ph_2AsGa(CH_2SiMe_3)_2]_n$, $Ph_2AsAsPh_2$, Me_4Si, H_2, and unreacted $(Me_3SiCH_2)_3Ga$; no evidence for the desired product was obtained when $(Me_3SiCH_2)_2AsH$ and $(Me_3SiCH_2)_3Ga$ (1:1 molar ratio) were heated at 100-120 °C for 1 month.

(5) For example, when Ph_2AsH and Me_3Ga (2:1 molar ratio) were heated at 80-100 °C for 2 days, no evidence for any product other than CH_4, $(Ph_2AsGaMe_2)_n$, and unchanged Ph_2AsH was obtained.

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Stimson, R. E.; Leopold, M.F.; Rubin, B.H. Inorg. Chem. 1982, 21, 1909. (g) Hoffmann, G.G. J. Organomet. Chem. 1984, 273, 187.

(7) See for example: (a) Abel, E.W.; Honigschmidt-Grossich, R.; Illingworth, S. M. J. Chem. Soc. (A) 1968, 2623. (b) Abel, E. W; Crow, J.P. J. Organomet. Chem. 1969, 17, 337. (c) Mislow, K.; Senkler, G.H.; Cook, R.J.; Casey, J.P.; Baechler, R. D. J. Am. Chem. Soc. 1972, 94, 2859. The new silylarsines used in this work were prepared under strict inert atmospheric conditions as follows. **$(Me_3SiCH_2)_2AsSiMe_3$.** A mixture of $(Me_3SiCH_2)_2AsH$[2c] (6.0 g, 24 mmol) and n-BuLi (10 mL, 2.4 M in hexane) was stirred at 60 °C for 1 day under nitrogen pressure and then cooled to 0 °C, before adding dropwise excess Me_3SiCl (4 mL in 20 mL pentane). After refluxing for 0.5 h, addition of 10 mL of Et_2O, and standing at room temperature for 1 day, the mixture was filtered; following solvent removal, distillation afforded the silylarsine as a colorless liquid (5.8 g, 75% yield), bp 40 °C/0.04-0.35 Torr. Anal. Calcd (Found) for $C_{11}H_{31}AsSi_3$: C, 40.96 (40.83); H, 9,69 (9.82). NMR: ^1H (80 MHz) (C_6D_6) δ 0.80 and 0.46 [AB pattern ($^2J_{HH}$ = 13.6 Hz) 4H, CH_2], 0.18 (s, 9H, $AsSiMe_3$), 0.15 (s, 18H, $CSiMe_3$); ^{13}C (22.5 MHz) (C_6D_6) δ 5.7 (s, CH_2), -1.5 (s, $AsSiMe_3$), 0.37 (s, $CSiMe_3$). **$Mes_2AsSiMe_3$.** (a) Mesitylmagnesium bromide (274 mmol) in THF (200 mL) was added over a 45 min period, with stirring, to $AsCl_3$ (25.0 g, 138 mmol) in THF; after 12 h, degassed water (125 mL) and conc HCl (60 mL) were added, and the mixture was stirred for 1 day. Following extraction with benzene, the volatiles were removed by distillation leaving crude, solid Mes_2AsCl (45.1 g, 94% yield). NMR: ^1H (80 MHz) (C_6D_6) δ 6.60 (s, 4H, ring CH), 2.35 (s, 12H, Me), 2.02 (s, 6H Me). (b) The crude Mes_2AsCl was dissolved in THF (500 ml) and $LiAlH_4$ (10.0 g, 263 mmole) was added. After stirring the solution for 46 h, addition of water (220 mL), extraction with

benzene, and removal of volatiles, distillation afforded Mes_2AsH as a colorless liquid (14.6 g, 58% yield), bp 145-150 ^{o}C/0.01 Torr. Anal. Calcd (Found) for $C_{18}H_{23}As$: C, 68.79 (68.66); H, 7.38 (7.55). NMR: ^{1}H (80 MHz) (C_6D_6) δ 6.70 (s, 4H ring CH), 4.83 (s, 1H, AsH), 2.27 (s, 12H, Me), 2.07 (s, 6H, Me). IR: (Nujol) 2130 cm^{-1} (s, AsH). (c) A mixture of Mes_2AsH (14.62 g, 46.42 mmol), n-BuLi (20 mL, 2.4 M in hexane), and ligroin (150 mL) was heated at 50 ^{o}C for 20 min. Filtration gave solid, yellow Mes_2AsLi which was dried under vacuum (14.41 g, 96.7% yield). Anal. Calcd (Found) for $C_{18}H_{22}AsLi$: C, 67.51 (67.15); H, 7.82 (7.95). NMR: ^{1}H (80 MHz) (C_6D_6 + 1 drop THF) δ 6.93 (s, 4H, ring CH), 2.61 (s, 12H, Me) 2.29 (s, 6H, Me). (d) A mixture of Mes_2AsLi (3.79 g, 11.8 mmol), Me_3SiCl (10 mL), and ligroin (100 mL) was heated to reflux, stirred at room temperature for 12 h, and filtered. The filtrate was concentrated in vacuo to an oil which eventually crystallized as colorless $Mes_2AsSiMe_3$ (4.46 g, 98% yield), mp 62-66 ^{o}C Anal. Calcd (Found) for $C_{21}H_{31}AsSi$: C, 65.26 (65.53); H, 8.08 (8.24). NMR: ^{1}H (80MHz) (C_6D_6) δ 6.74 (s. 4H, ring CH), 2.31 (s, 12H, Me), 2.10 (s, 6H, Me), 0.28 (s, 9H, $SiMe_3$).

(8) The arsinogallanes were prepared under strict inert atmospheric conditions as follows. **$[(Me_3SiCH_2)_2AsGaCl_2]_3$.** A solution of $(Me_3SiCH_2)_2AsSiMe_3$ (0.5 g, 1.55 mmol) in pentane (6 mL) was added to a solution of $GaCl_3$ (0.27 g, 1.55 mmol) in pentane (6 mL). After several min, a precipitate formed. Removal of the liquid phase, washing with pentane, and drying in vacuo gave the arsinogallane as a white solid (0.40 g, 67% yield), mp 170-184 ^{o}C (decomp.). Anal. Calcd (Found) for $C_{24}H_{66}As_3Cl_6Ga_3Si_6$: C, 24.64 (24.82); H, 5.68 (5.97); Cl, 18.18 (17.84); mol wt (cryoscopic in benzene), 1170 (1070 80); NMR spectrum shows one species. NMR: ^{1}H (250 MHz) (C_6D_6) δ 1.78 (s, 12H, CH_2), 0.23 (s, 54H, $SiMe_3$); ^{13}C (22.5 MHz) (C_6D_6) δ 7.4 (s, CH_2)

1.2 (s, $SiMe_3$). **$\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$.** A solution of $(Me_3SiCH_2)_2AsSiMe_3$ (1.0 g, 3.10 mmol) in pentane (10 mL) was added to a solution of $GaCl_3$ (0.27 g, 1.55 mmol) in benzene (10 mL) and, after 1 day, the mixture was brought to a boil. Removal of the volatiles under vacuum gave a white solid that on slow recrystallization from ligroin (bp 95-110) afforded the bisarsinogallane as colorless crystals that were dried in vacuo (0.67 g, 80% yield), mp 101-128 °C (decomp.). Anal. Calcd (Found) for $C_{32}H_{88}As_4Cl_2Ga_2Si_8$: C, 31.82 (31.66); H, 7.34 (7.23); mol wt (cryoscopic in cyclohexane), 1207 (1100 ± 55). **$(Mes_2AsGaCl_2)_n$.**[2d] A solution of $Mes_2AsSiMe_3$ (0.39 g, 1.0 mmol) in pentane (3 mL) was added to a solution of $GaCl_3$ (0.24 g, 1.36 mmol) in pentane (5 mL) and, after 5 min, the volatiles were removed. Washing the remaining solid with ligroin and drying in vacuo gave the arsinogallane as a white solid (0.46 g, 100% yield), mp 145-146 °C (decomp.). Anal.[2d] Calcd (Found) for $C_{18}H_{22}AsCl_2Ga$: C, 47.63 (47.91); H, 4.89 (5.07). NMR: ^1H (80 MHz) (C_6D_6 + 2 drops THF) δ 6.69 (s, 4H, ring CH), 2.45 (s, 12H, Me), 2.06 (s, 6H, Me). **$[(Mes_2As)_2GaCl]_n$.**[2d] Addition of a solution of $Mes_2AsSiMe_3$ (0.82 g, 2.1 mmol) in benzene (10 mL) to a solution of $GaCl_3$ (0.35 g, 2.0 mmol) in benzene (10 mL) gave a white precipitate of $(Mes_2AsGaCl_2)_n$. Addition of more $Mes_2AsSiMe_3$ (0.75 g, 1.9 mmol) resulted in a yellow-orange solution. Removal of volatiles after 3 h gave a yellow solid that on recrystallization from ligroin/benzene (1:1) afforded the bisarsinogallane as a yellow solid (0.35 g, 24% yield), mp 120-125 °C (decomp.). Anal. Calcd (Found) for $C_{36}H_{44}As_2ClGa$: C, 59.09 (59.27); H,6.06 (6.02). NMR: ^1H (80 MHz) (C_6D_6) δ 6.68 (s, 8H, ring CH), 2.31 (s, 24H, Me), 2.06 (s, 12H, Me). **$(Mes_2As)_3Ga$.**[2d] Addition of a solution of $Mes_2AsSiMe_3$ (0.67 g, 1.7 mmol) in benzene (10 mL) to a solution of $GaCl_3$ (0.15 g, 0.85 mmol) in benzene (10 mL) gave a yellow solution. Removal of volatiles after 3 days gave a yellow solid which was shown by NMR to be an impure mixture of mono- and bisarsinogallane. Addition of more $Mes_2AsSiMe_3$ (0.21 g, 0.54 mmol) dissolved in benzene (10 mL) gave a yellow solid and orange solution. Filtration and removal of volatiles gave an orange oil to which ligroin (10 mL) was added. The resulting mixture was heated and allowed to cool; after 1 day the trisarsinogallane precipitated as an orange solid (0.11 g, 13% yield), mp 130-160 °C (decomp). Anal.[2d] Calcd (Found) for $C_{54}H_{66}As_3Ga$: C, 64.24 (64.55); H, 6.59 (6.59). NMR: ^1H (80MHz) (C_6H_6) δ 6.63 (s, 12H, ring CH), 2.32 (s, 36H, Me) 2.05(s, 18H, Me).

(9) Based on NMR, same peaks as in spectra of authentic samples of the arsine[2c] and the diarsine. The diarsine was prepared by the reduction of $(Me_3SiCH_2)_2AsCl$[2c, 13] with zinc amalgam in refluxing methanol. Anal. Calcd (Found) for $C_{16}H_{44}As_2Si_4$: C, 38.54 (38.11); H, 8.89 (8.61). NMR: ^1H (80 MHz) (C_6D_6) δ 0.75 and 0.61 [AB pattern ($^2\underline{J}_{HH}$ = 13.6), 8H, CH_2], 0.12 (s, 36H, $SiMe_3$); ^{13}C (22.5 MHz) (C_6D_6) δ 10.2 (s, CH_2), 0.5 (s, $SiMe_3$).

(10) (a) The ^{13}C (75.429 MHz) Me_3Si resonances from spectra at eleven temperatures (304, 309, 314, 319, 325, 330, 349, 350, 351, 352, and 365 °K) were compared with the simulations from the modified DNMR3[10b] program, using $\Delta\nu$ = 83.5 Hz, and a natural line width of 1.0 Hz, and the rate constants (5, 5, 11, 14.5, 29, 35, 150, 170, 185, 195, and 500 sec^{-1}) were obtained. A plot and least-squares analysis of ln (k/T) versus 1/T yielded a slope (m = -8295 ± 218) and an intercept (b = 22.98 ± 0.66). The equations[10c] $\Delta H^\ddagger = -mR$, $\Delta S^\ddagger = R(b - 23.76)$, and $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ were used to obtain $\Delta H^\ddagger$ (16.5 ± 0.4 kcal/mole), $\Delta S^\ddagger$ (-1.55 ± 1.3 cal/mol-°K), and $\Delta G^\ddagger$. (b) Binsch, G.; Kleier, D.A. The Computation of Complex Exchange-Broadened NMR Spectra, Program 165, Quantum Chemistry Program Exchange, Indiana University, 1970; revised by

Bushweller, C.H.; Bhat, G.; Letendre. L.J.; Brunelle,J.A.; Bilofsky, H.S.; Ruben, H.; Templeton, D.H.; Zalkin, A. J. Am. Chem. Soc. 1975, 97, 65; and by Caves, T. (North Carolina State University). (c) Sandstrom, J. "Dynamic NMR Spectroscopy"; Academic Press Inc.: London, England, 1982.

(11) $\Delta G_c^{\ddagger}$ = 17.0 ± 0.1 kcal/mol; obtained (in cal/mol) from the equation $\Delta G_c^{\ddagger} = T_c[45.67 + 4.58 \log (T_c/\Delta\nu)]$, where $T_c = 351 \pm 1$ °K, and $\Delta\nu = 83.3$ 0.2 Hz.

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Figure 1. (a) ^1H NMR Spectra and (b) ^{13}C NMR Spectra of $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$.

Figure 2. Exchange of the Endo- and Exocyclic Arsino Groups.

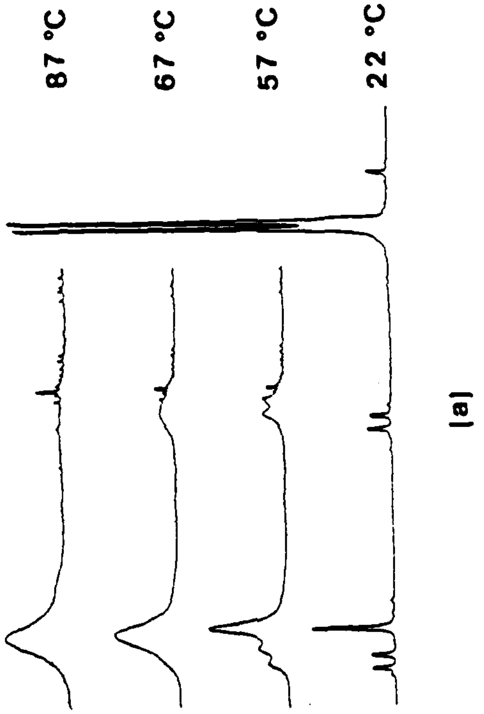

Figure 1 (a)

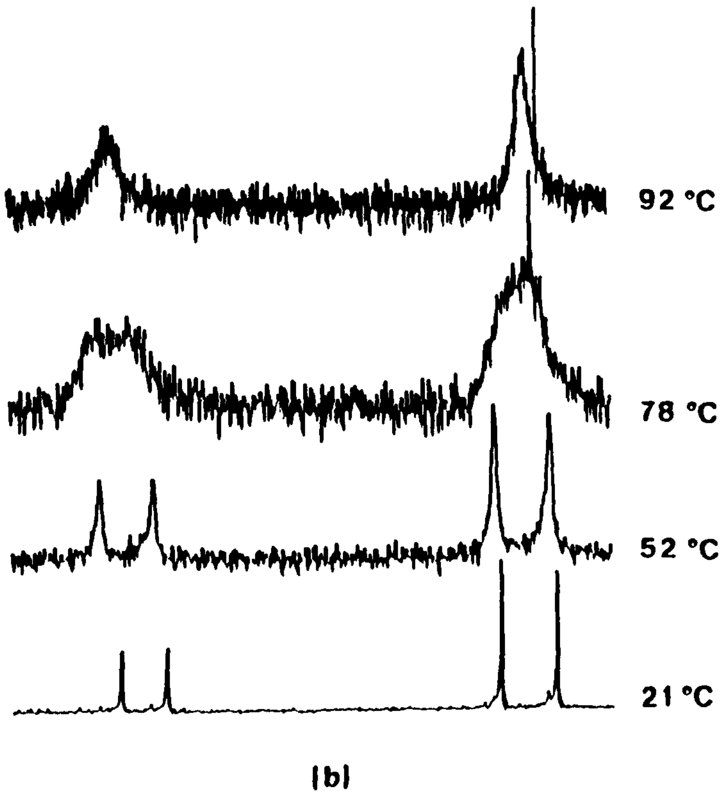

Figure 1 (b)

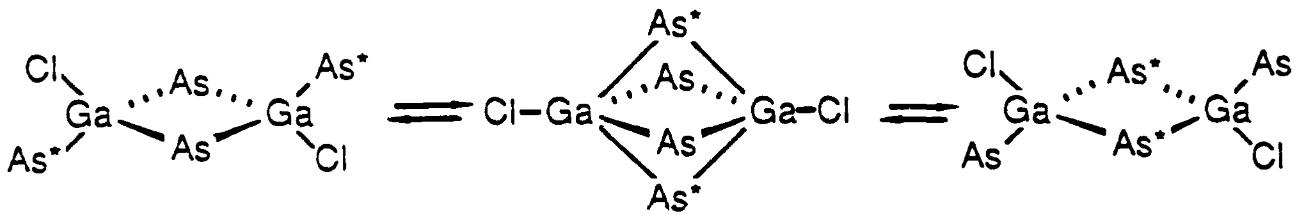

Figure 2

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