Primary and secondary neopentyl arsines and their reactions with trimethylgallium. Crystal and molecular structure of $[Me_2GaAs(CH_2CMe_3)_2]_2$

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Abstract

The primary and secondary neopentylarsines, $NpAsH_2$ and Np_2AsH ($Np = CH_2CMe_3$) have been prepared from the reaction of the corresponding bromide ($NpAsBr_2$ and Np_2AsBr) with lithium aluminum hydride in ether or tetraglyme solution. Reaction of the primary or secondary arsine with $GaMe_3$ yielded a colorless, crystalline arsino(gallane) with empirical formula $Me_2GaAs(H)Np$ or $Me_2GaAsNp_2$, respectively. The new compounds have been fully characterized according to elemental analysis, physical and solubility properties, IR, ^1H and ^{13}C NMR spectroscopies. Single crystal X-ray diffraction studies of $Me_2GaAsNp_2$ have shown the compound to be dimeric in the solid state. The compound $[Me_2GaAsNp_2]_2$ crystallized in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 8.688(4)$, $b = 9.817(4)$, $c = 9.910(4)$ Å, $V = 774.7(6)$ Å^3 and $Z = 2$. The planar $(Ga–As)_2$ ring of the dimer lies on an inversion center with Ga–As bond lengths of 2.529(1) and 2.532(1) Å. The endocyclic angles at As and Ga are 94.3(1) and 85.7(1)°, respectively.

Introduction

In recent years, investigations of the synthesis and characterization of Group 13 and 15 compounds have been driven by the potential of these compounds as precursors for the OMCVD (organometallic chemical vapor deposition) production of compound semiconductors. These investigations have yielded a variety of new and interesting compounds. A number of new neopentylaluminum [1], -gallium [2] and -indium [3] compounds, including the monomeric aluminum compound $AlNp_3$ ($Np = CH_2CMe_3$), have been described. Wells and co-workers described the first monomeric arsinogallane [4], $Ga(AsR_2)_3$ (R = mesityl), as well as several other heterometallic 13/15 compounds [5]. Theopold and co-workers reported the monomeric arsino(gallane) [6], $(C_5Me_5)_2GaAs(SiMe_3)_2$, the first example of a monomeric 13/15 compound containing only one Group 13 element and one Group 15 element. A notable feature of $(C_5Me_5)_2GaAs(SiMe_3)_2$ was the ease in which it underwent decomposition in butanol to form GaAs. Cowley, Jones and co-workers investigated the synthesis of a number of 13/15 compounds [7], including the mixed metal derivative $Me_2AsGa_2(t\text{-}Bu)_4InMe_2$, and have investigated the potential of these compounds as precursors for 13/15 semiconductors [8].

Primary and secondary arsines are of interest since they have been shown to be viable alternatives to AsH_3 for the OMCVD fabrication of GaAs [9]. Beachley and Coates [10] utilized primary and secondary arsines in alkane elimination reactions with trimethylaluminum, -gallium or -indium which resulted in the first examples of 13/15 compounds. However, little of the current work has been devoted to examining the preparation and properties of new primary and secondary arsines that might be useful in semiconductor synthesis. Notable exceptions include R_2AsH and $RAsH_2$ (R = mesityl, [trimethylsilyl]methyl) [5a, b, 11, 12]. In our previous studies [13] we investigated the synthesis and properties of the new arsines, Np_nAsBr_{3-n} (Np = neopentyl; $n = 1–3$) and Np_nAsBr_{5-n} ($n = 2, 3$). We report here the synthesis of the new primary and secondary arsines, $NpAsH_2$ and Np_2AsH, which have been fully characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopies. Since these compounds have potential as alternate OMCVD sources, their vapor pressures have also been measured. In addition, the

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reactions of Np_nAsH_{3-n} ($n=1, 2$) with $GaMe_3$ have also been examined and have yielded $[Me_2GaAs(H)Np]_x$* and $[Me_2GaAsNp_2]_2$, respectively. The solid state structure of $[Me_2GaAsNp_2]_2$ has been determined by X-ray diffraction studies. The syntheses of these new compounds now allows comparisons between the neopentyl- and (trimethylsilyl)methylarsine systems.

Experimental

General data

All compounds described in this investigation were manipulated in a vacuum system or under a purified helium atmosphere. Diethyl ether was vacuum distilled from sodium diphenylketal immediately prior to use. Tetraglyme was refluxed over sodium, vacuum distilled and stored over molecular sieves in a glove box. Pentane and benzene, dried over CaH_2 and P_4O_{10}, were stored in sodium mirrored flasks and were vacuum distilled as needed. The synthesis and purification of the neopentylarsenic(III) bromides, Np_2AsBr and $NpAsBr_2$, have been described previously [13]. Lithium aluminum hydride was obtained from Aldrich Chemical Co. and was used as received. Trimethylgallium was obtained from Morton Thiokol/CVD. Analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, NY or E+R Microanalytical Laboratory, Corona, NY. IR spectra were recorded either as Nujol mulls between cesium iodide plates, as neat liquids, or in the gas phase by using a Perkin-Elmer model 1430 spectrophotometer. Absorption intensities were measured by the method of Durkin *et al.* [14] and are reported with the abbreviations: w (weak), m (medium), s (strong), sh (shoulder) and v (very). The ^1H NMR spectra were recorded at 90 MHz with a Varian EM390 spectrometer or at 300 MHz using a Bruker MSL-300 spectrometer. Proton decoupled ^{13}C spectra were recorded on a Bruker MSL-300 spectrometer at 75.5 MHz. Proton chemical shifts were referenced to benzene at 7.13 ppm and carbon chemical shifts were referenced to deuterobenzene at 128.00 ppm. All NMR tubes were sealed under vacuum.

Synthesis of $NpAsH_2$

Method A

A modification of the method of Becker *et al.* [15] was used. A 100 ml two-necked flask was charged with *c.* 20 ml of tetraglyme in which lithium aluminum hydride (LAH) (0.090 g, 2.4 mmol) was suspended. An addition tube containing $NpAsBr_2$ (1.4061 g, 4.6 mmol) in 5 ml of tetraglyme was connected to one neck of the flask and the system was evacuated. After the tetraglyme/LAH mixture was degassed and cooled to 0 °C for 30 min, the $NpAsBr_2$ solution was added slowly. Evolution of a non-condensable gas (presumably H_2) was observed. **Caution**: large scale reactions require a pressure release for the evolving H_2. The reaction mixture was stirred for 30 min at 0 °C, 20 min at ambient temperature and finally for an additional 30 min at 40 °C. A mobile colorless liquid, $NpAsH_2$ (0.4240 g, 2.9 mmol, 62% based on $NpAsBr_2$) was easily isolated from the non-volatile reaction solvent by vacuum distillation (*c.* 0.001 torr) at room temperature.

Method B

In addition to the synthetic route described above, reactions between LAH and $NpAsBr_2$ were carried out at various temperatures (−78, −20 and 25 °C), in diethyl ether, by utilizing a reaction stoichiometry of 1:2 ($NpAsBr_2$:LAH), similar to the method of Wells *et al.* [12]. After the reaction was complete, the reaction mixture was hydrolyzed by slow addition of water to the reaction mixture. $NpAsH_2$ was separated from diethyl ether and most excess water by fractionation distillation. The ether/water/$NpAsH_2$ mixture was passed through a series of traps (−30, −65 and −196 °C traps). The $NpAsH_2$ collected in the −65 °C trap was dried over CaH_2 while the water collected in the −35 °C trap was fractionated a second time to remove small quantities of $NpAsH_2$. The ether collected in the −196 °C trap was discarded. In all cases, yields of $NpAsH_2$ were 10–17% lower than when Method A was employed.

$NpAsH_2$: colorless liquid, b.p. 96.5 °C (calc.). *Anal.* Calc.: C, 40.56; H, 8.85. Found: C, 40.74; H, 8.87%. ^1H NMR (C_6H_6, ppm): 1.98 (t, AsH_2, 2H, $J=6.4$ Hz), 1.48 (t, $-CH_2-$, 2H, $J=6.4$ Hz), 0.80 (s, $-CH_3$, 9H). $^{13}C\{^1H\}$ (C_6D_6, ppm): 30.30 ($-CMe_3$), 30.20 ($-CH_3$), 27.55 ($-CH_2-$). IR (gas, cm^{-1}): 2965vs, 2915s, 2875s, 2170w, 2100vs, 2040w, 1477m, 1400sh, 1372m, 1248m, 1178m, 1020w, 978m, 912vw, 862m, 770w.

Synthesis of Np_2AsH

Method A

The secondary arsine was produced in 79% yield by reaction of Np_2AsBr (1.6144 g, 5.4 mmol) and LAH (0.051 g, 1.3 mmol) in diethyl ether. The synthesis was similar to that described for the preparation of $NpAsH_2$. A diethyl ether solution of Np_2AsBr was slowly added to a cooled suspension of LAH in diethyl ether. The reaction mixture was stirred at 0 °C for 30 min followed by an additional

*x indicates an oligomeric mixture of unknown composition.

18 h of reaction at ambient temperature. Non-condensable gas was observed upon addition of the reagents. The reaction mixture again was cooled to 0 °C and the ether removed by vacuum distillation. The product, a mobile, colorless liquid, was purified by vacuum distillation at 25–30 °C in a short path still, and collected (0.9268 g, 4.2 mmol, 79% based on Np_2AsBr) in a receiving flask cooled in an ethanol/ice bath.

Method B

Alternatively, the reaction was performed by using a 1:1 stoichiometry (Np_2AsBr:LAH) in diethylether at −78 °C. After 18 h, the reaction mixture was slowly hydrolyzed by addition of water to the reaction mixture. Hydrogen was removed as it evolved. When no additional hydrogen evolution was observed, the most volatile materials were removed by vacuum distillation and set aside for later work-up. The remaining reaction mixture was heated with a heat gun and all volatile compounds were distilled under dynamic vacuum into a −196 °C trap. Residual ether and some water were removed by vacuum distillation and the remaining crude Np_2AsH was vacuum distilled into a flask containing CaH_2. The flask containing the most volatile compounds, set aside earlier, was cooled to −30 °C and the ether was then removed by vacuum distillation. The resulting second portion of crude Np_2AsH was distilled into the flask containing CaH_2. Final traces of water were removed from Np_2AsH by stirring over CaH_2. Pure Np_2AsH was obtained by vacuum distillation from the Np_2AsH/CaH_2 mixture. Reaction yield of 76% was comparable to that obtained utilizing method A described above.

Np_2AsH: colorless liquid, b.p. 173 °C (calc.). *Anal.* Calc.: C, 55.04; H, 10.62. Found: C, 54.68; H, 10.55%. ^1H NMR (C_6D_6, ppm): 2.39 (m, As–H, 1H), 1.89 and 1.19 (m, $-CH_2-$, 4H), 0.97 (s, $-CH_3$, 17H), $J_{AX}=6.5$ Hz, $J_{BX}=7.8$ Hz, $J_{AB}=12.4$ Hz. $^{13}C\{^1H\}$ NMR (C_6D_6, ppm): 36.50 ($-CH_2-$), 31.18 ($-CMe_3$), 30.97 ($-CH_3$). IR (neat liquid, cm^{-1}): 3880vw, 3405vw, 3365w, 3345w, 3285w, 3220m, 3180m, 2910vs,br, 2740m, 2710m, 2685w, 2405vw, 2380w, 2290w, 2070vs, 1990w, 1467vs, 1445sh, 1413m, 1387vs, 1362vs, 1270m, 1240vs, 1157vs, 1108s, 1015s, 933w, 917m, 864vs, 856vs, 804m, 776m, 748w, 722m, 693m, 627m, 387m.

Synthesis of [$Me_2GaAs(H)Np$]$_x$

In a typical reaction a 100 ml reaction bulb with a high-vacuum stopcock was charged with $NpAsH_2$ (0.4155 g, 2.806 mmol). The flask was evacuated and 10 ml of pentane was vacuum distilled into the bulb. Trimethylgallium (0.2939 g, 2.559 mmol) was weighed into a tared tube and then also vacuum distilled into the reaction bulb. The reaction bulb containing all the reactants was then weighed. After stirring for 5 days at room temperature, the reaction vessel was cooled to −196 °C and the methane was removed by vacuum distillation. The reaction bulb was then reweighed to determine the amount of methane evolved. Methane (0.0367 g, 2.29 mmol, 89% yield based on $GaMe_3$) was identified by its vapor pressure of 10 mm at −196 °C and by its IR spectrum. Removal of the reaction solvent yielded a colorless, crystalline solid. The product was dissolved in a fresh portion of pentane and the faintly cloudy solution was filtered through a medium frit. A white, crystalline solid, [$Me_2GaAs(H)Np$]$_x$ (0.477 g, 1.93 mmol) was isolated in 75% yield (based on $GaMe_3$) after removal of the pentane.

[$Me_2GaAs(H)Np$]$_x$: colorless solid, m.p. 94–97.5 °C. *Anal.* Calc.: C, 34.06; H, 7.35; As, 30.35; Ga, 28.24. Found: C, 34.28; H, 7.33; As, 30.08; Ga, 28.80%. ^1H NMR (C_6H_6, ppm): 1.94, 1.87, 1.81 ($-CH_2-$, As–H, 3H), 0.93 ($-C-CH_3$, 10.2H), 0.26, 0.22, 0.19 (Ga–CH_3, 7.3H). ^{13}C NMR (C_6D_6, ppm): 31.38 (CMe_3), 30.90 ($-CH_2-$), 30.57 ($-CH_3$), −1.89 and −3.66 (Ga–CH_3) (see 'Results and discussion' for details on the ^1H and ^{13}C spectra). IR (Nujol mull, cm^{-1}): 2735w, 2705w, 1975br,vw, 1848vw, 1825vw, 1732w, 1358vs, 1264m, 1237vs, 1158w, 1126vs, 1093m, 1070m, 1007m, 978m, 944w, 931w, 914w, 785w, 752vs, 733vs, 676m, 602vs, 565w, 510w, 448w, 415vw, 384m, 254m.

Synthesis of [$Me_2GaAsNp_2$]$_2$

A 100 ml reaction bulb was charged with a sample of Np_2AsH (0.8127 g, 3.72 mmol). The flask was fitted with a high-vacuum stopcock and evacuated. A previously weighed sample of trimethylgallium (1.1250 g, 9.80 mmol) was vacuum distilled into the reaction bulb. The reaction mixture was stirred and heated to 85–95 °C for 3 days. Methane (0.0585 g, 3.65 mmol), identified by its IR spectrum and vapor pressure at −196 °C, was produced in 98% yield. The excess trimethylgallium was removed by vacuum distillation yielding a colorless crystalline solid. The product was dissolved in pentane and the solution was filtered through a fine frit. The solvent was removed yielding [$Me_2GaAsNp_2$]$_2$ (1.075 g, 3.391 mmol) in 91% yield. Colorless crystals of [$Me_2GaAsNp_2$]$_2$ suitable for X-ray analysis were grown by recrystallization from a saturated pentane solution.

[$Me_2GaAsNp_2$]$_2$: colorless solid, m.p. 124–134 °C. *Anal.* Calc.: C, 45.47; H, 8.90. Found: C, 45.36; H, 9.00%. ^1H NMR (C_6H_6, ppm): 2.07 (s, $-CH_2-$, 4H), 0.98 (s, C–CH_3, 18H), 0.23 (s, Ga–CH_3, 6H). $^{13}C\{^1H\}$ (C_6D_6, ppm): 38.14 ($-CH_2-$), 32.36 ($-CMe_3$), 31.65 ($-CH_3$), −3.21 (Ga–CH_3). IR (Nujol mull, cm^{-1}): 2370br,vw, 2075vw, 1359s, 1274vw, 1240m, 1196m, 1180m, 1165s, 1118m, 1015m, 947vw, 932vw, 909w, 812s, 750vs, 725vs, 673m, 642m, 588w, 554m, 523m, 462vw, 385vw.

Vapor pressures of $NpAsH_2$ and Np_2AsH

Vapor pressure measurements were obtained by immersion of a tensimeter containing the sample in a constant temperature bath and monitoring the change in height of the mercury (using a cathetometer) with change in temperature [16]. The heat of vaporization of $NpAsH_2$ and Np_2AsH was determined by plotting the log of the vapor pressure (in atmospheres) versus the temperature (K) (Figs. 1 and 2, respectively). The slope was equal to $-\Delta H_{vap}/2.303RT$, defined in eqn. (1). Thus ΔH_{vap} for $NpAsH_2$

$$\log P = -\Delta H_{vap}/2.303RT + C \quad (1)$$

was calculated to be 8.76 ± 0.17 kcal/mol with C equal to 5.17 in the temperature range of 34–50 °C (errors were calculated as standard deviations). Extrapolation of the data gave a calculated normal boiling point of 97 °C and a vapor pressure of 43 mm Hg at 25 °C. In a similar manner, the ΔH_{vap} for Np_2AsH was calculated from eqn. (1) to be 14.5 ± 0.72 kcal/mol with C equal to 7.12 in a temperature range of 54–100 °C. The normal boiling point was then calculated to be 173 °C with a vapor pressure of 0.22 mm Hg at 25 °C.

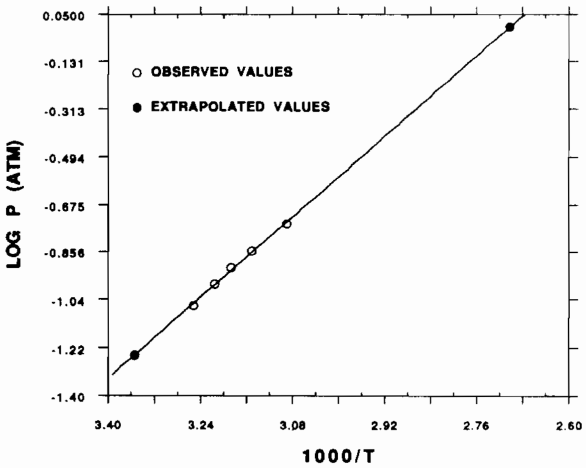

Fig. 1. Plot of the log P vs. $1/T$ for $NpAsH_2$. The observed data points were fit to $\log P = -1914/T + 5.17$ ($-H_{vap}/2.303R = -1914$). Vapor pressure at 25 °C and the normal boiling point are shown as extrapolated data points.

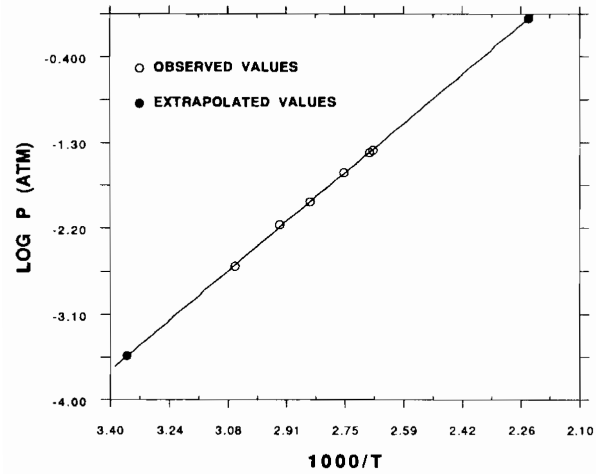

Fig. 2. Plot of the log P vs. $1/T$ for Np_2AsH. The observed data points were fit to $\log P = -3177/T + 7.12$ ($-H_{vap}/2.303R = -3177$). Vapor pressure at 25 °C and the normal boiling point are shown as extrapolated data points.

Crystallographic studies

A crystal of $[Me_2GaAsNp_2]_2$ was sealed under helium gas in a thin walled capillary for data collection on an automated Nicolet R3m/V diffractometer using an incident beam monochromator with Mo Kα radiation. Data were corrected for Lorentz and polarization effects and an empirical absorption correction based on the φ-dependence of 17 reflections with $\chi \sim 90°$ was applied. Maximum and minimum transmittance was 0.98 and 0.69. The structure was determined by direct methods with the aid of the program SHELXTL [17] and was refined with full matrix least-squares [17]. The parameters refined include the atom coordinates and anisotropic thermal parameters for all non-hydrogens. The methyl groups were treated as rigid groups and allowed to rotate about the C–C bond. Coordinate shifts of the carbon atoms were applied to the bonded hydrogens with C–H distances and H–C–H angles fixed at 0.96 Å and 109.5°, respectively, and the isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$. Additional data collection and refinement parameters are listed in Table 1. Atomic scattering factors are from the International Tables for X-ray Crystallography [18]. Atomic coordinates and equivalent isotropic displacement coefficients are given in Table 2. Bond lengths are listed in Table 3 and bond angles in Table 4. Anisotropic displacement coefficients are given in Table 5. Hydrogen atom coordinates and isotropic displacement coefficients are given in Table 6.

Results and discussion

A modification of the method described by Becker *et al.* [15] was investigated for the synthesis of $NpAsH_2$. Reactions were carried out in tetraglyme solution, where the separation of the volatile $NpAsH_2$ was expected to proceed readily. Acceptable yields of $NpAsH_2$ (*c.* 62%) were achieved by performing the reaction in tetraglyme solution at 0 °C using an

TABLE 1. Crystal and refinement data

Formula	$C_{12}H_{28}GaAs$
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.688(4)
b (Å)	9.817(4)
c (Å)	9.910(4)
α (°)	87.90(3)
β (°)	78.38(3)
γ (°)	69.46(3)
V (Å^3)	774.7(6)
Z	2
Formula weight	317.0
$F(000)$	328
ρ(calc.) (g cm^{-3})	1.359
Temperature (°C)	−5
Crystal dimensions (mm)	0.27×0.41×0.52
λ, wavelength (Å)	0.71073
μ, absorption coefficient (cm^{-1})	38.6
2θ max (°)	50
Scan speed (°/min)	variable 10–30
2θ scan range (°)	$1.6+\Delta_{\alpha1\alpha2}$
Data collected, h k l	−10 to 10, −11 to 0, −11 to 11
Unique data	2724
R_{int}	0.029
Unique data, $F_o > 3\sigma(F_o)$	2365
Total reflections	2893
Standard reflections	1.8% random variation
Parameters refined	152
Weighting function, g[a]	0.00023
R[b], R_w[c], S[d]	0.041, 0.043, 1.653
Fourier excursions (e Å^{-3})	0.28, −0.57

[a]$w^{-1}=\sigma^2(F_o)+gF_o^2$. [b]$\Sigma|\Delta|/\Sigma|F_o|$. [c]$\Sigma[(w\Delta^2)/\Sigma(wF_o^2)]^{1/2}$. [d]$[\Sigma w(\Delta^2)/(N_o-N_p)]^{1/2}$.

TABLE 2. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2×10^3)

	x	y	z	U_{eq}[a]
Ga	−1377(1)	4226(1)	9331(1)	42(1)
As	1386(1)	4589(1)	8439(1)	37(1)
C(1)	−1663(5)	2327(4)	9259(4)	61(2)
C(2)	−2984(5)	5832(5)	8499(4)	66(2)
C(3)	1211(5)	5517(4)	6639(3)	53(2)
C(4)	1566(4)	6937(4)	6369(4)	49(1)
C(5)	1508(7)	7285(6)	4856(5)	87(3)
C(6)	235(6)	8168(5)	7298(5)	79(2)
C(7)	3285(5)	6775(4)	6618(5)	62(2)
C(8)	3609(4)	3030(3)	7941(4)	48(1)
C(9)	3708(4)	1476(3)	7663(4)	48(1)
C(10)	2999(5)	865(5)	8965(5)	75(2)
C(11)	5562(5)	540(4)	7195(5)	67(2)
C(12)	2755(6)	1441(4)	6540(5)	71(2)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Bond lengths (Å)

Ga–As	2.529(1)	Ga–As′	2.532(1)
Ga–C(1)	1.971(5)	Ga–C(2)	1.985(4)
As–C(3)	1.982(4)	As–C(8)	1.978(3)
C(3)–C(4)	1.534(6)	C(4)–C(5)	1.532(6)
C(4)–C(6)	1.522(5)	C(4)–C(7)	1.516(6)
C(8)–C(9)	1.529(5)	C(9)–C(10)	1.512(6)
C(9)–C(11)	1.532(4)	C(9)–C(12)	1.522(6)

TABLE 4. Bond angles (°)

As–Ga–C(1)	123.2(1)	As–Ga–C(2)	102.9(1)
C(1)–Ga–C(2)	114.9(2)	As–Ga–As′	85.7(1)
C(1)–Ga–As′	122.6(1)	C(2)–Ga–As′	102.4(1)
Ga–As–C(3)	106.2(1)	Ga–As–C(8)	126.0(1)
C(3)–As–C(8)	100.3(1)	Ga–As–Ga′	94.3(1)
C(3)–As–Ga′	126.9(1)	C(8)–As–Ga′	106.0(1)
As–C(3)–C(4)	120.1(3)	C(3)–C(4)–C(5)	107.5(4)
C(3)–C(4)–C(6)	110.1(3)	C(5)–C(4)–C(6)	109.6(3)
C(3)–C(4)–C(7)	111.1(3)	C(5)–C(4)–C(7)	109.1(4)
C(6)–C(4)–C(7)	109.5(4)	As–C(8)–C(9)	119.4(3)
C(8)–C(9)–C(10)	110.5(3)	C(8)–C(9)–C(11)	107.8(3)
C(10)–C(9)–C(11)	108.5(3)	C(8)–C(9)–C(12)	110.6(3)
C(10)–C(9)–C(12)	109.7(4)	C(11)–C(9)–C(12)	109.6(3)

′Indicates a symmetry related atom.

$NpAsBr_2$:LAH mol ratio of 2:1. The product, $NpAsH_2$, was easily isolated from the non-volatile reaction solvent by vacuum distillation at room temperature with no hydrolysis being necessary. Similar results were obtained by Tzschach and Deylig [19] for the synthesis of tert-butylarsine. The primary arsine, $NpAsH_2$, was soluble in a variety of organic solvents including ether, tetraglyme, pentane and benzene, but was insoluble in water.

The reaction of $NpAsBr_2$ with LAH in a 1:2 mol ratio in diethyl ether solution was examined at several temperatures. Reactions between $NpAsBr_2$ and LAH were performed at −78, −20 and 25 °C with yields of 52%, 45% and 47%, respectively. It was apparent that reaction temperature had little effect on product yield. Despite the use of a hydrolysis step, which was reported to improve yields of tert-butylarsine [15] and phenylarsine [20], the yields were consistently well below those obtained when performing the reaction of $NpAsBr_2$ and LAH in tetraglyme using a 2:1 ($NpAsBr_2$:LAH) mol ratio. Thus, the reduced yields were likely due to product losses during the separation of the relatively volatile $NpAsH_2$ from ether and/or side reactions available because of the utilization of a 1:2 ($NpAsBr_2$:LAH) reaction stoichiometry. A reaction stoichiometry of 1:2 may result in the formation of AlH_3 which can then react with $NpAsH_2$ (eqns. (2) and (3)). It is of interest that similar side reactions have been suggested to

TABLE 5. Anisotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ga	38(1)	43(1)	47(1)	−6(1)	−11(1)	−16(1)
As	36(1)	38(1)	37(1)	−3(1)	−7(1)	−13(1)
C(1)	65(2)	61(2)	68(3)	−13(2)	−5(2)	−38(2)
C(2)	49(2)	84(3)	58(2)	−6(2)	−22(2)	−8(2)
C(3)	63(2)	64(2)	43(2)	10(2)	−19(2)	−30(2)
C(4)	47(2)	50(2)	50(2)	9(2)	−13(2)	−16(2)
C(5)	112(4)	105(4)	67(3)	37(3)	−36(3)	−59(3)
C(6)	68(3)	56(3)	93(3)	8(2)	0(2)	−7(2)
C(7)	54(2)	63(2)	76(3)	8(2)	−11(2)	−31(2)
C(8)	36(2)	51(2)	54(2)	−11(2)	−3(2)	−13(2)
C(9)	42(2)	44(2)	53(2)	−7(2)	−4(2)	−11(2)
C(10)	65(3)	60(3)	86(3)	17(2)	−3(2)	−13(2)
C(11)	52(2)	52(2)	79(3)	−10(2)	3(2)	−5(2)
C(12)	87(3)	55(2)	73(3)	−16(2)	−26(2)	−21(2)

The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$.

TABLE 6. Hydrogen atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\text{Å} \times 10^3$)

	x	y	z	U
H(1A)	−928	1560	9704	72
H(1B)	−1475	2065	8300	72
H(1C)	−2808	2475	9684	72
H(2A)	−2792	6723	8610	78
H(2B)	−4130	5959	8899	78
H(2C)	−2762	5576	7535	78
H(3A)	85	5711	6520	57
H(3B)	1983	4814	5946	57
H(5A)	1642	8208	4667	95
H(5B)	440	7328	4692	95
H(5C)	2388	6540	4265	95
H(6A)	−804	8252	7047	92
H(6B)	429	9071	7144	92
H(6C)	180	7946	8254	92
H(7A)	4123	5986	6047	74
H(7B)	3327	6582	7569	74
H(7C)	3496	7662	6392	74
H(8A)	4179	2994	8684	52
H(8B)	4202	3317	7120	52
H(10A)	1859	1503	9264	88
H(10B)	3628	861	9659	88
H(10C)	3022	−104	8815	88
H(11A)	5955	864	6310	79
H(11B)	5660	−459	7110	79
H(11C)	6225	629	7830	79
H(12A)	3189	1830	5708	84
H(12B)	1609	2042	6882	84
H(12C)	2813	469	6352	84

$$NpAsH_2 + AlH_3 \longrightarrow [H_2AlAs(H)Np]_n + H_2 \qquad (2)$$

$$[H_2AlAs(H)Np]_n \longrightarrow [HAlAsNp]_n + H_2 \qquad (3)$$

account for reduced yields during the preparation of $PhAsH_2$ (Ph = phenyl) from LAH and $PhAsCl_2$ [20]. Wells *et al.* [12] also observed low yields for the analogous trimethylsilylmethyl compound $(Me_3SiCH_2)AsH_2$ using similar procedures.

Reaction stoichiometry and solvent did not appear to play a significant role in the synthesis of the secondary neopentyl arsine. Hydrolysis of the product mixture did not lead to an increased yield of the secondary arsine. In addition, changes in reaction stoichiometry from 1:1 (Np_2AsBr:LAH) to 4:1 also had no effect on product yield. The increased steric demands of two neopentyl groups have presumably hindered secondary reactions of the type described in eqns. (4) and (5). Also, the lower vapor pres-

$$Np_2AsH + AlH_3 \longrightarrow [H_2AlAsNp_2]_n + H_2 \qquad (4)$$

$$[H_2AlAsNp_2]_n \longrightarrow [HAlAsNp]_n + NpH \qquad (5)$$

sure of Np_2AsH compared to that of the reaction solvent (diethyl ether) facilitate the separation. The secondary arsine, Np_2AsH was soluble in organic solvents such as pentane, hexane, benzene and ether but was insoluble in water.

The (trimethylsilyl)methyl analogs of the primary and secondary neopentyl arsine have been synthesized by either a reduction of $(Me_3SiCH_2)_nAsH_{3-n}$ ($n = 1$, 2) with Cu/Zn/Hg in an aqueous acid environment [11] or with LAH [5a, 12]. Yields reported for $(Me_3SiCH_2)_2AsH$ using the Cu/Zn/Hg reduction method were comparable to those now reported for Np_2AsH, but yields of $(Me_3SiCH_2)AsH_2$ were significantly lower than those obtained for the neopentyl derivative. Recent reports showed an improvement in the yield of $(Me_3SiCH_2)AsH_2$ by the reaction of $(Me_3SiCH_2)AsCl_2$ with LAH in diethyl ether solution at low temperature [12], but the reported yields of 47% for $(Me_2SiCH_2)AsH_2$ were still 10–15% lower than those obtained for $NpAsH_2$. Also, yields of

$NpAsH_2$ were not as dependent on reaction temperature as they were in the case of $(Me_3SiCH_2)AsH_2$.

The data provided in the vapor pressure curves shown in Figs. 1 and 2 are exceedingly important if these compounds are to be used as new OMCVD sources. Specifically, vapor pressure data is critical for determining flow rates and III/V ratios for compound semiconductor production. As expected there is a considerable difference in the vapor pressure between the primary and secondary neopentylarsines. The primary arsine, $NpAsH_2$, has an extrapolated vapor pressure of 43 torr at 25 °C while the vapor pressure of Np_2AsH is only 0.22 torr (Figs. 1 and 2) ($\Delta H_{vap} = 8.76 \pm 0.17$ and 14.5 ± 0.72 kcal/mol for $NpAsH_2$ and Np_2AsH, respectively). The relatively high vapor pressure of $NpAsH_2$ makes it a potential OMCVD arsenic source. For comparison, tert-butylarsine (TBA, a commercially available OMCVD source) has a $\Delta H_{vap} = 7.15$ kcal/mol and a vapor pressure of 124 torr at 20 °C [21]. Although complete vapor pressure data is not available for $(Me_3SiCH_2)AsH_2$ and $(Me_3SiCH_2)_2AsH$, their vapor pressures seem to be comparable to those of $NpAsH_2$ and Np_2AsH, with the neopentyl arsines having slightly lower boiling points than the analogous (trimethylsilyl)methyl arsines.

The large difference in vapor pressures between the primary and secondary neopentyl arsines can be exploited in their syntheses. A typical synthesis [13] of $NpAsH_2$ is outlined in eqns. (6)–(11). The $NpAsBr_2$

$$AsCl_3 + 3NpMgCl \longrightarrow AsNp_3 + 3MgCl_2 \quad (6)$$

$$AsNp_3 + Br_2 \longrightarrow Np_3AsBr_2 \quad (7)$$

$$Np_3AsBr_2 \xrightarrow{\Delta} Np_2AsBr + NpBr \quad (8)$$

$$Np_2AsBr + Br_2 \longrightarrow Np_2AsBr_3 \quad (9)$$

$$Np_2AsBr_3 \xrightarrow{\Delta} NpAsBr_2 + NpBr \quad (10)$$

$$2NpAsBr_2 + LiAlH_4 \longrightarrow 2NpAsH_2 + LiBr + AlBr_3 \quad (11)$$

obtained from this sequence of reactions is typically contaminated with Np_2AsBr, which is tedious to remove. However, because of the large differences in the vapor pressures of the primary and secondary neopentylarsines, an impurity of Np_2AsBr in $NpAsBr_2$ does not present a problem in the synthesis and purification of $NpAsH_2$, since any Np_2AsH formed is easily removed by fractional distillation. Attempts to prepare Np_2AsCl or $NpAsCl_2$ directly, from a stoichiometric reaction of $AsCl_3$ and NpMgCl, invariably result in inseparable mixtures of the two chlorides in ratios of approximately 2:1 [22]. Preliminary results* indicate that this mixture can now be used for the simultaneous preparation of primary and secondary neopentyl arsines, and that the resulting mixture of primary and secondary arsines are easily separated by fractionation.

The IR and ^1H and ^{13}C NMR spectra of the primary and secondary neopentyl arsines were quite similar to those reported for the (trimethylsilyl)methyl analogs. The neopentyarsines, $NpAsH_2$ and Np_2AsH exhibited strong absorptions at 2100 and 2070 cm^{-1}, respectively, which were assigned to As–H stretching modes. The corresponding values for $(Me_3SiCH_2)AsH_2$ [11] and $(Me_3SiCH_2)_2AsH$ [5a] are 2080 and 2050 cm^{-1}, respectively. Likewise, phenylarsine exhibited an As–H stretching frequency at a higher frequency than the As–H stretching frequency for diphenylarsine [23]. The ^1H NMR spectrum of $NpAsH_2$, in benzene solution, exhibited two triplets for the $-AsH_2$ and $-CH_2-$ protons and a singlet for the $-CH_3$ protons which was consistent with the formulation $NpAsH_2$. For Np_2AsH, the ^1H NMR spectrum exhibited a complex pattern of lines for the As–H and the $-CH_2-$ protons, and a singlet for the methyl protons. This complex pattern of lines was also reported for $(Me_3SiCH_2)_2AsH$ and was attributed to an AA'BB'X type spectrum [5a]. The ^{13}C NMR spectrum of $NpAsH_2$ exhibited lines at 30.20 and 30.30 ppm for the primary and quaternary carbons, respectively. Likewise, the lines for the primary and quaternary carbons of Np_2AsH appeared at 30.97 and 31.18 ppm, respectively. A more pronounced difference in position of the ^{13}C NMR lines for the secondary carbons of $NpAsH_2$ and Np_2AsH, 36.50 and 27.55 ppm, respectively, was observed.

The (arsino)gallanes, $[Me_2GaAs(H)Np]_x$ and $[Me_2GaAsNp_2]_2$ were isolated in high yields from the reaction of the primary or secondary neopentylarsine, respectively, and trimethylgallium. Elemental analyses were consistent with the formulations given. Beachley and Coates [10] showed that $PhAsH_2$ and $MeAsH_2$ react with trimethylgallium to eliminate 1.79 and 1.43 mol of methane, respectively. Therefore, the reaction to produce $[Me_2GaAs(H)Np]_x$ was performed in pentane solution at room temperature in order to moderate the reaction and prevent further elimination of alkane to produce $[MeGaAsNp]_n$. The successful synthesis of $[Me_2GaAs(H)Ph]_3$ and $[Me_2GaAs(H)(CH_2SiMe_3)]_3$ utilized a similar synthetic route [11, 12]. In contrast, $[Me_2GaAsNp_2]_2$ was produced by heating Np_2AsH in a large excess

*A mixture of $AsNpCl_2$ and $AsNp_2Cl$ (2:1 ratio based on ^1H NMR integration) were reacted with LAH suspended in tetraglyme. With subsequent workup $AsNpH_2$ was isolated in 84% yield and $AsNp_2H$ was obtained in 33% yield.

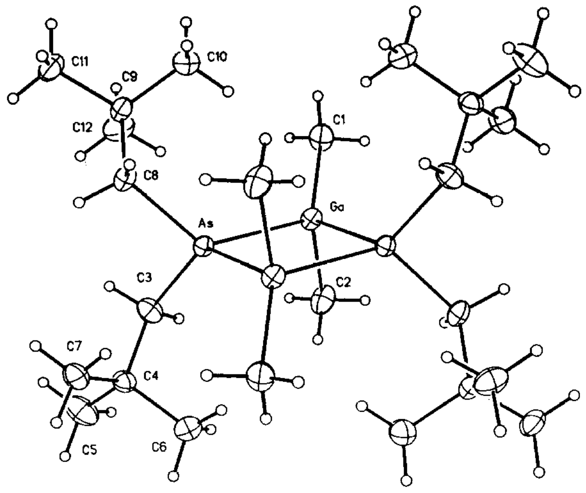

Fig. 3. Thermal ellipsoid plot of $[Me_2GaAsNp_2]_2$ drawn at the 20% probability level. Unlabeled ellipsoids are related by an inversion center located at the center of the GaAs ring.

of $GaMe_3$. The ability to perform the reaction under harsher conditions was due to the lack of a second reactive hydrogen. Both $[Me_2GaAs(H)Np]_x$ and $[Me_2GaAsNp_2]_2$ were soluble in pentane and benzene.

The ^1H NMR spectrum of $[Me_2GaAsNp_2]_2$, exhibited lines at 2.07 and 0.98 ppm for methylene and methyl protons, respectively, of the neopentyl moiety, in addition to a singlet at 0.23 ppm for the methylgallium protons. Unlike the analogous (trimethylsilyl)methyl derivative, $[Me_2GaAs(CH_2SiMe_3)_2]_2$ [11], there was no NMR evidence for a dimer/trimer equilibrium in solution. In the $^{13}C\{^1H\}$ NMR spectrum, singlets for the primary, secondary and quaternary carbons on the neopentyl group were observed at 31.65, 38.14 and 32.36 ppm, respectively, as well as a singlet at −3.21 pm for the methyl carbon bound to gallium. The (arsino)gallane was soluble in hydrocarbons. The ^1H NMR spectrum of $[Me_2GaAs(H)Np]_x$ was much more complicated than that observed for $[Me_2GaAsNp_2]_2$. The spectrum exhibited a fairly broad resonance at 1.87 ppm with smaller secondary lines on each side (the most prominent secondary lines were 1.94 and 1.81 ppm). These resonances were assigned to the $-CH_2-$ and $-AsH_2$ protons, believed to be coincident. A singlet corresponding to the methyl groups of the neopentyl ligand was observed at 0.93 ppm and the signal for the methyl groups on gallium appeared as three resonances at 0.26, 0.22 and 0.19 ppm. The integration ratio of 2.4:1:3.4 for $Ga-Me_2$:As–H + $-CH_2-$:CMe_3 was consistent with the formulation $[Me_2GaAs(H)Np]_x$. The similarity of this spectrum with that reported for the trimeric compound $[Me_2GaAs(H)(CH_2SiMe_3)]_3$ [12] suggests a value of $x = 3$ for the neopentyl derivative, $[Me_2GaAs(H)Np]_x$. We were unable to grow crystals of $[Me_2GaAs(H)Np]_x$ suitable for X-ray analysis.

In the solid state $Me_2GaAsNp_2$ is a dimer (Fig. 3) with one molecule in the $P\bar{1}$ unit cell. The planar $(As–Ga)_2$ ring lies on an inversion center with As–Ga bonds of 2.529(1) and 2.532(1) Å for the four coordinated atoms and endocyclic angles at the As and Ga atoms of 94.3(1) and 85.7(1)°, respectively. Dimers with $(As–Ga)_2$ planar rings have a limited range of values for the ring parameters which vary due to steric crowding of ring substituents. The compounds $\{BrGa[As(CH_2SiMe_3)_2]_2\}_2$ [5c], $[Ph_2GaAs(CH_2CMe_3)_2]_2$ [5a] and $[Ga(AsBu_2)Me_2)]_2$ [7b] have a range of As–Ga values from 2.513(1)–2.558(1) Å, and endocyclic angles at the As and Ga atoms that range from 94.9(1)–95.7(1)° and 84.3(1)–85.1(1)°, respectively. A somewhat larger variation is evident in the As–C bonds to ring substituents where the range is 1.956 [5c]–2.046 [7b] Å. For $[Me_2GaAsNp_2]_2$ the average As–C is 1.980(3)

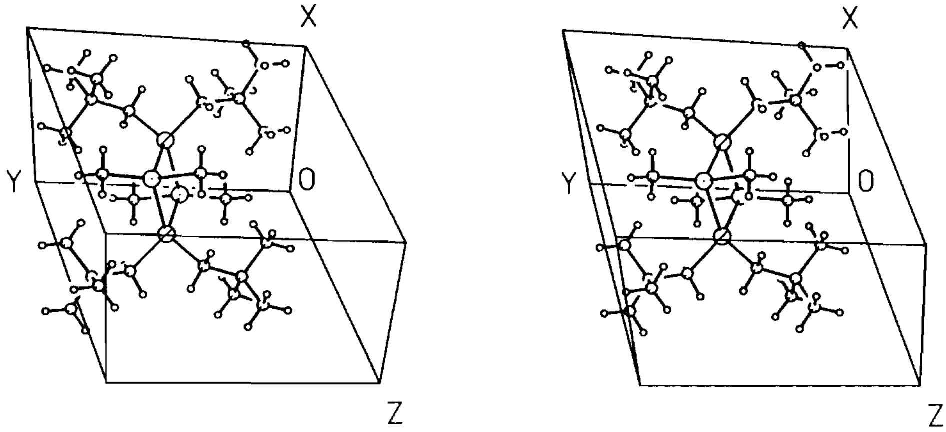

Fig. 4. Stereoscopic view of the unit cell for $[Me_2GaAsNp_2]_2$.

Å. In monomeric $[(C_5Me_5)_2GaAs(SiMe_3)_2]$ [6], $(t\text{-}Bu)_2GaAs(t\text{-}Bu)_2$ [24] and $Ga(AsMes_2)_3$ (Mes = mesityl) [4] tricoordinated As–Ga bonds are 2.49(2), 2.466(3) and 2.433(4) Å, respectively. The orientation of the Np and Me groups to the ring plane may be described by the dihedral angle between the ring planes and the C–Ga–C and C–As–C planes for the respective Me and Np moieties. The C–Ga–C plane is perpendicular to the ring with an axial and an equatorial Ga–C bond, while the dihedral angle between the C–As–C plane and the ring is 73.6(3)°. In this conformation there are several intramolecular contacts between the methyl hydrogens on respective Np and Me groups of 2.36(1) Å for the equatorially bonded Me groups. A stereoscopic view of the unit cell for $[Me_2GaAsNp_2]_2$ is given in Fig. 4.

Supplementary material

A listing of observed and calculated structure amplitudes (10 pages) is available from author C.G. upon request.

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