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Alternate Arsenic and Antimony Sources for the  
OMCVD Fabrication of Semiconductors

a

Final Technical Report

prepared  
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### Comments on the ONT Postdoctoral Program

My appointment as an ONT postdoctoral fellow has been very rewarding and I consider myself fortunate to have participated in the program. I have and will continue to recommend this program to individuals seeking to further their training. A few of what I consider to be the highlights of the program within NRL are discussed below.

A strong feature of this program was the great deal of freedom that the participant was given to choose and develop a research project. In my particular case this freedom was enhanced by my advisor, Dr. Alan Berry, who strongly encouraged my ideas, yet offered additional options when problems arose. In many regards our association was that of colleagues rather than as advisor/postdoc. In terms of funding through the chemistry division, there was no difficulty in obtaining supplies or equipment which were needed for the project. In addition, access was available to a variety of equipment on a "hands-on" basis and when necessary under the direction of a specialist. Interaction with other divisions was strongly encouraged and has resulted in joint publications.

The management of the program through ASEE and the benefits provided have been quite good throughout my tenure. However, I must comment that I've noticed a new energy and interest in assisting the program participants with the appointment of the new program manager, Mr. Bob Davis.

While I was quite pleased with this program there are few areas which might be improved. Treating the participants as self-employed causes an increased tax burden (i.e. self employment tax) on the participant as well as the burden of preparing and filling out more complex tax forms. If there was some way participants could be employed by an independent agency, the ONT program would become even more attractive. Travel as a ONT-fellow is handled well in terms of payment and arrangements. Unfortunately the allowance of \$1000. is not always sufficient for even one trip per year within the United States considering

the current cost of air fares and that participants cannot qualify for reduced travel fares through government travel offices. Perhaps a maximum of \$1000./year (or even less) should be set for travel only when an individual is not presenting a paper. Presentation of papers at meetings could then be encouraged by raising the maximum to perhaps \$2000-2500./year. Finally, I strongly agree that participants should submit progress reports to ASEE on a regular basis but I think quarterly is too frequent. Perhaps requiring a more structured report biannually would be a reasonable compromise.

In closing, I want to again thank ONT, NRL and ASEE for the opportunity to participate in their outstanding program. I have greatly appreciated the efforts of Alan Berry, Bob Davis and Jessica Hileman.

### Introduction

There has been considerable interest in the effect of sterically demanding ligands on the synthesis and properties of organometallic derivatives of the main group elements. Organometallic compounds incorporating such ligands have been shown to exhibit some unusual properties. For example, aluminum compounds incorporating neopentyl<sup>1</sup> and mesityl<sup>2</sup> ligands have been shown to be monomeric in the solid state. Also, mesityl<sup>3</sup>, pentamethylcyclopentadienyl<sup>4</sup> and neopentyl<sup>5</sup> derivatives of gallium exhibit significantly reduced Lewis acidities. In addition, sterically demanding ligands have been used to stabilize a variety of low valent group 14 and group 15 derivatives.<sup>6</sup> In arsenic chemistry, Lappert and co-workers<sup>7</sup> have examined the utility of the bis(trimethylsilyl)methyl and (trimethylsilyl)amino ligands in stabilizing radicals of the type,  $\cdot\text{AsR}_2$ . The effect of the bulky mesityl group on rotation about the As-C bond has also been investigated.<sup>8</sup> Particular interest has focused on arsenic derivatives incorporating the (trimethylsilyl)methyl moiety. Tris[(trimethylsilyl)methyl]arsine and bis[(trimethylsilyl)methyl]arsenic(III) chloride were first described by Seyferth.<sup>9</sup> Reactivity patterns of arsenic(V) compounds incorporating the (trimethylsilyl)methyl ligand have also been examined.<sup>10</sup> More recently, Wells and co-workers have investigated a route to the silylarsine,  $(\text{Me}_2\text{SiCH}_2)_2\text{AsSiMe}_2$  from reaction of  $(\text{Me}_2\text{SiCH}_2)_2\text{AsLi}$  and  $\text{Me}_2\text{SiCl}$ .<sup>11</sup> The silylarsine was then used to prepare a series

of novel (arsino)gallanes.<sup>11,12</sup>

Substituting the neopentyl moiety for the (trimethylsilyl)methyl ligand in aluminum<sup>1,13</sup> and gallium<sup>5,14</sup> compounds resulted in pronounced differences in properties and reactivities. Arsenic compounds incorporating the neopentyl ligand ( $\text{CH}_2\text{CMe}_2=\text{Np}$ ) have not previously been described. Thus, in our initial studies, trineopentyl arsine ( $\text{AsNp}_3$ ), dineopentylarsenic(III) bromide ( $\text{AsNp}_2\text{Br}$ ), neopentylarsenic(III) dibromide ( $\text{AsNpBr}_2$ ), trineopentylarsenic(V) dibromide ( $\text{AsNp}_3\text{Br}_2$ ) and dineopentylarsenic(V) tribromide ( $\text{AsNp}_2\text{Br}_3$ ) have been synthesized and fully characterized. Characterization data include elemental analyses, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and physical properties. The synthesis and properties of the neopentyl arsenic compounds were compared with those analogous compounds incorporating the (trimethylsilyl)methyl moiety. In addition, the solid state structures of  $\text{AsNp}_3$  and  $\text{AsNp}_2\text{Br}_2$  have been defined by X-ray diffraction studies.

Once isolated, the neopentylarsenic(III) bromides were used as starting materials for synthesis of the primary and secondary arsines,  $\text{AsNpH}_2$  and  $\text{AsNp}_2\text{H}$ . Since these compounds were of direct interest as OMCVD precursors for the growth of GaAs, vapor pressure measurements were made in addition to the characterization data described above. In addition the reactivity of the primary and secondary arsines with trimethylgallium was examined and resulted in the preparation

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of the new compounds,  $\text{Np}(\text{H})\text{AsGaMe}_2$  and  $\text{Np}_2\text{AsGaMe}_2$ . The properties of these new (arsino)gallanes were described and were compared to those of the (trimethylsilyl)methyl analogs.

There has been considerable interest in providing alternate sources to arsine for the OMCVD formation of GaAs. Thus, the usefulness of these new arsines in GaAs growth has also been examined. GaAs films were grown using  $\text{AsNpH}_2$  and  $\text{Np}_2\text{AsGaMe}_2$  as sources.

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## Experimental Section

### General Data

All compounds described in this investigation were manipulated in a vacuum system or under a helium atmosphere. Diethyl ether was vacuum distilled from sodium diphenylketal immediately prior to use. Pentane and benzene, dried by standard methods, were stored in sodium mirrored flasks and were vacuum distilled as needed. Arsenic trichloride and neopentyl chloride were purified by vacuum distillation. Bromine was used as received. Analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra were recorded either as Nujol mulls between cesium iodide plates or as neat liquids, using a Perkin-Elmer Model 1430 spectrophotometer. Absorption intensities were measured by the method of Durkin, DeHayes and Glore<sup>15</sup> and are reported with the abbreviations: w(weak), m(medium), s(strong), sh(shoulder) and v(very). The <sup>1</sup>H NMR spectra were recorded at 90 MHz with a Varian EM390 spectrometer or at 59.75 MHz using a Jeol FX60-Q spectrometer. Proton decoupled <sup>13</sup>C spectra were recorded on a Jeol FX60-Q spectrometer at 15 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 AsNp<sub>2</sub>. The synthesis of the neopentyl Grignard reagent was carried out in a 100 mL reaction bulb equipped with a glass/Teflon stopcock and charged with Mg powder (2.203 g, 90.61 mmol). Neopentyl chloride (9.055 g, 85.23 mmol) and diethyl ether (ca. 40 mL) were then vacuum distilled into the reaction bulb. The reaction mixture was subjected to ultrasound (60 Hz, 80 Watts) for one hour and then stirred and refluxed in the sealed bulb for 15 h. The solution of NpMgCl was added over the course of 30 min to a 0°C solution of AsCl<sub>3</sub> (4.044 g, 22.31 mmol). A voluminous precipitate of MgCl<sub>2</sub> was observed during the addition of the Grignard reagent. After warming to room temperature, the reaction mixture was stirred for 24 h before removing the ether by vacuum distillation. Trineopentylarsine was vacuum distilled at 120°C into a cooled (-196°C) side arm flask connected to the reaction flask by means of an 80° elbow. Residual quantities of ether were removed by vacuum distillation. Final traces of MgCl<sub>2</sub> were removed by filtration through a fine glass frit yielding AsNp<sub>2</sub> (5.877 g, 20.38 mmol, 91% yield based on AsCl<sub>3</sub>) as a colorless pentane soluble product. Additional purification was carried out by vacuum sublimation at 50-60°C (0.001 mm Hg). Crystals of AsNp<sub>2</sub> suitable for an X-ray structural study were grown by slow sublimation at 33°C.

AsNp<sub>2</sub>. Colorless solid, mp 68-71°C. Anal. Calcd.: %C, 62.48; %H, 11.54. Found: %C, 62.21; %H, 11.66. <sup>1</sup>H NMR (C<sub>6</sub>H<sub>6</sub>, ppm): 1.43 (-CH<sub>2</sub>-, 2H) and 1.01 (-CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>,

ppm): 46.50 (-CH<sub>2</sub>-), 32.13 (CMe<sub>3</sub>) and 31.32 (-CH<sub>3</sub>). IR (Nujol mull, cm<sup>-1</sup>): 2735w, 2710w, 1416m, 1360vs, 1271m, 1243vs, 1158vs, 1108m, 1022w, 1009m, 948w, 913m, 791vs, 788vs, 747m, 652s, 643m, 460vw, 391m, 290w.

Synthesis of AsNp<sub>2</sub>Br<sub>2</sub>. In a typical reaction, a 100 mL flask was charged with AsNp<sub>2</sub> (4.582 g, 12.42 mmol) and approximately 50 mL of pentane. Bromine (2.043 g, 12.79 mmol) was then vacuum distilled into the reaction flask. The reaction mixture was allowed to warm slowly to room temperature yielding a pale yellow precipitate of AsNp<sub>2</sub>Br<sub>2</sub>. After stirring between 24-48 h at room temperature, the pentane was removed by vacuum distillation. The product was purified by washing twice with a 15 mL portion of pentane. Trineopentylarsenic(V) dibromide (5.091 g, 11.36 mmol) was isolated in 91% yield as a sparingly pentane-soluble, air-sensitive colorless solid. Crystals of AsNp<sub>2</sub>Br<sub>2</sub> suitable for X-ray analysis were grown from a saturated solution of benzene by slow evaporation.

AsNp<sub>2</sub>Br<sub>2</sub>. Colorless solid, mp 177-186°C (dec). Anal. Calcd.: %C, 40.20; %H, 7.42; %Br, 35.66. Found: %C, 40.37; %H, 7.41; %Br, 35.32. <sup>1</sup>H NMR (C<sub>6</sub>H<sub>6</sub>, ppm): 3.83 (-CH<sub>2</sub>-, 2H) and 1.15 (-CH<sub>3</sub>, 9H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 73.69 (-CH<sub>2</sub>-), 34.89 (-CMe<sub>3</sub>), 32.05 (-CH<sub>3</sub>). IR (Nujol mull, cm<sup>-1</sup>): 2738w, 2720w, 1413m, 1248s, 1238vs, 1179vs, 1136vs, 1033s, 940w, 897m, 827s, 753w, 726w, 653s, 472w, 390vw, 315m.

Synthesis of  $\text{AsNp}_2\text{Br}$ . A tube with a glass/Teflon valve was charged with a sample of  $\text{AsNp}_2\text{Br}_2$  (3.4871 g, 7.7757 mmol), evacuated and heated to 140–150°C for 4–5 h producing a yellowish brown liquid (an uncharacterized gray precipitate was sometimes observed at this point). The most volatile product, neopentyl bromide, was then removed by vacuum distillation. The  $^1\text{H}$  NMR and IR spectra were consistent with those of an authentic sample of neopentyl bromide. Vacuum distillation (0.001 mm Hg) of the less volatile product in a short-path still yielded a sample of crude  $\text{AsNp}_2\text{Br}$  (2.2810 g, 7.6773 mmol, 99% yield) boiling between 35–45°C. An analytically pure sample of  $\text{AsNp}_2\text{Br}$  was obtained by recrystallization from pentane at -78°C.

Alternatively, a reaction tube containing  $\text{AsNp}_2\text{Br}_2$  (2.4294 g, 5.4208 mmol) was placed in a 190–195°C bath for 15 min. A yellow liquid and a small quantity of gray precipitate were obtained. The most volatile product, neopentyl bromide (0.8206 g, 5.433 mmol, 100% yield), was collected and characterized. The yellow liquid was vacuum distilled (0.001 mm Hg) in a short-path still yielding crude  $\text{AsNp}_2\text{Br}$  (1.5277 g, 5.1419 mmol, 95% yield) as a pale yellow liquid.

$\text{AsNp}_2\text{Br}$ . Pale yellow liquid, bp 35–45°C (0.001 mm Hg). Anal. Calcd.: %C, 40.43; %H, 7.46; %Br, 26.89. Found: %C, 40.46; %H, 7.46; %Br, 27.25.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ , ppm): 2.43 and 1.82 ( $J_{\text{AB}}=13.5\text{Hz}$ ,  $-\text{CH}_2-$ , 2H) and 0.90 (s,  $-\text{CH}_3$ , 9H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 52.75 ( $-\text{CH}_2-$ ), 32.13 ( $-\text{CMe}_2$ ), 31.07 ( $-\text{CH}_3$ ). IR (neat,

cm<sup>-1</sup>): 2955vs, 2905m, 2890m, 2865s, 1473s, 1468s, 1442w, 1405w, 1388m, 1365vs, 1270w, 1241s, 1154w, 1105vw, 773w, 745vw, 658w, 648w, 390vw, 279m.

Synthesis of AsNpBr<sub>2</sub> via AsNp<sub>2</sub>Br<sub>3</sub>. A sample of AsNp<sub>2</sub>Br (4.2601 g, 14.338 mmol) was quantitatively transferred to a 100 ml flask. Pentane was vacuum distilled into the flask, followed by bromine (2.3725 g, 14.846 mmol), for a total volume of ca. 50 mL. The reaction mixture was slowly warmed from -196°C to 0°C with stirring. A voluminous yellow/orange precipitate of AsNp<sub>2</sub>Br<sub>2</sub> formed immediately. The reaction was stirred for 45 min at 0°C followed by an additional 1.5 h of stirring at room temperature. Dineopentylarsenic(V) tribromide was isolated as a yellow-orange solid after removal of the reaction solvent. The compound, AsNp<sub>2</sub>Br<sub>2</sub>, proved to be unstable at room temperature, reductively eliminating neopentyl bromide and forming AsNpBr<sub>2</sub>. A <sup>1</sup>H NMR spectrum of the arsorane taken immediately after preparation exhibited resonances at 4.08 and 1.12 ppm indicative of the methylene and methyl protons, respectively, of AsNp<sub>2</sub>Br<sub>2</sub>. However, lines for the methyl protons of neopentyl bromide and AsNpBr<sub>2</sub> were also noted and were observed to grow in intensity with time. The crude sample of AsNp<sub>2</sub>Br<sub>2</sub> exhibited a melting/decomposition range of 68-71°C.

A flask containing the above prepared sample of AsNp<sub>2</sub>Br<sub>2</sub> was placed in a 45-50°C oil bath for 5h yielding a yellow liquid and a small amount of white precipitate. Neopentyl

bromide (2.0968 g, 13.882 mmol) was collected in 97% yield. The less volatile product,  $\text{AsNpBr}_2$ , was vacuum distilled at 30–40°C (0.001 mm Hg) in a short-path still and was isolated in 83% yield (3.6537g, 11.945mmol) as a pale yellow liquid. Additional purification was achieved by recrystallization from pentane at -78°C.

$\text{AsNpBr}_2$ . Pale yellow liquid, bp (0.001 mm Hg) 30–40°C. Anal. Calcd.: %C, 19.63; %H, 3.63; %Br, 52.25. Found: %C, 19.23; %H, 3.32; %Br, 52.63.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ , ppm): 2.75 (s,  $-\text{CH}_2-$ , 2H), 0.67 (s,  $-\text{CH}_3$ , 9H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 60.30 ( $-\text{CH}_2-$ ), 32.94 ( $-\text{CMe}_3$ ), 30.91 ( $-\text{CH}_3$ ). IR (neat,  $\text{cm}^{-1}$ ): 2950s, 2880m, 2860m, 2720vw, 1960vw, 1468s, 1440w, 1403w, 1384s, 1367s, 1265w, 1238s, 1155m, 1100w, 1022vw, 1008w, 931vw, 808vw, 782m, 743w, 646m, 540vw, 405vw, 388vw, 285sh, 274vs.

Synthesis of  $\text{AsNpH}_2$ . Using a modification of the method of Becker, Gutekunst and Wessely (Z. Anorg. Allg. Chem. 1980, **462**, 113), a pure sample of  $\text{AsNpH}_2$  was isolated in 62% yield from the reaction of  $\text{AsNpBr}_2$  and lithium aluminum hydride (LAH) in tetraglyme. Thus, a tetraglyme solution of  $\text{AsNpBr}_2$  (1.4061g, 4.597mmol) was added at 0°C to a suspension of LAH (0.09g, 2.37mmol) in tetraglyme. The reaction mixture was stirred for 30 min at 0°C followed by 20 min at ambient temperature and then for an additional 30 min at 40°C. The product was easily isolated from the non-volatile reaction solvent by vacuum distillation at room temperature. No hydrolysis of the

reaction mixture was required to obtain the product in 62% yield. More  $\text{AsNpH}_2$  might have been isolated if the remaining reaction mixture was hydrolyzed as Becker and co-workers reported. However, the yield of 62% was sufficient such that the purification problems and potential hazards associated with the hydrolysis reaction were avoided.

$\text{AsNpH}_2$ : Colorless liquid, bp.  $96.5^\circ\text{C}$ . Anal. Calcd.: %C, 40.56; %H, 8.85. Found: %C, 40.74; %H, 8.87.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ , ppm): 1.98 (t,  $\text{AsH}_2$ , 2H,  $J=6.4$  Hz), 1.48 (t,  $-\text{CH}_2-$ , 2H,  $J=6.4$  Hz) and 0.80 (s,  $-\text{CH}_3$ , 9H).  $^{13}\text{C}$  ( $^1\text{H}$ ) ( $\text{C}_6\text{D}_6$ , ppm): 30.30 ( $-\text{CMe}_2$ ), 30.20 ( $-\text{CH}_2$ ) and 27.55 ( $-\text{CH}_2-$ ). IR (Gas,  $\text{cm}^{-1}$ ): 2965vs, 2915s, 2875s, 2170w, 2100vs, 2040w, 1477m, 1400sh, 1372m, 1248m, 1178m, 1020w, 978m, 912vw, 862m, 770w.

Synthesis of  $\text{AsNp}_2\text{H}$ . The secondary arsine was produced in 79% yield by reaction of  $\text{AsNp}_2\text{Br}$  (1.6144g, 5.4336 mmol) and LAH (0.051g, 1.34 mmol) in diethyl ether. The reagents were mixed at  $0^\circ\text{C}$  and stirred for 1/2 h followed by an additional 18 h of reaction at ambient temperature. The reaction mixture was again cooled to  $0^\circ\text{C}$  and the ether then removed by vacuum distillation. The product,  $\text{AsNp}_2\text{H}$ , was purified by vacuum distillation at  $25-30^\circ\text{C}$  in a short path still. It is of interest that no hydrolysis was required to isolate the secondary arsine and that it was easily separated from the reaction solvent.

$\text{AsNp}_2\text{H}$ : Colorless liquid, bp.  $173^\circ\text{C}$ . Anal. Calcd.: %C,

55.04; %H, 10.62. Found: %C, 54.68; %H, 10.55.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 2.39 (As-H, 1H), 1.89 and 1.19 ( $-\text{CH}_2-$ , 4H), 0.97 ( $-\text{CH}_3$ , 17H),  $J_{\text{Ax}} = 6.5$  Hz,  $J_{\text{Bx}} = 7.8$  Hz,  $J_{\text{AB}} = 12.4$  Hz.  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR ( $\text{C}_6\text{D}_6$ , ppm): 36.50 ( $-\text{CH}_2-$ ), 31.18 ( $-\text{CMe}_2$ ), 30.97 ( $-\text{CH}_3$ ). IR (neat,  $\text{cm}^{-1}$ ): 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  $\text{Np}(\text{H})\text{AsGaMe}_2$ . The room temperature reaction of  $\text{AsNpH}_2$  (0.4155g, 2.8059 mmol) with TMG (0.2939 g, 2.5595 mmol) in pentane solution (ca. 10 mL) has been investigated. After stirring for 5 d at room temperature, methane (0.0367 g, 22.9 mmol) was observed in 89% yield and was identified by its vapor pressure of 10 mm at  $-196^\circ\text{C}$  and by its IR spectrum. The white, crystalline solid,  $\text{Np}(\text{H})\text{AsGaMe}_2$  (0.477 g, 1.93 mmol) was isolated in 75% yield.

$\text{Np}(\text{H})\text{AsGaMe}_2$ : Colorless solid, mp. 94-97.5 $^\circ\text{C}$ . Anal. Calcd.: %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.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ , ppm): 1.94, 1.87, 1.81 ( $-\text{CH}_2-$ , As-H, 3H), 0.93 ( $-\text{C}-\text{CH}_3$ , 10.2H), 0.26, 0.22, 0.19 (Ga- $\text{CH}_3$ , 7.3H). IR (Nujol mull,  $\text{cm}^{-1}$ ): 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  $\text{Np}_2\text{AsGaMe}_2$ . The reaction of  $\text{AsNp}_2\text{H}$  (0.8127 g, 3.724 mmol) and TMG (1.1250 g, 9.7975 mmol) at 85–95°C, in the absence of solvent, resulted in the isolation of  $\text{Np}_2\text{AsGaMe}_2$  (1.075 g, 3.391 mmol) in 91% yield. Methane (0.0585 g, 3.65 mmol), identified by its IR spectrum and vapor pressure at –196°C, was produced in 98% yield. Colorless crystals of  $\text{Np}_2\text{AsGaMe}_2$  suitable for X-ray analysis have been grown.

$\text{Np}_2\text{AsGaMe}_2$ : Colorless solid, mp. 124–134°C. Anal. Calcd.: %C, 45.47; %H, 8.90. Found: %C, 45.36; %H, 9.00.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ , ppm): 2.07 (s,  $-\text{CH}_2-$ , 4H), 0.98 (s,  $\text{C}-\text{CH}_3$ , 18H) and 0.23 (s,  $\text{Ga}-\text{CH}_3$ , 6H).  $^{13}\text{C}$  ( $^1\text{H}$ ) ( $\text{C}_6\text{D}_6$ , ppm): 38.14 ( $-\text{CH}_2-$ ), 32.36 ( $-\text{CMe}_3$ ), 31.65 ( $-\text{CH}_3$ ) and –3.21 ( $\text{Ga}-\text{CH}_3$ ). IR (Nujol mull,  $\text{cm}^{-1}$ ): 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  $\text{AsNpH}_2$  and  $\text{AsNp}_2\text{H}$ . The heat of vaporization of  $\text{AsNpH}_2$  and  $\text{AsNp}_2\text{H}$  were determined by plotting the natural logarithm of the vapor pressure (in atmospheres) versus the temperature (K). The slope was equal to  $-\Delta H_{\text{vap}}/RT$ , defined in equation 1.

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

Thus  $\Delta H_{vap}$  was calculated to be 8.80 +/- 0.17 kcal/mol with C equal to 12.0 for AsNpH<sub>2</sub> providing a calculated normal boiling point of 96.5°C and a vapor pressure of 43 mm Hg at 25°C. The vapor pressure of AsNp<sub>2</sub>H was determined to be much lower than that observed for AsNpH<sub>2</sub>. The  $\Delta H_{vap}$  was calculated from equation 1 to be 14.5 +/- 0.72 kcal/mol with C equal to 16.3. Therefore, AsNp<sub>2</sub>H has a calculated normal boiling point of 173°C and a vapor pressure of 0.224 mm Hg at 25°C.

OMVPE of GaAs. Epitaxial films of GaAs were grown by chemical vapor deposition utilizing the new arsine AsNpH<sub>2</sub>. Films were deposited on Cr doped GaAs<100>. Deposition temperature was approximated at 625°C. The substrates were etched with 5:1:1 (H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O) prior depositing the film. V/III ratios ranged between 2-3. Trimethylgallium (TMG) was purified by complexation with diphos prior to use. The arsenic source was maintained at ambient temperature and the TMG was kept at -5 - -15°C. Typical TMG flow rates were 7-8 ccm while AsNpH<sub>2</sub> flow rates were kept between 20-25 ccm. Both technical grade and high purity hydrogen were used as the carrier gas.

Crystallographic Studies. Colorless crystals of AsNp<sub>2</sub> and AsNp<sub>2</sub>Br<sub>2</sub> were sealed under helium gas in thin walled capillaries for data collection on an automated Nicolet R3m/v diffractometer using an incident beam monochromator with Mo K $\alpha$  radiation. Data were corrected for Lorentz and polarization

effects and an empirical absorption correction based on the  $\psi$ -dependence of 9 reflections with  $\chi$  ca.  $90^\circ$  was applied for both  $\text{AsNp}_2$  and  $\text{AsNp}_2\text{Br}_2$ . Maximum and minimum transmittance for  $\text{AsNp}_2$  and  $\text{AsNp}_2\text{Br}_2$  were 0.82 and 0.65, and 0.78 and 0.22, respectively. The space group determinations were based on extinctions present and E value statistics and were confirmed by the structure solutions. The structures of both compounds were determined by direct methods with the aid of the program SHELXTL<sup>16</sup> and were refined with a full matrix least squares.<sup>16</sup> The parameters refined include the atom coordinates and anisotropic thermal parameters for all non-hydrogens. The methyl groups were treated as rigid groups and were allowed to rotate about the C-C bond. Coordinate shifts of the carbon atoms were applied to the bonded hydrogens, C-H distances and H-C-H angles were constrained to be 0.96Å and  $109.5^\circ$ , respectively, and the isotropic thermal parameters set at  $U(\text{H})=1.2U_{\text{eq}}(\text{C})$ . Determination of the absolute configuration using the method suggested by Rogers<sup>17</sup> was inconclusive for both compounds. Additional data collection and refinement parameters are listed in Table I. Atomic scattering factors are from the International Tables for X-ray Crystallography (1974).

### Results and Discussion

The new compound,  $\text{AsNp}_3$ , was synthesized in high yield and was fully characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies, melting point data, elemental analysis and an X-ray structural study. Addition of  $\text{Br}_2$  to  $\text{AsNp}_3$  resulted in the formation of the  $\text{AsNp}_3\text{Br}_2$ . Thermal decomposition of  $\text{AsNp}_3\text{Br}_2$  yielded  $\text{AsNp}_2\text{Br}$  to which  $\text{Br}_2$  was added to form  $\text{AsNp}_2\text{Br}_2$ . Reductive elimination of neopentyl bromide from  $\text{AsNp}_2\text{Br}_2$  resulted in the production of  $\text{AsNpBr}_2$ . The bromide derivatives have been isolated in high yields and have also been fully characterized, including a single-crystal X-ray diffraction study of  $\text{AsNp}_2\text{Br}_2$ .

Trineopentylarsine has been prepared from the reaction of the Grignard reagent,  $\text{NpMgCl}$ , with  $\text{AsCl}_3$  in ether solution. A calculated excess of Grignard reagent was used since earlier studies<sup>5</sup> indicated incomplete reaction of neopentyl chloride and magnesium. The  $\text{NpCl}/\text{Mg}/\text{ether}$  mixture was therefore subjected to ultrasound treatment for one hour followed by refluxing for an additional 18h. The slow reaction of  $\text{NpCl}$  with magnesium is contrasted to that of  $\text{Me}_2\text{SiCH}_2\text{Cl}$  and magnesium, the latter maintaining reflux without external heating.<sup>14</sup> Trineopentylarsine was isolated as a colorless, non-pyrophoric, crystalline solid which slowly oxidized in air. Sublimation of  $\text{AsNp}_3$  occurred readily at  $50^\circ\text{C}$  but the compound could also be slowly transferred in the vacuum line at room temperature. The properties of  $\text{AsNp}_3$  appeared to be quite similar to those of the analogous (trimethylsilyl)methyl

compound.<sup>9</sup>

The sterically demanding neopentyl ligand did not sufficiently hinder halogen addition reactions with  $\text{AsNp}_3$ , which was also noted for the (trimethylsilyl)methyl analogs.<sup>9</sup> Thus,  $\text{AsNp}_3\text{Br}_2$  was readily prepared by reaction of stoichiometric quantities of  $\text{AsNp}_3$  and  $\text{Br}_2$ . Reaction was quantitative with only small losses resulting from purification and isolation. Since the formation of  $\text{AsNp}_3\text{Br}_2$  was exothermic, the initial reaction was performed at low temperature (ca.  $0^\circ\text{C}$ ). The  $\text{AsNp}_3\text{Br}_2$  was initially yellow, but after continuous stirring at room temperature (up to a total of 48 h) a white product was obtained. Washing the product twice with a portion of pentane ensured there was no contamination with unreacted  $\text{AsNp}_3$ . Trineopentylarsenic(V) dibromide was isolated as a white powder which recrystallized from a saturated benzene solution as colorless crystals suitable for X-ray analysis. The compound,  $\text{AsNp}_3\text{Br}_2$ , had limited solubility in hydrocarbons and ether, but was somewhat more soluble in benzene.

Although a variety of trialkylarsenic(III) and trialkylarsenic(V) dihalides have been described,<sup>10</sup> limited structural data on these simple compounds is available. In the  $\text{AsNp}_3$  crystal, the molecular  $C_{3v}$  symmetry is lost by the rotation of the neopentyl group by approximately  $23^\circ$  from the three-fold axis which is maintained in the crystal. The pyramidal arsenic(III) atom lies on a three-fold axis and only those atoms labelled in Figure 1 are crystallographically unique (1/3

of a molecule in the asymmetric unit). The value of the C-As-C bond angle is  $94.6(4)^\circ$  and the C-As bond distance is  $1.998(10)\text{\AA}$ . These values are near the  $96.2^\circ$  and  $1.979\text{\AA}$  observed in a gas electron diffraction study of trimethylarsine<sup>19</sup> and the  $97.4^\circ$  and  $1.992\text{\AA}$  observed about the 3-coordinate exocyclic arsenic in the X-ray diffraction study of  $\{[(\text{Me}_2\text{SiCH}_2)_2\text{As}]_2\text{GaBr}\}_2$ <sup>12</sup>. In comparison, the value of the C-As-C angle in trimesitylarsine increases significantly, averaging  $107.6^\circ$  with an average As-C bond distance of  $1.976\text{\AA}$ .<sup>20</sup>

Although the symmetry for  $\text{AsNp}_2\text{Br}_2$  may be  $C_{2h}$ , this symmetry is not present in the crystal and the three-fold symmetry about the Br-As-Br axis is only approximate and not a crystallographic three-fold axis of symmetry. This five-coordinate, nonionic compound has a nearly regular trigonal bipyramidal geometry (TBP) with respect to the As atom (Figure 2). This geometry is consistent with the structural analyses of several trialkylarsenic(V) dichlorides and difluorides<sup>19a, 21</sup>. However, it is of interest that the compounds  $\text{Me}_2\text{AsX}_2$  ( $X=\text{Br}, \text{I}$ )<sup>21, 22</sup> and  $\text{Et}_2\text{AsBr}_2$ <sup>22</sup> have been shown to be ionic with a tetrahedral geometry about the arsenic atom. Deviations from regular TBP geometry are small for  $\text{AsNp}_2\text{Br}_2$ . The Br-As-Br bond angle is  $179.6(1)^\circ$  and the As-Br bond lengths differ [ $\text{As-Br}(1)=2.530(2)\text{\AA}$  and  $\text{As-Br}(2)=2.597(2)\text{\AA}$ ]. A plane through the methylene carbons shows the As atom displaced from that plane  $0.026\text{\AA}$  towards Br(1). These deviations from

regularity are likely due to crystal packing effects as are the relative differences in orientation of the Np groups which may be described by the torsion angles  $\text{As-C(1)-C(2)-C(3)}=177.6^\circ$ ,  $\text{As-C(1')-C(2')-C(3')}=177.4^\circ$  and  $\text{As-C(1'')-C(2'')-C(3'')}=175.3^\circ$ . The average of the As-C bond distances is  $1.98(1)\text{\AA}$  and the As-Br distances range from  $2.530(2)$ - $2.597(2)\text{\AA}$ ; respective values from single bond covalent radii data<sup>24</sup> are  $1.98\text{\AA}$  and  $2.35\text{\AA}$ . The increase for the As-Br bonds is due to the crowding of the methylene hydrogens and bromine ligands. The closest intermolecular contacts are near Van der Waals separations on both  $\text{AsNp}_2$  and  $\text{AsNp}_2\text{Br}_2$ . Trineopentylarsine has only a few close contacts,  $\text{H(1a)-H(5a)}[y, y-z, z+0.5]=2.54\text{\AA}$  and  $\text{H(3a)-H(4a)}[y-x-1.0, -x, z]=2.62\text{\AA}$ . In  $\text{AsNp}_2\text{Br}_2$  the shortest intermolecular contact is  $\text{H(4'a)-H(5'a)}[x, -y, z-0.5]=2.46\text{\AA}$ .

Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. Bond distances and bond angles in  $\text{AsNp}_2$  and  $\text{AsNp}_2\text{Br}_2$  are given in Table 3. Packing of  $\text{AsNp}_2$  and  $\text{AsNp}_2\text{Br}_2$  in their unit cells is shown in Figures 3 and 4, respectively.

Trineopentylarsenic(V) dibromide melts with decomposition in the range of  $177$ - $186^\circ\text{C}$ . This decomposition is represented by the reductive-elimination reaction described in equation 1.



Elimination of alkylhalides from trialkylarsenic(V) dihalides

is a well documented<sup>25</sup> route to the synthesis of dialkylarsenic(III) halides. It is, however, of interest that the analogous compound,  $\text{As}(\text{CH}_2\text{SiMe}_3)_2\text{Br}_2$ , does not decompose by reductive elimination of  $\text{Me}_3\text{SiCH}_2\text{Br}$ , but rather eliminates  $\text{Me}_3\text{SiBr}$  to produce  $(\text{Me}_3\text{SiCH}_2)_2\text{AsCH}_2\text{Br}$ .<sup>10</sup> On a preparative scale, the best conditions for the formation of  $\text{AsNp}_2\text{Br}$  involves the heating of  $\text{AsNp}_2\text{Br}_2$  at  $190^\circ\text{C}$  in a sealed reaction bulb for 15–20 min. Although the reductive-elimination reaction of  $\text{AsNp}_2\text{Br}_2$  does proceed at a lower temperature, the purity of the product,  $\text{AsNp}_2\text{Br}$ , was not significantly better than that obtained from reaction at  $190^\circ\text{C}$ . In addition to the formation of  $\text{AsNp}_2\text{Br}$  from the reductive-elimination reaction, small quantities of  $\text{AsNpBr}_2$  and  $\text{AsNp}_3$  were also observed. These products are likely the result of a ligand redistribution reaction at high temperature (equation 2). Redistribution



reactions have also been observed for phenyl<sup>26</sup> and vinyl<sup>27</sup> arsenic(III) derivatives at high temperature.

Dineopentylarsenic(III) bromide was initially purified by vacuum distillation. An analytically pure sample of the pale yellow liquid,  $\text{AsNp}_2\text{Br}$ , was obtained after recrystallization from pentane at  $-78^\circ\text{C}$ . The monobromide derivative is soluble in hydrocarbons and ethers.

Reaction of  $\text{AsNp}_2\text{Br}$  and  $\text{Br}_2$  in pentane solution for 2h

yielded  $\text{AsNp}_2\text{Br}_3$  as a yellow powder. However,  $\text{AsNp}_2\text{Br}_3$  has limited stability at room temperature, reductively eliminating neopentyl bromide and forming  $\text{AsNpBr}_2$ . This observation is consistent with the trend in arsenic(V) chemistry, where increased halide substitution results in lower reductive elimination temperatures.<sup>256</sup> The poor thermal stability of  $\text{AsNp}_2\text{Br}_3$  has precluded characterization other than melting point and  $^1\text{H}$  NMR spectroscopic data. While complete decomposition of  $\text{AsNp}_2\text{Br}_3$  occurred over a period of several days at room temperature, the reaction could be accelerated to completion within 5 h by heating between 45–50°C. The neopentyl bromide was isolated by vacuum distillation and its properties were consistent with those of a commercial sample of neopentyl bromide. Neopentylarsenic(III) dibromide was purified by vacuum distillation in a short path still and was isolated as a pale yellow liquid, soluble in ether and hydrocarbons. Initial analytical results suggested slight contamination of the distilled  $\text{AsNpBr}_2$  with  $\text{AsBr}_3$ . Although  $\text{AsBr}_3$  could be envisioned to arise from the equilibrium described in equation 3, the mild reductive-elimination



conditions and the absence of  $\text{AsNp}_2\text{Br}$  makes this unlikely. The presence of  $\text{AsBr}_3$  was therefore attributed to an impurity of  $\text{AsNpBr}_2$  in the starting material,  $\text{AsNp}_2\text{Br}$ . Addition of  $\text{Br}_2$  to

$\text{AsNpBr}_2$  would produce  $\text{AsNpBr}_4$  which would undergo facile elimination of  $\text{NpBr}$  at ambient temperature to yield  $\text{AsBr}_3$  in the final product. However, an analytically pure sample of  $\text{AsNpBr}_2$ , free of  $\text{AsBr}_3$ , was obtained by recrystallization from pentane at  $-78^\circ\text{C}$ .

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra have been obtained in benzene solution for the arsenic(III) and arsenic(V) compounds. With the exception of  $\text{AsNp}_2\text{Br}$ , the  $^1\text{H}$  NMR spectra of the neopentyl arsines and arsoranes exhibit two singlets in the ratio of 2:9 for the methylene and methyl protons, respectively. The inequivalency of the methylene protons in  $\text{AsNp}_2\text{Br}$  results in an AB pattern with  $J_{\text{AB}}=13.5\text{Hz}$ . The chemical shift for the methylene protons was consistently downfield that of the methyl resonances for all the neopentyl arsenic compounds. The change in chemical shift,  $\Delta\delta$  ( $^1\text{H}$  NMR), was defined as  $\delta\text{CH}_2 - \delta\text{CH}_3$  and was used to describe the environment about the arsenic center. The change in chemical shift between methyl and methylene protons has been used to approximate the environment about arsenic<sup>20</sup> compounds incorporating the ethyl group. Thus the  $\Delta\delta$  for the neopentyl arsenic(III) compounds was shown to increase with halide substitution at the arsenic center as expected for the addition of electronegative substituents (Table 4). For comparison, the series  $\text{AsR}_n\text{Cl}_{3-n}$  ( $\text{R}=\text{Et}, \text{CH}_2\text{SiMe}_3$ ;  $n=1-3$ )<sup>20, 29</sup> exhibit similar increases in  $\Delta\delta$  upon halide substitution. The  $\Delta\delta$ 's for the neopentylarsenic(V) derivatives were greater than those observed for the neopentylarsenic(III)

compounds, consistent with the lowering of electron density at the arsenic center. Similarly, increased halide substitution at the As(V) center resulted in the expected increase in  $\Delta\delta$ . The  $^{13}\text{C}$  NMR spectra exhibit similar trends for the secondary carbons, while the quaternary and primary carbons exhibit little change in chemical shift with halide substitution or change in oxidation state.

Having obtained relatively pure samples of the arsenic(III) mono- and di- bromides, reduction of these materials to produce the secondary and primary arsine, respectively, were investigated. The reaction of  $\text{AsNpBr}_2$  with LAH ( $\text{LiAlH}_4$ ) in a 1:2 mol ratio, respectively, has been examined at several temperatures.  $\text{AsNpH}_2$  was isolated from the reaction of  $\text{AsNpBr}_2$  and LAH at  $-78^\circ\text{C}$  (18 h) however, yields of  $\text{AsNpH}_2$  were low, ca. 52%. Room temperature reaction of  $\text{AsNpBr}_2$  and LAH (18 h) resulted in isolation of  $\text{AsNpH}_2$  in ca. 47%. Reaction at  $-20^\circ\text{C}$  for 2.5 h yields the primary arsine in ca. 42%. Thus, there does not appear to be a significant dependence of yield on reaction temperature. The lowest yield at  $-20^\circ\text{C}$  was more likely a result of the short reaction time rather than a temperature effect. Two problems associated with the preparative route to  $\text{AsNpH}_2$  may be responsible for the low yields.

- a. Use of ether as a reaction solvent.
- b. Reaction stoichiometry.

Separation of the primary arsine from ether is somewhat tedious even though ether has a higher vapor pressure. Losses of  $\text{AsNpH}_2$  may be a result of the fractionation procedure. To test this hypotheses, subsequent reactions were carried out in tetraglyme where the separation of the volatile  $\text{AsNpH}_2$  was expected to proceed much more readily. Also, previous work (Becker, Gutekunst and Wessely, *Z. Anorg. Allg. Chem.* 1980, 462, 113) on the synthesis of  $\text{As}(\text{tBu})\text{H}_2$  in yields of 83% utilized a 2:1 stoichiometry of  $\text{As}(\text{tBu})\text{Cl}_2$  to LAH. By using a lower reaction stoichiometry the could also be eliminated since the formation of arsino allanes was perceived to be less likely. Thus, an acceptable yield of  $\text{AsNpH}_2$  (ca. 62%) was achieved by performing the the reaction in tetraglyme solution at  $-5^\circ\text{C}$  and using an LAH: $\text{AsNpBr}_2$  mol ratio of 1:2. The product was easily isolated from the non-volatile reaction solvent by vacuum distillation at room temperature. No hydrolysis of the reaction mixture was required to obtain the product in 62% yield. More  $\text{AsNpH}_2$  might have been isolated if the remaining reaction mixture was hydrolyzed as Becker and co-workers reported. However, the yield of 62% was sufficient such that the purification problems and potential hazards associated with the hydrolysis reaction were avoided.

The proton NMR spectrum in benzene solution consisted of two triplets and one singlet as expected. Difficulty was encountered observing the quaternary carbon in the  $^{13}\text{C}$  NMR

spectrum of  $\text{AsNpH}_2$  since the signal was very close to the resonance for the methyl carbon. The use of long relaxation times and collecting data over a narrow region of the spectrum eventually resulted in the observation of the quarternary carbon signal.

Bisneopentylarsine ( $\text{AsNp}_2\text{H}$ ) has been similarly prepared by the initial low temperature ( $-78^\circ\text{C}$ ) reaction of  $\text{AsNp}_2\text{Br}$  and LAH in ether solution. After reaction for 18h at room temperature, any intermediate aluminum arsenides were hydrolyzed to afford  $\text{AsNp}_2\text{H}$ , in 76% yield, as a colorless, slightly volatile liquid. The  $\text{AsNp}_2\text{H}$  was isolated by removing the ether and fractionating it through a  $-40^\circ\text{C}$  trap and also by subjecting the reaction products (after removal of the ether) to dynamic vacuum for 90min and collecting the volatile components in a  $-196^\circ\text{C}$  trap. Water was removed from the sample of  $\text{AsNp}_2\text{H}$  by stirring over  $\text{CaH}_2$ . It is of interest that later experiments showed that hydrolysis was not required to isolate equivalent yields of the secondary arsine. Also, unlike the primary arsine, there was no problem separating  $\text{AsNp}_2\text{H}$  from the reaction solvent,  $\text{Et}_2\text{O}$ . The  $^1\text{H}$  NMR spectrum of the  $\text{AsNp}_2\text{H}$  exhibits a complex pattern of lines for the As-H and the  $-\text{CH}_2-$ protons, in addition to the singlet for the methyl protons. This pattern of lines was also reported for the analagous compound,  $\text{As}(\text{CH}_2\text{SiMe}_2)_2\text{H}$ , and was attributed to a  $\text{AA}'\text{BB}'\text{X}$  type spectrum. In the  $^{13}\text{C}$  NMR spectrum all carbon signals were observed but as in the case of the primary arsine, the quarternary carbon was very close in

chemical shift to that of the methyl carbon.

The hydrido(arsino)gallane,  $\text{Np}(\text{H})\text{AsGaMe}_2$  was prepared in a manner similar to that used to prepare the analogous (trimethylsilylmethyl) compound. The Coates reaction used to prepare the neopentyl arsine is rather slow. This is due likely to the use of a reaction solvent and low reaction temperatures. While such condition tend to make the reaction slow, they also make it less likely to lose an additional mole of methane and thus form a polymeric arsinogallane of the type,  $[\text{NpAsGaMe}]_n$ . The mild reaction conditions may be responsible for the reaction not going to completion but side reactions cannot be ruled out (vide infra). The  $^1\text{H}$  NMR of  $\text{Np}(\text{H})\text{AsGaMe}_2$  consists of a fairly broad resonance at 1.87ppm with smaller peaks on each side (1.94 and 1.81 ppm), which are assigned to the  $-\text{CH}_2-$  and  $\text{As}-\text{H}$  protons, believed to be coincident. A singlet corresponding to the methyl groups of the neopentyl ligand was observed at 0.93ppm while the signal for the methyl groups on gallium was split into three resonances at 0.26, 0.22 and 0.19 ppm. These multiple resonances are likely the result of isomers associated with a trimeric structure in solution. A very small line at 0.81 ppm has also been observed in the spectra of this compound and may be evidence of an adduct of the type  $\text{Np}(\text{H})\text{AsGaMe}_2 \text{AsNpH}_2$ , formed from the product ( $\text{Np}(\text{H})\text{AsGaMe}_2$ ) and the excess  $\text{AsNpH}_2$ . It is also of interest that elimination of a second  $\text{CH}_4$  molecule does not occur readily at room temperature as evidenced by no change in the

proton NMR spectra with time.

By using reaction temperature of ca. 95°C and performing the reaction neat, the reaction of TMG and AsHp<sub>2</sub>H goes to completion within 48h. Colorless crystals of Np<sub>2</sub>AsGaMe<sub>2</sub> suitable for X-ray analysis have been grown. The proton NMR was as expected for an associated species, likely a dimer. It is of interest that the related trimethylsilylmethyl compound exhibits a dimer/trimer equilibrium in solution as evidenced by its <sup>1</sup>H NMR spectra. However, no equilibrium is observed when the neopentyl ligand is substituted for the (trimethylsilyl)methyl ligand.

A final goal of this project was to demonstrate of GaAs using the new arsines which have been prepared. Thus film growth was achieved in a chemical vapor deposition (CVD) apparatus designed specifically to test these new compounds. Using AsNpH<sub>2</sub> as a substitute films of GaAs of reasonable quality have been grown. Thus Using high purity H<sub>2</sub>, p-type GaAs doped ca. mid 10<sup>16</sup> cm<sup>-3</sup> and with fair electron mobility has been obtained. For comparison, GaAs grown with AsH<sub>3</sub> yields p-type GaAs doped in the low 10<sup>16</sup> cm<sup>-3</sup>, the mobility was improved over that of GaAs grown using the primary arsine. The morphology of the films prepared with the primary arsine was fairly good. GaAs has also been grown utilizing the one source material, Np<sub>2</sub>AsGaMe<sub>2</sub>. Film quality in this case was very poor and was not epitaxial. However, Auger measurements indicated that the material was indeed GaAs. No electrical measurements

were made on this film.

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Table (1) Crystal and Refinement Data

formula	C <sub>15</sub> H <sub>33</sub> As	C <sub>15</sub> H <sub>33</sub> AsBr <sub>2</sub>
crystal system	hexagonal	monoclinic
space group	P6 <sub>3</sub>	Cc
a, Å	9.929(2)	9.894(3)
b, Å		17.038(5)
c, Å	10.373(3)	12.147(3)
β, deg.		108.0(2)
γ, deg.	120.0	
V, Å <sup>3</sup>	885.7(4)	1947.9(9)
Z	2	4
formula weight	288.35	448.22
F(000)	312	904
ρ(calc), g cm <sup>-3</sup>	1.081	1.528
temp, C°	22	22
crystal dim., mm	0.45 x 0.73 x 0.40	0.71 x 0.64 x 0.18
λ, wavelength, Å	0.71073	0.71073
μ, absorption coef., cm <sup>-1</sup>	19.0	57.8
2θ max., deg.	45	45
scan speed, deg./min.	variable 10 to 30	variable 30 to 60
2θ scan range, deg.	1.6 + Δα1α2	1.8 + Δα1α2
data collected, h k l	0 to 9, 0 to 9, 0 to 11	-10 to 10, 0 to 18, -12 to 12
unique data	419	2579*
R <sub>int</sub>	0.056	*
unique data, F <sub>o</sub> > 3σ(F <sub>o</sub> )	318	2226 *
standard refl.	3.2% random variation	3.0% random variation
parameters refined	57	183
weighting function, g <sup>a</sup>	0.00023	0.00025
R <sup>b</sup> , wR <sup>c</sup> , S <sup>d</sup>	0.041, 0.043, 1.653	0.045, 0.043, 1.417
Fourier excursions, e Å <sup>-3</sup>	0.28, -0.57	0.65, -0.89

\* Friedels not merged

$$a \ w^{-1} = \sigma^2(F_o) + g F_o^2$$

$$b \ \sum |\Delta| / \sum |F_o|$$

$$c \ \sum [(w \Delta^2) / \sum (w F_o^2)]^{1/2}$$

$$d \ [\sum w(\Delta^2) / (N_o - N_p)]^{1/2}$$

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA} \times 10^3$ )

AsNp<sub>3</sub>

	x	y	z	U(eq)
As	0	0	0	45(1)
C(1)	-1919(10)	-567(11)	1018(11)	46(4)
C(2)	-3088(12)	-176(12)	388(11)	51(6)
C(3)	-4437(14)	-606(15)	1361(15)	79(8)
C(4)	-2345(13)	1548(12)	105(31)	87(6)
C(5)	-3768(15)	-1129(17)	-838(14)	75(8)

AsNp<sub>3</sub>Br<sub>2</sub>

	x	y	z	U(eq)
As	5787	1359(1)	7163	31(1)
Br(1)	5089(2)	995(1)	5042(1)	62(1)
Br(2)	6491(2)	1741(1)	9336(1)	57(1)
C(1)	7300(10)	2049(6)	6975(8)	39(4)
C(2)	7025(11)	2913(7)	6645(10)	48(5)
C(3)	8460(14)	3236(8)	6643(13)	72(6)
C(4)	6011(15)	3005(9)	5402(12)	90(7)
C(5)	6495(15)	3389(7)	7479(14)	82(7)
C(1')	6247(12)	245(6)	7614(9)	44(4)
C(2')	7728(11)	-94(6)	7738(9)	38(4)
C(3')	7614(18)	-966(7)	8034(15)	85(8)
C(4')	8133(13)	-47(8)	6641(9)	57(5)
C(5')	8871(12)	314(8)	8710(9)	62(6)
C(1'')	3878(10)	1784(6)	6970(9)	36(4)
C(2'')	2664(11)	1247(6)	7060(10)	48(5)
C(3'')	1402(14)	1805(9)	6966(14)	89(7)
C(4'')	2196(15)	656(9)	6089(11)	83(7)
C(5'')	2989(14)	839(9)	8207(11)	77(7)

\* Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

Table 3. Bond distances (Å), and bond angles (deg.)

AsNp<sub>3</sub>

As-C(1)	1.998 (10)	C(1)-C(2)	1.541 (14)
C(2)-C(3)	1.557 (14)	C(2)-C(4)	1.515 (16)
C(2)-C(5)	1.526 (15)		
C(1)-As-C(1')	94.6(4)	C(2)-C(1)-As	115.9(7)
C(3)-C(2)-C(1)	108.0(10)	C(4)-C(2)-C(1)	111.3(9)
C(4)-C(2)-C(3)	107.6(12)	C(5)-C(2)-C(1)	110.7(9)
C(5)-C(2)-C(3)	108.4(9)	C(5)-C(2)-C(4)	110.7(15)

AsNp<sub>3</sub>Br<sub>2</sub>

As-Br(1)	2.530 (2)	As-Br(2)	2.597 (2)
As-C(1)	1.971 (10)	As-C(1')	1.989 (10)
As-C(1'')	1.968 (10)	C(1)-C(2)	1.528 (14)
C(2)-C(3)	1.523 (16)	C(2)-C(4)	1.541 (16)
C(2)-C(5)	1.512 (17)	C(1')-C(2')	1.539 (14)
C(2')-C(3')	1.540 (15)	C(2')-C(4')	1.508 (14)
C(2')-C(5')	1.528 (14)	C(1'')-C(2'')	1.542 (14)
C(2'')-C(3'')	1.546 (15)	C(2'')-C(4'')	1.511 (16)
C(2'')-C(5'')	1.500 (15)		
Br(2)-As-Br(1)	179.6(1)	C(1)-As-Br(1)	90.4(3)
C(1)-As-Br(2)	89.6(3)	C(1')-As-Br(1)	90.8(3)
C(1')-As-Br(2)	89.6(3)	C(1')-As-C(1)	118.9(4)
C(1'')-As-Br(1)	91.0(3)	C(1'')-As-Br(2)	88.6(3)
C(1'')-As-C(1)	120.1(4)	C(1'')-As-C(1')	120.9(4)
C(2)-C(1)-As	121.7(7)	C(3)-C(2)-C(1)	105.0(9)
C(4)-C(2)-C(1)	111.4(10)	C(4)-C(2)-C(3)	106.7(10)
C(5)-C(2)-C(1)	114.3(10)	C(5)-C(2)-C(3)	108.8(11)
C(5)-C(2)-C(4)	110.2(11)	C(2')-C(1')-As	121.0(7)
C(3')-C(2')-C(1')	104.4(9)	C(4')-C(2')-C(1')	113.5(9)
C(4')-C(2')-C(3')	108.5(10)	C(5')-C(2')-C(1')	111.1(9)
C(5')-C(2')-C(3')	110.4(10)	C(5')-C(2')-C(4')	108.9(10)
C(2'')-C(1'')-As	120.9(7)	C(3'')-C(2'')-C(1'')	105.0(9)
C(4'')-C(2'')-C(1'')	113.4(10)	C(4'')-C(2'')-C(3'')	107.8(11)
C(5'')-C(2'')-C(1'')	113.1(9)	C(5'')-C(2'')-C(3'')	106.9(11)
C(5'')-C(2'')-C(4'')	110.1(11)		

Table 4. Effect of halide substitution on  $\Delta\delta$  ( $^1\text{H}$  NMR) of neopentyl-, ethyl- and (trimethylsilyl)methyl-arsenic compounds.

R, X, n	$\Delta\delta$	
	$\text{AsR}_n\text{X}_{3-n}$	$\text{AsR}_n\text{X}_{5-n}$
Np <sup>a</sup> , Br, 1	2.08	-
2	1.23	2.96
3	0.42	2.68
Et <sup>b</sup> , Cl, 1	0.85 <sup>c</sup>	-
2	0.45 <sup>c</sup>	-
3	0.00 <sup>c</sup>	2.50 <sup>d</sup>
Me <sub>3</sub> SiCH <sub>2</sub> , <sup>a,e</sup> Cl, 1	1.57	-
2	1.16	-
3	0.59	2.46

a. Benzene solution. b. Ref. 28, 30. c. CH<sub>2</sub>Cl<sub>2</sub> solution. d. Neat, TMS reference. e. Ref 29

### Legends

Figure 1. Thermal ellipsoid plot of  $\text{AsNp}_3$  drawn from experimental coordinates. The unlabeled atoms are related by symmetry to those labelled.

Figure 2. Thermal ellipsoid plot of  $\text{AsNp}_3\text{Br}_2$  drawn from experimental coordinates.

Figure 3. Molecular packing of  $\text{AsNp}_3$  viewed down c axis, hydrogen atoms omitted for clarity.

Figure 4. Molecular packing of  $\text{AsNp}_3\text{Br}_2$  viewed down a axis.



Figure 2.





