Neopentylarsenic chemistry: synthesis and characterization of As(CH2CMe3)nBr3-n (n = 1-3) and As(CH2CMe3)nBr5-n (n = 2 or 3). Crystal and molecular structure of As(CH2CMe3)3 and As(CH2CMe3)3Br2

John C. Pazik, and Cliff. George

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Supplementary Material Available: Table SI, coordinates and isotropic thermal parameters for the hydrogen atoms, and Table SII, thermal parameters for the non-hydrogen atoms (2 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Neopentylarsenic Chemistry: Synthesis and Characterization of $As(CH_2CMe_3)_nBr_{3-n}$ (n = 1–3) and $As(CH_2CMe_3)_nBr_{5-n}$ (n = 2 or 3). Crystal and Molecular Structure of $As(CH_2CMe_3)_3$ and $As(CH_2CMe_3)_3Br_2$

John C. Pazik* and Cliff George

Chemistry Division and the Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375-5000

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The new compound $As(CH_2CMe_3)_3$ has been prepared in 91% yield from the reaction of $(Me_3CCH_2)MgCl$ with $AsCl_3$ in ether solution. Addition of bromine to a pentane solution of $As(CH_2CMe_3)_3$ yielded $As(CH_2CMe_3)_3Br_2$ as a colorless, crystalline solid. Reductive elimination of neopentyl bromide, at 190–195 °C, from $As(CH_2CMe_3)_3Br_2$ produced the pale yellow liquid $As(CH_2CMe_3)_2Br$. Reaction of $As(CH_2CMe_3)_2Br$ with bromine resulted in formation of the yellow solid $As(CH_2CMe_3)_2Br_3$. The arsorane reductively eliminates neopentyl bromide at room temperature, but more readily at 50 °C, yielding $As(CH_2CMe_3)Br_2$ as a pale yellow liquid. The neopentylarsines and -arsoranes have been fully characterized according to physical and solubility properties and IR and ^1H and ^{13}C NMR spectroscopic properties. Also, single-crystal X-ray diffraction studies of $As(CH_2CMe_3)_3$ and $As(CH_2CMe_3)_3Br_2$ have been carried out. The compound $As(CH_2CMe_3)_3$ crystallizes in the hexagonal space group $P6_3$ with unit-cell parameters $a = 9.929\ (2)$ Å, $b = 9.929\ (2)$ Å, $c = 10.373\ (3)$ Å, $V = 885.7\ (4)$ Å^3, and $Z = 2$. The geometry about arsenic is pyramidal with the C–As–C angle equal to 94.6 (4)° and As–C distances of 1.998 (10) Å. The addition compound $As(CH_2CMe_3)_3Br_2$ crystallizes in the monoclinic space group Cc with unit-cell parameters $a = 9.894\ (3)$ Å, $b = 17.038\ (5)$ Å, $c = 12.147\ (3)$ Å, $V = 1947.9\ (9)$ Å^3, and $Z = 4$. A nearly regular trigonal-bipyramidal geometry is observed about As with the Br–As–Br angle equal to 179.6 (1)° and an average C–As–C equal to 120 (1)°. The average As–C bond distance is 1.98 (1) Å, and As–Br bond distances range from 2.530 (2) to 2.597 (2) Å.

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[1] and mesityl[2] ligands have been shown to be monomeric in the solid state. Also, mesityl,[3] pentamethylcyclopentadienyl,[4] and neopentyl[5] 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.[6] In arsenic chemistry, Lappert and coworkers[7] have examined the utility of the bis(trimethylsilyl)methyl and (trimethylsilyl)amino ligands in stabilizing radicals of the type $^{\bullet}AsR_2$. The effect of the bulky mesityl group on rotation about the As–C bond has also been investigated.[8] 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.[9] Reactivity patterns of arsenic(V) compounds incorporating the (trimethylsilyl)methyl ligand have also been examined.[10] More recently, Wells and co-workers have investigated a route to the silylarsine $(Me_3SiCH_2)_2AsSiMe_3$ from reaction of $(Me_3SiCH_2)_2AsLi$ and Me_3SiCl.[11] The silylarsine was then used to prepare a series of novel (arsino)gallanes.[11,12]

Substituting the neopentyl moiety for the (trimethylsilyl)methyl ligand in aluminum[1,13] and gallium[5,14] compounds resulted in pronounced differences in properties

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and reactivities. Arsenic compounds incorporating the neopentyl ligand (CH_2CMe_3 = Np) have not previously been described. Thus, in our initial studies, trineopentylarsine ($AsNp_3$), dineopentylarsenic(III) bromide ($AsNp_2Br$), neopentylarsenic(III) dibromide ($AsNpBr_2$), trineopentylarsenic(V) dibromide ($AsNp_3Br_2$), and dineopentylarsenic(V) tribromide ($AsNp_2Br_3$) have been synthesized and fully characterized. Characterization data include elemental analyses, IR and ^1H and ^{13}C NMR spectroscopy, and physical properties. The synthesis and properties of the neopentylarsenic compounds were compared with those analogous compounds incorporating the (trimethylsilyl)methyl moiety. In addition, the solid-state structures of $AsNp_3$ and $AsNp_3Br_2$ have been defined by X-ray diffraction studies.

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 diphenyl ketal 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[15] 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 59.75 MHz using a JEOL FX60-Q spectrometer. Proton-decoupled ^{13}C NMR 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 deuteriobenzene at 128.00 ppm. All NMR tubes were sealed under vacuum.

Synthesis of $AsNp_3$. 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 W) for 1 h and then stirred and refluxed in the sealed bulb for 15 h. *Note*: Caution must be exercised when performing the Grignard reaction in a sealed bulb. The solution of NpMgCl was added over the course of 30 min to a 0 °C solution of $AsCl_3$ (4.044 g, 22.31 mmol). A voluminous precipitate of $MgCl_2$ was observed during the addition of the Grignard reagent. After being warmed to room temperature, the reaction mixture was stirred for 24 h before the ether was removed 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 $MgCl_2$ were removed by filtration through a fine glass frit yielding $AsNp_3$ (5.877 g, 20.38 mmol, 91% yield based on $AsCl_3$) as a colorless pentane-soluble product. Additional purification was carried out by vacuum sublimation at 50–60 °C (0.001 mmHg). Crystals of $AsNp_3$ suitable for an X-ray structural study were grown by slow sublimation at 33 °C.

$AsNp_3$: colorless solid; mp 68–71 °C. Anal. Calcd: C, 62.48; H, 11.54. Found: C, 62.21; H, 11.66. ^1H NMR (C_6H_6, ppm): 1.43 ($-CH_2-$, 2 H), 1.01 ($-CH_3$, 9 H). ^{13}C NMR (C_6D_6, ppm): 46.50 ($-CH_2-$), 32.13 (CMe_3), 31.32 ($-CH_3$). IR (Nujol mull, cm^{-1}): 2735 w, 2710 w, 1416 m, 1360 vs, 1271 m, 1243 vs, 1158 vs, 1108 m, 1022 w, 1009 m, 948 w, 913 m, 791 vs, 788 vs, 747 m, 652 s, 643 m, 460 vw, 391 m, 290 w.

Synthesis of $AsNp_3Br_2$. In a typical reaction, a 100-mL flask was charged with $AsNp_3$ (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 $AsNp_3Br_2$. After the solution was stirred between 24 and 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 $AsNp_3Br_2$ suitable for X-ray analysis were grown from a saturated solution of benzene by slow evaporation.

$AsNp_3Br_2$: 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. ^1H NMR (C_6H_6, ppm): 3.83 ($-CH_2-$, 2 H), 1.15 ($-CH_3$, 9 H). ^{13}C NMR (C_6D_6, ppm): 73.69 ($-CH_2-$), 34.89 ($-CMe_3$), 32.05 ($-CH_3$). IR (Nujol mull, cm^{-1}): 2738 w, 2720 w, 1413 m, 1248 s, 1238 vs, 1179 vs, 1136 vs, 1033 s, 940 w, 897 m, 827 s, 753 w, 726 w, 653 s, 472 w, 390 vw, 315 m.

Synthesis of $AsNp_2Br$. A tube with a glass/Teflon valve was charged with a sample of $AsNp_3Br_2$ (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 ^1H NMR and IR spectra were consistent with those of an authentic sample of neopentyl bromide. Vacuum distillation (0.001 mmHg) of the less volatile product in a short-path still yielded a sample of crude $AsNp_2Br$ (2.2810 g, 7.6773 mmol, 99% yield) boiling between 35 and 45 °C. An analytically pure sample of $AsNp_2Br$ was obtained by recrystallization from pentane at −78 °C.

Alternatively, a reaction tube containing $AsNp_3Br_2$ (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 mmHg) in a short-path still yielding crude $AsNp_2Br$ (1.5277 g, 5.1419 mmol, 95% yield) as a pale yellow liquid.

$AsNp_2Br$: pale yellow liquid; bp 35–45 °C (0.001 mmHg). Anal. Calcd: C, 40.43; H, 7.46; Br, 26.89. Found: C, 40.46; H, 7.46; Br, 27.25. ^1H NMR (C_6H_6, ppm): 2.43 and 1.82 (J_{AB} = 13.5 Hz, $-CH_2-$, 2 H), 0.90 (s, $-CH_3$, 9 H). ^{13}C NMR (C_6D_6, ppm): 52.75 ($-CH_2-$), 32.13 ($-CMe_3$), 31.07 ($-CH_3$). IR (neat, cm^{-1}): 2955 vs, 2905 m, 2890 m, 2865 s, 1473 s, 1468 s, 1442 w, 1405 w, 1388 m, 1365 vs, 1270 w, 1241 s, 1154 w, 1105 vw, 773 w, 745 vw, 658 w, 648 w, 390 vw, 279 m.

Synthesis of $AsNpBr_2$ via $AsNp_2Br_3$. A sample of $AsNp_2Br$ (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 to 0 °C with stirring. A voluminous yellow/orange precipitate of $AsNp_2Br_3$ 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 $AsNp_2Br_3$ proved to be unstable at room temperature, reductively eliminating neopentyl bromide and forming $AsNpBr_2$. A ^1H 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 $AsNp_2Br_3$. However, lines for the methyl protons of neopentyl bromide and $AsNpBr_2$ were also noted and were observed to grow in intensity with time. The crude sample of $AsNp_2Br_3$ exhibited a melting/decomposition range of 68–71 °C.

A flask containing the above prepared sample of $AsNp_2Br_3$ was placed in a 45–50 °C oil bath for 5 h 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 $AsNpBr_2$ was vacuum distilled at 30–40 °C (0.001 mmHg) in a short-path still and was isolated in 83% yield (3.6537 g, 11.945 mmol) as a pale yellow liquid. Additional purification was achieved by recrystallization from pentane at −78 °C.

$AsNpBr_2$: pale yellow liquid; bp 30–40 °C (0.001 mmHg). Anal. Calcd: C, 19.63; H, 3.63; Br, 52.25. Found: C, 19.23; H, 3.32; Br, 52.63. ^1H NMR (C_6H_6, ppm): 2.75 (s, $-CH_2-$, 2 H), 0.67

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Table I. Crystal and Refinement Data

	$C_{15}H_{33}As$	$C_{15}H_{33}AsBr_2$
cryst system	hexagonal	monoclinic
space group	$P6_3$	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^3	885.7 (4)	1947.9 (9)
Z	2	4
fw	288.35	448.22
$F(000)$	312	904
ρ(calcd), g cm^{-3}	1.081	1.528
temp, °C	22	22
cryst dimens, mm	0.45 × 0.73 × 0.40	0.71 × 0.64 × 0.18
λ, wavelength, Å	0.710 73	0.710 73
μ, abs coeff, cm^{-1}	19.0	57.8
$2\theta_{max}$, deg	45	45
scan speed, deg/min	variable 10–30	variable 30–60
2θ scan range, deg	$1.6 + \Delta_{\alpha_1\alpha_2}$	$1.8 + \Delta_{\alpha_1\alpha_2}$
data collected, *hkl*	0 to 9, 0 to 9, 0 to 11	−10 to +10, 0 to 18, −12 to +12
unique data	419	2579^e
R_{int}	0.056	e
unique data, $F_0 > 3\sigma(F_o)$	318	2226^e
std reflctn	3.2% random variation	3.0% random variation
parameters refined	57	183
weighting function, g^a	0.000 23	0.000 25
R,^{b}, wR,^{c} S^d	0.041, 0.043, 1.653	0.045, 0.043, 1.417
Fourier excursions, e Å^{-3}	0.28, −0.57	0.65, −0.89

$^a w^{-1} = \sigma^2(F_o) + gF_o^2$. $^b \sum|\Delta|/\sum|F_o|$. $^c \sum[(w\Delta^2)/\sum(wF_o^2)]^{1/2}$. $^d [\sum w(\Delta^2)/(N_o - N_p)]^{1/2}$. ^{e} Friedels not merged.

(s, $-CH_3$, 9 H). ^{13}C NMR (C_6D_6, ppm): 60.30 ($-CH_2-$), 32.94 ($-CMe_3$), 30.91 ($-CH_3$). IR (neat, cm^{-1}): 2950 s, 2880 m, 2860 m, 2720 vw, 1960 vw, 1468 s, 1440 w, 1403 w, 1384 s, 1367 s, 1265 w, 1238 s, 1155 m, 1100 w, 1022 vw, 1008 w, 931 vw, 808 vw, 782 m, 743 w, 646 m, 540 vw, 405 vw, 388 vw, 285 sh, 274 vs.

Crystallographic Studies. Colorless crystals of $AsNp_3$ and $AsNp_3Br_2$ 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 Kα radiation. Data were corrected for Lorentz and polarization effects and an empirical absorption correction based on the φ-dependence of nine reflections with χ ca. 90° was applied for both $AsNp_3$ and $AsNp_3Br_2$. Maximum and minimum transmittance for $AsNp_3$ were 0.82 and 0.65, respectively, and for $AsNp_3Br_2$ were 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[16] and were refined with a full-matrix least squares.[16] 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 0.96 Å and 109.5°, respectively, and the isotropic thermal parameters set at $U(H) = 1.2U_{eq}(C)$. Determination of the absolute configuration using the method suggested by Rogers[17] was inconclusive for both compounds. Additional data collection and refinement parameters are listed in Table I. Atomic scattering factors are from ref 31.

Results and Discussion

The new compound $AsNp_3$ was synthesized in high yield and was fully characterized by IR and ^1H and ^{13}C NMR spectroscopies, melting point data, elemental analysis, and an X-ray structural study. Addition of Br_2 to $AsNp_3$ resulted in the formation of the $AsNp_3Br_2$. Thermal decomposition of $AsNp_3Br_2$ yielded $AsNp_2Br$ to which Br_2 was added to form $AsNp_2Br_3$. Reductive elimination of neopentyl bromide from $AsNp_2Br_3$ resulted in the production of $AsNpBr_2$. The bromide derivatives have been isolated in high yields and have also been fully characterized, including a single-crystal X-ray diffraction study of $AsNp_3Br_2$.

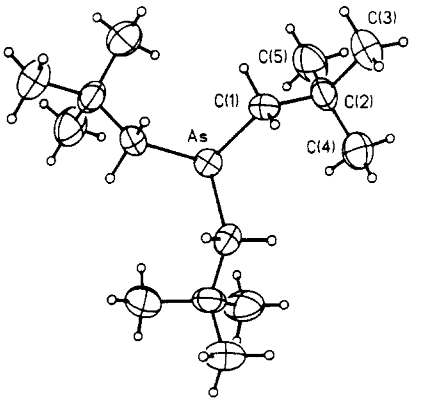

Figure 1. Thermal ellipsoid plot of $AsNp_3$ drawn from experimental coordinates. The unlabeled atoms are related by symmetry to those labeled.

Trineopentylarsine has been prepared from the reaction of the Grignard reagent NpMgCl with $AsCl_3$ in ether solution. A calculated excess of Grignard reagent was used since earlier studies[5] indicated incomplete reaction of neopentyl chloride and magnesium. The NpCl/Mg/ether mixture was therefore subjected to ultrasound treatment for 1 h followed by refluxing for an additional 18 h. The typically slow reaction of NpCl with magnesium is contrasted to that of Me_3SiCH_2Cl and magnesium, the latter maintaining reflux without external heating.[14] Trineopentylarsine was isolated as a colorless, nonpyrophoric, crystalline solid which slowly oxidized in air. Sublimation of $AsNp_3$ occurred readily at 50 °C, but the compound could also be slowly transferred in the vacuum line at room temperature. The properties of $AsNp_3$ appeared to be quite similar to those of the analogous (trimethylsilyl)methyl compound.[9]

The sterically demanding neopentyl ligand did not sufficiently hinder halogen addition reactions with $AsNp_3$, which was also noted for the (trimethylsilyl)methyl analogues.[9] Thus, $AsNp_3Br_2$ was readily prepared by reaction of stoichiometric quantities of $AsNp_3$ and Br_2. Reaction was quantitative with only small losses resulting from purification and isolation. Since the formation of $AsNp_3Br_2$ was exothermic, the initial reaction was performed at low temperature (ca. 0 °C). The $AsNp_3Br_2$ 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 $AsNp_3$. 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 $AsNp_3Br_2$ 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,[18] limited structural data on these simple compounds is available. In the $AsNp_3$ crystal, the molecular C_{3v} symmetry is lost by the rotation of the neopentyl group by approximately 23° from

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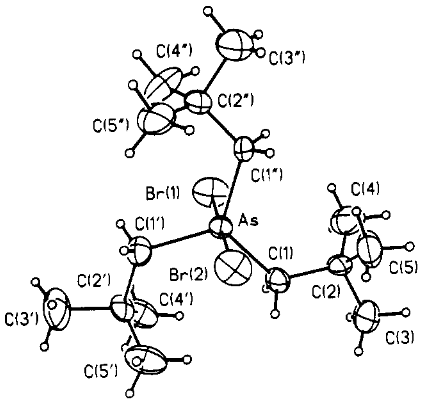

Figure 2. Thermal ellipsoid plot of $AsNp_3Br_2$ drawn from experimental coordinates.

the threefold axis which is maintained in the crystal. The pyramidal arsenic(III) atom lies on a threefold axis, and only those atoms labeled 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)°, and the C–As bond distance is 1.998 (10) Å. These values are near the 96.2° and 1.979 Å observed in a gas electron diffraction study of trimethylarsine[19] and the 97.4° and 1.992 Å observed about the three-coordinate exocyclic arsenic in the X-ray diffraction study of $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$.[12] In comparison, the value of the C–As–C angle in trimesitylarsine increases significantly, averaging 107.6° with an average As–C bond distance of 1.976 Å.[20]

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10³)

	x	y	z	U(eq)[a]
		$AsNp_3$		
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)
		$AsNp_3Br_2$		
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)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Bond Distances (Å) and Bond Angles (deg)

	$AsNp_3$		
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)
	$AsNp_3Br_2$		
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)		

Although the symmetry for $AsNp_3Br_2$ may be C_{3h}, this symmetry is not present in the crystal and the threefold symmetry about the Br–As–Br axis is only approximate and not a crystallographic threefold 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.[18a,21] However, it is of interest that the compounds Me_3AsX_2 (X = Br, I)[21,22] and Et_3AsBr_2[23] have been shown to be ionic with a tetrahedral geometry about the arsenic atom. Deviations from regular TBP geometry are small for $AsNp_3Br_2$. The Br–As–Br bond angle is 179.6 (1)°, and the As–Br bond lengths differ [As–Br(1) = 2.530 (2) Å and As–Br(2) = 2.597 (2) Å]. A plane through the methylene carbons shows the As atom displaced from that plane 0.026 Å toward 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 As–C(1)–C(2)–C(3) = 177.6°, As–C(1′)–C(2′)–C(3′) = 177.4° and As–C(1″)–C(2″)–C(3″) = 175.3°. The average of the As–C bond distances is 1.98 (1) Å, and the As–Br distances range from 2.530 (2) to 2.597 (2) Å; respective values from single bond covalent radii data[24] are 1.98 and 2.35 Å. 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 $AsNp_3$ and $AsNp_3Br_2$. Trineopentylarsine has only a few close contacts, H(1a)···H(5a)[y, $y - x$, $z + 0.5$] = 2.54 Å and H(3a)···H(4a)[$y - x - 1.0$, $-x$, z] = 2.62 Å. In $AsNp_3Br_2$ the shortest intermolecular contact is H(4′a)···H(5′a)[x, $-y$, $z - 0.5$] = 2.46 Å.

Atomic coordinates and equivalent isotropic thermal parameters are listed in Table II. Bond distances and

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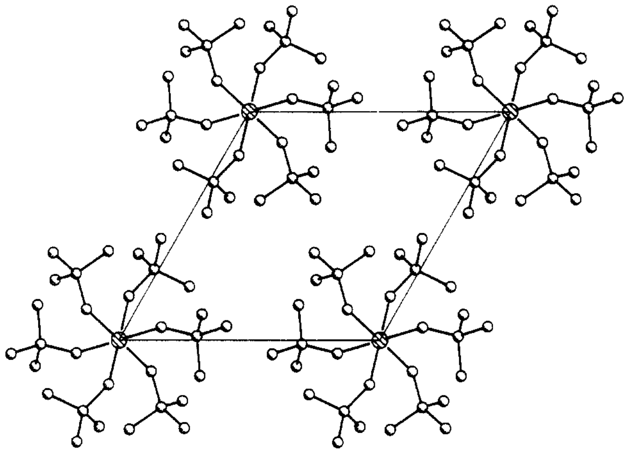

Figure 3. Molecular packing of $AsNp_3$ viewed down *c* axis, (hydrogen atoms omitted for clarity).

bond angles in $AsNp_3$ and $AsNp_3Br_2$ are given in Table III. Packing of $AsNp_3$ and $AsNp_3Br_2$ in their unit cells is shown in Figures 3 and 4, respectively.

Trineopentylarsenic(V) dibromide melts with decomposition in the range of 177–186 °C. This decomposition is represented by the reductive-elimination reaction described in eq 1. Elimination of alkyl halides from trialkylarsenic(V) dihalides is a well-documented[25] route to the synthesis of dialkylarsenic(III) halides. It is, however, of interest that the analogous compound $As(CH_2SiMe_3)_3Br_2$ does not decompose by reductive elimination of Me_3SiCH_2Br but rather eliminates Me_3SiBr to produce $(Me_3SiCH_2)_2AsCH_2Br$.[10] On a preparative scale, the best conditions for the formation of $AsNp_2Br$ involves the heating of $AsNp_3Br_2$ at 190 °C in a sealed reaction bulb for 15–20 min. Although the reductive-elimination reaction of $AsNp_3Br_2$ does proceed at a lower temperature, the purity of the product, $AsNp_2Br$, was not significantly better than that obtained from reaction at 190 °C. In addition to the formation of $AsNp_2Br$ from the reductive-elimination reaction, small quantities of $AsNpBr_2$ and $AsNp_3$ were also observed. These products are likely the result of a ligand redistribution reaction at high temperature (eq 2).

$$AsNp_3Br_2 \rightarrow AsNp_2Br + NpBr \qquad (1)$$

$$2AsNp_2Br \rightleftharpoons AsNp_3 + AsNpBr_2 \qquad (2)$$

Redistribution reactions have also been observed for phenyl[26] and vinyl[27] arsenic(III) derivatives at high temperature. Dineopentylarsenic(III) bromide was initially purified by vacuum distillation. An analytically pure sample of the pale yellow liquid $AsNp_2Br$ was obtained after recrystallization from pentane at −78 °C. The monobromide derivative is soluble in hydrocarbons and ethers.

Reaction of $AsNp_2Br$ and Br_2 in pentane solution for 2 h yielded $AsNp_2Br_3$ as a yellow powder. However, $AsNp_2Br_3$ has limited stability at room temperature, reductively eliminating neopentyl bromide and forming $AsNpBr_2$. This observation is consistent with the trend in arsenic(V) chemistry, where increased halide substitution results in lower reductive-elimination temperatures.[25b] The poor thermal stability of $AsNp_2Br_3$ has precluded characterization other than melting point and ^1H NMR spectroscopic data. While complete decomposition of $AsNp_2Br_3$ occurred over a period of several days at room temperature, the reaction could be accelerated to completion within 5 h by heating between 45 and 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 $AsNpBr_2$ with $AsBr_3$. Although $AsBr_3$ could be envisioned to arise from the equilibrium described in eq 3, the mild reductive-elimination conditions and the absence of $AsNp_2Br$ makes this unlikely. The presence of $AsBr_3$ was therefore attributed to an impurity of $AsNpBr_2$ in the starting material $AsNp_2Br$. Addition of Br_2 to $AsNpBr_2$ would produce $AsNpBr_4$ which would undergo facile elimination of NpBr at ambient temperature to yield $AsBr_3$ in the final product. However, an analytically pure sample of $AsNpBr_2$, free of $AsBr_3$, was obtained by recrystallization from pentane at −78 °C.

$$2AsNpBr_2 \rightleftharpoons AsNp_2Br + AsBr_3 \qquad (3)$$

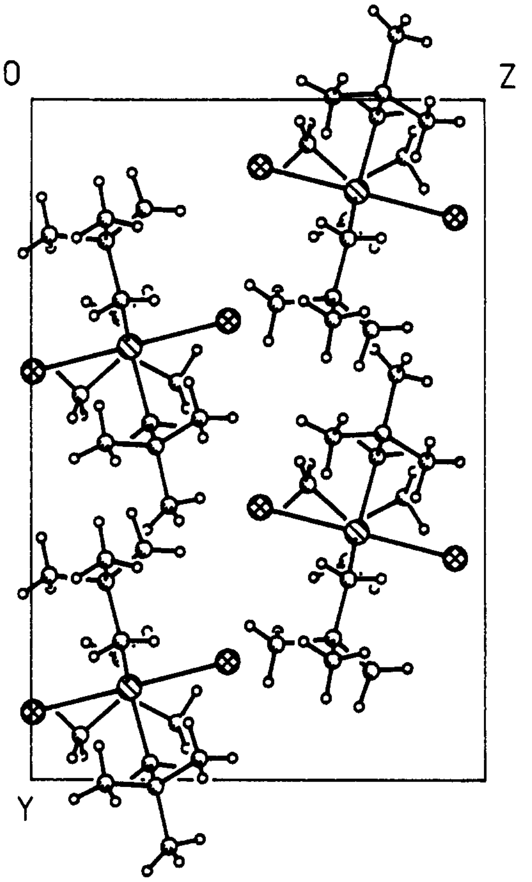

Figure 4. Molecular packing of $AsNp_3Br_2$ viewed down *a* axis.

^1H and ^{13}C NMR spectra have been obtained in benzene solution for the arsenic(III) and arsenic(V) compounds. With the exception of $AsNp_2Br$, the ^1H NMR spectra of the neopentylarsines 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 $AsNp_2Br$ results in an AB pattern with J_{AB} = 13.5 Hz. The chemical shift for the methylene protons was con-

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Table IV. Effect of Halide Substitution on Δδ (^1H NMR) of Neopentyl-, Ethyl-, and [(Trimethylsilyl)methyl]arsenic Compounds

	Δδ	
R, X, *n*	AsR_nX_{3-n}	AsR_nX_{5-n}
Np,[a] Br, 1	2.08	
2	1.23	2.96
3	0.42	2.68
Et,[b] Cl, 1	0.85[c]	
2	0.45[c]	
3	0.00[c]	2.50[d]
Me_3SiCH_2,[a,e] Cl, 1	1.57	
2	1.16	
3	0.59	2.46

[a] Benzene solution. [b] References 28 and 30. [c] CH_2Cl_2 solution. [d] Neat, TMS reference. [e] Reference 29.

sistently downfield that of the methyl resonances for all the neopentyl arsenic compounds. The change in chemical shift, Δδ (^1H NMR), was defined as $\delta(CH_2) - \delta(CH_3)$ 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[28] compounds incorporating the ethyl group. Thus, the Δδ for the neopentylarsenic(III) compounds was shown to increase with halide substitution at the arsenic center as expected for the addition of electronegative substituents (Table IV). For comparison, the series AsR_nCl_{3-n} (R = Et, CH_iSiMe_3; $n = 1–3$)[28,29] exhibit similar increases in Δδ upon halide substitution. The Δδ'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 Δδ. The ^{13}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.

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Registry No. $AsNp_3$, 99715-59-0; $AsNP_3Br_2$, 118299-85-7; $AsNp_2Br$, 118299-86-8; $AsNpBr_2$, 118299-87-9; $AsNp_2Br_3$, 118299-88-0; NpMgCl, 13132-23-5; $AsCl_3$, 7784-34-1; neopentyl chloride, 753-89-9.

Supplementary Material Available: Tables of anisotropic displacement parameters and hydrogen atom coordinates (5 pages); a listing of observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

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Lewis Base Adducts to Diorganosilylenes

Gregory R. Gillette, George H. Noren, and Robert West*

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

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Silylenes **2a–d** were generated photolytically at 77 K in 3-MP matrices doped with ethers, amines, sulfides, phosphines, and alcohols. The initially formed free silylenes react upon annealing of the matrix to give acid–base complexes observed by electronic spectroscopy. For R_2O, R_3N, and R_2S further warming of the matrix leads to the disilenes **3a–d**. Use of *i*-PrOH or *sec*-BuOH as bases led to silylene–alcohol complexes which ultimately yielded products of silylene insertion into the O–H bond.

Introduction

In the rapidly advancing field of silylene chemistry,[1,2] a topic of current interest is the formation of silaylides from the reaction of silylenes with Lewis bases. Acid–base complexes of silylenes were first proposed as intermediates by Seyferth et al. in 1978.[3] Beginning in 1980, Weber published a series of papers presenting evidence for the formation of silylene–donor adducts with a number of oxygen- and sulfur-substituted compounds.[4] The first spectroscopic evidence for complex formation came from an infrared spectroscopic study of the reaction of Si atoms with H_2O in Ar matrices in which a complex of hydroxysilylene (H–Si–OH) and H_2O was observed.[5] In the last

Table I. Absorption Maxima for Ether, Amine, and Sulfide Complexes (λ_{max} (nm))

	substituents on silicon			
base	Mes, Mes	Mes, *t*-Bu	Mes, OAr	Me, Me
3-MP	580	505	395	450
Et_2O	320	348	332	299
THF	328	350	330	280
2-MeTHF	326	350	330	294
2,5-MeTHF	327	350	322	290
Et_3N	350	345	348	287
n-Bu_3N	325	345	346	287
i-Pr_2NEt	329	339	328	288
t-Bu_2S	316	368	350	322
$\overline{\Delta\lambda}(R_2O)$	256	155	65	160
$\overline{\Delta\lambda}(R_3N)$	225	162	55	162

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