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III/V Precursors with P–H or As–H Bonds. A Low-Temperature Route to Gallium Arsenide and Gallium Phosphide

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The trimers $[t\text{-}Bu_2Ga(\mu\text{-}EH_2)]_3$ (E = P, As) have been prepared via the reaction of $t\text{-}Bu_3Ga$ with EH_3 at low temperatures. The structure of $[t\text{-}Bu_2Ga(\mu\text{-}PH_2)]_3$ has been established by X-ray crystallography. These are the first $\mu\text{-}PH_2$ and $\mu\text{-}AsH_2$ derivatives of gallium to be reported. Both compounds react with H_2O to give the hydroxygallium trimer $[t\text{-}Bu_2Ga(\mu\text{-}OH)]_3$. The structure of $[t\text{-}Bu_2Ga(\mu\text{-}PH_2)]_3$ features a planar six-membered Ga_3P_3 ring. Crystal data for $[t\text{-}Bu_2Ga(\mu\text{-}PH_2)]_3$: $C_{24}H_{60}Ga_3P_3$, $M_n = 650.83$, hexagonal, space group $P\bar{6}2m$ (No. 189), $a = 11.127$ (4) Å, $c = 16.506$ (6) Å, $V = 1769.7$ (5) Å^3, $Z = 3$, $D_{calc} = 0.867$ g cm^{-3}, μ(Mo Kα) = 13.4 cm^{-1}, 880 unique reflections measured over the range $3.0 \leq 2\theta \leq 55.0°$ (θ–2θ scan mode), 446 reflections with $I > 3\sigma(I)$ used in the refinements to give R and R_w = 0.064 and 0.075, respectively. Thermal decomposition studies in solution and in the solid state show that both compounds afford the corresponding III/V semiconductor material at a relatively low temperature. $[t\text{-}Bu_2Ga(\mu\text{-}PH_2)]_3$ produces GaP at 248 °C in the solid state and at 110 °C when heated in toluene solution. $[t\text{-}Bu_2Ga(\mu\text{-}AsH_2)]_3$ gives GaAs at 250 °C in the solid state and slowly at room temperature in hexane but more rapidly at 110 °C when heated in toluene solution. The products are polycrystalline, as shown by X-ray powder diffraction studies.

Introduction

There is currently considerable interest in compounds containing group 13 and group 15 elements as these may serve as single source precursors to compound semiconductors such as GaAs and InP.[1] The original studies of Coates[2] and Beachley[3] et al. established that compounds of the formula $[Me_2MER'_2]_3$ (M = Ga, In; E = P, R′ = Me, Et; E = As, R′ = Me) may be prepared by the thermal reaction of Me_3M with R'_2EH. More recent work by Wells and others showed that if the steric demands of the alkyl groups are increased, dimeric materials e.g. $[(Me_3SiCH_2)_2AsGaPh_2]_2$,[4] $[(Me_3SiCH_2)_2InPPh_2]_2$,[5] and $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$[6] may be characterized. In addition to these oligomers, Wells and co-workers[7] have also characterized novel group 13 and group 15 binary compounds such as $Ga[As(Mes)_2]_3$[8] (Mes = mesityl) and $[Ga(As(CH_2SiMe_3)_2)_3]_2$.

We recently reported the use of the dinuclear complexes $[Me_2Ga(\mu\text{-}As(t\text{-}Bu)_2)]_2$ and $[Me_2In(\mu\text{-}P(t\text{-}Bu)_2)]_2$ for the organometallic chemical vapor deposition (OMCVD) of thin films of GaAs and InP, respectively.[9] These compounds and other analogues of the type $[Me_2M(\mu\text{-}E(t\text{-}Bu)_2)]_2$ (M = Al, Ga, In; E = P, As) offer advantages over the currently employed OMCVD processes, which typically employ mixtures of group 13 alkyls (e.g. Me_3Ga, Me_3In) with group 15 sources such as AsH_3 or $AsMe_3$ (e.g. eq 1).[10]

$$Me_3Ga + AsH_3 \rightarrow GaAs + 3CH_4\uparrow \qquad (1)$$

The major advantages are increased stability toward air and moisture, hydrocarbon solubility, and decreased toxicity, yet sufficient volatility for OMCVD processes. Our deposition studies indicate that an important feature of such precursors is the availability of a low-energy decomposition pathway.[9] In the case of the t-Bu-substituted compounds the primary decomposition mode involves the elimination of isobutylene. Since the t-Bu substituent can therefore be considered to be a "masked" hydrogen, there was obvious interest in preparing precursors with group 15–hydrogen bonds. It was anticipated that such hydrogen-substituted precursor clusters would possess even lower decomposition temperatures than the corresponding alkylated compounds. We were also aware of the significance that compounds of this class might have in regard to the mechanism of the reaction of Me_3Ga with PH_3[11] or AsH_3.[12] With these points in mind we investigated the chemistry of single-source precursors that feature t-Bu substituents on the group 13 elements (Al, Ga, In) in addition to $-PH_2$ and $-AsH_2$ groups. We report here the synthesis, characterization, and preliminary decomposition studies of $[t\text{-}Bu_2Ga(\mu\text{-}EH_2)]_3$ (E = P (1), As (2)). To the best of our knowledge, 1 and 2 constitute the first examples of group 13/15 precursors bearing $-EH_2$ (E = P, As) units.

Results and Discussion

Synthesis and Structure of $[t\text{-}Bu_2Ga(\mu\text{-}PH_2)]_3$ (1). The condensation of excess PH_3 onto frozen (−196 °C) $t\text{-}Bu_3Ga$ (neat or in a benzene solution), followed by warming to 25 °C, results in the formation of 1 in essentially quantitative yield based on Ga. Interestingly when THF was employed as solvent, no reaction took place. Colorless 1 may be recrystallized from toluene at −20 °C.

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[8] Pitt, C. G.; Higa, K. T.; McPhail, A. T.; Wells, R. L. *Inorg. Chem.* **1986**, *25*, 2483.

[9] Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248. Bradley et al. have also investigated the deposition of InP from $[Me_2In(\mu\text{-}P(t\text{-}Bu)_2)]_2$ (using the MOMBE technique): Aitchison, K. A.; Backer-Dirks, J. D. J.; Bradley, D. C.; Factor, M. M.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B.; Short, R. L. *J. Organomet. Chem.* **1989**, *366*, 11.

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[11] Schlyer, D. J.; Ring, M. A. *J. Electrochem. Soc.* **1977**, *124*, 569.

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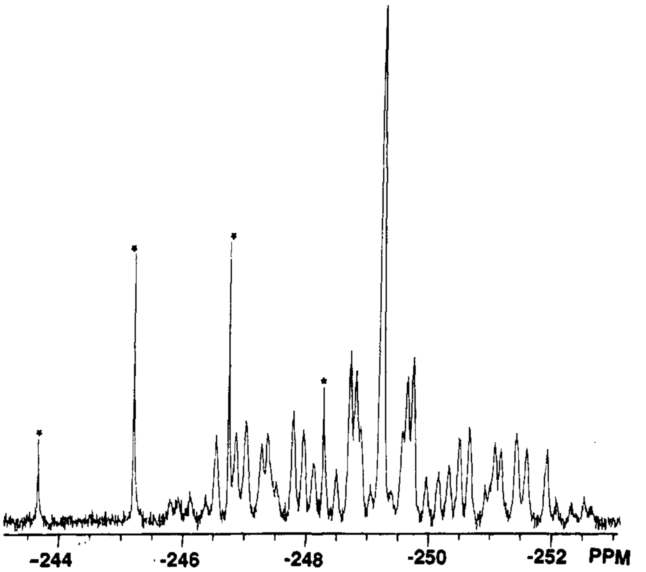

Figure 1. ^{31}P NMR spectrum of 1 at 121.47 MHz in THF/C_6D_6 (10%) at 35 °C. Signals marked with asterisks are due to traces of free PH_3.

Table I. Bond Lengths (Å) for [*t*-$Bu_2Ga(\mu\text{-}PH_2)]_3$ (1)[a]

Ga-P	2.439 (3)	C1-C2	1.56 (2)
Ga-C1	2.02 (2)	C1-C3	1.56 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table II. Bond Angles (deg) for [*t*-$Bu_2Ga(\mu\text{-}PH_2)]_3$ (1)[a]

P-Ga-P	101.5 (3)	Ga-C1-C3	111 (1)
P-Ga-C1	107.9 (3)	C2-C1-C2	111 (2)
C1-Ga-C1′	122.0 (7)	C2-C1-C3	111 (1)
Ga-P-Ga′	138.5 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The compound is extremely air and moisture sensitive and must be handled with care, since it liberates phosphine gas (PH_3) upon hydrolysis. Infrared spectroscopic data indicate the presence of the PH_2 units [ν_{P-H}(sym) 2343 cm^{-1} and ν_{P-H}(asym) 2335 cm^{-1}]. The computed H-P-H angle is 96 (3)°.[13] The ^1H NMR spectrum exhibits a singlet at δ 1.08, assigned to the *t*-Bu units. Attempts at locating the phosphine protons were unsuccessful due to the spectral complexity and also because of the presence of traces of overlapping signals due to [*t*-$Bu_2Ga(\mu\text{-}OH)]_3$ (3).[14] No resonances corresponding to the solvent of crystallization were detected. The $^{31}P\{^1H\}$ NMR spectrum of 1 in THF/10% C_6D_6 at 35 °C comprises a singlet at δ −249.3. The corresponding proton-coupled spectrum is a broad multiplet characteristic of the nine-spin system [AA′A″XX′X″X‴X⁗X″‴] (see Figure 1), consistent with the presence of the trimeric species in solution. Moreover, very little changes are apparent in the variable-temperature $^{31}P\{^1H\}$ NMR spectrum, thus indicating that 1 exists in the same state of aggregation from −20 to +80 °C. The $^{13}C\{^1H\}$ NMR data are also consistent with the proposed structure.

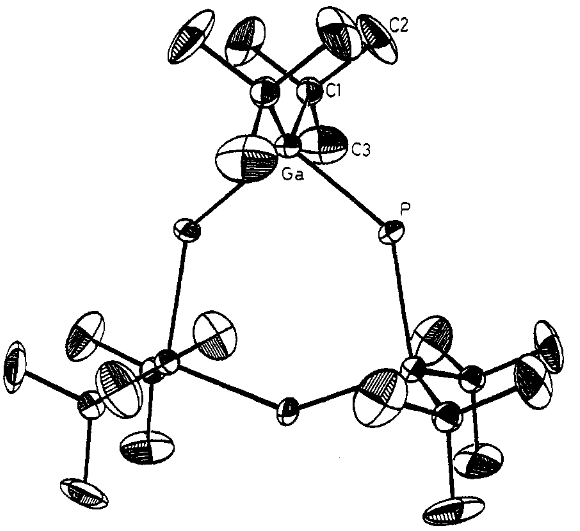

Figure 2. ORTEP view of 1, showing the atom-numbering scheme.

Table III. Summary of Crystal Data, Collection Data, and Refinement for [*t*-$Bu_2Ga(\mu\text{-}PH_2)]_3$ (1)

Description of Crystal	
color	clear
habit	prism
max cryst dimens, mm	0.30 × 0.30 × 0.20
cryst system	hexagonal
space group	$P\bar{6}2m$
unit cell params	
a, Å	11.127 (4)
c, Å	16.506 (6)
V, $Å^3$	1769.7 (5)
Z	3
formula	$C_{24}H_{60}Ga_3P_3$
M_r	650.83
D_{calcd}, g cm^{-3}	0.867
μ(Mo Kα), cm^{-1}	13.4
Data Collection	
radiation (λ, Å)	Mo Kα (0.71073)
scan technique	$\theta/2\theta$
scan width, deg	0.80 + 0.35 tan θ
range of indices *h*,*k*,*l*	±14,±14,±21
2θ range, deg	3.0–55.0
no. of reflcns measd	1644
std reflcns	
intens	525, 0,0,12
orientation	409, 049
decay of stds, %	−27.6
agreement factor for averaged reflcns	5.3 (*I*) 3.3 (F_o)
Structure Determination	
no. of reflections used ($I > 3\sigma(I)$)	446
no. of params varied	42
data/param ratio	10.6
esd of an observn of unit wt	2.736
R^a	0.064
$R_w{}^a$	0.075
highest peak of resid electron density, e $Å^{-3}$	0.86 (due to disordered toluene)

[a] *R* and R_w are defined as $R = \sum|F_o| - |F_c|/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$.

In the solid state 1 crystallizes in the hexagonal space group $P\bar{6}2m$ as a planar trimer, consistent with the solution-phase spectroscopic data. A view of the molecule is shown in Figure 2, and important bond lengths and angles are presented in Tables I and II. Crystallographic details are given in Table III. The molecular geometry is D_{3h}, and the structure comprises a planar Ga_3P_3 ring with the *t*-Bu groups eclipsed above and below the molecular plane.

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(13) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: London, 1980; p 1074. The reverse assignment was considered by us, but the calculation of the enclosing H-E-H angle (where E = P, As) gave the values 84 (3)° for 1 and 79 (3)° for 2, both of which are unrealistically small. This assignment is not uncommon (see figure in ref 13).

(14) Details of the synthesis and characterization of 3 will be the subject of a future publication.

The coordination geometry at each Ga atom is approximately tetrahedral; however, there is a wide scatter of angles (P–Ga–P = 101.5 (3)°, P–Ga–C(1) = 107.9 (3)°, C(1)–Ga–C(1)′ = 122.0 (7)°). The Ga–P distance (2.439 (3) Å) is shorter than that of $[t\text{-Bu}_2Ga(\mu\text{-P}(C_5H_9)H)]_2$ (2.451 Å)[15] but is not significantly different from those found in the trimer $[Me_2Ga(\mu\text{-P}(i\text{-Pr})_2)]_3$, which was recently synthesized in these laboratories[16] and in which the Ga–P distances range from 2.43 to 2.44 Å. The Ga–C distance of 2.02 (2) Å is comparable with those found in the dimeric complexes $[R_2Ga(\mu\text{-P}(t\text{-Bu})_2)]_2$ (R = *n*-Bu, Me; ca. 2.02 Å).[17] Another point of interest is the large angle subtended at the P atom (Ga–P–Ga = 138.5 (4)°). This is significantly larger than the In–As–In angle in the planar conformer of $[Me_2In(\mu\text{-As}(Me)_2)]_3$ (126.64 (9)°).[18] Of related interest is the aluminum amide $[(t\text{-Bu})_2Al(\mu\text{-NH}_2)]_3$ recently characterized by Interrante and co-workers in which the Al–N–Al angle is 133.9 (5)°.[19]

Synthesis and Characterization of $[t\text{-Bu}_2Ga(\mu\text{-AsH}_2)]_3$ (2). Colorless crystalline 2 can be prepared in virtually quantitative yield by replacing PH_3 with AsH_3 in the procedure described above for 1. Compound 2 can be recrystallized from toluene at −20 °C. In the solid state 2 is stable for several months in the dark under an inert atmosphere. However, toluene or hexane solutions of 2 are light sensitive. Exposure of these solutions to normal light (fluorescent tube) at 25 °C results in coloration over a period of several hours and deposition of an orange film. Compound 2 is extremely moisture and air sensitive and liberates AsH_3 upon hydrolysis and must therefore be handled with extreme caution.

On the basis of the spectroscopic data for 2, we propose a similar structure to that of 1. In order to confirm this, we attempted to determine the molecular weight of 2 in solution by the isothermal distillation method using a modified Signer apparatus.[20] A variety of solvents was tried, including diethyl ether, toluene, and dichloromethane. No value of meaningful accuracy could be obtained, due to the poor solubility and inherent instability of 2. However, the chemical ionization mass spectrum (CIMS) confirmed the trimeric nature of 2 in the gas phase (m/e for M^+ = 782 amu). Infrared spectroscopy confirms the presence of AsH_2 units [ν_{As-H}(sym) 2145 cm^{-1} and ν_{As-H}(asym) 2132 cm^{-1}] and leads to a calculated H–As–H angle of 101 (3)°.[13] This is the same (to within experimental error) as the corresponding H–P–H value for 1. The ^1H NMR spectrum in C_6D_6 at 35 °C exhibits a singlet at δ 1.16, assigned to *t*-Bu protons, and a less intense singlet at δ 1.04, which is attributable to the As–H protons. The spectrum remains unchanged from +35 °C to −90 °C, indicating that 2 is either planar in solution or undergoes an interchange of conformers (e.g. boat, chair, twist-boat, etc.) that is rapid on the NMR time scale. The $^{13}C\{^1H\}$ NMR spectrum contains a singlet at δ 29.96 assigned to the (As–C–CH_3) groups; the quaternary carbons were not observed.

Thermal Decomposition Studies of 1 and 2. (a) Solid State. Solid-state pyrolysis studies were carried out under a low pressure (ca. 100 Torr) of nitrogen gas in a static system. Under these conditions both 1 and 2 produced a mirror on the internal surfaces of the decomposition vessels. Compound 1 decomposes slowly at 200 °C but rapidly at its melting point (243–248 °C). The layer, deposited onto an unetched silicon wafer, was analyzed by XPS. The corrected Ga(3d) and P(2p) signals, at 20.3 and 128.6 eV, respectively, compare well with the literature values of 19–20 and 129 eV.[21] The XPS experiment also revealed the presence of carbon (ca. 10%), which varied from sample to sample. We have, so far, made no attempts to optimize the decomposition conditions in order to lower the carbon content, since our main goal was to demonstrate a lower temperature route to the semiconductors than had previously been described. The film did not give an X-ray diffraction pattern, thus indicating that an amorphous layer had been grown. Mass spectroscopic and ^1H NMR analysis of the volatiles produced during decomposition revealed the presence of mostly isobutane and isobutylene. NMR analysis showed the isobutane to isobutylene ratio to be 3.67:1.00.

Compound 2 decomposes slowly at 155 °C in the solid state. However, the rate of decomposition is significantly more rapid at 250 °C. The residual film was also analyzed by XPS. The corrected Ga(3d) signal at 20.2 eV compares well with the literature value of 19.5 eV. The corrected As(3d) region showed two overlapping signals, one at 41.0 eV attributed to GaAs (literature value 40.7 eV)[21] and a shoulder at 44.1 eV assigned to elemental arsenic (literature value 44.0 eV).[21] XPS again revealed significant carbon incorporation; however, the carbon-containing species could not be identified. This film was also shown to be amorphous by X-ray diffraction. The volatile byproducts consisted mainly of isobutane, which suggests a reaction pathway involving the evolution of alkane groups from adjacent *t*-BuGa and EH units (E = P, As).

(b) Solution. Compounds 1 and 2 both undergo decomposition in solution. Thus, vigorous refluxing of 1 in toluene solution for 24 h produces a yellow-orange suspension. Examination of the resulting solid by EI mass spectrometry indicated the presence of organophosphorus oligomers. Low-intensity *tert*-butyl C–H stretching vibrations were evident in the infrared spectra. Refluxing of a toluene solution of 2 for 20 min resulted in quantitative conversion to a red-brown suspension. Infrared spectra of the dried solid again showed only low intensity *tert*-butyl vibrations. While EI mass spectrometry of this material shows peaks consistent with the presence of organoarsenic oligomers, subsequent annealing under N_2 at 350–400 °C resulted in positive identification of the residue as polycrystalline GaAs by X-ray power diffraction. We therefore conclude that in solution, 2 decomposes to amorphous GaAs, which contains trapped organic impurities. Of related interest are materials prepared by Theopold et al. via the reaction of $Cp^*{}_2GaAs(SiMe_3)_2$ with *t*-BuOH.[22] Exposure of hexane solutions of 2 at room temperature to room light over a period of hours also affords amorphous GaAs.

In studies of reactions of Me_3Ga with PH_3 or AsH_3 it was concluded that, while several different mechanisms may be in operation under different conditions, the prevalent mechanism is of the Langmuir–Hinshelwood

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type, in which the surface bound species undergo the following reactions:

$$Me_3Ga + EH_3 \rightarrow Me_2GaEH_2 + CH_4$$

$$Me_2GaEH_2 \rightarrow MeGaEH + CH_4$$

$$MeGaEH \rightarrow GaE + CH_4$$

The isolation of $[t\text{-}Bu_2GaEH_2]_3$ in this present work supports the idea that the Me_3Ga/EH_3 reactions proceed via the formation of $[Me_2GaEH_2]_n$ species. Attempts at isolating species of composition $[t\text{-}BuGaEH]_n$, analogous to the iminoalanes $[RAlNR']_n$,[23] by careful heating gave only insoluble residues.

Experimental Section

All manipulations were performed under dry, oxygen-free N_2 under vacuum (with standard vacuum-line techniques) or in a Vacuum Atmospheres drybox under argon. Microanalyses were conducted by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Pentane and THF were distilled from sodium benzophenone ketyl under N_2. Toluene was distilled from sodium under N_2. C_6D_6 was dried initially over 4-Å molecular sieves, stirred over Na/K alloy overnight, and then vacuum-transferred for storage over Na/K alloy. Instruments: IR, Digilab FTS-40; NMR, GE QE-300 (^1H, ^{13}C, ^{31}P); EI-MS, Bell & Howell CEC 24-491; 70-eV CI-MS, Finnigan MAT 4023; XPS, Leybold-Heraeus LHS-12 surface analysis system equipped with a rapid entry load-lock system (base pressure 1.5×10^{-9} Torr). IR spectra were run as KBr pellets, and the solvent of crystallization was removed under reduced pressure before sample preparation. NMR spectra recorded in C_6D_6 at ambient temperature unless otherwise stated and are in ppm referenced to Me_4Si (δ 0.0, ^1H, ^{13}C) and 85% H_3PO_4 (aq) (δ 0.0, ^{31}P). The solvent of crystallization was again removed under reduced pressure before sample preparation, and there was no evidence of toluene in any of the spectra. XPS spectra were taken by using a dual X-ray anode (Mg and Al) and an EA-11 hemispherical analyzer. The data were obtained with Mg Kα radiation (1253.6 eV) at 200 W (10 keV, 20 mA) along with 40-eV pass energy, which gave an overall energy resolution of 0.95 eV. The resolution was checked by measuring the line width of the Ag $3d_{5/2}$ peak. No sample charging was observed in any of the samples, as evidenced by the constant position of the "adventitous" carbon (1s) peak (binding energy = 284.9 eV). Melting points were determined on an Electrothermal melting point apparatus in sealed capillaries under argon (1 atm) and are uncorrected.

$t\text{-}Bu_3Ga$ was made in accordance with the literature.[24] PH_3 and AsH_3 gases were purchased from Scott Specialty Gases and Linde (division of Union Carbide), respectively, and used as supplied. Satisfactory elemental analyses (C, H) were obtained for both compounds.

Caution! AsH_3 and PH_3 are colorless, highly toxic gases, and compounds 1 and 2 liberate these gases upon contact with moisture. All manipulations should be carried out in a drybox or in a well-ventilated hood. Procedures for the manipulation of PH_3 and AsH_3 have been described.[25,26]

Synthesis and Characterization of $[t\text{-}Bu_2Ga(\mu\text{-}PH_2)]_3$ (1). Onto a frozen benzene solution of $t\text{-}Bu_3Ga$ (1.0 mL of a 1.83 M solution, 1.83 mmol) at −196 °C was condensed excess PH_3 (0.50 mL, 11 mmol). The mixture was allowed to warm until the PH_3 melted and exerted ca. 0.5 atm of pressure, as measured by a mercury manometer, before being recooled to −196 °C. This cycle was repeated 2–3 times to ensure completion of reaction. Excess PH_3 was allowed to boil off under a vigorous stream of nitrogen into a sodium hypochlorite bubbler solution (1% w/w), as the mixture was warmed to room temperature (3 h). Benzene was removed under reduced pressure, the colorless residue was extracted with toluene (30 mL), the solution was filtered, and the filtrate was concentrated under vacuum (15 mL). Upon cooling (−20 °C), clear colorless crystals of 1 were formed in essentially quantitative yield. Mp: 243–248 °C dec. IR (KBr disk): 2948 m, 2923 w, 2861 w, 2838 m, 2712 w, 2342 m, 2335 m, 1464 s, 1456 s, 1394 w, 1360 s, 1258 w, 1182 w, 1167 w, 1047 s, 1009 s, 939 w, 810 vs, 651 w, 523 w, 515 cm^{-1} w. ^1H NMR (300.15 MHz, THF/10% C_6D_6, 35 °C): δ 1.08 (s, 18 H, *t-Bu*Ga); P*H* protons not observed. $^{31}P\{^1H\}$ NMR (121.47 MHz): δ −249.30 (s, μ-*P*H_2). ^{31}P NMR: δ −249.30 (br mult, μ-*P*H_2). $^{13}C\{^1H\}$ NMR (75.48 MHz): δ 30.70 (s, $(H_3C)_3CGa$); $(H_3C)_3$*C*Ga quaternary carbons not observed. EIMS: *m/e* 593 amu ($C_{20}H_{51}Ga_3P_3$, M^+ − {*t*-Bu})

Synthesis and Characterization of $[t\text{-}Bu_2Ga(\mu\text{-}AsH_2)]_3$ (2). An excess of AsH_3 was condensed onto frozen neat $t\text{-}Bu_3Ga$ (0.5 mL, ca. 4 mmol) at −196 °C. The mixture was allowed to warm to 0 °C, whereupon it rapidly solidified before being recooled to −196 °C. This cycle was repeated 2–3 times to ensure completion of the reaction. Excess AsH_3 was allowed to boil off under a vigorous stream of nitrogen into a series of sodium hypochlorite (1% w/w) and bromine–water (1% w/w) bubblers, as the mixture was warmed to room temperature (1 h). The colorless residue was extracted with toluene (80 mL), the solution was filtered, and the filtrate was concentrated under vacuum (50 mL). Upon cooling (−20 °C), clear colorless crystals of 2 were formed in essentially quantitative yield. Mp: 155–162 °C dec. IR (KBr disk): 2950 s, 2925 s, 2916 s, 2864 s, 2842 s, 2761 w, 2733 w, 2706 w, 2703 w, 2145 m, 2132 m, 1464 s, 1438 w, 1387 w, 1360 s sh, 1262 w, 1189 w, 1167 m, 1094 w br, 1008 s, 942 m, 845 w, 808 s, 594 cm^{-1} m. ^1H NMR (300.15 MHz, C_7D_8, 35 °C): δ 1.16 (s, 18 H, *t-Bu*Ga), 1.04 (s, 2 H, As*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz): δ 29.96 (s, $(CH_3)_3CGa$); $(H_3C)_3CGa$ quaternary carbons not observed. CIMS (Me^+): *m/e* 782 amu ($C_{24}H_{60}Ga_3As_3$, M^+).

X-ray Experimental Details for 1. Crystals of 1 were obtained by careful cooling of a saturated toluene solution. A colorless, prismatic crystal (0.30 × 0.30 × 0.20 mm) was mounted into a thin-walled glass capillary with Dow-Corning high-vacuum grease. The capillary was sealed under argon. Crystallographic details are given in Table III. Cell constants, their standard deviations, and the orientation matrix were obtained by least-squares treatment of the angular coordinates of 25 intense independent reflections in the range $28° < 2\theta < 30°$. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 24 ± 2 °C, employing graphite-monochromated Mo Kα radiation. The intensities of two check reflections were measured after every 100 reflections. Corrections were made by assuming linear decay, and the data were also corrected for Lorentz and polarization effects. An empirical absorption correction was also applied to the data, based on φ scans (φ 0–360° every 10°) of suitable reflections with χ values close to 90°. Of the 880 unique reflections measured, 446 reflections were considered observed with $I > 3\sigma(I)$.

Calculations were performed on a MICROVAX II computer using the "SDP-PLUS" software package.[27] Since the X-ray data displayed no systematic absences, the structure was refined under all five possible space groups ($P\bar{6}m2$, $P\bar{6}2m$, $P6mm$, $P622$, and $P6/mmm$) by direct methods (Patterson)[28] using successive cycles of difference Fourier maps followed by least-squares refinement. The best agreement (goodness of fit = 2.736) was obtained for the hexagonal space group, $P\bar{6}2m$ (No. 189). When the refinement was terminated, the maximum shift of any parameter was 3% of its estimated standard deviation, and at this point R and R_w were 0.064 and 0.075, respectively. On this basis, the space group was assigned as $P\bar{6}2m$. The presence of poorly resolved and badly disordered toluene, intercalating the trimers, was evident in the final difference Fourier map. We were unable to find a satisfactory model for it. A non-Poisson contribution weighting scheme, with an instability factor P set at 0.08, was used in the final stages of

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refinement.[29] No hydrogen atoms were located in the structure, but their contributions were included in the refinements. Scattering factors were taken from ref 30. Supplementary material is available.[31]

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Supplementary Material Available: For 1, complete listings of positional and thermal parameters (2 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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(29) *P* is used in calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\sum w(|F_o|-|F_c|)^2$, where $w = 4(F_o)^2/[\sum(F_o)^2]^2$, $[\sum(F_o)^2]^2 = [S^2(C + R^2B) + (P(F_o)^2)^2]/Lp^2$, and *S* is the scan rate, *C* is the total integrated peak count, *R* is the ratio of scan time to background counting time, *B* is the total background count, and *Lp* is the Lorentz–polarization factor.

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Synthesis and NMR Spectroscopy of Permethylpolysilane Oligomers $Me(SiMe_2)_{10}Me$, $Me(SiMe_2)_{16}Me$, and $Me(Me_2Si)_{22}Me$

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Compounds $Me(SiMe_2)_{10}Me$ (Si10), $Me(SiMe_2)_{16}Me$ (Si16), and $Me(Me_2Si)_{22}Me$ (Si22) were synthesized by coupling a toluene solution of $Me_3SiSiMe_2Cl$ and $Cl(SiMe_2)_6Cl$ with sodium–potassisum alloy. The ^1H, ^{13}C, and ^{29}Si NMR spectra of Si10 were fully assigned by 2D ^1H–^{13}C and ^1H–^{29}Si NMR spectroscopy; the latter method is useful for obtaining Si–Si as well as Si–H connectivities. Si–Si coupling constants for Si10 were determined with use of INEPT-INADEQUATE NMR spectroscopy.

Introduction

The linear permethylpolysilane oligomers $Me(SiMe_2)_nMe$ (n = 2–12) were prepared in the 1960s by Kumada and his students,[1] but polysilane oligomers with longer chains are almost unknown. The only exceptions are the compounds $Me(SiMe_2)_{18}Me$ and $Me(SiMe_2)_{24}Me$, which were reported by Boberski and Allred from the coupling reaction of eq 1.[2] Oligomeric polysilanes of this type can serve as model compounds for the polysilane polymers, which have now acquired considerable interest.[3]

$$Me(SiMe_2)_6Cl + Cl(SiMe_2)_6Cl \xrightarrow[\text{toluene}]{\text{Na/K}} Me(SiMe_2)_{6n}Me \quad n = 2\text{–}4 \tag{1}$$

$$Me_3SiSiMe_2Cl + Cl(SiMe_2)_6Cl \xrightarrow[\text{toluene}]{\text{Na/K}} Me(SiMe_2)_nMe \quad \begin{matrix} n = 10,\ \text{Si10} \\ n = 16,\ \text{Si16} \\ n = 22,\ \text{Si22} \end{matrix} \tag{2}$$

We have synthesized permethylsilane oligomers Si10, Si16, and Si22 according to eq 2 and studied these molecules by ^1H, ^{13}C and ^{29}Si NMR spectroscopy. The NMR spectra of Si10 were reported earlier[4,5] but could not be decisively assigned. This has now been accomplished with use of two-dimensional NMR methods. One-, two-, and three-bond coupling constants between silicon atoms in Si10 were determined with use of INEPT-INADEQUATE NMR spectroscopy,[6] modified for ^{29}Si.[7,8] The coupling constants may be important for understanding the electron delocalization in polysilanes.[3]

Experimental Section

NMR Spectroscopy. NMR spectra were recorded on a Bruker AM-500 spectrometer at 125.3 MHz for ^{13}C and 99.36 MHz for ^{29}Si. Silicon-29 NMR spectra were recorded with use of the proton-decoupled INEPT pulse sequence D1 = 3.0 s, D2 = 37 ms, and D3 = 12 ms. 2D NMR spectra were acquired with the XHCORR microprogram D1 = 3.0 s, D3 = 74 ms, and D4 = 24 ms. The COLOC microprogram gave similar results. Experimental times were 2.5 h.

The INEPT-INADEQUATE pulse sequence was used for ^{29}Si–^{29}Si couplings with repetition delay 3.0 s, τ_1 = 37 ms, τ_2 = 10 ms, and $\tau_3 = \tau_4$ = 7.2 ms. The notation corresponds to that in Figure 1. Acquisition time was 12 h. Experimental manipulations were carried out in oven-dried glassware under a nitrogen atmosphere.

1,6-Dichlorohexasilane (1). Dodecamethylcyclohexasilane, $(Me_2Si)_6$ (30 g, 0.082 mol), synthesized from Me_2SiCl_2 by a standard procedure,[9] was treated with Cl_2 in CCl_4 at 0 °C to give 1 and smaller chlorinated permethylsilanes.[10] After Kugelrohr distillation of the mixture, 6.3 g (18%) of 1 was isolated pure.

Pentamethylchlorodisilane (2). $Me_2PhSiCl$ (17 g, 0.10 mol) was added to 1.75 g (0.25 mol) of Li wire in 150 mL of THF to

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