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Cyclic Trimeric Hydroxy, Amido, Phosphido, and Arsenido Derivatives of Aluminum and Gallium. X-ray Structures of $[t\text{-}Bu_2Ga(\mu\text{-}OH)]_3$ and $[t\text{-}Bu_2Ga(\mu\text{-}NH_2)]_3$

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Reaction of t-Bu_3Al with PH_3 or AsH_3 produces cyclic trimeric complexes of formula $[t\text{-}Bu_2Al(\mu\text{-}EH_2)]_3$ (E = P (**1**), As (**2**), which were identified by their IR, NMR, and mass spectra. From infrared data the ∠H–P–H and ∠H–As–H angles are calculated to be 97 (3) and 105 (3)°, respectively. The adduct t-Bu_3GaNH_3 (**3**) may be isolated from mixtures of t-Bu_3Ga and NH_3 at room temperature. Heating **3** to 160 °C results in the formation of $[t\text{-}Bu_2Ga(\mu\text{-}NH_2)]_3$ (**4**), whose cyclic trimeric structure was confirmed in the solid state by X-ray crystallography. The analogous μ-ND_2 complex **5** can be prepared by substituting ND_3 for NH_3. Reaction of t-Bu_3Ga with H_2O in pentane solution at 25 °C gives the cyclic trimer $[t\text{-}Bu_2Ga(\mu\text{-}OH)]_3$ (**6**) in 90% yield. The deuterium-labeled compound $[t\text{-}Bu_2Ga(\mu\text{-}OD)]_3$ (**7**) may be prepared in a similar fashion using D_2O. Compound **6** is also formed by the hydrolysis of $[t\text{-}Bu_2Ga(\mu\text{-}PH_2)]_3$, $[t\text{-}Bu_2Ga(\mu\text{-}AsH_2)]_3$, and $[t\text{-}Bu_2Ga(\mu\text{-}As(t\text{-}Bu)H)]_3$. The cyclic trimeric structure of **6** was confirmed by X-ray crystallography, which showed a planar Ga_3O_3 ring with t-Bu groups extending above and below the plane. Crystal data for **4**: $C_{24}H_{60}N_3Ga_3$; $M_n = 600.03$; rhombohedral space group $R\bar{3}c$; $a = 10.443$ (2) Å; $c = 50.836$ (13) Å; $V = 4801$ (5) Å^3; $Z = 6$, $D_{calc} = 1.250$ g cm^{-3}; μ(Cu Kα) = 11.26 cm^{-1}; 932 unique reflections over the range of $2 < 2\theta < 110°$ ($\omega/2\theta$ scan mode) were measured; 652 unique observed reflections were used in the refinement with $I > 3\sigma(I)$; R and $R_w = 0.0310$ and 0.0329, respectively. Crystal data for **6**: $C_{24}H_{57}Ga_3$; $M_n = 602.17$; rhombohedral space group $R\bar{3}c$; $a = 10.362$ (2) Å; $c = 50.927$ (10) Å; $V = 4735.89$ (15) Å^3; $Z = 6$, $D_{calc} = 1.262$ g cm^{-3}; μ(Mo Kα) = 13.4 cm^{-1}, 1117 reflections over the range $3.0 \leq 2\theta \leq 50.0°$ ($\theta/2\theta$ scan mode) were measured; 610 reflections with $I > 3\sigma(I)$ were used in the refinement; R and $R_w = 0.044$ and 0.0548, respectively.

Introduction

Recent interest in the chemistry of compounds containing group 13 to group 15 bonds has been partly due to their potential to serve as single-source precursors to the corresponding III/V compound semiconductor materials.[1] We recently reported the use of $\{Me_2Ga[\mu\text{-}As(t\text{-}Bu)_2]\}_2$ and $\{Me_2In[\mu\text{-}P(t\text{-}Bu)_2]\}_2$ as single-source precursors to GaAs and InP thin films via OMCVD (organometallic chemical vapor deposition).[2] These complexes are thought to undergo a β-hydrogen elimination pathway during decomposition to their respective III/V materials (GaAs, InP). One suggested mechanistic pathway involves the elimination of isobutylene from the group V atom to form a transient hydride species, as shown in eq 1.[2] Therefore, an interest developed in preparing hydride species of formula $[R_2GaEH_2]$ (E = P, As) which might also act as single-source precursors to thin films. Further interest in these complexes stems from their role as possible intermediates in the proposed mechanism of reaction between Me_3Ga and EH_3 (E = P, As) to produce GaP and GaAs.[3-5] In an earlier paper we reported the preparation and structures of gallium phosphido and arsenido complexes of formula $[t\text{-}Bu_2Ga(\mu\text{-}EH_2)]_3$ (E = P, As) and described their decomposition in both solid and solution state to form GaP and GaAs.[6] We now report the extension of this research to include PH_2 and AsH_2 complexes of t-Bu_2Al as well as a series of related gallium amido complexes derived from t-Bu_3Ga and ammonia. Also reported is the synthesis and structural characterization

$$Me_2GaAs(t\text{-}Bu_2) \xrightarrow[-2(CH_3)_2C{=}CH_2]{\Delta} Me_2GaAsH_2 \xrightarrow[-2CH_4]{\Delta} GaAs \qquad (1)$$

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of the cyclic trimer [t-Bu$_2$Ga(μ-OH)]$_3$, which was originally identified as an impurity in the synthesis of [t-Bu$_2$Ga(μ-PH$_2$)]$_3$.[6]

Results and Discussion

Synthesis and Characterization of μ-EH$_2$ Complexes of Al. Exposure of t-Bu$_3$A (neat or benzene solution) to excess PH$_3$ at 0 °C and subsequent heating to 80 °C results in the formation of [t-Bu$_2$Al(μ-PH$_2$)]$_3$ (**1**). Compound **1** may be recrystallized from toluene at −20 °C. This colorless compound is both air- and moisture-sensitive and must be handled with care, since it liberates phosphine gas (PH$_3$) upon hydrolysis. A structure similar to that of the previously reported cyclic trimer [t-Bu$_2$Ga(μ-PH$_2$)]$_3$ is proposed for **1** on the basis of spectroscopic data.[6] The electron impact mass spectrum indicates the existence of a trimer in the gas phase ($M^+ - \{t\text{-Bu}\} = 465$ amu). Infrared spectroscopic data indicate the presence of PH$_2$ units ($\nu_{\text{P-H}}$(sym) 2347 cm^{-1} and $\nu_{\text{P-H}}$(asym) 2339 cm^{-1}) with a computed ∠H–P–H angle of 97 (3)°,[7] which is the same, within experimental error, as that found for [t-Bu$_2$Ga(μ-PH$_2$)]$_3$ (96(3)°).[6] The ^{1}H NMR spectrum exhibits a singlet at δ 1.08, assigned to the t-Bu units. We were unable to unequivocally assign protons due to the PH$_2$ units, since the spectrum also contained overlapping signals arising from traces of PH$_3$. The ^{31}P{^{1}H} NMR spectrum of **1** in C$_6$D$_6$ at 31 °C comprises a singlet at δ −250.2. The corresponding proton-coupled spectrum is a broad multiplet characteristic of the nine-spin system AA′A″XX′X″X‴X⁗X′′′′′ also found for [t-Bu$_2$Ga(μ-PH$_2$)]$_3$ and is consistent with the presence of a trimeric species in solution. Like [t-Bu$_2$Ga(μ-PH$_2$)]$_3$, compound **1** may exist in a rigidly planar conformation or a rapidly interchanging one (e.g. boat, chair, twist-boat, etc.) at room temperature. The ^{13}C{^{1}H} NMR data are also consistent with the proposed structure.

Exposure of t-Bu$_3$Al (neat or benzene solution) to excess AsH$_3$ at 0 °C and subsequent heating to 50 °C results in the formation of [t-Bu$_2$Al(μ-AsH$_2$)]$_3$ (**2**). Compound **2** is also colorless and can be recrystallized from toluene at −20 °C. Unlike its gallium counterpart, [t-Bu$_2$Ga(μ-AsH$_2$)]$_3$,[6] **2** is stable to light in both the solid state and in solution. Toluene solutions of **2** show no observable discoloration, even after several days of exposure to room light. Compound **2** is extremely moisture- and air-sensitive and liberates AsH$_3$ upon hydrolysis and must therefore be handled with extreme caution.

A structure similar to that of **1** is proposed for **2** on the basis of the spectroscopic data. The electron impact mass spectrum (EIMS) confirmed the trimeric nature of **2** in the gas phase ($M^+ - \{t\text{-Bu}\} = 597$ amu). Infrared spectroscopy shows the presence of AsH$_2$ units ($\nu_{\text{As-H}}$(sym) 2155 cm^{-1} and $\nu_{\text{As-H}}$(asym) 2144 cm^{-1}) and leads to a calculated ∠H–As–H angle of 105 (3)°.[7] This is the same, within experimental error, as the corresponding ∠H–As–H value for [t-Bu$_2$Ga(μ-AsH$_2$)]$_3$.[6] The ^{1}H NMR spectrum in C$_6$D$_6$ at 35 °C exhibits a singlet at δ 1.11, assigned to t-Bu protons, and a less intense singlet at δ 1.08, which is attributable to the AsH$_2$ protons. The ^{13}C{^{1}H} NMR contains a singlet at δ 30.37, assigned to the Ga–C–CH$_3$ groups; the quaternary carbons were not observed.

Synthesis and Characterization of NH$_3$ and μ-NH$_2$ Complexes. Exposure of t-Bu$_3$Ga (neat or benzene solution) to excess NH$_3$ at room temperature results in the formation of t-Bu$_3$GaNH$_3$ (**3**) in quantitative yield as a colorless, low-melting solid (mp 42–46 °C) which may be purified by sublimation. The formula was assigned on the basis of the following spectroscopic data. Three weak N–H stretching frequencies were identified in the infrared spectrum of **3** ($\nu_{\text{N-H}}$ 3387, 3334, 3289 cm^{-1}). The ^{1}H NMR spectrum contains the expected singlet due to the t-Bu groups on the gallium atom (δ 1.10) as well as a broad singlet for the hydrogen atoms of the NH$_3$ moiety (δ 0.95). In addition, chemical ionization mass spectrometry allowed the monomeric formulation to be assigned (CIMS (Me$^+$), *m/e* 257 amu). Other well-characterized examples are limited to Me$_3$GaNH$_3$[8] and Pr$_3$GaNH$_3$.[9]

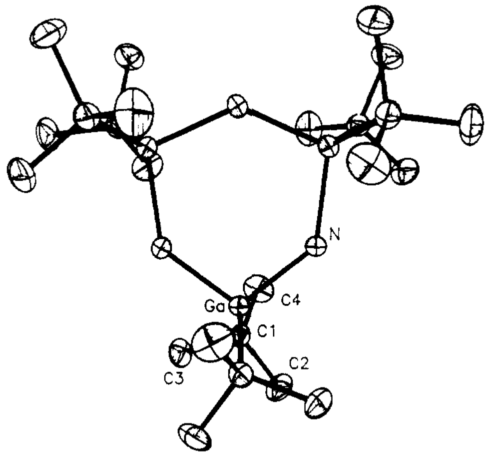

Figure 1. ORTEP view of **4**, showing the atom-numbering scheme.

Heating of **3** to 160–170 °C results in the formation of [t-Bu$_2$Ga(μ-NH$_2$)]$_3$ (**4**) in essentially quantitative yield with respect to Ga. In a similar manner, but using ND$_3$, the compound [t-Bu$_2$Ga(μ-ND$_2$)]$_3$ (**5**) was synthesized. Although IR spectroscopy of **4** shows the presence of N–H stretching frequencies ($\nu_{\text{N-H}}$(sym) 3328 cm^{-1} and $\nu_{\text{N-H}}$(asym) 3272 cm^{-1}), they were too weak for the H–N–H angle to be accurately determined. An alternative synthesis of **4** involves a salt elimination reaction using t-Bu$_2$GaCl and NaNH$_2$ (see Experimental Section). Crystals of **4** can be isolated from saturated Et$_2$O solutions in essentially quantitative yield.

The ^{1}H NMR spectrum of **4** exhibits a singlet at δ 1.12, assigned to the t-Bu units, and a less intense broad singlet at δ 0.41 which is assigned to the N–H protons. The ^{13}C{^{1}H} NMR spectrum of **4** at 23 °C contains a singlet at δ 31.62 assigned to the Ga–C–(CH$_3$)$_3$ groups. The spectroscopic data for **5** are consistent with deuteration at all nitrogen atoms, although the N–D stretching modes were not observed.

X-ray Structure of 4. In the solid state **4** crystallizes in the rhombohedral space group $R\bar{3}c$ as a planar trimer. A view of the molecule is shown in Figure 1, 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_3, in which the t-BuGa groups are staggered above and below the Ga$_3$N$_3$ plane. The coordination geometry at each Ga atom is approximately tetrahedral; however, there is a wide scatter of angles (∠N–Ga–N′ = 106.4 (1)°, ∠N–Ga–C(1) = 107.7 (1)°, ∠C(1)–Ga–

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Table I. Bond Lengths (Å) for [*t*-Bu$_2$Ga(μ-NH$_2$)]$_3$ (4)[a]

Ga″–Ga	3.719 (3)	C1–C3	1.541 (6)
Ga–N	2.017 (2)	C1–C4	1.514 (7)
Ga–C1	2.012 (4)	N–H	1.05 (5)
C1–C2	1.527 (6)		

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

Table II. Selected Bond Angles (deg) for [*t*-Bu$_2$Ga(μ-NH$_2$)]$_3$ (4)[a]

N–Ga–N	106.4 (1)	Ga–C1–C3	109.3 (3)
N–Ga–C1	107.7 (1)	Ga–C1–C2	110.8 (3)
C1′–Ga–C1	119.9 (2)	Ga–C1–C4	112.9 (3)
Ga″–N–Ga	134.5 (3)	Ga–N–H	101.0 (3)

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

Table III. Summary of Crystal Data, Collection Data, and Refinement of [*t*-Bu$_2$Ga(μ-NH$_2$)]$_3$ (4) and [*t*-Bu$_2$Ga(μ-OH)]$_3$ (6)

	4	6
	Description of Crystal	
color	colorless	colorless
habit	prism	irregular
max cryst dimens (mm)	0.21 × 0.31 × 0.35	0.30 × 0.30 × 0.30
cryst syst	rhombohedral	trigonal
space group	$R\bar{3}c$	$R\bar{3}c$
unit cell params		
a (Å)	10.443 (2)	10.362 (2)
c (Å)	50.83 (1)	50.927 (10)
V (Å^3)	4801 (5)	4735.89 (15)
Z	6	6
formula	$C_{24}H_{60}N_3Ga_3$	$C_{24}H_{57}Ga_3O_3$
mw	600.03	602.17
D_{calc} (g cm^{-3})	1.250	1.262
μ_{calc} (cm^{-1})	30.3	25.5
	Data Collection	
radiation (λ, Å)	Mo Kα (0.710 73)	
scan technique	$\omega/2\theta$	$\theta/2\theta$
scan width (deg)	0.8 = 0.15 (tan θ)	
2θ range (deg)	$2 < 2\theta < 110$	3.0
no. of rflns measd	932	1117
	Structure Determination	
no. of reflns used ($I > 3\sigma(I)$)	652 [$F > 6\sigma(F)$]	610 [$I > 3\sigma(I)$]
no. of params varied	51	47
data/param ratio	12.8	13.0
R[a]	0.0310	0.044
R_w[a]	0.0329	0.058
highest peak of residual electron density (e Å^{-3})	0.28[b]	0.48[c]

[a] R and R_w are defined as $R = \sum|F_o| - |F_c|/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. [b] Located near Ga. [c] Due to disordered toluene.

C(1)′ = 119.2 (2)°). The Ga–N distance (2.017 (2) Å) is slightly longer than those found in [(Me$_2$Ga(μ-N(Me)-H)$_2$(MeGa(μ_3-NMe)]$_6$ (1.95–2.00 Å)[10] or [Me$_2$Ga(μ-N=C-(CH$_3$))]$_2$ (1.978 (3) Å).[11] The Ga–C distance of 2.012 (4) Å is also longer than those found in the above complexes (1.986 (4) and 1.966 (6) Å). Also of interest is the large angle subtended at the N atom (Ga–N–Ga′ = 134.5 (3)°). While quite large compared to ∠M–E–M angles found in other planar trimers, the angle is within experimental error of that reported for the analogous aluminum amide [*t*-Bu$_2$Al(μ-NH$_2$)]$_3$ recently characterized by Interrante and co-workers (Al–N–Al = 133.9 (5)°).[12]

The hydrogen atoms were also located and refined in the structure of 4. The N–H length is 1.05 (5) Å, which is significantly longer than in the aluminum analog (0.87 (7) Å).[12] The ∠H–N–H angle of 114 (3)° in the gallium species **4** is slightly larger than that of the aluminum species (103 (6)°).

Synthesis and Characterization of a μ-OH Complex of Ga. Small quantities of [*t*-Bu$_2$Ga(μ-OH)]$_3$ (**6**) were originally observed in the base line of the ^{1}H and ^{13}C{^{1}H} NMR spectra of the compounds [*t*-Bu$_2$Ga(μ-E(*t*-Bu)H)]$_n$[13] (E = P, As; n = 2, 3) and [*t*-Bu$_2$Ga(μ-EH$_2$)]$_3$[6] (E = N, P, As). Compound **6** is formed by the hydrolysis of these dimers and trimers by traces of H$_2$O present in hydrocarbon solvents.

Compound **6** could also be synthesized in 90% yield by careful addition of a slight excess of H$_2$O to toluene or pentane solutions of *t*-Bu$_3$Ga at 25 °C.[14] The resulting white microcrystalline solid was recrystallized from toluene at −20 °C as clear colorless crystals which are solvent-dependent but not particularly air- or moisture-sensitive. The ^{1}H NMR spectrum of **6** exhibits a singlet at δ 1.20, assigned to the *t*-*Bu*Ga units, and a less intense singlet at δ 0.73, which is assigned to the GaO*H* protons. The integration (18:1) is consistent with the proposed formulation.

Very little change is apparent in the variable-temperature ^{1}H NMR spectra of **6**, thus indicating that it exists in this rapidly interchanging state from +25 to −90 °C. The ^{13}C{^{1}H} NMR spectrum of **6** contains a singlet at δ 31.70 assigned to the GaC(*C*H$_3$)$_3$ groups; the quaternary carbons were not observed. Infrared spectroscopic data for **6** confirm the presence of the O–H group (ν_{O-H} = 3613 cm^{-1}).

The deuterated analog of **6**, [*t*-Bu$_2$Ga(μ-OD)]$_3$ (**7**), may be prepared in a manner similar to that employed for **6** using D$_2$O. The O–D stretching frequency is observed (ν_{O-D} 2666 cm^{-1}). The ^{1}H NMR spectrum of **7** exhibits only a singlet at δ 1.20, assigned to the *t*-*Bu*Ga units. The ^{13}C{^{1}H} NMR spectrum of **7** is similar to that of **6**. Spectroscopic data are consistent with deuteration at the oxygen.

Compound **6** is readily soluble in hexane and may be recrystallized from this solvent. The solubility of **6** in aqueous media was determined by ^{1}H NMR spectroscopy to be 30 μM (with respect to the monomeric unit *t*-Bu$_2$GaOH).[15] The O*H* signal of compound **6** in D$_2$O slowly disappeared over 120 h, indicating slow proton exchange with the solvent. Solutions of **6** in toluene or D$_2$O are air-stable but deompose thermally at 25 °C (ca. 10%, 120 h). Partial elimination of isobutane, isobutylene, and presumably hydrogen results in the formation of an insoluble material which is sparingly soluble in CDCl$_3$. The ^{1}H NMR of this material exhibits a complex pattern between δ 1.44 and 1.20 and has at least two distinct GaO*H* resonances. Further characterization of this material was not attempted.

Crystals of **6** suitable for X-ray crystallographic analysis were grown from toluene at −20 °C. A view of the molecule is shown in Figure 2, and important bond lengths and

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(15) *Snell-Hilton-Encyclopedia of Industrial Chemical Analysis*; 1st ed.; Wiley: New York, 1966; Vol. 2, pp 720–723 (method adapted from the principles therein).

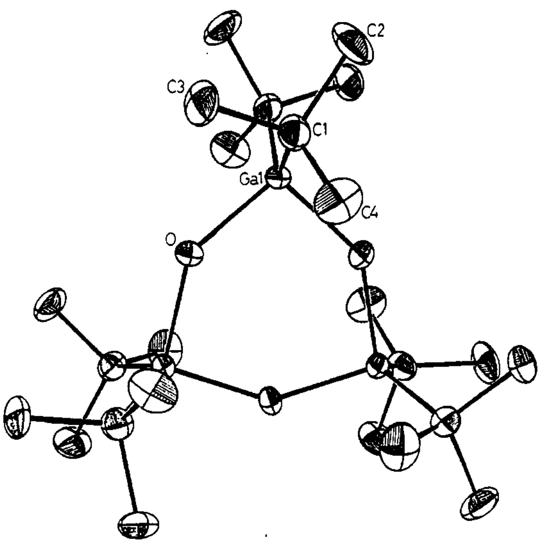

Figure 2. ORTEP view of **6**, showing the atom-numbering scheme.

Table IV. Bond Lengths (Å) for $[t\text{-}Bu_2Ga(\mu\text{-}OH)]_3$ (6)[a]

Ga1–O	1.957 (5)	C1–C3	1.58 (1)
Ga1–C1	1.987 (9)	C1–C4	1.54 (1)
C1–C2	1.58 (2)		

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

Table V. Selected Bond Angles (deg) for $[t\text{-}Bu_2Ga(\mu\text{-}OH)]_3$ (6)[a]

C1–Ga1–C1′	122.9 (4)	Ga1–C1–C4	112.6 (7)
Ga1–O–G1′	143.0 (2)	O–Ga1–O′	97.0 (2)
Ga1–C1–C2	110.6 (6)	O–Ga1–C1	108.3 (3)
Ga1–C1–C3	108.6 (6)	O–Ga1–C1′	108.0 (2)

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

angles are presented in Tables IV and V with crystallographic details given in Table III. As for **4**, the molecular geometry of **6** is D_3. The structure comprises a planar six-membered ring consisting of alternating Ga and O atoms. The *t*-Bu ligands attached to the gallium atoms are positioned above and below the Ga_3O_3 plane. The coordination geometry about each gallium atom may be described as distorted tetrahedral with a range of angles (∠O–Ga(1)–O = 97.0 (2)°, ∠O–Ga(1)–C(1) = 108.2 (3)°, ∠O–Ga(1)–C(1′) = 108.0 (2)°, ∠C(1′)–Ga(1)–C(1) = 122.9 (4)°). The Ga–O distance of 1.957 (5) Å is within the range found for the Ga–O separation in $[Me_2Ga(\mu\text{-}OH)]_4$ (1.94–1.99 Å).[16] The Ga–C distance of 1.987 (9) Å is also the same, within experimental error, as that found in $[Me_2Ga(\mu\text{-}OH)]_4$ (1.97 (4) Å). If the molecule exhibits the full crystallographic symmetry, then the geometry around O should be trigonal planar.

Experimental Section

All manipulations were performed under dry, oxygen-free N_2, under vacuum (using 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); EIMS, Bell & Howell CEC 24-491, 70 eV; CIMS, Finnigan MAT 4023. IR spectra were run as KBr pellets with any solvent of crystallization removed under reduced pressure before sample preparation. NMR spectra were 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; there was no evidence of toluene in any of the spectra. Melting points were determined on a Electrothermal melting point apparatus in sealed capillaries under argon (1 atm) and are uncorrected.

The trialkyl compounds $t\text{-}Bu_3Ga$ and $t\text{-}Bu_3Al$ were made according to literature methods.[17,18] Gaseous PH_3 and AsH_3 were purchased from Scott Specialty Gases and Linde (Division of Union Carbide), while ND_3 and NH_3 gases were purchased from Volk Radiochemical Co. and Matheson Gas Products, respectively. All gases were used as supplied. Satisfactory elemental analyses (C, H, N) were obtained for all compounds.

*Caution! AsH_3 and PH_3 are colorless, highly toxic gases, and compounds **1, 2, 6,** and **7** 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.*[19,20]

$[t\text{-}Bu_2Al(\mu\text{-}PH_2)]_3$ (1). A frozen benzene solution of $t\text{-}Bu_3Al$ (1.0 mL of a 1.96 M solution, 1.96 mmol) at 0 °C was exposed to an atmosphere of PH_3. This mixture was heated (80 °C, 4 h) and cooled to room temperature. Excess PH_3 was vented under a vigorous stream of nitrogen into a sodium hypochlorite bubbler solution (1% w/w) at room temperature (15 min). Benzene was removed under reduced pressure, and the colorless residue was extracted with toluene (20 mL) and the resulting solution filtered and concentrated under vacuum (12 mL). Upon cooling (−20 °C) colorless crystals of **1** were formed. Further concentration and cooling of the mother liquor yielded additional crops of **1**. The combined yield was 80% (with respect to Al). Mp: 229–232 °C dec. IR (KBr disk): 2962 s, 2943 s, 2921 s, 2908 s, 2863 m, 2836 s, 2764 w, 2730 w, 2712 w, 2701 w, 2347 w br, 2339 w, 1465 s, 1359 w, 1263 s sh, 1174 w, 1097 s br, 1036 s, 1021 s, 939 w, 809 w br, 802 vs cm^{-1}. ^1H NMR (300.15 MHz, C_6D_6, 31 °C): δ 1.08 (s, 18 H, *t*-BuGa); P*H* protons not observed. $^{31}P\{^1H\}$ NMR (121.47 MHz, C_6D_6, 31 °C): δ −250.21 (s, μ-PH_2). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 31 °C): δ 30.46 (s, $(H_3C)_3Ga$); $(H_3C)_3CGa$ quaternary carbons not observed. EIMS; *m/e* 465 amu ($C_{20}H_{51}Al_3P_3$, $M^+ - \{t\text{-}Bu\}$). Anal. Calcd: C, 55.16; H, 11.57. Found: C, 54.86; H, 12.01.

$[t\text{-}Bu_2Al(\mu\text{-}AsH_2)]_3$ (2). A frozen benzene solution of $t\text{-}Bu_3Al$ (1.5 mL of a 1.96 M solution, 2.9 mmol) at 0 °C was exposed to an atmosphere of AsH_3. This mixture was heated (55 °C, 10 min) and cooled to room temperature. Excess AsH_3 was vented under a vigorous stream of nitrogen into a sodium hypochlorite bubbler solution (1% w/w) and bromine–water (1% w/w) bubblers at room temperature (15 min). Benzene was removed under reduced pressure, and the colorless residue was extracted with toluene (60) mL). The resulting solution was filtered and concentrated under vacuum (45 mL). When this solution was cooled (−20 °C), colorless crystals of **2** were formed in essentially quantitative yield with respect to Al. Mp: 148–153 °C dec. IR (KBr disk): 2962 s, 2945 s, 2921 s, 2908 s, 2869 m, 2833 s, 2763 w, 2731 w, 2704 w, 2155 m, 2144 m, 1465 s, 1445 w, 1399 m, 1387 m, 1372 m, 1361 m, 1261 m, 1175 m, 1089 w br, 1042 m, 1021 m, 1002 m, 938 w, 904 m br, 813 m, 807 m cm^{-1}. ^1H NMR (300.15 MHz, C_6D_6, 31 °C): δ 1.11 (s, 18 H, *t*-*Bu*Ga), 108 (s, 2 H, As *H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 31 °C): δ 30.37 (s, $(CH_3)_3CGa$);

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$(H_3C)_3C$Ga quaternary carbons not observed. EIMS: *m/e* 597 amu ($C_{20}H_{51}Al_3P_3$, $M^+ - \{t\text{-Bu}\}$). Anal. Calcd: C, 50.88; H, 10.67. Found: C, 51.06; H, 10.98.

***t*-Bu$_3$GaNH$_3$ (3).** Exposure of a benzene solution containing freshly distilled *t*-Bu$_3$Ga (2.0 mL, ca. 4.0 M, 8.0 mmol) to an atmosphere of anhydrous ammonia results in a slight warming and the quantitative formation of the adduct *t*-Bu$_3$GaNH$_3$ (**3**). Colorless crystals of **3** may be isolated by sublimation (25 °C, 10^{-2} Torr, 14 h). Mp: 42–46 °C. IR (KBr disk): 3387 w, 3334 vw, 3289 w, 2972 m, 2953 s, 2924 s, 2871 m, 2840 s, 2768 w, 2704 w, 1608 w br, 1468 m, 1445 w, 13403 vw, 1385 w, 1363 m, 1258 w, 1244 w, 1190 m br, 1024 w, 1009 w, 974 w, 938 w, 832 w, 814 m, 749 w cm^{-1}. ^{1}H NMR (300.15 MHz, C_6D_6, 30 °C): δ 1.10 (s, 27 H, *t*-B*u*Ga), 1.95 (br s, 3 H, N*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 30 °C): δ 32.53 (s, $(CH_3)_3$CGa); $(H_3C)_3C$Ga quaternary carbons not observed. CIMS (Me^+); *m/e* 257 amu ($C_{12}H_{29}GaN$, M^+). Anal. Calcd: C, 55.84; H, 11.72; N, 5.43. Found: C, 54.75; H, 11.26; N, 5.29.

[*t*-Bu$_2$Ga(μ-NH$_2$)]$_3$ (4). Method 1. Compound **3** in solution or the solid state was exposed to NH$_3$, stirred, and heated (160–170 °C, 24 h). The flask was then cooled, and the resulting colorless solid was dissolved in diethyl ether (15 mL). The volume of the solution was reduced to 10 mL by evaporation under vacuum, and cooling (−20 °C, 48 h) gave colorless rhombic crystals. Further concentration and cooling of the mother liquor yielded additional crops of **1**. The combined yield was essentially quantitative with respect to Ga. Mp: 182–186 °C. IR (KBr disk): 3328 w, 3272 w, 2948 s, 2866 m, 2835 s, 2703 w, 1836 w br, 1505 w, 1464 m, 1386 w, 1359 m, 1236 w, 1192 w, 1007 w, 953 m, 934 w, 840 vw, 812 m, 746 m cm^{-1}. ^{1}H NMR (300.15 MHz): δ 1.12 (s, 18 H, *t*-B*u*Ga), 0.41 (br s, 2 H, N*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 30 °C): δ 31.62 (s, $(CH_3)_3$CGa); $(H_3C)_3C$Ga quaternary carbons not observed. EIMS: *m/e* 540 amu ($C_{20}H_{51}Ga_3N_3$, $M^+ - \{t\text{-Bu}\}$). Anal. Calcd: C, 48.10; H, 10.08; N, 7.01. Found: C, 47.96: H, 11.13; N, 6.65.

Method 2. A solution of *tert*-butyllithium (62.6 mL of a 0.74 M solution, 46 mmol) in diethyl ether was added dropwise to a stirred, −78 °C solution of GaCl$_3$ (4.08 g, 23.17 mmol) in Et$_2$O (50 mL). The reaction mixture was warmed to 25 °C and then stirred for 6 h before filtration. To the filtrate was added, at −78 °C, 1 equiv of NaNH$_2$. The resulting mixture was warmed to 25 °C and then stirred for 12 h. Volatile materials were removed under reduced pressure, the residue was extracted with hexane (50 mL), and the resulting solution was filtered. Cooling (−30 °C) of the filtrate gave colorless crystals of **4**.

[*t*-Bu$_2$Ga(μ-ND$_2$)]$_3$ (5). Compound **5** was synthesized in a manner similar to that used for **4**, by replacing NH$_3$ with ND$_3$. Mp: 182–186 °C. IR (KBr disk): 2948 s, 2918 s, 2866 m, 2835 s, 2703 w, 1836 w br, 1505 w, 1464 m, 1386 w, 1359 m, 1236 w, 1192 w, 1007 w, 953 m, 934 w, 840 vw, 812 m, 746 m cm^{-1}. ^{1}H NMR (300.15 MHz): δ 1.12 (s, 18 H, *t-Bu*Ga). $^{13}C\{^1H\}$ NMR (75.48 MHz, C_6D_6, 30 °C): δ 31.62 (s, $(CH_3)_3$CGa); $(H_3C)_3C$Ga quaternary carbons not observed. EIMS: *m/e* 546 amu ($C_{20}H_{45}D_6Ga_3N_3$, $M^+ - \{t\text{-Bu}\}$). Anal. Calcd: C, 47.65; H, 9.99; N, 6.94. Found: C, 46.27; H, 10.02; N, 6.68.

[*t*-Bu$_2$Ga(μ-OH)]$_3$ (6). Distilled water (200 μL, 11 mmol) was added dropwise over 5 min to a stirred toluene solution of *t*-Bu$_3$Ga (30 mL of a 0.35 M solution, 10.5 mmol) at room temperature. The mixture was stirred (30 min) before volatile materials were removed under reduced pressure. The white powder was extracted with toluene (20 mL), the extract was filtered, and the resulting solution was concentrated under vacuum (15 mL); cooling (−20 °C, 24 h) gave colorless rhombic crystals of **6**. Further concentration and cooling of the mother liquor yielded additional crops of **6**. Careful collection of all crops of crystals showed the yield to be 90% with respect to Ga. Mp: 253–255 °C dec. IR (KBr disk): 3613 s vs, 295 s br, 2925 s br, 2869 s, 2844 s, 2976 w, 2766 w, 2738 w, 2710 w, 2643 w br, 1466 m, 1442 w, 1392 w, 1361 m, 1020 m, 1009 m, 943 w, 918 w, 534 w br cm^{-1}. ^{1}H NMR (300.15 MHz, CDCl$_3$, 32 °C): δ 1.20 (s, 18 H, *t-Bu*Ga), 10.73 (s, 1 H, GaO*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz): δ 31.70 (s, $(CH_3)_3$CGa); $(CH_3)C$Ga quaternary carbons not observed. EIMS: *m/e* 543 amu ($C_{20}H_{48}Ga_3O_3$, $M^+ - \{t\text{-Bu}\}$). Anal. Calcd: C, 47.81; H, 9.53. Found: C, 48.23; H, 9.39.

[*t*-Bu$_2$Ga(μ-OD)]$_3$ (7). Compound **7** was synthesized in a manner similar to that of **6** by replacing H$_2$O with D$_2$O. Mp: 253–255 °C dec. IR (KBr disk): 2954 s br, 2927 s, br, 2869 s, 2844 s, 2769 w, 2833 s, 2738 w, 2709 w, 2666 m sh, 1467 m, 1392 w, 1367 m, 1262 m, 1023 m, 944 w, 867 w, 818 m, 804 m, 761 m, 525 w br, 508 m cm^{-1}. ^{1}H NMR (300.15 MHz): δ 1.20 (s, 18 H, *t-Bu*Ga). $^{13}C\{^1H\}$ NMR (75.48 MHz, CDCl$_3$, 32 °C): δ 31.70 (s, $(CH_3)_3$CGa), $(CH_3)C$Ga quaternary carbons not observed. EIMS: *m/e* 546 amu ($C_{20}H_{45}D_3Ga_3O_3$, $M^+ - \{t\text{-Bu}\}$). Anal. Calcd: C, 47.58; H, 10.03. Found: C, 46.01; H, 10.53.

X-ray Structure Determination for 4. Details of crystal data and a summary of intensity data collection parameters for **4** are given in Table III. The crystals were mounted in thin-walled glass capillaries and sealed under argon. Unit cell parameters were obtained by centering 25 reflections having 2θ values between 22 and 26°. Data were collected on an Enraf-Nonius CAD-4 diffractometer at $2\theta = 2$–$50°$ using graphite-monochromated Cu Kα radiation for **4**. Intensity data were recorded in the usual manner.[21] The intensity standards for each data collection indicated a <2% decrease in intensity over the course of data collection, and no correction was applied, unless otherwise indicated. All calculations were performed on a MICROVAX 3100 computer using SHELX software.[22] The data were corrected for Lorentz and polarization effects. The observed structure factors of equivalent reflections were averaged. The structures were solved by direct and Patterson methods with successive interpretation of difference Fourier maps, followed by least-squares refinement. Data with intensities less than $3.0\sigma(I)$ and $(\sin\theta)/\lambda$ less than 0.10 were excluded, and a weighting scheme ($[(\sigma F)^2 + 0.000625F^2]^{-1}$) was used in the final stages of the refinement.

Crystals suitable for X-ray diffraction were grown by cooling a diethyl ether solution to −30 °C. The rhombohedral space group $R\bar{3}c$ was uniquely determined by the systematic absences $h0l$ ($l = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$). Data were collected in the $+h$ quadrant between 2θ values of 2 and 50°. A ψ scan of four reflections having χ values between 80 and 90° showed a minimum transmission of 78% and a maximum transmission of 93%. An empirical absorption correction was applied. The gallium atom was found using a Patterson search, and subsequent location of the other non-hydrogen atoms was achieved using difference Fourier maps. The nitrogen hydrogen atom was located from difference Fourier maps, assigned a fixed thermal parameter, and then refined with the nitrogen atom. The other hydrogen atoms were not located, but their contributions were included in the final refinements. The atoms were refined to final values of 0.0310 and 0.0329 for R and R_w, respectively.

X-ray Structure Determination for 6. Crystals of **6** were obtained by careful cooling of a saturated toluene solution. A colorless, irregular crystal (0.30 × 0.30 × 0.30 mm) was mounted into a thin-walled glass capillary and 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 assuming linear decay; the data were also corrected for Lorentz and polarization effects. An empirical absorption correction was also applied to the data, on the basis of φ scans (φ 0–360° every 10°) of suitable reflections with χ values close to 90°. Of the 1117

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unique reflections measured, 610 reflections were considered observed with $I > 3\sigma(I)$.

Calculations were performed on a MICROVAX II computer using the "SDP-PLUS" software package.[23] The systematic absences displayed by the X-ray data ($-h + k + l = 3n$; $-h + k = 3n$; $l = 3n$; $h + l = 3n$; $l = 2n$; $2l = 6n$, $h = 3n$) indicate two possible space groups ($R\bar{3}c$ and $R3c$); the structure was refined under both by direct methods (Patterson),[24] using successive cycles of difference Fourier maps followed by least-squares refinement. The best agreement (goodness of fit 4.627) was obtained for the rhombohedral space group $R\bar{3}c$ (No. 167). When the refinement was terminated, the maximum shift of any parameter was 0.38% of its estimated standard deviation, and at this point R and R_w were 0.044 and 0.058, respectively. On this basis, the space group was assigned as $R\bar{3}c$. The presence of poorly resolved and badly disordered toluene was evident in the final difference Fourier map. No satisfactory model could be found for the solvent disorder. A non-Poisson contribution weighting scheme, with the instability factor P set at 0.04, was used in the final stages of refinement.[25] No hydrogen atoms were located in the structure, but their contributions were included in the refinements. Scattering factors were taken from ref 26.

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Supplementary Material Available: Listings of bond distances and angles and positional and thermal parameters for 4 and 6 (8 pages). Ordering information is given on any current masthead page.

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[25] P is used in the calculation of $\sigma(I)$ to downweight intense reflection 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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