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Synthesis and characterization of bridged dimeric and trimeric Group 13/15 complexes containing primary phosphido $[(^{t}Bu)PH]^-$ and arsenido $[(^{t}Bu)AsH]^-$ units

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Abstract

Addition of the primary phosphine $^{t}BuPH_2$ or the primary arsine $^{t}BuAsH_2$ to $^{t}Bu_3M$ (M = Ga, Al) followed by heating or photolysis affords the complexes $[^{t}Bu_2M(\mu\text{-}E(^{t}Bu)H)]_n$ (**1**: M = Ga, E = P; $n = 2$; **2**, M = Al, E = P, $n = 2$; **3**, M = Ga, E = As, $n = 3$; **4**, M = Al, E = As, $n = 3$). For each compound, the degree of association was assessed on the basis of ^{1}H, ^{31}P, ^{13}C NMR and mass spectroscopy. The *anti*-isomer of **1** (**1a**) was also characterized by X-ray crystallography. Crystal data for **1a**: $C_{24}H_{56}Ga_2P_2$, monoclinic, space group $C2/m$, a 17.124(7), b 11.755(7), c 8.700(3) Å, V 1561.94(15) Å^3, $Z = 4$, D_{calc} 1.157 g cm^{-3}, μ(Mo Kα) 18.3 cm^{-1}. A total of 1501 unique reflections was measured over the range $3.0 \leq 2\theta \leq 50.0°$ (θ–2θ scan mode) and 1263 of these with $I > 3\sigma(I)$ were used in the refinement to afford final R and R_w values of 0.059 and 0.070, respectively.

1. Introduction

There is an increasing interest in compounds featuring bonding between the Group 13 and 15 elements. In large measure, this is due to the potential of these compounds to serve as single-source precursors for the organometallic chemical vapor deposition (OMCVD) of 13/15 electronic materials. Currently, the most common sources for the Group 15 elements, As and P, used in thin film production of 13/15 materials such as GaAs and InP, are AsH_3 and PH_3 [1]. More recently, $^{t}BuAsH_2$ and $^{t}BuPH_2$ have been explored as alternative sources for the production of thin films of GaAs and InP, respectively [2,3]. The use of alkylated group 15 hydrides has several key advantages over the simple hydrides, namely lower volatilities, ease of handling, and ease of purification. Single-source precursors in which both the Group 13 and Group 15 elements are incorporated into a single molecule offer additional advantages in regard to lower toxicities, lower decomposition temperatures, and greater resistance to oxidation and environmental degradation [4].

Compounds of empirical formula $R_2MER'_2$ (M = Group 13 element, E = Group 15 element) have been known for almost three decades [5]. More recent, structurally authenticated examples of this class of compound include monomeric $(^{t}Bu)_2GaAs(^{t}Bu)_2$ [6] and $(C_5Me_5)_2GaAs(SiMe_3)_2$ [7], dimeric $[(Me_3CCH_2)_2Ga(\mu\text{-}PPh_2)]_2$ [8] $[Me_2Al(\mu\text{-}P(SiMe_3)_2]_2$ [9], $[Et_2Al(\mu\text{-}As(SiMe_3)_2)]_2$ [10], $[(PhMe_2CCH_2)_2Ga(\mu\text{-}N(H)(Pr))]_2$ [11], $[(Me_3SiCH_2)_2In(\mu\text{-}P(SiMe_3)_2)]_2$ [12] and $[(Me_3SiCH_2)_2In(\mu\text{-}As(SiMe_3)_2)]_2$ [13], and trimeric $[H_2Al(\mu\text{-}NMe_2)]_3$ [14]. Thus far, most of the single-source precursors developed in our laboratory involve bulky substituents, typically ^{t}Bu and ^{i}Pr [4,15]. Compounds such as $[Me_2Ga(\mu\text{-}As^{t}Bu_2)]_2$ undergo thermolysis via alkane/alkene elimination to afford the corresponding 13/15 electronic materials [16]. The evolution of alkene implies a β-hydride shift mechanism and thus the transient existence of species with E–H bonds (eqn. (1)).

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$$\text{“}Me_2M(E^tBu)_2\text{”} \xrightarrow[-2(CH_3)_2C{=}CH_2]{\Delta} Me_2MEH_2 \xrightarrow[-2CH_4]{\Delta} ME$$

$$(M = Al, Ga, In; E = P, As) \qquad (1)$$

In effect, the ^tBu (or other β-hydride emitting group) plays the role of a “masked hydrogen”. As a consequence, our attention was drawn to the possibility of synthesizing precursors with P–H or As–H functionalities. In a previous study [17], we found that EH_2-bridged trimers, $[^tBu_2M(\mu\text{-}EH_2)]_3$, can be isolated and characterized. However, these compounds undergo thermal decomposition during sublimation and are thus not suitable as conventional OMCVD sources. The next logical step, therefore, was to attempt the preparation of 13–15 compounds with primary phosphido or arsenido units. Herein we report the synthesis and characterization of compounds with empirical formula $^tBu_2M(\mu\text{-}E(^tBu)H)$ (M = Al, Ga; E = P, As). To our knowledge, the only previous examples of Group 13–15 compounds with primary phosphido or arsenido groups are $[^tBu_2Ga(\mu\text{-}P(C_5H_9)H]_2$ [18], $[^iBu_2Al(\mu\text{-}P(SiPh_3)H]_2$ [19], and $[Ph_2Ga(\mu\text{-}As(CH_2SiMe_2)H]_3$ [20].

2. Results and discussion

2.1. Synthesis and characterization of $[^tBu_2Ga(\mu\text{-}P(^tBu)H)]_2$ (1a,b)

The reaction of $^tBu_3Ga$ with an excess of $^tBuPH_2$ in the absence of light results initially in adduct formation [21*]. Thermolysis of this $^tBu_3Ga \cdot P(^tBu)H_2$ intermediate in refluxing toluene, followed by sublimation, affords a mixture of isomers (**1a** and **1b**) in 45% yield. The **1a,b** mixture can be sublimed without decomposition or change in isomeric abundance. However compound **1a** can be separated from **1b** by fractional crystallization from toluene. Solutions of **1a,b** are readily hydrolyzed by atmospheric moisture to $^tBuPH_2$ and $[^tBu_2Ga(\mu\text{-}OH)]_3$ [17,22]. The **1a,b** mixture can also be prepared in comparable overall yield (40%) by treatment of $GaCl_3$ with $LiP(^tBu)H$, followed by reaction with Li^tBu (eqns. (2) and (3)).

$$GaCl_3 + LiP(^tBu)H \longrightarrow [Cl_2Ga(\mu\text{-}P(^tBu)H)] + 2\,LiCl \qquad (2)$$

$$2[Cl_2GaP(^tBu)H] + 4\,Li^tBu \longrightarrow [^tBu_2Ga(\mu\text{-}P(^tBu)H)]_2 + 4\,LiCl \qquad (3)$$

Crystals of **1a** suitable for X-ray diffraction were grown from a cooled (−10°C) toluene solution of the **1a,b** mixture. The solid state of **1a** comprises individual molecules of the *anti*-isomer and there are no short intermolecular interactions. A view of the molecule is shown in Fig. 1, and listings of important bond lengths and angles appear in Table 1. Crystallographic details are summarized in Table 3. As a consequence of the monoclinic space group $C2/m$, there is a crystallographically imposed two-fold axis of rotation which passes through both Ga atoms, and a mirror plane which contains both P atoms and the C(1) atoms of the ^tBu groups. The Ga–P distance in the Ga_2P_2 rhombus (2.459(3) Å) is virtually identical to that in $[^tBu_2Ga(\mu\text{-}P(C_5H_9)H)]_2$, (2.451(1) Å) [18], the only other primary phosphido-gallium dimer for which structural information is available.

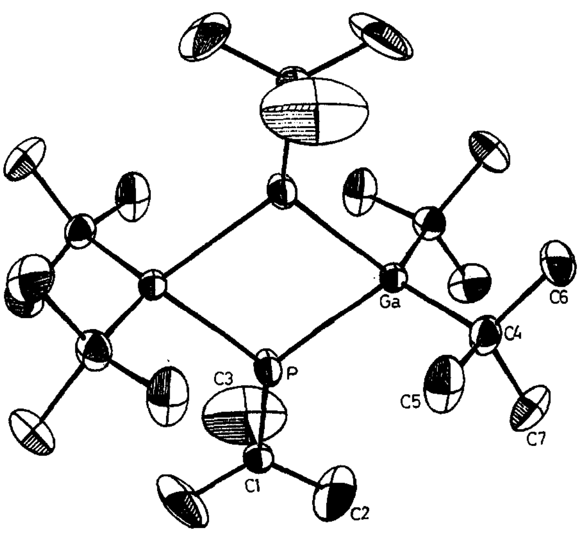

Fig. 1. ORTEP view of **1a** showing the atom numbering scheme.

NMR data indicate that the *syn* and *anti* isomers persist in solution in the temperature range −90 to 25°C. Thus, both **1a** and **1b** exhibit [AA′XX′] proton-coupled ^{31}P spectra which collapse to singlets upon ^1H

TABLE 1. Bond distances (Å) and angles (°) for $[^tBu_2Ga(\mu\text{-}P(^tBu)H]_2$ (**1a**) (Numbers in parenthesis are estimated standard deviations in the least significant digit)

Ga–P	2.459(2)
Ga–C4	2.036(9)
P–C1	1.863(9)
P–Ga–P′	78.79(3)
P–Ga–C4′	114.2(2)
C4–Ga–C4′	120.1(3)
Ga–P–Ga	101.2(4)
Ga–P–C1	129.01(7)
P–C1–C2	112.4(6)
P–C1–C3	103.7(9)

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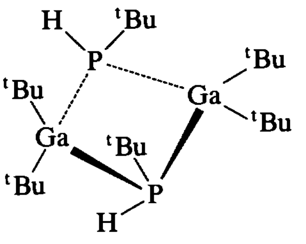
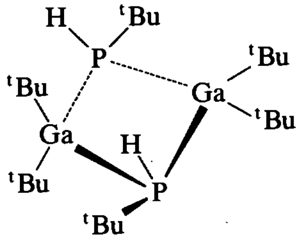
* Reference number with asterisk indicates a note in the list of references.

irradiation. Moreover, as anticipated on the basis of the following structures, the ^{1}H and ^{13}C{^{1}H} spectra of **1a** exhibit only one Ga^{t}Bu methyl resonance, while **1b** exhibits two such resonances.



1a (*anti*)



1b (*syn*)

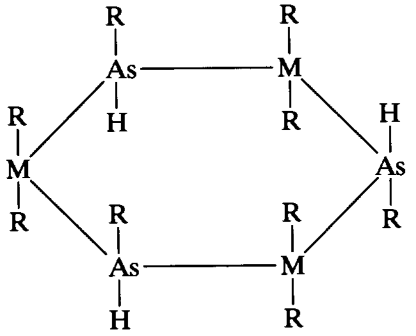
Small ^{31}P couplings are apparent in the ^{1}H and ^{13}C{H} resonances of both isomers. Integration of the Ga^{t}Bu ^{1}H resonances in the **1a,b** mixture reveals a **1a**/**1b** isomer ratio of 1.8/1.0. Finally, the mass spectral data indicate that dimeric **1a,b** persist in the vapor phase.

2.2. Synthesis and characterization of [^{t}Bu$_2$AlP(^{t}Bu)H]$_2$ (2a,b)

The reaction of ^{t}Bu$_3$Al with ^{t}BuPH$_2$ proceeded in a similar manner to that described above for the corresponding ^{t}Bu$_3$Ga reaction. Unfortunately, it was not possible to separate the geometric isomers in this case. Nevertheless, the dimeric formulation [^{t}Bu$_2$Al(μ-P(^{t}Bu)H)]$_2$ (*anti*, **2a**; *syn*, **2b**) is established by (i) the similarity of ^{31}P chemical shifts to those of **1a** and **1b** (see Table 2), (ii) the [AA′XX′] nature of the proton-coupled ^{31}P spectra, (iii) the pattern of ^{1}H and ^{13}C{^{1}H} resonances in the Al^{t}Bu region (*cf.* above for the Ga^{t}Bu resonances of **1a** and **1b**), and (iv) the fact that, like **1a,b**, **2a,b** exhibits a mass spectral peak corresponding to M$^+$−^{t}Bu. Integration of the Ga^{t}Bu resonances reveals that the **2a**/**2b** isomer ratio is 1.9/1.0. As in the case of **1a,b**, the **2a,b** isomer mixture sublimes without decomposition or changes in relative isomeric abundance. Exposure to moist air converts **2a,b** to ^{t}BuPH$_2$ and [^{t}Bu$_2$Al(μ-OH)]$_3$ [22].

2.3. Synthesis and characterization of [^{t}Bu$_2$MAs(^{t}Bu)-H]$_3$ (M = Ga, 3; Al, 4)

As in the case of the ^{t}BuPH$_2$ reactions described above, treatment of ^{t}Bu$_3$Ga or ^{t}Bu$_3$Al with an excess of ^{t}BuAsH$_2$ in benzene solution results in initial adduct formation. Both adducts undergo slow alkane elimination at 25°C; however, mild heating is necessary to obtain useful yields (~ 70%) of [^{t}Bu$_2$Ga(μ-As(^{t}Bu)H)]$_3$ (**3**) and [^{t}Bu$_2$Al(μ-As(^{t}Bu)H]$_3$ (**4**). Both compounds are solids; however, in neither case were the crystals suitable for X-ray analysis. Nevertheless, the trimeric formulation is indicated by the fact that mass spectroscopic peaks were detected that correspond to M^+−^{t}Bu. Confirmation is provided by ^{1}H and ^{13}C{^{1}H} NMR data (see Table 2). Previous studies [4] have established that six-membered M$_3$E$_3$ rings (a) adopt a wide range of conformations in the solid state, and (b) undergo facile ring-flexing processes in solution. The ^{1}H and ^{13}C{^{1}H} NMR data for **3** and **4** are consistent with either planar or time-averaged planar structures for the M$_3$E$_3$ rings.



(R = ^{t}Bu; M = Al, Ga)

TABLE 2. Spectroscopic data for **1–4**

Compound	^{31}P	^{13}C ^{a}		^{1}H			IR ν(PH) (cm^{-1})	MS
		^{t}BuM	^{t}BuE	^{t}BuM	^{t}BuE	EH		
[^{t}Bu$_2$GaP(^{t}Bu)H]$_2$ (**1a**) (*anti*)	−68.3(dd)	32.11(s)	34.33(s)	1.14(s)	1.29–1.39(m)	3.73(d)	2329	M$^+$−^{t}Bu
[^{t}Bu$_2$GaP(^{t}Bu)H]$_2$ (**1b**) (*syn*)	−74.4(dd)	31.56(s)	34.25(s)	1.25(s) 1.08(s)	1.29–1.39(m)	3.22(d)	2329	M$^+$−^{t}Bu
[^{t}Bu$_2$AlP(^{t}Bu)H]$_2$ (**2a**) (*anti*)	−84.84(dd)	32.05(s)	34.43(s)	1.05(s)	1.32–1.42(m)	–	2325	M$^+$−^{t}Bu
[^{t}Bu$_2$AlP(^{t}Bu)H]$_2$ (**2b**) (*syn*)	−91.07(dd)	31.56(s) 31.28(s)	34.46(s)	1.15(s) 0.98(s)	1.32–1.42(m)	–	2325	M$^+$−^{t}Bu
[^{t}Bu$_2$GaAs(^{t}Bu)H]$_3$ (**3**)	–	31.56(s) 31.09(s)	35.85(s) 32.64(s)	1.18(s) 1.08(s) 1.02(s)	1.38(s) 1.34(s)	2.47(s) 2.17(s)	–	M$^+$
[^{t}Bu$_2$AlAs(^{t}Bu)H]$_3$ (**4**)	–	31.06(s) 30.77(s)	35.02(s) 31.73(s)	1.14(s) 1.05(s) 0.99(s)	1.49(s) 1.46(s)	2.34(s) 2.09(s)	–	M$^+$

[a] The quaternary carbons were not observed.

As anticipated on the basis of the above structure, there are two As-H and two As-^{t}Bu ^{1}H signals in relative 2/1 abundance and Ga-^{t}Bu signals in 2/2/1 relative abundance. The appropriate number of environments was also evident in the $^{13}C\{^1H\}$ NMR spectra.

Finally, OMCVD experiments on these new compounds will be reported in a future paper.

3. Experimental details

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: NMR, GE QE-300 (^{1}H, ^{13}C and ^{31}P); EIMS, Bell & Howell CEC 24-491, 70 eV. CI-MS, Finnigan MAT 4023. NMR spectra were recorded in C_6D_6 solution at ambient temperature unless otherwise stated and are in ppm referenced to Me_4Si (δ 0.0, ^{1}H, and ^{13}C) and 85% H_3PO_4 (aq) (δ 0.0, ^{31}P). In each case, the solvent of crystallization was removed under reduced pressure prior to NMR sample preparation; there was no evidence of toluene or hexane in any of the spectra. Melting points were determined in sealed capillaries on an Electrothermal Melting Point apparatus and are uncorrected.

Both $^tBuPH_2$ and $^tBuAsH_2$ were made by an adaptation (see below) of the method first described by Hoff and Hill [23]. The compounds $^tBu_3Ga$ and $^tBu_3Al$ were prepared and purified according to the literature [24]. Phosphine, AsH_3 and isobutylene were purchased from Scott Specialty Gases, Linde (Division of Union Carbide), and Matheson Gas Products, respectively. All gases were used as supplied.

Caution: *AsH_3 and PH_3 are colorless, highly toxic gases. 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 [24].*

3.1. Preparation of $^tBuAsH_2$ and $^tBuPH_2$

Molten *p*-toluenesulfonic acid (200 g, dried at 10^{-2} torr, 12 h, 110°C) was poured into a hot (150°C), previously leak-tested (H_2 (g), 1500 psi), stainless steel pressure reactor (1 L). A magnetic stir-bar was added and the pressure reactor was assembled rapidly under a stream of dry nitrogen. It was then evacuated (10^{-2} torr) and allowed to cool to room temperature (2 h). The pressure reactor was then cooled to −78°C and a previously trapped volume of isobutylene (130 mL, 81 g, 1.5 mol) was vacuum transferred into it. The pressure reactor was then cooled to −196°C, and, in similar manner, AsH_3 (92 mL, 151 g, 1.9 mol) was transferred into it. The autoclave was allowed to warm to room temperature (2 h) and then heated in an oil bath, initially to 100°C (1 h), and then at 80°C (3 h). At this temperature, all the volatiles were carefully vacuum transferred onto anhydrous $MgSO_4$ (2 g) in a 1 L Schlenk flask at −196°C. After the volatiles were removed, the autoclave was allowed to cool and was disassembled; the residues (mostly *p*-toluenesulfonic acid, and elemental arsenic) were allowed to stand in a well-ventilated hood (6 h) before cleaning with NaOH.

The volatiles were allowed to warm slowly to room temperature and excess AsH_3 was allowed to boil off under a vigorous stream of nitrogen into a series of sodium hypochlorite (5% w/w) and bromine-water (1% w/w) bubblers. The remaining colorless, noxious smelling oil, crude t-butylarsine, was filtered and distilled (65–67°C) to give 80 g (40% yield with respect to isobutylene) of 95% pure (^{1}H NMR) t-butylarsine [25*].

The t-butylphosphine was prepared in a similar manner [26], except the pressure reactor must be heated more vigorously (110°C, 14 h). The yield of distilled (53–55°C) $^tBuPH_2$ is 37% (33 g) based on the isobutylene consumed.

Caution: *$^tBuPH_2$ and $^tBuAsH_2$ are colorless, noxious smelling, air sensitive liquids; $^tBuPH_2$ is also pyrophoric. The toxicology of these materials has been poorly studied, but their similarity to PH_3 and AsH_3 is clear. Compounds 1–4 liberate these volatile oils upon contact with moisture. All manipulations should be carried out in a drybox or in a well-ventilated hood. Where possible, bubblers similar to the ones described above should be used.*

3.2. Preparation of $[^tBu_2Ga(\mu\text{-}P(^tBu)H)]_2$ (1a,b) by method A

Excess $^tBuPH_2$ (0.20 mL, 1.6 mmol) was added to a stirred benzene solution of $^tBu_3Ga$ (0.50 mL *ca.* 1.82 M, 0.91 mmol) at room temperature. The mixture was allowed to stir overnight (13 h); benzene and excess $^tBuPH_2$ were removed under reduced pressure. The colorless residue was dissolved in toluene (20 mL) and refluxed (12 h). The toluene was removed under reduced pressure and the resulting colorless residue was sublimed slowly under 1 atmosphere of nitrogen (120°C, 48 h). The sublimate was redissolved in toluene (15 mL), filtered and concentrated under vacuum (10 mL). Slow cooling (−10°C, 120 h) afforded clear colorless crystals of **1a,b**. EIMS, *m/e* 489 amu ($C_{20}H_{47}Ga_2P_2$, $M^+ - \{^tBu\}$). Analyses. Found: C, 52.25; H, 10.08. Calc.: C, 52.79; H, 10.34%.

1a: (*anti*) ^{1}H NMR (300.15 MHz, $CDCl_3$, 23°C): δ 3.73 (br d, ^1J(P–H) = 80–90 Hz, P*H*); 1.39–1.29 (br mult., ^{t}BuP, **1a** and **2b**); 1.14 (t, ^4J(P–H) = 0.90 Hz, ^{t}BuGa). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 28°C): δ 34.33 (t, ^2J(C–P) = ^4J(C–P) = 2.52 Hz, $(CH_3)_3CP$); 32.11 (t, ^2J(C–P) = 1.36 Hz, $(CH_3)_3CGaP$). The quaternary carbons were not observed. ^{31}P NMR (121.49 MHz): δ −68.30 (br, dd, ^1J(P–H) = 86 Hz, ^2J(P–P) = 168 Hz, μ-*P*(^{t}Bu)H). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 35°C): δ −68.30 (s, μ-P(^{t}Bu)H).

1b: (*syn*) ^{1}H NMR (300.15 MHz, $CDCl_3$, 23°C): δ 3.22 (br d, ^1J(P–H) = 80–90 Hz, P*H*); 1.39–1.29 (br mult., ^{t}BuP, **1a** and **1b**); 1.25, 1.08 (t, ^4J(P–H) = 0.90 Hz, ^{t}BuGa). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 28°C): δ 34.25 (t, ^2J(C–P) = ^4J(C–P) = 2.57 Hz, $(CH_3)_3CP$), 32.93 (t, ^2J(C–P) = 1.62 Hz, $(CH_3)_3CGaP$), 31.56 (t, ^2J(C–P) = 0.98 Hz, $(CH_3)_3CGaP$). The quaternary carbons were not observed. ^{31}P NMR (121.49 MHz): δ −74.42 (br, dd, ^1J(P–H) = 91 Hz, ^2J(P–P) = 172 Hz, μ-*P*(^{t}Bu)H). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 35°C): δ −74.42 (s, μ-*P*(^{t}Bu)H).

3.3. Preparation of [$^tBu_2Ga(\mu$-$P(^tBu)H)]_2$ (1a,b) by method B

A solution of $GaCl_3$ (2.75 g, 15.6 mmol) in THF (72 mL) was cooled to −78°C. A THF solution of LiP(^{t}Bu)H (34.7 mL, 0.45 M, 15.6 mmol) was added dropwise via syringe. The solution was allowed to warm to room temperature (45 min), stirred (8 h) and recooled to −78°C. A freshly titrated solution of ^{t}BuLi in pentane (20.3 mL, 1.54 M, 31.3 mmol) was added dropwise to the suspension and the yellow mixture was allowed to warm slowly to room temperature (45 min). Upon stirring (14 h) the mixture decolorized. The volatiles were removed *in vacuo* and the residue extracted with toluene (2 × 30 mL). The combined and filtered solutions were refluxed (12 h). Toluene was removed under reduced pressure and the resulting colorless residue was sublimed slowly under 1 atmosphere of nitrogen (120°C, 48 h). The sublimate was redissolved in toluene (30 mL), filtered and concentrated under vacuum (20 mL). Slow cooling (−10°C, 120 h) afforded clear colorless crystals of **1a,b**. The yield with respect to Ga was 40%.

3.4. Preparation of [$^tBu_2Al(\mu$-$P(^tBu)H)]_2$ (2a,b)

Excess ^{t}BuPH$_2$ (0.20 mL, 1.6 mmol) was added to a stirred benzene solution of ^{t}Bu$_3$Al (0.50 mL *ca.* 2.00 M, 1.0 mmol) at room temperature. The mixture was refluxed (12 h). Toluene and excess ^{t}BuPH$_2$ were removed under reduced pressure and the resulting colorless residue was sublimed slowly under 1 atmosphere of nitrogen (130°C, 48 h). The sublimate was redissolved in hexane (15 mL), filtered and concentrated under vacuum (10 mL). Slow cooling (−10°C, 120 h) afforded clear colorless crystals of **2a,b**. The yield with respect to Al was 60%. EIMS, *m/e* 633 amu ($C_{32}H_{75}Al_3P_3$, $M^+ - \{^tBu\}$). Analyses. Found: C, 62.86; H, 11.95. Calc.: C, 62.58; H, 12.25%.

2a: (*anti*) ^{1}H NMR (300.15 MHz, $CDCl_3$, 23°C): δ 1.42–1.32 (br, mult., ^{t}BuP) and 1.05 (s, ^{t}BuAl). The P*H* protons were not observed. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 28°C): δ 34.45 (t, ^2J(C–P) = ^4J(C–P) = 2.42 Hz, $(CH_3)_3CP$); 31.56 (s, $(CH_3)_3CAlP$). The quaternary carbons were not observed. ^{31}P NMR (121.49 MHz): δ −84.84 (br dd, ^1J(P–H) = 83 Hz, ^2J(P–P) = 163 Hz, μ-*P*(^{t}Bu)H). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 35°C): δ −84.84 (s, μ-*P*(^{t}Bu)H).

2b: (*syn*) ^{1}H NMR (300.15 MHz, $CDCl_3$, 23°C): δ 1.42–1.32 (br mult., ^{t}BuP, 1.15 (s, ^{t}BuAl), 0.98 (s, ^{t}BuAl). The P*H* protons were not observed. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 28°C): δ 34.46 (t, ^2J(C–P) = ^4J(C–P) = 2.38 Hz, $(CH_3)_3CP$); 32.05 (s, $(CH_3)_3CAlP$); 31.28 (s, $(CH_3)_3CAlP$). The $(CH_3)_3CAl$ and $(CH_3)_3CP$ quaternary carbons were not observed. ^{31}P NMR (121.49 MHz): δ −91.07 (br dd ^1J(P–H) = 87 Hz, ^2J(P–P) = 172 Hz, μ-*P*(^{t}Bu)H). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, 35°C): δ −91.07 (s, μ-*P*(^{t}Bu)H).

3.5. Preparation of [$^tBu_2Ga(\mu$-$As(^tBu)H)]_3$ (3)

Excess ^{t}BuAsH$_2$ (0.90 mL, 7.6 mmol) was added to a stirred benzene solution of ^{t}Bu$_3$Ga (2.0 mL, 3.5 M, 7.0 mmol) at room temperature. The mixture was stirred (15 min, 80°C); benzene and excess ^{t}BuAsH$_2$ were removed under reduced pressure. The pale yellow residue was extracted with toluene (30 mL), filtered and concentrated under vacuum (10 mL). Upon cooling (−20°C, 48 h), clear colorless crystals of **3** were produced. Careful collection of all crops of crystals afforded a yield of 70% with respect to Ga. M.p. 170–175°C (dec.). ^{1}H NMR (300.15 MHz, $CDCl_3$, 25°C): δ 2.47 9s, 2H, As*H*); 2.17 (s, 1H, As*H*); 1.38 (s, 9H, As(^{t}*Bu*)); 1.34 (s, 18H, As(^{t}Bu)); 1.18 (s, 18H, ^{t}BuGa); 1.08 (s, 36H, ^{t}BuGa); 1.02 (s, 18H, ^{t}BuGa). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 35°C): δ 35.85 (s, $AsC(CH_3)_3$); 34.92 (s, $AsC(CH_3)_3$); 32.64 (s, $(CH_3)_3CGa$); 31.85 (s, $(CH_3)_3CGa$); 31.09 (s, $(CH_3)_3CGa$). The quaternary carbons were not observed. EIMS, *m/e* 891 amu ($C_{32}H_{75}Ga_3As_3$, M^+). CIMS, *m/e* 834 amu ($C_{32}H_{75}Ga_3As_3$, $M^+ - \{^tBuH\}$). Analyses. Found: C, 45.75; H, 8.82. Calc. C, 45.47; H, 8.90%.

3.6. Preparation of [$^tBu_2Al(\mu$-$As(t$-$Bu)H)]_3$ (4)

Excess ^{t}BuAsH$_2$ (0.90 mL, 7.6 mmol) was added to a stirred benzene solution of ^{t}Bu$_3$Al (2.5 mL, 2.8 M, 7.0 mmol) at room temperature. The mixture was stirred (15 min, 80°C); benzene and excess ^{t}BuAsH$_2$ were removed under reduced pressure. The pale yellow residue was extracted with toluene (30 mL), filtered and concentrated under vacuum (10 mL). Upon cooling (−20°C, 48 h) clear colorless crystals of **4** were produced. Careful collection of all crops of crystals afforded a yield of 70% with respect to Al. M.p. 163–166°C (dec.). ^{1}H NMR (300.15 MHz, CDCl$_3$, 25°C): δ 2.34 (s, 2H, As*H*); 2.09 (s, 1H, As*H*); 1.49 (s, 9H, As(^{t}*Bu*)); 1.46 (s, 18H, As(^{t}*Bu*)); 1.14 (s, 18H, ^{t}*Bu*Al); 1.05 (s, 36H, ^{t}*Bu*Al); 0.99 (s, 18H, ^{t}*Bu*Al). ^{13}C{^{1}H} NMR (75.48 MHz, CDCl$_3$, 33°C): δ 35.02 (s, AsC(CH$_3$)$_3$); 31.73 (s, (CH$_3$)$_3$CAl); 31.06 (s, (CH$_3$)$_3$-CAl); 30.77 (s, (CH$_3$)$_3$CAl). CIMS, m/e 765 amu ($C_{32}H_{75}Al_3As_3$, $M^+ - \{^{t}Bu\}$). Analyses, Found: C, 52.81; H, 10.38. Calc.: C, 52.55; H, 10.29%.

3.7. X-Ray analysis of 1a

Crystals of **1a** were obtained by careful cooling of a saturated toluene solution of **1a** and **1b**. A colorless, prismatic crystal (0.30 × 0.30 × 0.30 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 3. 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 $26° < 2\theta < 32°$. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 24 ± 1°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, based on ϕ-scans (ϕ 0–360° every 10°) of suitable reflections with χ values close to 90°. Of the 1450 unique reflections measured, 1263 reflections were considered observed with $I > 3\sigma(I)$.

All 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 three possible space groups (Cm, $C2$, and $C2/m$) by direct methods using successive cycles of difference Fourier maps followed by least-squares refinement. The best agreement (goodness of fit = 2.667) was obtained for the monoclinic space group, $C2/m$ (No. 12). When the refinement was terminated, the maximum shift of any parameter was 0.93% of its estimated standard deviation; at this point, R and R_w were 0.059 and 0.070, respectively. On this basis, the space group was assigned as $C2/m$. The presence of a poorly resolved and badly disordered toluene molecule 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 an instability factor P set at 0.04, was used in the final stages of refinement [28*]. No hydrogen atoms were located in the structure; their contributions were included in the refinements. Scattering factors were taken from the usual sources [29].

TABLE 3. Summary of crystal data, collection data, and refinement for [^{t}Bu$_2$Ga(μ-P(^{t}Bu)H)]$_2$ (**1a**)

Description of crystal	
Color	colorless
Habit	prism
Max. crystal dimensions (mm)	0.30 × 0.30 × 0.30
Crystal system	monoclinic
Space group	$C2/m$
Unit cell parameters:	
a (Å)	17.124(7)
b (Å)	11.755(7)
c (Å)	8.700(3)
β (°)	116.89(3)
U (Å^3)	1561.94(15)
Molecules per unit cell	4
Formula	$C_{24}H_{56}Ga_2P_2$
Molecular weight (g mol^{-1})	545.44
Calculated density (g cm^{-3})	1.157
$\mu_{calc.}$ (cm^{-1})	18.3
Data collection	
Radiation (Å)	Mo Kα (0.71073)
Scan technique	$\theta/2\theta$
Scan width (°)	0.80 + 0.35 (tan θ)
Range of indices h, k, l	0–20, 0–13, −10–9
2θ range (°)	3.0–50.0
No. reflections measured	1501
Standard reflections	
intensity	12 0 −1, 0 0 −5
orientation	9 3 −6, 8 2 −5
Decay of standards	−3.5%
Structure determination	
No. reflections used ($I > 3\sigma(I)$)	1263
No. parameters varied	69
R	0.059
R_w	0.070

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