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Syntheses and Characterization of the Gallium–Phosphorus Cages {(Et$_2$O)$_2$Li}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$} and {(*t*-Bu)$_2$Ga}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$}

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The novel cage compounds {(Et$_2$O)$_2$Li}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$} (1) and {(*t*-Bu)$_2$Ga}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$} (2) were synthesized in Et$_2$O solution by the reaction of Li$_2$P(*t*-Bu) with 1 or 2 equiv of (*t*-Bu)$_2$GaCl. They were characterized by X-ray crystallography and variable-temperature (VT) ^{1}H and ^{31}P NMR spectroscopy. In the crystal, 1 and 2 have a distorted-trigonal-bipyramidal LiGa$_2$P$_2$ or Ga$_3$P$_2$ core structure. Each compound contains four-coordinate phosphorus and both three- and four-coordinate gallium centers. A proposed mechanism for the formation of 1 and 2 and related compounds is also discussed. Crystal data with Mo Kα radiation (λ = 0.710 69 Å) at 130 K: 1, C$_{28}$H$_{65}$Ga$_2$LiO$_2$P$_2$, a = 10.277(5) Å, b = 17.439(7) Å, c = 11.212(5) Å, β = 115.12(3)°, monoclinic, space group $P2_1$, Z = 2, R = 0.059; 2, C$_{28}$H$_{63}$Ga$_3$P$_2$, a = 17.236(4) Å, b = 11.970(3) Å, c = 16.958(4) Å, β = 91.98(2)°, monoclinic, space group $C2/c$, Z = 4, R = 0.063.

Introduction

Much of the recent impetus in the study of heavier main-group 3–5 compounds has been their possible use as single-source precursors to semiconducting materials.[1] Most of the currently available data on molecular heavier main-group 3–5 species concern dimeric compounds of formula (R$_2$MER$'_2$)$_2$.[1] Less information is availale for species that have higher aggregation numbers (e.g. cubanes or various other cages). Only a few structurally characterized examples of these compounds are currently known. They include the cubanes [*t*-BuM(μ_3-PSiPh$_3$)]$_4$ (M = Al, Ga, In) the cage species (*t*-Bu)$_6$Ga$_2$P$_4$·(*t*-BuGaCl$_2$),[3] [(PhAsH)(R$_2$Ga)(PhAs)$_6$(RGa)$_4$] (R = CH$_2$SiMe$_3$),[4] [Ga$_4$(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_3${P(1-Ad)}$_4$P(H)(1-Ad)],[5] and (*t*-Bu)$_2$GaP$_4$(*t*-Bu)$_2$.[6] The results described here originated during attempts to synthesize gallium–phosphorus analogues of multiply-bonded boryl phosphide and arsenides. These are species of the general formulas LiE(R$'$)BR$_2$ (E = P, As) and RP(BR$'_2$)$_2$ (R, R$'$ = alkyl or aryl groups) which were synthesized by the reaction of R$_2$BX with lithium phosphides and arsenides.[7–9] However, it is shown here that the reaction of 1 or 2 equiv of the diorganogallium halide (*t*-Bu)$_2$GaCl with Li$_2$P(*t*-Bu) in Et$_2$O gives new types of cage compounds, {(Et$_2$O)$_2$Li}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$} (1) and {(*t*-Bu)$_2$Ga}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$} (2). They were characterized by variable-temperature ^{1}H and ^{31}P NMR as well as X-ray crystallography.

Experimental Section

General Procedures. All work was performed by using modified Schlenk techniques or a Vacuum Atmospheres HE 43-2 drybox under N$_2$. Solvents were freshly distilled from a Na/K alloy and degassed twice prior to use. ^{31}P and ^{1}H NMR spectra were recorded in C$_6$D$_6$ or C$_7$D$_8$ solutions using a General Electric QE-300 spectrometer. The phosphine (*t*-Bu)PH$_2$ was prepared from reduction of (*t*-Bu)PCl$_2$ by LiAlH$_4$ in diglyme. (*t*-Bu)$_2$GaCl[10] was synthesized by a literature method.

Synthesis. {(Et$_2$O)$_2$Li}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$} (1). Li$_2$P(*t*-Bu) was synthesized by the addition of 2 equiv of *n*-BuLi (1.6 M in hexane) to (*t*-Bu)PH$_2$ in Et$_2$O at 0 °C. After this mixture was warmed to room temperature and stirred for 1 h, a finely divided yellow precipitate of Li$_2$P(*t*-Bu) was isolated by filtration and dried under reduced pressure. One equivalent of (*t*-Bu)$_2$GaCl (0.65 g, 3 mmol) in Et$_2$O (30 mL) was added slowly via double-tipped needle to a slurry of Li$_2$P(*t*-Bu) (0.31 g, 3 mmol) in Et$_2$O (30 mL) at ambient temperature. After it was stirred for 4 h, the solution was filtered through Celite and concentrated under reduced pressure to ca. 5 mL. Slow cooling in a −20 °C freezer gave product 1 as colorless crystals: yield 0.41 g, 43% (based on P); mp >120 °C dec; ^{1}H NMR (C$_6$D$_6$) δ 1.02 (t, Et$_2$O, 12 H), 1.50 (s, Ga(C(CH$_3$)$_3$)$_2$ or GaC(CH$_3$)$_3$, 9 H), 1.62 (s, Ga(C(CH$_3$)$_3$)$_2$ or GaC(CH$_3$)$_3$, 9 H), 3.14 (q, Et$_2$O, 8 H); ^{31}P NMR (C$_6$D$_6$) δ −77. Anal. Calcd for C$_{28}$H$_{65}$Ga$_2$LiO$_2$P$_2$: C, 52.37; H, 1.02. Found: C, 52.8, 10.6.

{(*t*-Bu)$_2$Ga}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$} (2). A slurry of Li$_2$P(*t*-Bu) (0.24 g, 2 mmol, prepared as for 1) in Et$_2$O (30 mL) was treated dropwise with 2 equiv of (*t*-Bu)$_2$GaCl (0.88 g, 4 mmol) in Et$_2$O (30 mL) at room temperature. After the mixture was stirred for 12 h, all volatile components were removed under reduced pressure. The residue was taken up in pentane (15 mL) and filtered. Slow cooling in a −20 °C freezer afforded colorless cubes of 2: yield 0.25 g, 38% (based on P); mp >200 °C dec; ^{1}H NMR (C$_7$D$_8$, 25 °C) δ 1.26 (t, P(C(CH$_3$)$_3$), 18 H, J_{P-H} = 8.5 Hz), 1.33 (s, GaC(CH$_3$)$_3$, 9 H), 1.36 (s, Ga(C(CH$_3$)$_3$)$_2$, 18 H), 1.57 (s, Ga(C(CH$_3$)$_3$)$_2$, 18 H); ^{31}P NMR (C$_7$D$_8$, 25 °C) δ −80. Anal. Calcd for C$_{28}$H$_{63}$Ga$_3$P$_2$: C, 50.12; H, 9.46. Found: C, 50.3; H, 9.6.

X-ray Data Collection and the Solution and Refinement of the Structure. Crystals of 1 and 2 were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fiber by silicone grease, and immediately placed in the low-temperature N$_2$

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Table I. Crystallographic Data for Compounds 1 and 2

compd	**1**	**2**
formula	$C_{28}H_{65}Ga_2LiO_2P_2$	$C_{28}H_{63}Ga_3P_2$
fw	642.1	670.9
temp, K	130	130
cryst syst	monoclinic	monoclinic
a, Å	10.277(5)	17.236(4)
b, Å	17.439(7)	11.970(3)
c, Å	11.212(5)	16.958(4)
β, deg	115.12(3)	91.98(2)
V, Å^3	1820.1(11)	3496.8(14)
space group	$P2_1$	$C2/c$
Z	2	4
D_{calc}, g cm^{-3}	1.172	1.257
μ, mm^{-1}	1.588	1.76
2θ range, deg	0–55	0–55
no. of obsd reflns	6077 ($I > 2\sigma(I)$)	3037 ($I > 2\sigma(I)$)
no. of variables	315	163
R, R_w	0.059, 0.057	0.063, 0.068

Table II. Atom Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Selected Atoms of 1 and 2

	x	y	z	U(eq)^a
		Compound **1**		
Ga(1)	2471(1)	620	5504(1)	17(1)
Ga(2)	−264(1)	276(1)	2926(1)	20(1)
P(1)	2083(2)	356(1)	3236(2)	18(1)
P(2)	253(2)	1338(1)	4263(2)	17(1)
O(1)	−602(5)	1983(3)	823(5)	25(2)
O(2)	2317(5)	2701(3)	2566(5)	30(2)
Li	1176(13)	1770(7)	2477(12)	23(5)
C(1)	2326(8)	−292(4)	6584(7)	23(3)
C(5)	4147(8)	1359(4)	6420(7)	26(3)
C(9)	−2014(8)	−334(4)	1813(8)	28(3)
C(13)	2981(8)	−481(4)	2810(7)	25(3)
C(17)	−1081(7)	1599(4)	4946(7)	21(3)
		Compound **2**		
Ga(1)	4210(1)	2216(1)	3231(1)	23(1)
Ga(2)	5000	4423(1)	2500	27(1)
P(1)	4451(1)	2877(1)	1842(1)	18(1)
C(1)	3420(3)	3255(6)	3720(4)	33(2)
C(5)	4082(3)	572(5)	3512(4)	30(2)
C(9)	5000	6114(6)	2500	49(4)
C(13)	3737(3)	2972(5)	985(3)	29(2)

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

stream.[11] X-ray data were collected with a Syntex P2$_1$ (**1**) or a Siemens R3m/V (**2**) diffractometer equipped with a graphite monochromator and a locally modified Enraf-Nonius low-temperature apparatus. Calculations were carried out on a Microvax 3200 computer using the SHELXTL PLUS program system. Neutral-atom scattering factors and the correction for anomalous dispersion were from ref 12. The structure of 1 was solved by direct methods in the space group $P2_1$, and that of 2 was solved from a Patterson map in the space group $C2/c$. Attempts to solve the structure of 2 in the noncentrosymmetric space group CC failed to resolve a disorder of the *tert*-butyl group bound to Ga(2). Details of the data collection and refinement and important atom coordinates are provided in Tables I and II, respectively. Important bond distances and angles for the molecules of 1 and 2 are provided in Table III.

Results

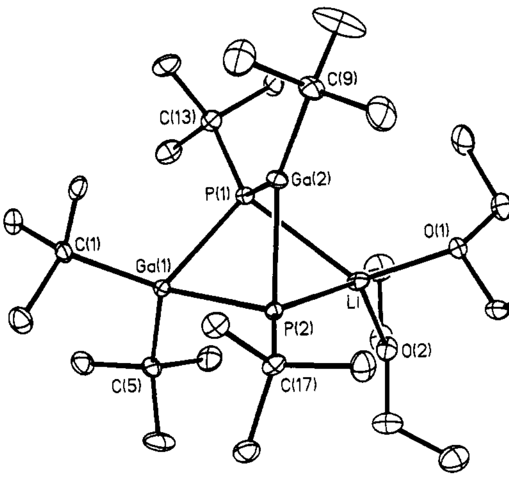

Figure 1. Computer-generated thermal ellipsoid (30%) plot of 1. Hydrogen atoms are omitted for clarity.

Table III. Selected Bond Distances (Å) and Angles (°) for 1 and 2

	Compound **1**		
Ga(1)–P(1)	2.444(2)	P(1)–C(13)	1.894(8)
Ga(1)–P(2)	2.450(2)	P(1)–Li	2.646(11)
Ga(1)–C(1)	2.042(8)	P(2)–C(17)	1.888(9)
Ga(1)–C(5)	2.045(7)	P(2)–Li	2.663(16)
Ga(2)–P(1)	2.290(2)	Li–O(1)	2.010(11)
Ga(2)–P(2)	2.298(2)	Li–O(2)	1.980(13)
Ga(2)–C(9)	2.005(7)		
P(1)–Ga(1)–P(2)	78.7(1)	Ga(2)–P(1)–C(13)	120.6(2)
P(1)–Ga(1)–C(1)	116.7(2)	Li–P(1)–C(13)	141.3(4)
P(2)–Ga(1)–C(1)	116.8(2)	Ga(1)–P(2)–Ga(2)	82.0(1)
P(1)–Ga(1)–C(5)	111.8(3)	Ga(1)–P(2)–Li	91.7(3)
P(2)–Ga(1)–C(5)	110.2(2)	Ga(2)–P(2)–Li	78.2(3)
C(1)–Ga(1)–C(5)	116.8(3)	Ga(1)–P(2)–C(17)	123.6(2)
P(1)–Ga(2)–P(2)	85.1(1)	Ga(2)–P(2)–C(17)	116.9(2)
P(1)–Ga(2)–C(9)	137.3(3)	Li–P(2)–C(17)	142.0(3)
P(2)–Ga(2)–C(9)	137.0(3)	P(1)–Li–O(1)	121.8(5)
Ga(1)–P(1)–Ga(2)	82.3(1)	P(2)–Li–O(1)	105.8(6)
Ga(1)–P(1)–Li	92.2(3)	P(1)–Li–O(2)	128.9(6)
Ga(2)–P(1)–Li	78.6(3)	P(2)–Li–O(2)	125.9(6)
Ga(1)–P(1)–C(13)	121.7(2)	O(1)–Li–O(2)	100.5(6)
	Compound **2**		
P(1)–Ga(1)	2.533(2)	Ga(1)–C(1)	2.041(6)
P(1)–Ga(2)	2.344(2)	Ga(1)–C(5)	2.038(6)
P(1)–C(13)	1.875(6)	Ga(2)–C(9)	2.024(7)
P(1)–Ga(1a)	2.447(2)		
Ga(1)–P(1)–Ga(2)	83.1(1)	C(1)–Ga(1)–C(5)	114.5(3)
Ga(1)–P(1)–C(13)	128.0(2)	P(1)–Ga(1)–P(1a)	70.5(1)
Ga(2)–P(1)–C(13)	124.3(2)	C(1)–Ga(1)–P(1a)	117.9(2)
Ga(1)–P(1)–Ga(1a)	97.5(1)	C(5)–Ga(1)–P(1a)	115.7(2)
Ga(2)–P(1)–Ga(1a)	85.0(1)	P(1)–Ga(2)–C(9)	142.2(1)
C(13)–P(1)–Ga(1a)	125.1(2)	P(1)–Ga(2)–P(1a)	75.7(1)
P(1)–Ga(1)–C(1)	108.7(2)		
P(1)–Ga(1)–C(5)	122.8(2)		

Structural Descriptions. {(Et$_2$O)$_2$Li}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$} (1). The structure of 1, which is represented in Figure 1, has no crystallographically imposed symmetry. The LiGa$_2$P$_2$ framework of 1 is formed from a nonplanar four-membered Ga$_2$P$_2$ ring coordinated to a Li$^+$ ion through the P atoms. The Li$^+$ ion is also coordinated by two Et$_2$O molecules. The 3- and 4-fold ligations of Ga(2) and Ga(1) are reflected in different bond lengths (2.29 and 2.44 Å) to the phosphorus centers. The phosphorus coordinations are distorted tetrahedral, with bond angles ranging from 78 to 142°. The interligand angles for four and three-coordinate Ga(1) and Ga(2) range from 78.7(1) to 116.8(2)° and 85.1(1) to 137.3(3)°, respectively. The P–Li and Li–O bonds are 2.65 and 1.99 Å in length, and the P(1)···P(2) and Ga(1)···Ga(2) distances are 3.103 and 3.119 Å.

{(*t*-Bu)$_2$Ga}{*t*-BuGa}{P(*t*-Bu)}$_2${Ga(*t*-Bu)$_2$} (2). The structure of 2 (Figure 2) has a crystallographically imposed 2-fold axis along the Ga(2)–C(9) bond. The core framework of the molecule is composed of the atoms Ga$_3$P$_2$ and is

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[11] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[12] This method is described in: Hope, H. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

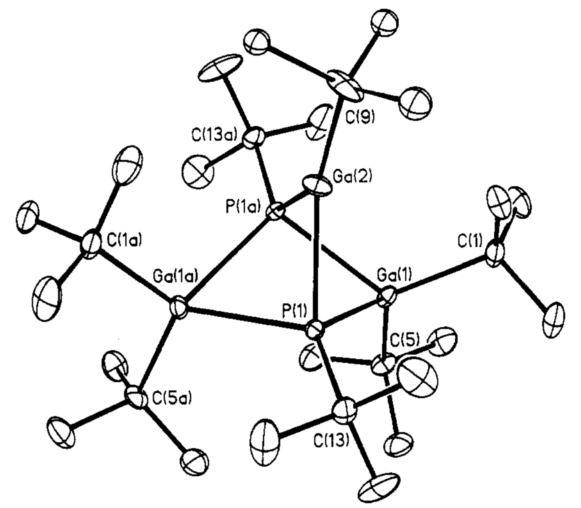
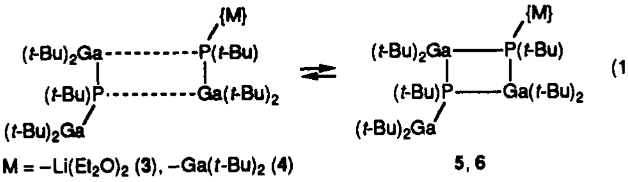


Figure 2. Computer-generated thermal ellipsoid (30%) plot of 2. Hydrogen atoms are omitted for clarity.

similar to that of 1 in the sense that the $-Li(Et_2O)_2$ group is replaced by $-Ga(t\text{-}Bu)_2$. As in 1, the four-coordinate Ga and P centers in 2 have bond angles that are severely distorted from regular tetrahedral values. The Ga(2) center has a coordination number of 3 and interligand angles that range from 75.7(1) to 142.2(1)°. In addition, the Ga(1)–P(1) and Ga(1)–P(1a) distances, 2.533(2) and 2.447(2) Å, are asymmetric and the Ga(2)–P bond is 2.344(2) Å. The P(1)···P(2) distance (2.88 Å) is shorter and the Ga(1)···Ga(2) distance (3.239 Å) is longer than the corresponding values in 1.

Discussion

The synthesis of 1 and 2 arose from attempts to isolate gallium–phosphorus compounds analogous to the known boryl phosphides of formula $LiP(R')BR_2$[7,8] and diborylphosphanes $R'P(BR_2)_2$.[13] This involved the treatment of $Li_2P(t\text{-}Bu)$ with 1 or 2 equiv of $(t\text{-}Bu)_2GaCl$. No Ga–P compounds corresponding to the formulas $LiP(R')BR_2$ or $R'P(BR_2)_2$ were isolated from these mixtures. The products 1 and 2 are consistently obtained from these reactions in a reasonably good yield. The isolation of 1 and 2 may be explained by assuming the presence of two different species in the reaction solution, the gallyl phosphide $t\text{-}BuP\{Ga(t\text{-}Bu)_2\}Li(Et_2O)_{2,3}$ (3) and digallylphosphane $t\text{-}BuP\{Ga(t\text{-}Bu)_2\}_2$ (4). The formation of dimers by the association of 3 and 4 gives 5, while the association of 4 with itself gives 6 as depicted in eq 1. Elimination of $Ga(t\text{-}Bu)_3$ (identified in the reaction mixture by comparison with an authentic sample[14]) (eq 2) from the intermediate 5 or 6 gives 1 or 2, respectively. The presence of the digallylphosphane 4 in the reaction mixture is supported by the isolation and structural (X-ray) characterization of small amounts of the related compound $MesP\{Ga(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2\}_2\cdot Et_2O$ (7; Mes = $2,4,6\text{-}Me_3C_6H_2$) from a similar reaction between Li_2PMes and 1 equiv of $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2GaCl$ in tetrahydrofuran.[15] Presumably, 7 and $t\text{-}BuP\{Ga(t\text{-}Bu)_2\}_2$ (4) are formed in small quantities from their respective reagents in a 1:1 ratio due to the low solubility of dilithium phosphide salts and high solubility of diorganogallium halides in etheral solvents. In addition, treatment of the reaction mixture of 1 with 2 equiv of 12-crown-4 resulted in a solvent-separated species, $[\{Li(12\text{-crown-}4)_2\}_2][\{P(t\text{-}Bu)Ga(t\text{-}Bu)_2\}_2]$.[16] This constitutes direct evidence for a $\{Li(Et_2O)_{2,3}\}\{P(t\text{-}Bu)Ga(t\text{-}Bu)_2\}$ species (probably present as a dimer) in the reaction mixture.



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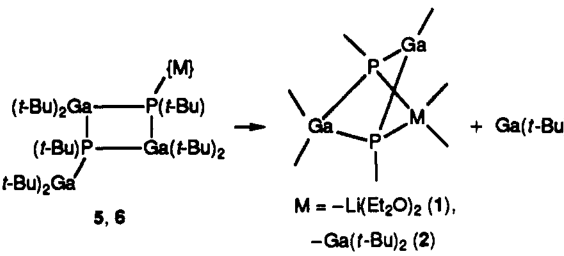
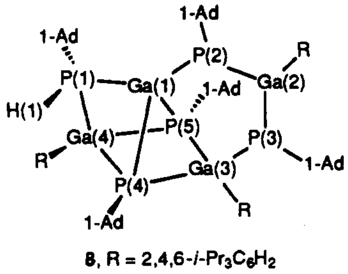


(2)

Reaction of $Li_2P(t\text{-}Bu)$ and $(t\text{-}Bu)_2GaCl$ in a 1:2 ratio affords 2. It is possible that 2 may simply be a derivative of 1; however, reaction may also proceed by initial formation of the dimer $\{t\text{-}BuP\{Ga(t\text{-}Bu)_2\}_2\}_2$ (eq 1, where M = $-Ga(t\text{-}Bu)_2$) followed by the loss of a $Ga(t\text{-}Bu)_3$ molecule (eq 2). For the analogous reaction, involving the reagents Li_2PMes and $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2GaCl$ in a 2:1 ratio, dimerization followed by elimination of $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3Ga$ might be expected to yield a product similar to 2. However, this reaction gives the digallylphosphane 7 in high yield.[15] Presumably, the formation of a dimer intermediate and further reaction is inhibited by the bulkiness of the gallium and phosphorus ligands (i.e. Mes and $2,4,6\text{-}i\text{-}Pr_3C_6H_2$). There is precedence for ligand redistribution among organogallium species with a tendency toward more symmetrical products (see refs 17 and 18). For example, Wells et al. have reported the ligand rearrangement product $Ph_3Ga\cdot As(SiMe_3)_3$ by reaction of $\overline{Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl}$ with $LiP(SiMe_3)_2$ in a 1:1 ratio.[19] Loss of organo groups from gallium were recently observed during the formation of the cluster $[Ga_4(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3\{P(1\text{-}Ad)\}_4P(H)(1\text{-}Ad)]$ (8). The latter cluster was synthesized in Et_2O/THF by reaction of $Li_2P(1\text{-}Ad)$ and 1 equiv of $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)GaCl_2(THF)$.[5] There is a structural similarity between a Ga_3P_2 cluster fragment in 8 consisting of Ga(1), Ga(3), Ga(4), P(4), and P(5) and the



8, R = $2,4,6\text{-}i\text{-}Pr_3C_6H_2$

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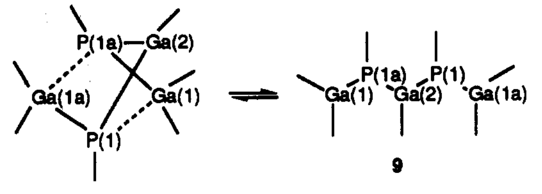
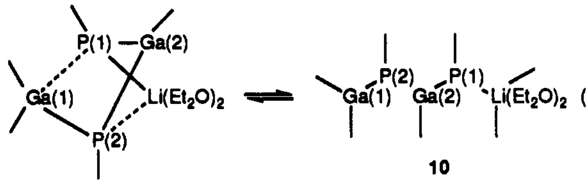
cages 1 and 2. Particularly intriguing is that Ga(1) in 8 has been stripped of an organo group (i.e. 2,4,6-i-$Pr_3C_6H_2$) in a manner similar to that of Ga(2) in 1 and 2. It may be possible that a step in the formation of this cluster involves a dimer species such as [1-AdP{Ga(Cl)-2,4,6-i-$Pr_3C_6H_2$}$_2$]$_2$ with subsequent elimination of (2,4,6-i-$Pr_3C_6H_2$)$_2$GaCl to form the intermediate species {2,4,6-i-$Pr_3C_6H_2$(Cl)Ga}{(Cl)Ga{P(1-Ad)}$_2$Ga(Cl)-2,4,6-i-Pr_3-C_6H_2}. Alternative pathways to 1 and 2 could involve t-BuGaCl$_2$, which implies impure (t-Bu)$_2$GaCl starting material or an equilibrium between these species in solution. However, this seems improbable, since, for the former, the ^{1}H NMR (C_6D_6) of (t-Bu)$_2$GaCl displays a singlet that is identical in shift to the literature value.[10] Furthermore, a recent ^{1}H NMR study provided no evidence for an equilibrium, in C_6D_6/Et_2O mixtures, between the related Mes$_2$GaCl and dichloride species MesGaCl$_2$.[20]

The structures of 1 and 2 are interesting for a number of reasons. They represent the first examples of heavier main-group 3–5 cages of their type and stoichiometry ($LiGa_2P_2$ in 1 and Ga_3P_2 in 2). In addition, to our knowledge, 1 is the first gallium–phosphorus cage compound in which lithium is incorporated into the Ga–P molecular framework. There is some precedent for the type of cage structure in 1 and 2 in the boron–phosphorus compound P_2(BN(i-Pr)$_2$)$_3$.[21] This species also has a quasi-trigonal-bipyramidal structure with the two phosphorus and three boron atoms occupying the axial and the equatorial positions, respectively, with both boron and phosphorus having three-coordination. In contrast, 1 and 2 have Ga centers that are three- or four-coordinate. The fairly short Ga(2)–P bond lengths observed in 1 (2.29 Å) and 2 (2.34 Å) result from three-coordination at Ga(2). The Ga(2)–P distances in 2, however, are ~0.05 Å longer than the corresponding distances in 1. The difference can be attributed to greater electron density on the phosphorus centers in 1 due to weak (long P–Li bonds, 2.65 Å) and largely ionic P–Li interactions. The weaker Ga(2)–P bonds in 2 may also arise from less efficient σ-orbital overlap owing to a narrower (by ~10°) P(1)–Ga(2)–P(2) angle, 75.7(1)°. Some of the Ga–P bond lengths involving four-coordinate gallium (Ga(1)–P in 1, Ga(1)–P(1a) and Ga(1a)–P(1) in 2) are consistent with distances (i.e. ~2.44 Å) observed in structures involving these coordination numbers.[1–3,5] In contrast the Ga(1)–P(1) and (by symmetry) Ga(1a)–(P1a) bands are considerably longer (2.533(2) Å) than the sum of the atomic radii of these elements, 2.46 Å.[22] In fact the Ga(1)–P(1) bond appears to be the longest Ga–P distance that has been observed to date. This may be due to considerable strain in the cage structure of 2. It is interesting to note that cleavage of these long Ga–P bonds would result in a gallium–phosphorus analogue of the pentadienyl cation (9 eq 3). The boron–phosphorus compound PhB[PMesBMes$_2$]$_2$, with the open type 9 structure, has recently been reported.[23] At least in the solid state, the steric protection afforded by the *tert*-butyl groups and the relative weakness of Ga–P π-bonding in this hypothetical species are, apparently, insufficient to prevent intramolecular association to 2.



In order to investigate the structure of 2 in solution, a variable-temperature ^{1}H NMR study was undertaken. Six proton resonances are observed at room temperature whose relative intensities are 2:2:1:0.5:1:0.5. The observation of a triplet (assigned to the phosphorus *tert*-butyl ligands in the case of both 1 and 2) has precedents in the ^{1}H and ^{13}NMR spectra of numerous {R_2M–PR'_2}$_2$ (M = Al, Ga, In) compounds and a gallium–phosphorus {(t-Bu)GaP-(2,4,6-t-$Bu_3C_6H_2$)}$_2$ four-membered ring.[24,25] Furthermore, a singlet (δ 1.33) due to the *tert*-butyl group on three-coordinate gallium is observed for 2 in addition to two well-resolved peaks (δ 1.36, 1.57) for the inequivalent *tert*-butyl ligands of the four-coordinate gallium centers. Cooling a d^8-toluene solution of 2 to T = –100 °C affords an unchanged spectrum. However, warming the solution results in a broadening of the Ga(t-Bu)$_2$ peaks and coalescence of these two signals at ca. 90 °C. Substitution of the parameters T_c = 363 K and peak separation at T = 273 K of $\Delta\nu$ = 64 Hz into an approximate formula[26] affords a $\Delta G^\ddagger$ value of 17.8 kcal mol^{-1} for the dynamic process. Assuming the cage structure of 2 is retained in solution at 26 °C, the magnetic equivalence of the Ga(t-Bu)$_2$ peaks at higher temperature may be explained by cleavage of the two weakened Ga(1)–P(1) and Ga(1a)–P(1a) bonds (see eq 3) to give the open structure 9, which would have essentially free rotation around the Ga(1)–P(1a) or P(1)–Ga(1a) bonds. The ^{31}P NMR signal shifts only slightly (~4 ppm) upfield as the temperature is increased. Although substantial asymmetry in the Ga(1)–P and Li–P bond lengths is not observed in 1, breaking of Li–P(2) and Ga(1)–P(1) bonds as in eq 4 would also result in a novel gallium–phosphorus analogue of butadiene, 10. However, increasing the temperature to T = 100 °C affords an unchanged spectrum, which suggests that the $LiGa_2P_2$ cage structure of 1 remains intact. In



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addition, the upfield ^{31}P NMR shift for 2 compared to 1 is unexpected, given that 1 is a phosphide salt. An explanation for this observation may involve the long Ga–P bonds (2.53 Å) seen in the crystal structure of 2.

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Supplementary Material Available: Full tables of data collection parameters, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters for 1 and 2 and a figure giving variable-temperature ^{1}H NMR spectra for 2 (19 pages). Ordering information is given on any current masthead page.

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