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[19. ABSTRACT]

A $\overline{\text{Ga-P-Ga-Cl}}$ ring containing compound, $Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}$ (1), is reported. Compound **1** is an example of a four-membered ring system with mixed bridging of the two gallium centers and was prepared *via* the reaction of Ph_2GaCl with $P(SiMe_3)_3$ in a 2:1 mole ratio in either toluene or pentane. Curiously, **1** was originally isolated as a minor product (ca 5% yield) from the reaction of $LiP(SiMe_3)_2$ with Ph_2GaCl in a 1:1 mole ratio. X-ray crystallographic analyses shows the $\overline{\text{Ga-P-Ga-Cl}}$ ring of **1** to be non- planar. The reaction of Ph_2GaCl and $P(SiMe_3)_3$ in a 1:1 mole ratio in either toluene or pentane yields $Ph_2(Cl)Ga{\bullet}P(SiMe_3)_3$ (**2**). Compound **3**, $Ph_3Ga{\bullet}P(SiMe_3)_3$, was also originally isolated as a minor product (ca. 10%) from the reaction of $LiP(SiMe_3)_2$ with Ph_2GaCl in a 1:1 mole ratio and is an additional reported example of an adduct formed through ligand redistribution involving $LiE(SiMe_3)_2$ (E = P or As) as a reactant. The straightforward synthesis of **3** can be accomplished by the 1:1 mole reaction of Ph_3Ga and $P(SiMe_3)_3$ in pentane. Both **2** and **3** are structural examples of adducts containing a Ga-P bond with aryl ligands on the gallium center. Compound **1** belongs to the monoclinic system, space group $P2_1/c$, with $z = 4$, $a = 10.579(2)$ Å, $b = 15.653(5)$ Å, $c = 20.428(4)$ Å, and $\beta = 91.80(2)°$. Compound **2** crystallizes in an orthorhombic system, space group $P2_12_12_1$, with $z = 4$, $a = 9.3320(10)$ Å, $b = 9.768(2)$ Å, and $c = 30.581(6)$ Å. Compound **3** belongs to the monoclinic system, space group $P2_1/n$, with $z = 4$, $a = 18.81(3)$ Å, $b = 19.25(2)$ Å, $c = 18.93(2)$ Å, and $\beta = 112.8(1)°$.

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X-Ray Crystal Structures of $Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}$, $Ph_2(Cl)Ga \bullet P(SiMe_3)_3$, and $Ph_3Ga \bullet P(SiMe_3)_3$

by

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Synthesis and Characterization of Novel Organogallium-Phosphorus Compounds: X-Ray Crystal Structures of $Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}$, $Ph_2(Cl)Ga\bullet P(SiMe_3)_3$, and $Ph_3Ga\bullet P(SiMe_3)_3$.

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A $\overline{Ga\text{-}P\text{-}Ga\text{-}Cl}$ ring containing compound, $Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}$ (1), is reported. Compound 1 is an example of a four-membered ring system with mixed bridging of the two gallium centers and was prepared *via* the reaction of Ph_2GaCl with $P(SiMe_3)_3$ in a 2:1 mole ratio in either toluene or pentane. Curiously, 1 was originally isolated as a minor product (ca 5% yield) from the reaction of $LiP(SiMe_3)_2$ with Ph_2GaCl in a 1:1 mole ratio. X-ray

crystallographic analyses shows the $\overline{\text{Ga-P-Ga-Cl}}$ ring of **1** to be non-planar. The reaction of Ph_2GaCl and $P(SiMe_3)_3$ in a 1:1 mole ratio in either toluene or pentane yields $Ph_2(Cl)Ga{\bullet}P(SiMe_3)_3$ (**2**). Compound **3**, $Ph_3Ga{\bullet}P(SiMe_3)_3$, was also originally isolated as a minor product (ca. 10%) from the reaction of $LiP(SiMe_3)_2$ with Ph_2GaCl in a 1:1 mole ratio and is an additional reported example of an adduct formed through ligand redistribution involving $LiE(SiMe_3)_2$ (E = P or As) as a reactant. The straightforward synthesis of **3** can be accomplished by the 1:1 mole reaction of Ph_3Ga and $P(SiMe_3)_3$ in pentane. Both **2** and **3** are structural examples of adducts containing a Ga-P bond with aryl ligands on the gallium center. Compound **1** belongs to the monoclinic system, space group $P2_1/c$, with $z = 4$, $a = 10.579(2)$ Å, $b = 15.653(5)$ Å, $c = 20.428(4)$ Å, and $\beta = 91.80(2)^\circ$. Compound **2** crystallizes in an orthorhombic system, space group $P2_12_12_1$, with $z = 4$, $a = 9.3320(10)$ Å, $b = 9.768(2)$ Å, and $c = 30.581(6)$ Å. Compound **3** belongs to the monoclinic system, space group $P2_1/n$, with $z = 4$, $a = 18.81(3)$ Å, $b = 19.25(2)$ Å, $c = 18.93(2)$ Å, and $\beta = 112.8(1)^\circ$.

Introduction

Previous research in our laboratory has shown the utility of dehalosilylation and lithium halide elimination reactions to prepare compounds containing the Ga-As bond.[1] Subsequently, we have employed reactions of this type to prepare analogous compounds containing In-As,[2] In-P,[3] and Al-As[4] bonds. From this line of investigation we have been able to isolate compounds whose core fragments contain two Group 13 metals bridged either by two pnictogen atoms [i.e., $\overline{\mathrm{M\text{-}E\text{-}M\text{-}E}}$ (M= Ga, E = As;[5,6] M = In, E = As[2] or P[3])], or by one pnictogen and one halogen atom [i.e., $\overline{\mathrm{M\text{-}E\text{-}M\text{-}X}}$ (M = Ga, E = As, X = Cl,[5,7] or Br;[7] M = In, E = As[2] or P,[3] X = Cl)]. As an ongoing effort in this area, we have begun to investigate similar gallium-phosphorus systems. Herein we report our initial findings, the syntheses and characterizations (partial elemental analyses, melting points, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra and X-ray analysis) of three compounds containing Ga-P bonds: $\mathrm{Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}}$ (**1**), $Ph_2(Cl)Ga{\cdot}P(SiMe_3)_3$ (**2**), and $Ph_3Ga{\cdot}P(SiMe_3)_3$ (**3**). Compound **1** is a structural example of a gallium-phosphorus mixed bridge system. Compounds **2** and **3** are examples of adducts containing the Ga-P bond and are the only adducts which contain aryl groups on the gallium center to be structurally analyzed. The original isolation of **3** involved an unusual ligand exchange process in which the symmetrization of both the metal and pnictide centers occurred. This rearrangement phenomenon has been observed previously in analogous gallium-arsenic and indium-phosphorus chemistry with the isolation of such compounds as $Ph_3Ga{\cdot}As(SiMe_3)_3$ and $(Me_3SiCH_2)In{\cdot}As(SiMe_3)_3$.[8]

Experimental Section

General Considerations. All manipulations were performed using general Schlenk, dry box, and/or high vacuum techniques. Solvents (including those for NMR spectra) were appropriately dried and distilled under argon prior to use. Literature methods were used to prepare Ph_3Ga[9] and $P(SiMe_3)_3$[10]. $GaCl_3$ was purchased from Alfa Products and purified by sublimation. Ph_2GaCl was prepared *via* the equilibration of Ph_3Ga and $GaCl_3$ in toluene in a 2:1 mole ratio and purified by recrystallization. $LiP(SiMe_3)_2$[11] was prepared *via* the 1:1 mole reaction of MeLi with $P(SiMe_3)_3$. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-300 at 300.0, 75.4, and 121.4 MHz, respectively. ^1H and ^{13}C spectra were referenced to TMS via the residual protons or carbons of C_6D_6. ^{31}P spectra were referenced to external 80% H_3PO_4 at δ 0.00 ppm. Melting points (uncorrected) were taken in sealed capillaries (Thomas-Hoover Unimelt). Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, N Y.

Preparation of $Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}$ (1). Method (a): Ph_2GaCl (0.379 g, 1.46 mmol) in 25 mL toluene was placed in the lower bulb of a two-bulb reaction flask equipped with Teflon valves and a micro-stirbar. $P(SiMe_3)_3$ (0.180 g, 0.73 mmol) in 10 mL of toluene was placed into the upper bulb. The lower bulb and its contents were degassed *via* a freeze-pump-thaw cycle. Next, the $P(SiMe_3)_3$ solution was slowly dripped into the stirred Ph_2GaCl solution held at 85 °C in an oil bath. The flask was attached to a N_2 bubbler, and allowed to stir at 100 °C overnight. From the resulting clear solution, the volatiles were removed *in vacuo*, affording a white solid. The volatiles were then hydrolyzed with deionized water and titrated with NaOH, (0.107M, 6.90 mL corresponding to the elimination of 0.73 mmol of Me_3SiCl). The white solid was dissolved in a small amount of warm toluene, and slow evaporation of the solvent in the dry box resulted in the formation of a clear crystalline product. Recrystallization from a 50:50 hexane/toluene solution afforded pure crystals of 1 (0.108 g, 22.4% yield); mp. 171-180 °C. Anal. Calcd. (found) for $C_{30}H_{38}ClGa_2PSi_6$: C, 54.54

(54.54); H, 5.79 (5.96); Cl, 5.37 (5.28). ^{1}H NMR: δ -0.06 (d, 18 H, Si*Me$_3$* ($J_{P\text{-}H}$ = 5.92 Hz)); δ 7.23-7.93 (m, 20 H, *Ph*). ^{13}C {^{1}H} NMR: δ 2.81 [d, PSi*Me$_3$* ($J_{P\text{-}C}$ = 8.60 Hz)], 128.73 (s, *Ph*), 128.32 (partially obscured by solvent, s, *Ph*), 135.88 (bs, *Ph*). ^{31}P {^{1}H} NMR: δ -214.74 (s).

Method (b): Compound 1 was prepared in a higher yield *via* the reaction of Ph_2GaCl (0.465 g, 1.80 mmol) and $P(SiMe_3)_3$ (0.235 g, 0.94 mmol) in 150 mL of dry pentane in a one necked 250 mL round-bottom flask equipped with a Teflon valve. The reaction was placed for 49 h in a sonicating water bath, volatiles were then removed *in vacuo*, and the crude product recrystallized from hot toluene to give 1 (0.251 g, 40.4% yield) as a crystalline product.

Isolation of 1 from the reaction Ph_2GaCl and $LiP(SiMe_3)_2$. In a similar apparatus as that used for 1 [method (a)], Ph_2GaCl (0.305 g, 1.17 mmol) in 30 mL toluene was placed into the lower bulb and $LiP(SiMe_3)_2$ (0.217 g, 1.17 mmol) in 20 mL THF was placed into the upper bulb. The $LiP(SiMe_3)_2$ solution was slowly added with stirring to the Ph_2GaCl solution at -78 °C. The mixture was allowed to stir and warm to room temperature for 14 h, after which time a clear yellow solution was obtained. The solution was filtered, and the volatiles removed *in vacuo*, affording a viscous yellow oil. Addition of 10 mL of hexane to the oil, resulted in the transitory formation of a white precipitate which quickly redissolved. Upon standing for several days at -15 °C, a yellow semi-crystalline material formed. This was collected, washed with hexane, and upon recrystallization from the same afforded clear X-ray quality crystals of 1 in ca. 5% yield.

Preparation of $Ph_2(Cl)Ga \bullet P(SiMe_3)_3$ (2). Method (a): Ph_2GaCl (0.097 g, 0.37 mmol) in 20 mL toluene and $P(SiMe_3)_3$ (0.098 g, 0.39 mmol) in 20 mL toluene were combined in a 100 mL round-bottomed flask equipped with a Teflon valve and a micro-stirbar. The contents of the flask were allowed to stir overnight at room temperature, after which, the volatiles of the clear solution were removed *in vacuo,* affording a white solid. This was redissolved in a small amount of warm toluene, and upon standing for several days at -15 °C afforded clear needles which were subsequently dissolved in a small amount of pentane. Upon evaporation, pure crystals of 2 were obtained, (0.071 g, yield 47.5 %); mp. 143-145 °C. Anal. Calcd (Found) for $C_{21}H_{36}ClGaPSi_3$: C, 49.56 (49.80); H, 7.12 (7.37). ^1H NMR: δ 0.19 (d, 27 H, Si*Me₃* (J_{P-H} = 4.94 Hz)) δ 7.22-8.18 (m, 10 H, *Ph*). ^{13}C {^1H} NMR: δ 2.82 [d, PSi*Me₃* (J_{P-C} = 7.50 Hz)], 128.34 (s,*Ph*), 128.23 (partially obscured by solvent, s, *Ph*), 137.22 (bs, *Ph*). ^{31}P {^1H} NMR: δ -214.78 (s).

Method (b): Ph_2GaCl (0.337 g, 1.30 mmol) and $P(SiMe_3)_3$ (0.33 g, 1.30 mmol) were similarly treated as with the preparation of 1 [method (b)] for 72 h in the sonicating bath. Upon recrystallization in toluene, needles of 2 (0.470g, 71.0% yield) were collected.

Preparation of $Ph_3Ga \bullet P(SiMe_3)_3$ (3). Ph_3Ga (0.250 g, 0.83 mmol) and $P(SiMe_3)_3$ (0.208 g, 0.83 mmol) were each dissolved in 10 mL of pentane and combined in a 25 ml glass vial in the dry box. The clear solution was capped and stirred for 8 h. Upon evaporation of the solvent, clear crystals of 3 formed in quantitative yield; mp. 192-197 °C. Anal. Calcd. (Found) for $C_{27}H_{42}GaPSi_3$: C, 58.79 (59.29); H, 7.67 (7.35). ^1H NMR: δ 0.14 (d, 27 H, Si*Me₃*(J_{P-H} = 4.77 Hz)) δ 7.25-8.13 (m, 15 H, *Ph*). ^{13}C {^1H}

NMR: δ 3.25 [d, PSi*Me*$_3$ ($J_{P\text{-}C}$ = 7.90 Hz)], 127.62 (s, *Ph*), 127.79 (partially obscured by solvent, s, *Ph*), 139.12 (bs, *Ph*). $^{31}P\{^1H\}$ NMR: δ -232.01 (s).

Isolation of 3 from the reaction of Ph_2GaCl and $LiP(SiMe_3)_2$. In a set-up similar to that used for the preparation of 1 [method (a)], Ph_2GaCl, (1.049 g, 4.05 mmol) was dissolved in 50 mL toluene and placed in the upper bulb and $LiP(SiMe_3)_2$, (0.746 g, 4.05 mmol) was dissolved in a 100 mL of an 80:20 toluene/THF mixture and placed into the lower bulb. The lower bulb and its contents were cooled to -78 °C, and the Ph_2GaCl solution was slowly added dropwise, with stirring. The mixture was allowed to stir and warm to ambient temperature overnight, after which the volatiles were removed *in vacuo*. Toluene (ca. 100 mL) was vacuum distilled onto the remaining yellowish-white semi-solid. The solution was filtered and the solvent removed to yield a yellow viscous solid. This was recrystallized from hot pentane, resulting in a small crop of colorless crystals of 3 (0.110 g, 10% yield).

Structural Analyses for 1, 2, and 3. Single crystals of 1, 2, and 3 were mounted in 0.7 mm thin-walled glass capillaries under an inert atmosphere of argon and flame sealed. Relevant crystallographic data are given in Table I. For 1 and 3, data were collected on a Rigaku AFC6S (MoKα 0.71069 Å) diffractometer at 23 °C. The structures were solved by direct methods and refined by full-matrix least-squares to convergence.[12] Neutral atom scattering factors were taken from Cromer and Waber.[13] Anomalous dispersion effects were included in F_{calc}; the values for Δf' and Δf'' were those of Cromer.[14] All calculations were performed using the TEXSAN[15] crystallographic software package of Molecular Structure Corporation.

For both **1** and **3**, cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections (in the range 22.77° < 2θ < 27.75° for **1** and 30.09° < 2θ < 33.89° for **2**), corresponded to a monoclinic cell. Intensity data were corrected for the usual Lorentz and polarization effects. A total of 4582 reflections for **1**, and 14863 reflections for **3** were recorded. An empirical absorption correction, based on azimuthal scans of several reflections, was applied. R_{int} = 0.085 on (I) to yield 4229 reflections and R_{int} = 0.136 on(I) to yield 14423 reflections, of which those 1615 with $I > 3\sigma(I)$ and those 3511 with $I > 3\sigma(I)$ were retained for analysis of **1** and **3**, respectively. In **3**, two molecules which are structurally identical but crystallographically independent lie in the four general positions of the asymmetric unit. The non-hydrogen atoms were refined using anisotropic thermal parameters; hydrogen atoms, in calculated positions, were included in structure factor calculations. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to downweight intense reflections. The final difference Fourier map of **1** contained a maxima and minima of 0.34 and -0.28 $e^{-}Å^{3}$, respectively, whereas that of **3** contained a maxima and minima of 1.27 and -0.98 $e^{-}Å^{3}$, respectively. Final fractional atomic coordinates are given in Tables II and IV. Selected bond distances and angles are given in Table V and VII. Thermal ellipsoid diagrams are presented in Figures 1 and 3.

For **2**, data were collected on a Siemens R3m/V (MoKα 0.71073 Å) diffractometer at 23 °C. Cell constants and an orientation matrix for data collection corresponded to an orthorhombic cell. Intensity data were corrected for the usual Lorentz and polarization effects. A total of 3849 reflections were recorded. An empirical absorption correction was applied

[R_{int} = 0.04 on (I)] to yield 3779 reflections out of which 2043 with $F > 3.0\sigma(F)$ were retained. The structure was solved by direct methods and refined using full-matrix least-squares to convergence using SHELXTL PLUS.[16] Non-hydrogen atoms were refined using anisotropic thermal parameters; hydrogen atoms, in calculated positions, were included in structure factor calculations. The weighting scheme ($w^{-1} = \sigma^2(F) + 0.0002F^2$) was based on counting statistics. The final difference map contained maxima and minima of 0.90 and -0.47 $e^-/Å^3$, respectively, located in close proximity to the Ga atom. Final fractional atomic coordinates are given in Table III. Selected bond distances and angles are given in Table VI. A thermal ellipsoid diagram is presented in Figure 2.

Results and Discussion

Dehalosilylation reactions between an organogallium halide and a silylarsine to form gallium-arsenic bonds now have ample precedent.[1] However, analogous reactions to form compounds containing the gallium-phosphorus bond have as yet been unreported. Reaction of Ph_2GaCl with $P(SiMe_3)_3$ in a 2:1 mole ratio in toluene at 100 °C also affords **1** *via* a dehalosilylation reaction (eq 1).

$$2Ph_2GaCl + P(SiMe_3)_3 \xrightarrow{\hspace{2cm}} Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl} + Me_3SiCl \qquad (1)$$

1

The core of **1** is that of a $\overline{\text{Ga-P-Ga-Cl}}$ ring, and is another example of an ever increasing class of compounds which contain a four-membered ring composed of the same two Group 13 metals bridged by a halogen atom and a pnictogen atom. These species are commonly referred to by us as "mixed-bridges" of the heavier Group 13 metals.[1] The relatively low yield of 1 (22.4% in toluene and 40.38% in pentane) can best be accounted for by its high solubility in both aromatic and aliphatic solvents. This high solubility has been noted previously for other related systems where these compounds tend to form oily materials when solvated which are rather difficult to purify.[3] Compound 1 is very stable in an inert atmosphere at room temperature for extended periods of time.

It is of interest to note that reaction of Ph_2GaCl with $LiP(SiMe_3)_2$ in toluene at -78 °C in a 1:1 mole ratio affords 1 in a very small yield. The isolation of 1 was first accomplished in this manner and it piqued our curiosity as to whether 1 could be synthesized in a more conventional method with an improved yield. Thus, *via* eq. (1), this was accomplished.

Though the isolation of 1 from the 1:1 mole reaction of Ph_2GaCl and $LiP(SiMe_3)_2$ (intended to produce $[Ph_2GaP(SiMe_3)_2]_2$) was unexpected, it is not surprising. Previous work in our laboratory[1-3] has shown that dimeric 13-15 compounds can easily be converted to their corresponding mixed-bridge counterparts by the reaction of the dimeric species with one mole equivalent of the appropriate diaryl or dialkyl Group 13 halide. Therefore, through the order of addition, an excess of Ph_2GaCl could immediately react with any synthesized $[Ph_2GaP(SiMe_3)_2]_2$ converting it to 1 (eq.2).

$$2Ph_2GaCl + [Ph_2GaP(SiMe_3)_2]_2 \longrightarrow 2Ph_2\underset{\mathbf{1}}{\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}} \qquad (2)$$

Surprisingly, we have as of yet not been able to isolate $[Ph_2GaP(SiMe_3)_2]_2$ though its arsenic analog $[Ph_2GaAs(SiMe_3)_2]_2$ is quite easy to prepare and stable.[7]

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of 1 are consistent with its solid state structure. In the ^1H NMR spectra the ^{31}P nucleus couples with the methyl protons of the adjacent trimethylsilyl groups and exhibits a doublet. Similarly, the $^{13}C\{^1H\}$ NMR spectrum exhibits a doublet corresponding to the carbon atoms of these same groups. As for the $^{31}P\{^1H\}$ NMR spectrum, the formation of a sharp single resonance implies the existence of only one species in solution at room temperature.

The Ga-P-Ga-Cl ring in 1 is distinctly nonplanar as is that for its isomorphous As analog, $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl$ (4).[7] As was observed for 4, compound 1 relieves substituent steric overcrowding which would be present with a planar four-membered ring and overall C_{2v} molecular symmetry by outward rotation of the Ga-C(111) and Ga-C(221) bond vectors, resulting in a mean dihedral angle about ring bonds of 6.4°. These effects are more pronounced in 1 than in 4 due to the shorter bond lengths involving phosphorus (mean Ga-P = 2.390 Å and mean P-Si = 2.272 Å) whereas for 4, the mean Ga-As and As-Si bonds are 2.466 Å and 2.363 Å, respectively. The Cl atom is displaced by 0.271 Å from the Ga-P-Ga plane. The mean Ga-Cl bond length of 2.410 Å is virtually identical to the mean Ga-Cl bond length of 2.411 Å in 4. The Ga-P-Ga, Ga-Cl-Ga, and mean P-Ga-Cl angles of 90.4(1)°, 89.4(1)°, and 89.7°, respectively, exhibit a slight rhombic distortion. The mean C-Ga-C bond angle of 120.3° is similar to that of 4 (mean C-Ga-C = 121.3°) and is likewise indicative of both steric effects and electronic factors.

rhombic distortion. The mean C-Ga-C bond angle of 120.3° is similar to that of 4 (mean C-Ga-C = 121.3°) and is likewise indicative of both steric effects and electronic factors.

The reaction of Ph_2GaCl with $P(SiMe_3)_3$ in a 1:1 mole ratio at room temperature in toluene yields 2. It is interesting that 2 is quite stable under an inert atmosphere at room temperature for extended periods of time even though it contains both a Cl atom and $SiMe_3$ groups. However, when 2 is heated in deuterated toluene to reflux in an NMR tube for 45 hours, the resultant ^1H NMR spectrum is complex and undecipherable, but does not exhibit resonances belonging to the parent compound. This behavior tends to demonstrate that 2 will undergo further thermal reaction to give additional Ga-P oligomers.

Surprisingly, compound 3 was originally isolated as the result of a ligand exchange process in the reaction of $LiP(SiMe_3)_2$ and Ph_2GaCl. This is an additional example reported by us of such a ligand redistribution product resulting from a lithium pnictide reaction [$Ph_3Ga{\cdot}As(SiMe_3)_3$ (5) and $(Me_3SiCH_2)In{\cdot}As(SiMe_3)_3$ (6) were previously reported[8]]. Though the precise pathway of these transformations is still not known, the isolation of 3, 5, and now 6 demonstrates the complex nature of these lithium chloride elimination reactions. As is expected, 3 can also be directly prepared from the reaction of Ph_3Ga and $P(SiMe_3)_3$ in pentane.

A review of the literature reveals that there are currently five structurally characterized neutral Ga-P adducts;[17-21] however, none have been reported which contain aromatic ligands on the gallium center. The Ga-P bond length of 2.459(2) Å in 2 and the mean for 3 of 2.540 Å are well within the established range of lengths previously observed [the shortest being 2.353(2) Å in $Cl_3Ga{\cdot}PMe_3$[20] and the longest being 2.683(5) Å in $(Me_3CCH_2)_3Ga{\cdot}P(H)Ph_2]$.[21] The slight elongation of the Ga-P bond length in **3** as compared with that of **2** is certainly due to its decreased Lewis acidity [Ph_3Ga versus Ph_2GaCl]. The Ga-Cl bond length in **2** of 2.240(3) Å is shorter than that observed for the mean (2.410 Å) in **1** and is to be expected given the nature of the bonding (terminal Cl versus bridging). The geometry about the gallium centers of **2** and **3** is that of a distorted tetrahedron. The steric demands of the bulky phenyl groups on each gives rise to enlarged C-Ga-C angles of 117.3(4)° in **2** and a mean of 113.4° in **3**, the sterically less demanding Cl atom in **2** allows greater distance between the two remaining phenyl groups, thus the angle is larger.

Conclusions

The isolation of **1** from a dehalosilylation reaction further expands the number of compounds which contain mixed-bridging of two group III atoms with a halogen and a pnictide atom. Certainly, compounds of this type, through the bridging halide, will come to fore as reagents for the introduction of other functionalities into the ring system. Additionally, the presence of the chlorine atoms and $SiMe_3$ groups in **1** and **2** could provide an avenue for further oligomerization through elimination reactions. Finally, the fact that **3** was originally isolated from the reaction of $LiP(SiMe_3)_2$ and Ph_2GaCl again shows that these reactions are not as straightforward as one would tend to believe. Further study in this area is warranted.

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Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, complete lists of interatomic distances and angles, including torsion angles for **1**, **2**, and **3** (42 pages). Ordering information is given on any current masthead page.

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Captions to Figures

Figure 1. A thermal ellipsoid diagram (30% probability level) showing the solid state conformation and atom numbering scheme of $Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}$ (1).

Figure 2. A thermal ellipsoid diagram (20% probability level) showing the solid state conformation and atom numbering scheme of $Ph_2(Cl)Ga{\bullet}P(SiMe_3)_3$ (2).

Figure 3. A thermal ellipsoid diagram (30% probability level) showing the solid state conformation of one of the molecules in the asymmetric crystal unit and atom numbering scheme of $Ph_3Ga{\bullet}P(SiMe_3)_3$ (3).

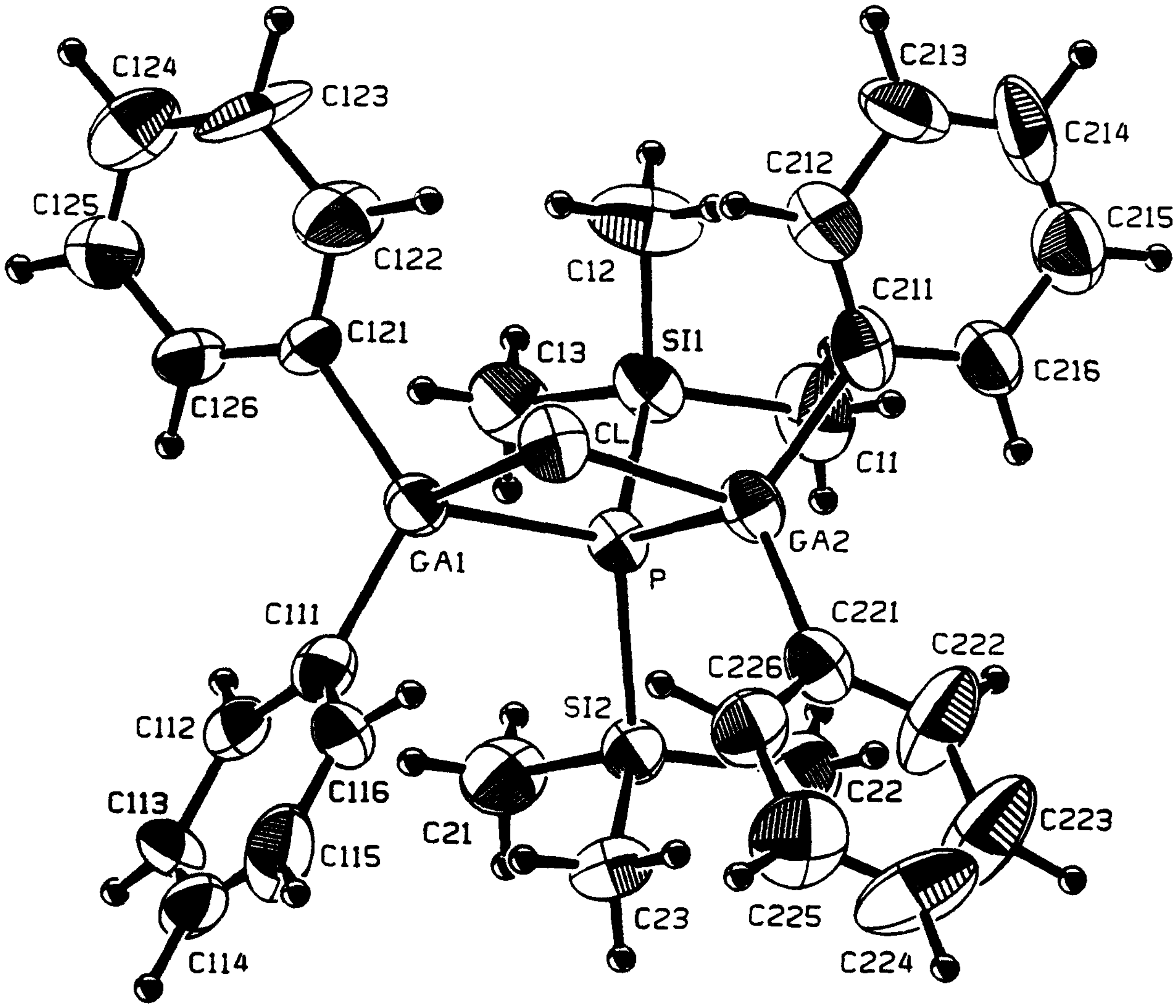
C124
C123
C213
C214
C125
C122
C212
C215
C12
C211
C121
C13
SI1
C216
C126
CL
C11
GA1
P
GA2
C111
C221
C222
C226
C112
SI2
C116
C22
C113
C223
C21
C115
C23
C225
C114
C224

Figure 1

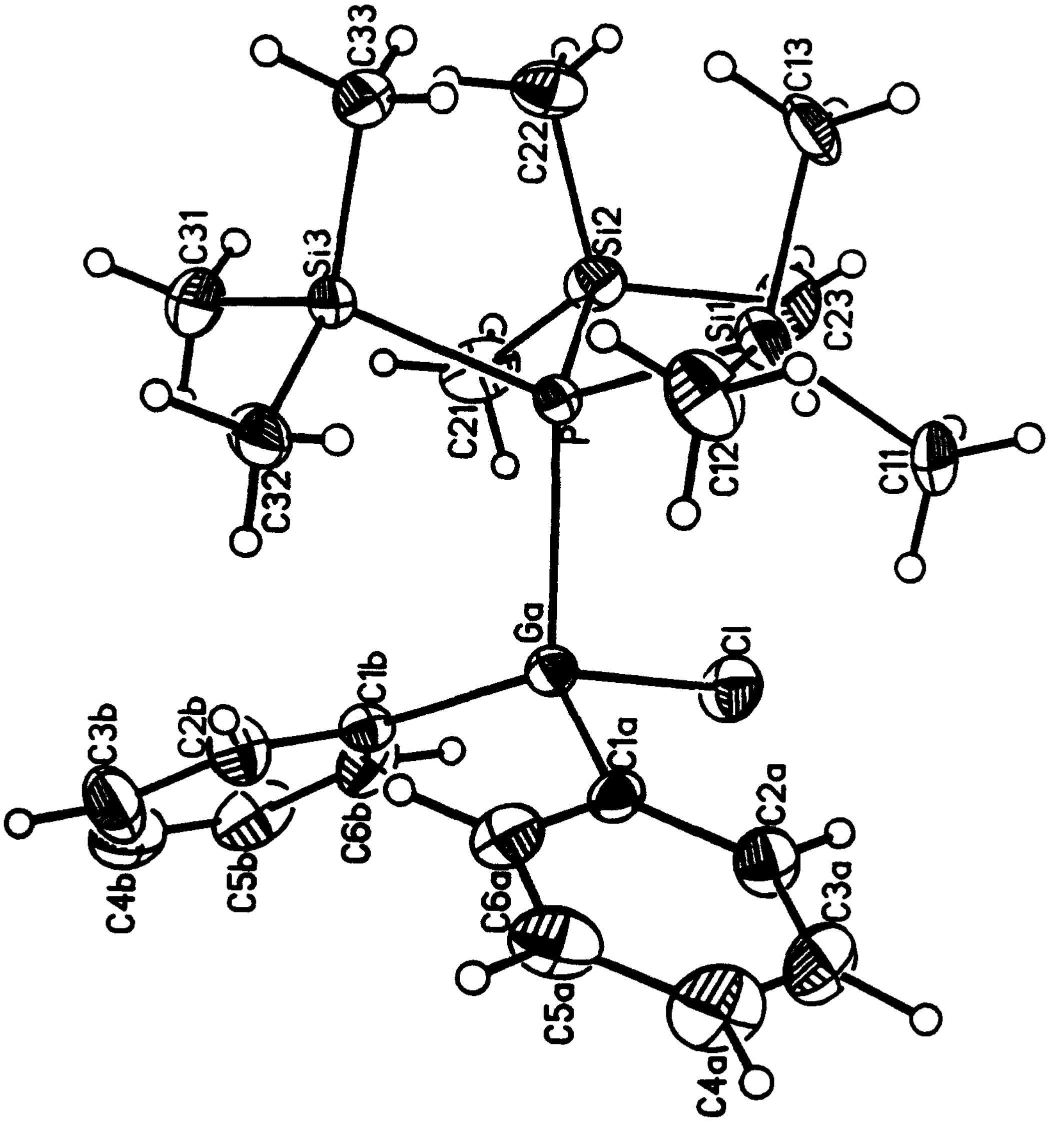
C33
C22
C13
C31
Si3
Si2
Si1
C23
C21
P
C12
C11
C32
Ga
Cl
C1b
C3b
C2b
C6b
C4b
C5b
C1a
C2a
C6a
C3a
C5a
C4a

Figure 2

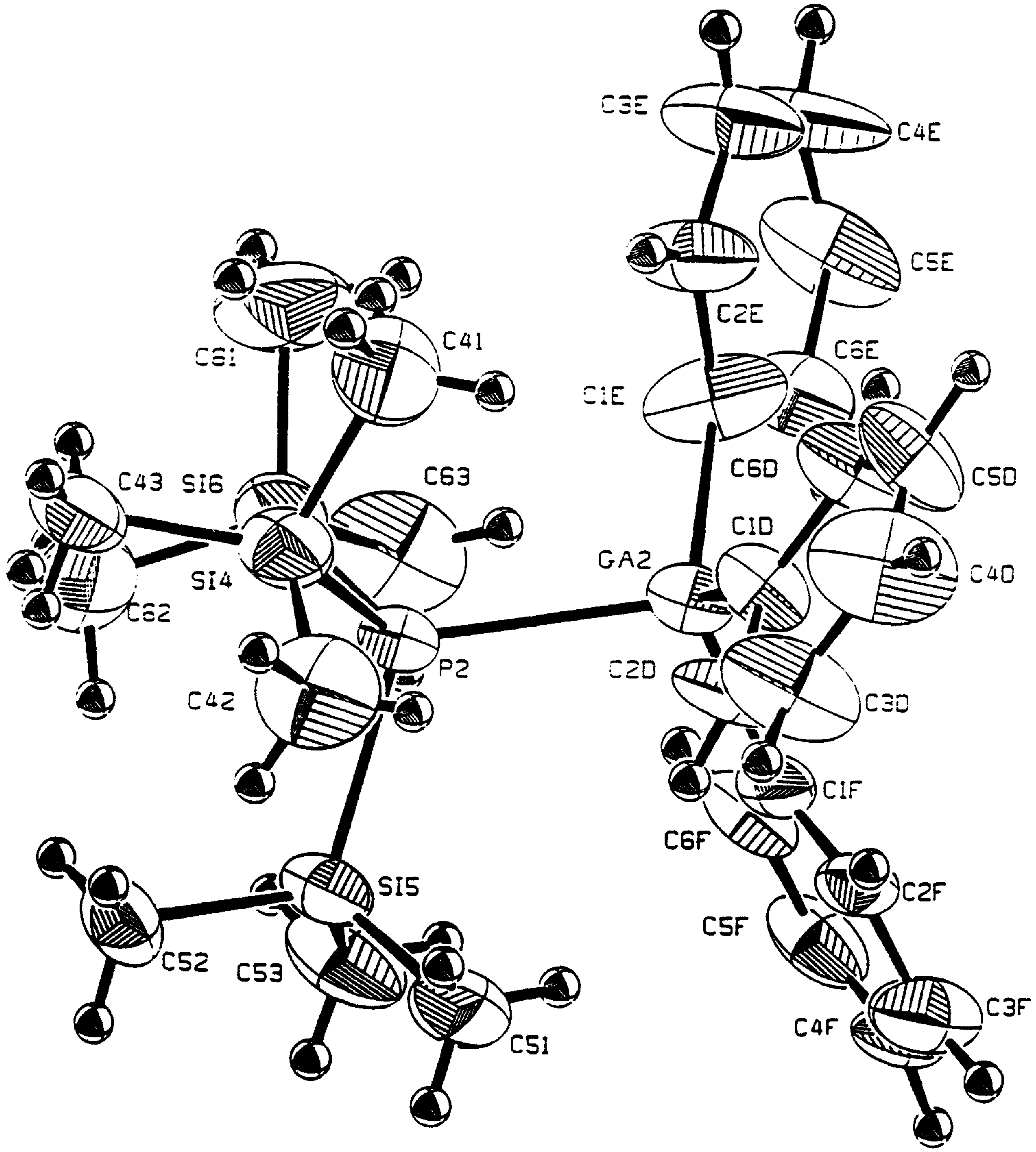
C3E
C4E
C5E
C2E
C6E
C61
C41
C1E
C43
SI6
C63
C6D
C5D
C1D
GA2
C4D
SI4
C62
P2
C2D
C3D
C42
C1F
C6F
SI5
C2F
C5F
C52
C53
C3F
C4F
C51

Figure 3

Table I. Crystallographic Data and Measurements for $\mathrm{Ph_2\overline{GaP(SiMe_3)_2Ga(Ph)_2Cl}}$ (1), $\mathrm{Ph_2(Cl)Ga{\bullet}P(SiMe_3)_3}$ (2), and $\mathrm{Ph_3Ga{\bullet}P(SiMe_3)_3}$ (3)

	1	2	3
molecular formula	$C_{30}H_{38}PSi_2Ga_2Cl$	$C_{21}H_{36}ClGaPSi_3$	$C_{54}H_{84}P_2Si_6Ga_2$
formula weight	660.67	508.9	1103.16
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$
a, Å	10.579(2)	9.3320(10)	18.81(3)
b, Å	15.653(5)	9.768(2)	19.25(2)
c, Å	20.428(4)	30.581(6)	18.93(2)
β, deg	91.80(2)	90	112.8(1)
V, $Å^3$	3381(1)	2787.6(8)	6319(9)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.298	1.213	1.160
crystal dimens, mm	0.5 x 0.4 x 0.7	0.5 x 0.4 x 0.15	0.4 x 0.4 x 1.0
F_{000}	1360	1068	2336
μ, cm^{-1}	18.00	12.68	10.41
scan type	ω	2Θ–Θ	ω
$2\Theta_{max}$, deg	50	55	55.0

Table I (continued)

	1	2	3
scan rate	8.0°/min in ω 2 rescans	variable 4.00 to 15.00°/min in ω	8.0°/min in ω 2 rescans
scan width	(0.98 + 0.30 tanΘ)°	0.80° plus Kα sep.	(1.26 + 0.30 tan Θ)°
R; R_w[a]	0.045; 0.042	0.062; 0.043	0.084; 0.090
goodness-of-fit[b]	1.31	1.32	2.50

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[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $\Sigma w\Delta^2[w = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|)]$ was minimized.

[b] Goodness-of-fit = $[\Sigma w\Delta^2 / (N_{observations} - N_{parameters})]^{1/2}$.

Table II. Non-hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, with estimated Standard Deviations in Parentheses.

atom	x	y	z	U_{eq}(Å^2)
Ga(1)	0.8123(1)	0.23547(8)	0.28673(7)	5.32(8)
Ga(2)	0.5222(1)	0.15113(9)	0.25291(8)	5.91(9)
Cl	0.6054(3)	0.2940(2)	0.2613(2)	6.6(2)
P	0.7222(3)	0.0957(2)	0.2908(2)	5.0(2)
Si(1)	0.7216(3)	0.0403(3)	0.3937(2)	6.2(2)
Si(2)	0.8100(3)	0.0028(2)	0.2201(2)	5.7(2)
C(11)	0.636(1)	-0.0629(9)	0.3936(7)	10(1)
C(12)	0.644(1)	0.112(1)	0.4494(7)	11(1)
C(13)	0.887(1)	0.0284(9)	0.4211(6)	9(1)
C(21)	0.975(1)	-0.0191(8)	0.2457(7)	9(1)
C(22)	0.717(1)	0.0958(8)	0.2188(7)	10(1)
C(23)	0.805(1)	0.0501(8)	0.1390(6)	7.7(9)
C(111)	0.915(2)	0.2520(8)	0.2108(8)	6(1)
C(112)	1.041(2)	0.2240(8)	0.2115(7)	6.7(9)
C(113)	1.117(1)	0.234(1)	0.157(1)	9(1)
C(114)	1.063(3)	0.273(1)	0.102(1)	10(2)
C(115)	0.942(2)	0.299(1)	0.099(1)	10(1)
C(116)	0.869(1)	0.289(1)	0.154(1)	8(1)
C(121)	0.862(2)	0.2912(7)	0.3688(6)	5.0(8)
C(122)	0.783(1)	0.330(1)	0.413(1)	10(1)
C(123)	0.826(2)	0.373(1)	0.4675(9)	12(1)
C(124)	0.953(2)	0.379(1)	0.4814(8)	10(1)
C(125)	1.032(1)	0.343(1)	0.440(1)	9(1)
C(126)	0.988(2)	0.2980(9)	0.3859(8)	7(1)
C(211)	0.396(1)	0.139(1)	0.3196(8)	7(1)
C(212)	0.371(1)	0.200(1)	0.367(1)	8(1)
C(213)	0.287(1)	0.182(1)	0.4171(8)	10(1)

Table II (continued)

atom	*x*	*y*	*z*	U_{eq}(Å^2)
C(214)	0.225(2)	0.107(2)	0.417(1)	12(2)
C(215)	0.242(2)	0.047(1)	0.372(1)	10(1)
C(216)	0.328(2)	0.063(1)	0.3233(8)	9(1)
C(221)	0.480(1)	0.136(1)	0.1605(7)	7(1)
C(222)	0.418(2)	0.066(1)	0.138(1)	12(2)
C(223)	0.387(2)	0.056(1)	0.072(1)	15(2)
C(224)	0.415(3)	0.117(2)	0.027(1)	14(2)
C(225)	0.477(2)	0.185(2)	0.048(1)	12(2)
C(226)	0.509(1)	0.196(1)	0.114(1)	8(1)

Table III. Non-hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters (x 10^3) for 2, with Estimated Standard Deviations in Parentheses.

atom	x	y	z	U_{eq}(Å^2)
Ga	0.7568(1)	0.6124(1)	0.1326(1)	47(1)
Cl	0.6663(3)	0.7704(3)	0.0873(1)	80(1)
P	1.0152(2)	0.6416(2)	0.1199(1)	43(1)
Si(1)	1.0758(3)	0.5294(3)	0.0569(1)	64(1)
Si(2)	1.0743(3)	0.8670(3)	0.1129(1)	65(1)
Si(3)	1.1529(3)	0.5536(3)	0.1751(1)	53(1)
C(1A)	0.6931(9)	0.4307(10)	0.1116(3)	53(4)
C(2A)	0.6207(11)	0.4150(10)	0.0729(3)	74(5)
C(3A)	0.5699(14)	0.2911(13)	0.0588(4)	100(6)
C(4A)	0.5873(16)	0.1780(14)	0.0836(5)	111(7)
C(5A)	0.6562(12)	0.1876(11)	0.1223(4)	90(5)
C(6A)	0.7086(9)	0.3119(10)	0.1369(3)	72(4)
C(1B)	0.7004(8)	0.6664(9)	0.1928(3)	48(3)
C(2B)	0.7208(11)	0.5799(10)	0.2267(3)	75(5)
C(3B)	0.6682(15)	0.6089(14)	0.2695(4)	114(6)
C(4B)	0.5915(15)	0.7239(16)	0.2773(5)	104(7)
C(5B)	0.5696(12)	0.8082(14)	0.2431(5)	104(6)
C(6B)	0.6246(11)	0.7811(11)	0.2019(4)	81(5)
C(11)	0.9353(10)	0.5709(11)	0.0152(3)	90(5)
C(12)	1.0775(12)	0.3447(10)	0.0693(3)	99(5)
C(13)	1.2515(10)	0.5869(10)	0.0371(3)	88(4)
C(21)	0.9763(10)	0.9607(10)	0.1566(3)	96(5)
C(22)	1.2700(10)	0.8932(9)	0.1191(3)	87(4)
C(23)	1.0158(12)	0.9274(9)	0.0581(3)	105(5)
C(31)	1.1433(10)	0.6723(10)	0.2230(3)	86(5)
C(32)	1.0767(9)	0.3819(9)	0.1903(3)	81(4)
C(33)	1.3399(9)	0.5321(10)	0.1555(3)	70(4)

Table IV. Non-hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 3, with Estimated Standard Deviations in Parentheses.

atom	x	y	z	B_{eq}(Å^2)
Ga(1)	0.2529(1)	0.0656(1)	-0.1020(1)	3.7(1)
Ga(2)	0.2613(1)	0.0731(1)	0.4026(1)	3.52(9)
P(1)	0.2561(3)	0.0561(2)	0.0330(3)	3.1(2)
P(2)	0.2636(3)	0.0591(3)	0.5369(3)	3.4(2)
Si(1)	0.1718(3)	0.1308(3)	0.0554(3)	3.8(2)
Si(2)	0.3747(3)	0.0833(3)	0.1224(3)	4.4(2)
Si(3)	0.2250(3)	-0.0515(3)	0.0637(3)	4.0(2)
Si(4)	0.3127(4)	0.1532(3)	0.6128(3)	5.2(3)
Si(5)	0.3354(3)	-0.0331(3)	0.6020(3)	4.4(3)
Si(6)	0.1424(3)	0.0428(3)	0.5329(3)	5.3(3)
C(1A)	0.337(1)	0.126(1)	-0.0962(9)	5(1)
C(1B)	0.149(1)	0.105(1)	-0.165(1)	4(1)
C(1C)	0.270(1)	-0.033(1)	-0.127(1)	6(1)
C(1D)	0.343(1)	0.140(1)	0.409(1)	3.9(9)
C(1E)	0.155(1)	0.111(1)	0.342(1)	6(1)
C(1F)	0.284(1)	-0.023(1)	0.373(1)	3.8(9)
C(2A)	0.335(1)	0.202(1)	-0.077(1)	6(1)
C(2B)	0.142(1)	0.165(1)	-0.208(1)	7(1)
C(2C)	0.212(1)	-0.067(1)	-0.188(1)	6(1)
C(2D)	0.420(1)	0.137(1)	0.458(1)	6(1)
C(2E)	0.134(1)	0.179(1)	0.343(1)	7(1)
C(2F)	0.351(1)	-0.033(1)	0.367(1)	3.9(9)
C(3A)	0.394(1)	0.245(1)	-0.076(2)	8(1)
C(3B)	0.069(1)	0.192(1)	-0.253(2)	9(1)
C(3C)	0.225(1)	-0.131(1)	-0.212(1)	8(1)
C(3D)	0.476(1)	0.181(1)	0.460(1)	8(1)
C(3E)	0.067(1)	0.207(1)	0.294(1)	8(1)

Table IV (continued)

atom	x	y	z	B_{eq}(Å^2)
C(3F)	0.371(1)	-0.097(1)	0.343(1)	6(1)
C(4A)	0.455(1)	0.220(2)	-0.091(1)	9(2)
C(4B)	0.007(1)	0.159(1)	-0.260(2)	9(2)
C(4C)	0.297(2)	-0.161(1)	-0.179(2)	8(1)
C(4D)	0.457(1)	0.236(1)	0.408(2)	9(1)
C(4E)	0.015(2)	0.166(1)	0.240(2)	12(2)
C(4F)	0.319(1)	-0.150(1)	0.330(1)	6(1)
C(5A)	0.459(1)	0.152(1)	-0.106(1)	7(1)
C(5B)	0.009(1)	0.101(1)	-0.219(2)	9(1)
C(5C)	0.353(1)	-0.130(1)	-0.119(1)	8(1)
C(5D)	0.382(1)	0.244(1)	0.359(1)	6(1)
C(5E)	0.034(1)	0.101(1)	0.231(1)	8(1)
C(5F)	0.249(1)	-0.143(1)	0.335(1)	6(1)
C(6A)	0.400(1)	0.110(1)	-0.106(1)	5(1)
C(6B)	0.080(1)	0.075(1)	-0.170(1)	7(1)
C(6C)	0.341(1)	-0.066(1)	-0.096(1)	6(1)
C(6D)	0.327(1)	0.197(1)	0.360(1)	6(1)
C(6E)	0.104(1)	0.072(1)	0.279(1)	6(1)
C(6F)	0.232(1)	-0.079(1)	0.359(1)	5(1)
C(11)	0.175(1)	0.213(1)	0.005(1)	6(1)
C(12)	0.201(1)	0.147(1)	0.159(1)	6(1)
C(13)	0.072(1)	0.094(1)	0.018(1)	6(1)
C(21)	0.390(1)	0.180(1)	0.128(1)	9(1)
C(22)	0.387(1)	0.055(1)	0.219(1)	8(1)
C(23)	0.448(1)	0.041(1)	0.093(1)	7(1)
C(31)	0.196(1)	-0.048(1)	0.148(1)	6(1)
C(32)	0.310(1)	-0.110(1)	0.085(1)	7(1)
C(33)	0.145(1)	-0.0861(9)	-0.022(1)	5(1)
C(41)	0.280(1)	0.231(1)	0.553(1)	7(1)
C(42)	0.422(1)	0.150(1)	0.650(1)	7(1)
C(43)	0.281(1)	0.156(1)	0.684(1)	7(1)

Table IV (continued)

atom	x	y	z	B_{eq}(Å^2)
C(51)	0.426(1)	-0.037(1)	0.584(1)	7(1)
C(52)	0.362(1)	-0.026(1)	0.708(1)	5(1)
C(53)	0.281(1)	-0.117(1)	0.566(1)	6(1)
C(61)	0.091(1)	0.127(1)	0.508(1)	10(2)
C(62)	0.144(1)	0.010(1)	0.624(1)	7(1)
C(63)	0.093(1)	-0.019(1)	0.456(1)	8(1)

Table V. Selected Bond Distances (Å) and Angles (°) for 1, with Estimated Standard Deviations in Parentheses.

Bond Lengths			
Ga1-Cl	2.414(3)	Ga2-C211	1.95(1)
Ga1-P	2.389(3)	Ga2-C221	1.94(1)
Ga1-C111	1.94(1)	P-Si1	2.275(5)
Ga1-C121	1.95(1)	P-Si2	2.270(5)
Ga2-Cl	2.407(3)	Si1-C11	1.85(1)
Ga2-P	2.392(3)	Si1-C12	1.82(1)
Si2-C21	1.83(1)	Si1-C13	1.83(1)
Si2-C22	1.83(1)	Si2-C23	1.81(1)
Mean C-C	1.37(2)		

Bond Angles			
Cl-Ga1-P	89.7(1)	Cl-Ga2-P	89.8(1)
Cl-Ga1-C111	107.8(6)	Cl-Ga2-C211	107.5(6)
Cl-Ga1-C121	103.6(5)	Cl-Ga2-C221	104.6(6)
P-Ga1-C111	112.6(4)	P-Ga2-C211	111.0(4)
P-Ga1-C121	118.6(4)	P-Ga2-C221	116.5(4)
C111-Ga1-C121	118.9(6)	C211-Ga2-C221	121.7(6)
Ga1-P-Ga2	90.4(1)	Ga1-Cl-Ga2	89.4(1)
Ga1-P-Si1	113.2(2)	P-Si1-C11	110.3(5)
Ga1-P-Si2	113.1(2)	P-Si1-C12	110.9(5)
Ga2-P-Si1	114.2(2)	P-Si1-C13	107.0(4)
Ga2-P-Si2	113.7(2)	C11-Si1-C12	108.1(7)
Si1-P-Si2	110.9(2)	C11-Si1-C13	111.9(6)

Table V (continued)

Bond Angles

P-Si2-C21	110.0(4)	C12-Si1-C13	108.6(7)
P-Si2-C22	108.5(4)	C21-Si2-C22	110.7(6)
P-Si2-C23	108.6(4)	C21-Si2-C23	109.6(7)
		C22-Si2-C23	109.3(7)

Torsion Angles[a]

(1)	(2)	(3)	(4)	angle
Ga1	Cl	Ga2	P	6.4(1)
Ga1	P	Ga2	Cl	-6.5(1)
Ga2	Cl	Ga1	P	-6.4(1)
Ga2	P	Ga1	Cl	6.5(1)

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[a] The sign is positive if when looking from atom 2 to atom 3, a clockwise motion of atom 1 would superimpose it on atom 4.

Table VI. Selected Bond Distances (Å) and Angles (°) for 2, with Estimated Standard Deviations in Parentheses.

Bond Lengths

Ga-Cl	2.240(3)	Si3-C31	1.869(10)
Ga-C1a	1.979(10)	Si3-C32	1.880(9)
Ga-C1b	1.986(9)	Si3-C33	1.857(9)
Si1-C11	1.875(9)	Mean C-C	1.370(16)
Si1-C12	1.843(10)	Ga-P	2.459(2)
Si1-C13	1.836(10)	P-Si1	2.288(4)
Si2-C21	1.859(10)	P-Si2	2.279(4)
Si2-C22	1.853(9)	P-Si3	2.289(3)
Si2-C23	1.860(10)		

Bond Angles

Cl-Ga-P	101.1(1)	Ga-P-Si1	108.6(1)
P-Ga-C1a	110.3(2)	Ga-P-Si2	111.4(1)
P-Ga-C1b	112.0(2)	Ga-P-Si3	113.0(1)
C1a-Ga-C1b	117.3(4)	Si1-P-Si2	108.9(1)
Cl-Ga-C1a	107.7(3)	Si1-P-Si3	107.6(1)
Cl-Ga-C(1B)	106.9(3)	Si2-P-Si3	107.2(1)
P-Si1-C11	107.3(3)	P-Si2-C21	106.8(3)
P-Si1-C12	107.3(4)	P-Si2-C22	111.3(3)
P-Si1-C13	110.6(3)	P-Si2-C23	108.7(3)

Table VI (continued)

Bond Angles			
C11-Si1-C12	110.9(5)	C21-Si2-C22	110.1(4)
C11-Si1-C13	109.5(4)	C21-Si2-C23	110.3(4)
C12-Si1-C13	111.1(5)	C22-Si2-C23	108.7(3)
P-Si3-C31	108.5(3)	C31-Si3-C32	110.0(4)
P-Si3-C32	107.7(3)	C31-Si3-C33	111.6(4)
P-Si3-C33	109.4(3)	C32-Si3-C33	109.5(4)

Table VII. Selected Bond Distances (Å) and Angles (°) for 3, with Estimated Standard Deviations in Parentheses.

Bond Lengths

Ga1-P1	2.539(6)	Ga2-P2	2.541(6)
Ga1-C1A	1.94(2)	Ga2-C1D	1.98(2)
Ga1-C1B	2.00(2)	Ga2-C1E	2.01(2)
Ga1-C1C	2.02(2)	Ga2-C1F	2.03(2)
P1-Si1	2.299(7)	P2-Si4	2.273(8)
P1-Si2	2.277(8)	P2-Si5	2.281(7)
P1-Si3	2.288(7)	P2-Si6	2.274(8)

Bond Angles

P1-Ga1-C1A	106.6(5)	P2-Ga2-C1D	107.2(5)
P1-Ga1-C1B	105.3(6)	P2-Ga2-C1E	103.9(7)
P1-Ga1-C1C	103.2(7)	P2-Ga2-C1F	104.9(5)
C1A-Ga1-C1B	113.1(8)	C1D-Ga2-C1E	112.0(8)
C1A-Ga1-C1C	112.3(9)	C1D-Ga2-C1F	111.9(8)
C1B-Ga1-C1C	115.2(8)	C1E-Ga2-C1F	116.0(8)
Ga1-P1-Si1	113.1(2)	Ga2-P2-Si4	113.1(3)
Ga1-P1-Si2	111.5(3)	Ga2-P2-Si5	113.6(3)
Ga1-P1-Si3	114.3(2)	Ga2-P2-Si6	110.7(3)
Si1-P1-Si2	105.4(3)	Si4-P2-Si5	105.6(3)
Si1-P1-Si3	104.9(3)	Si4-P2-Si6	106.7(3)
Si2-P1-Si3	107.0(3)	Si5-P2-Si6	106.6(3)

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