Organometallics **1996,** *15,* 91−97

Synthesis and Structural Characterization of Alkylgallium−Phosphorus Compounds. X-ray Crystal Structures of $(Me_3CCH_2)_2(Cl)Ga\cdot P(SiMe_3)_3$, $R_2\overline{GaP(SiMe_3)_2GaR_2Cl}$ ($R = Me_3CCH_2$, Me_3SiCH_2), and $[(R)(X)GaP(SiMe_3)_2]_2$ ($R = Me_3CCH_2$, $X = Cl$; $R = Me_3CCH_2$, $X = Me_3CCH_2$; $R = Me_3SiCH_2$, $X = Br$)

Richard L. Wells* and Ryan A. Baldwin

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27708

Peter S. White

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514

William T. Pennington

Department of Chemistry, Clemson University, Clemson, South Carolina 29634

Arnold L. Rheingold and Glenn P. A. Yap

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received September 25, 1995⊗

Reaction of $(Me_3CCH_2)_2GaCl$ with $(Me_3Si)_3P$ in a 1:1 mole ratio does not result in any intermolecular dehalosilylation but affords the adduct $(Me_3CCH_2)_2(Cl)Ga\cdot P(SiMe_3)_3$ (**1**) in nearly quantitative yield. Mixing $(Me_3CCH_2)_2GaCl$ and $(Me_3Si)_3P$ in a 2:1 mole ratio yields as the only isolable product the dimeric compound $[(Me_3CCH_2)(Cl)GaP(SiMe_3)_2]_2$ (**2**), which contains three different substituents on the gallium center. This type of product is also observed in the 2:1 reaction of $(Me_3SiCH_2)_2GaBr$ and $(Me_3Si)_3P$, where $[(Me_3SiCH_2)(Br)GaP(SiMe_3)_2]_2$ (**3**) is obtained. The salt elimination reaction between $(Me_3CCH_2)_2GaCl$ and $LiP(SiMe_3)_2$ leads to the dimer $[(Me_3CCH_2)_2GaP(SiMe_3)_2]_2$ (**4**) in good yield. Equilibration of compound **4** with 2 molar equiv of $(Me_3CCH_2)_2GaCl$ produces the mixed-bridge species $(Me_3CCH_2)_2\overline{GaP(SiMe_3)_2Ga(CH_2CMe_3)_2Cl}$ (**5**) in nearly quantitative yield. The mixed-bridge compound $(Me_3SiCH_2)_2\overline{GaP(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}$ (**6**) results from the 2:1 dehalosilylation reaction of $(Me_3SiCH_2)_2GaCl$ and $(Me_3Si)_3P$. Various physical and spectroscopic data are presented for compounds **1**−**6**, as well as the results of their X-ray crystal structure determinations.

Introduction

Continued activity in the development of single-source precursors to group 13−group 15 semiconductor materials[1] has motivated our laboratory to investigate the synthesis of novel organogallium−phosphorus compounds which might serve as potential precursors to GaP. Recently, our efforts to produce the gallium-phosphorus bond have led to the formation of interesting ring compounds and simple adducts. For example, the ring compounds $[X_2GaP(SiMe_3)_2]_2$ (X = Cl,[2] Br,[3] I[3]) and $Ph_2\overline{GaP(SiMe_3)_2GaPh_2Cl}$ (**7**)[4] have been isolated in our laboratory through dehalosilylation reactions, along with the adducts $R_3Ga\cdot P(SiMe_3)_3$ (R = Ph (**8**),[4] Me_3SiCH_2 (**9**)[5]) and $Ph_2(Cl)Ga\cdot P(SiMe_3)_3$ (**10**).[4] As part of a continuing effort to expand our knowledge of the gallium−phosphorus system, we wanted to further investigate reactions involving $(Me_3Si)_3P$ and its monolithium salt $LiP(SiMe_3)_2$ with alkylgallium halides. The bulky neopentyl and (trimethylsilyl)methyl ligands were chosen as the alkyl substituents on the gallium atom, in hopes of affecting the oligomerization or structural conformation of the resulting products. Our goal was to produce compounds which could serve as effective intermediates to species containing novel mixtures of group 13 and group 15 atoms. Through these efforts, we were able to isolate several new compounds and to

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* To whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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0276-7333/96/2315-0091$12.00/0

observe some interesting chemical phenomena; herein, we report the results obtained from our investigations.

Experimental Section

General Considerations. All manipulations of air- and moisture-sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by general Schlenk techniques. Benzene was distilled from sodium benzophenone ketyl under dry dinitrogen. Pentane was distilled over $LiAlH_4$ under dry dinitrogen. $(Me_3CCH_2)_2GaCl$,[6] $(Me_3SiCH_2)_2GaCl$,[7] $(Me_3SiCH_2)_2GaBr$,[7] and $(Me_3Si)_3P$[8] were synthesized by literature procedures. $LiP(SiMe_3)_2$ was prepared via the 1:1 reaction of $(Me_3Si)_3P$ and MeLi. The integrity of all materials used was confirmed via ^1H NMR spectra and by melting points. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300, 75.4, and 121.4 MHz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm, respectively, or the upfield pentet of C_7D_8 at δ 2.09 ppm for ^1H NMR spectra. All NMR samples were prepared in 5-mm tubes which were septum-sealed under argon. Melting points (uncorrected) were obtained with a Thomas-Hoover Uni-melt apparatus, and capillaries were flame-sealed under argon. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Mass spectral data were collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV. X-ray crystallographic data for compounds **1**−**6** were obtained as follows: data for **1**−**3** were obtained at −135 °C on a Rigaku AFC6/S diffractometer utilizing graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) radiation; data for **4** and **5** were obtained at 25 °C on a Siemens P4 diffractometer utilizing graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) radiation; data for **6** were obtained at −140 °C on a Rigaku AFC-7R diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) radiation.

Preparation of $(Me_3CCH_2)_2(Cl)Ga\cdot P(SiMe_3)_3$ (1). $(Me_3CCH_2)_2GaCl$ (0.247 g, 1.00 mmol) in 25 mL of pentane and $(Me_3Si)_3P$ (0.250 g, 0.998 mmol) in 25 mL of pentane were combined in a 250-mL one-necked round-bottomed flask equipped with a Teflon valve and a magnetic stirbar. The resulting clear solution was stirred at room temperature outside of the drybox for 48 h. The volatiles were removed *in vacuo* to yield a white crystalline solid, which was dissolved in 5 mL of warm pentane. Cooling the resulting solution to −15 °C for several days afforded colorless crystals of **1** suitable for X-ray analysis (0.487 g, 98% yield); mp 89−96 °C. Anal. Calcd (found) for $C_{19}H_{49}ClGaPSi_3$: C, 45.82 (46.04); H, 9.92 (9.79); Cl, 7.12 (6.90). ^1H NMR (C_6D_6): δ 0.29 [d, $SiMe_3$ (J_{P-H} = 4.8 Hz)], 1.14 (s, CH_2), 1.32 (s, C−Me_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.33 [d, $SiMe_3$ (J_{P-C} = 8.4 Hz)], 33.03 (s, −CMe_3), 34.38 (s, Me_3), 40.39 (s, CH_2). $^{31}P\{^1H\}$ NMR: δ −230.12. Mass spectrum: *m/z* 496, $(C_{19}H_{47}ClGaPSi_3)^+ = (M - 2H)^+$.

Preparation of $[(Me_3CCH_2)(Cl)GaP(SiMe_3)_2]_2$ (2). Compound **2** was synthesized using a procedure similar to that used for **1**. Reactants: $(Me_3CCH_2)_2GaCl$ (0.495 g, 2.00 mmol), $(Me_3Si)_3P$ (0.250 g, 0.998 mmol). Product: 0.163 g, 46% yield (based on P); mp 29−44 °C. X-ray-quality crystals were grown from a pentane/chlorobenzene mixture. Anal. Calcd (found) for $C_{22}H_{58}Cl_2Ga_2P_2Si_4$: C, 37.30 (36.83); H, 8.26 (8.19). ^1H NMR (C_6D_6): δ 0.50 [t, P−$SiMe_3$ (J_{P-H} = 3.6 Hz)], 1.21 (s, CH_2), 1.30 (s, CMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.21 (s, CMe_3), 4.13 (s, CH_2), 6.77 [t, P-$SiMe_3$ (J_{P-C} = 4.7 Hz)]. $^{31}P\{^1H\}$ NMR: δ −233.86.

Preparation of $[(Me_3SiCH_2)(Br)GaP(SiMe_3)_2]_2$ (3). Compound **3** was synthesized using a procedure similar to that used for **1**. Reactants: $(Me_3SiCH_2)_2GaBr$ (0.648 g, 2.00 mmol), $(Me_3Si)_3P$ (0.250g, 0.998 mmol). Product: 0.170 g, 41% yield (based on P); mp 87−101 °C. X-ray-quality crystals were grown from pentane. Anal. Calcd (found) for $C_{20}H_{58}Br_2Ga_2P_2Si_6$: C, 28.99 (32.65); H, 7.06 (7.59); Br, 19.29 (21.15). ^1H NMR (C_6D_6): δ 0.24 (s, CH_2), 0.35 (s, $SiMe_3$), 0.50 [t, P-$SiMe_3$ (J_{P-H} = 2.7 Hz)]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.42 (s, $SiMe_3$), 2.80 (s, CH_2), 3.87 [t, P-$SiMe_3$ (J_{P-C} = 3.7 Hz)]. $^{31}P\{^1H\}$ NMR: δ −227.61. Mass spectrum: *m/z* 829, $(C_{20}H_{59}Br_2Ga_2P_2Si_6)^+ = (M + H)^+$

Preparation of $[(Me_3CCH_2)_2GaP(SiMe_3)_2]_2$ (4). $(Me_3CCH_2)_2GaCl$ (0.247 g, 1.00 mmol) in 25 mL of benzene and $LiP(SiMe_3)_2$ (0.184 g, 0.999 mmol) in 25 mL of benzene were combined in a 250-mL one-necked round-bottomed flask equipped with a Teflon valve and a magnetic stirbar. The resulting yellow solution was stirred at room temperature outside of the drybox for 48 h. The volatiles were removed *in vacuo* to yield a yellow powder, which was extracted with 25 mL of pentane. Upon filtration, concentration, and cooling of the extract to −15 °C for several days, colorless crystals of **4** suitable for X-ray analysis were obtained (0.618 g, 79% yield); mp 49 - 58 °C. Anal. Calcd (found) for $C_{32}H_{80}Ga_2P_2Si_4$: C, 49.94 (50.11); H, 10.33 (10.68). ^1H NMR (C_6D_6): δ 0.42 [t, $SiMe_3$ (J_{P-H} = 4.8 Hz)], 1.11 (s, CH_2), 1.25 (s, C−Me_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.89 [t, $SiMe_3$ (J_{P-C} = 2.6 Hz)], 32.82 [d, Me_3 (J_{P-C} = 3.8 Hz)], 34.82 (s, −CMe_3). $^{31}P\{^1H\}$ NMR: δ −215.24.

Preparation of $(Me_3CCH_2)_2\overline{GaP(SiMe_3)_2Ga(CH_2CMe_3)_2Cl}$ (5). Compound **4** (0.637 g, 1.00 mmol) in 25 mL of pentane and $(Me_3CCH_2)_2GaCl$ (0.594 g, 2.00 mmol) in 25 mL of pentane were combined in a 250-mL one-necked round-bottomed flask equipped with a Teflon valve and a magnetic stirbar. The resulting clear solution was stirred at room temperature outside of the drybox for 48 h. The volatiles were removed *in vacuo* to yield a white crystalline solid, which was dissolved in 5 mL of warm pentane. Cooling the resulting solution to −30 °C for several days afforded colorless crystals of **5** suitable for X-ray analysis (1.206 g, 98% yield); mp 44−48 °C. Anal. Calcd (found) for $C_{26}H_{62}ClGa_2PSi_2$: C, 49.04 (48.84); H, 9.81 (9.69); Cl, 5.57 (5.25). ^1H NMR (C_6D_6): δ 0.38 [d, $SiMe_3$ (J_{P-H} = 4.8 Hz)], 1.24 (s, C-Me_3), 1.30 (s, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 4.59 [d, $SiMe_3$ (J_{P-C} = 7.6 Hz)], 34.55 (s, Me_3), 39.67 [d, CH_2 (J_{P-C} = 14.0 Hz)]. $^{31}P\{^1H\}$ NMR: δ −210.22.

Preparation of $(Me_3SiCH_2\overline{GaP(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}$ (6). Compound **6** was synthesized using a procedure similar to that used for **1**. Reactants: $(Me_3SiCH_2)_2GaCl$ (0.559 g, 2.00 mmol), $(Me_3Si)_3P$ (0.250 g, 0.998 mmol). Product: 0.694 g, 75% yield; mp. 68−75 °C. X-ray-quality crystals were grown from pentane. Anal. Calcd (found) for $C_{22}H_{62}ClGa_2PSi_6$: C, 37.68 (37.48); H, 8.84 (8.74); P, 4.57 (4.18). ^1H NMR (C_6D_6): δ 0.25 (s, −CH_2SiMe_3), 0.34 [d, $SiMe_3$ (J_{P-H} = 5.4 Hz)]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.32 (s, −$SiMe_3$), 3.37 [d, P-$SiMe_3$ (J_{P-C} = 7.8 Hz)], 7.81 [d, CH_2 (J_{P-C} = 10.7 Hz)]. $^{31}P\{^1H\}$ NMR: δ −213.27. Mass spectrum: *m/z* 697, $(C_{22}H_{61}ClGa_2PSi_6)^+ = (M - H)^+$.

X-ray Structural Solution and Refinement. Crystallographic data are summarized in Table 1. The structural analyses were performed as follows.

Compounds 1−3. Colorless crystals of **1**−**3** were mounted on a glass fiber with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at −135 °C on a Rigaku AFC6/S diffractometer utilizing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å), and the structures were solved by direct methods. Full-matrix least-squares refinement with weights based upon counting statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement, which converged at $R = 0.043$ ($R_w = 0.051$) for **1**, $R = 0.063$ ($R_w = 0.075$) for **2**, and $R = 0.036$ ($R_w = 0.041$) for **3**. A final difference-Fourier synthesis revealed no unusual features. Crystallographic calculations were performed using the NRCVAX[9] suite of structure determination programs. For all structure-factor calculations, neutral atom scattering fac-

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Table 1. Crystallographic Data and Measurements for $(Me_3CCH_2)_2Ga(Cl){\cdot}P(SiMe_3)_3$ (1), $[(Me_3CCH_2)(Cl)GaP(SiMe_3)_2]_2$ (2), $[(Me_3SiCH_2)(Br)GaP(SiMe_3)_2]_2$ (3), $[(Me_3CCH_2)_2GaP(SiMe_3)_2]_2$ (4), $(Me_3CCH_2)_2GaP(SiMe_3)_2Ga(CH_2CMe_3)_2Cl$ (5), and $(Me_3SiCH_2)_2GaP(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl$ (6)

	1	**2**	**3**
mol formula	$C_{19}H_{49}ClGaPSi_3$	$C_{22}H_{58}Cl_2Ga_2P_2Si_4$	$C_{20}H_{58}Br_2Ga_2P_2Si_6$
fw	497.99	707.32	828.38
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	12.320(7)	12.000(4)	9.705(4)
b, Å	12.308(5)	10.191(5)	19.020(5)
c, Å	19.550(8)	17.402(3)	11.268(4)
β, deg	101.97(4)	92.910(20)	111.61(3)
V, Å^3	2900.0(23)	2125.4(13)	1933.8(11)
Z	4	2	2
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm^{-1}	12.2	16.6	37.1
temp, °C	−135	−135	−135
D_{calcd}, g cm^{-3}	1.141	1.273	1.423
crystal dimens, mm	0.40 × 0.35 × 0.35	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.25
T_{max}, T_{min}	0.725:0.577	0.707:0.469	0.450:0.289
scan type	ω	ω	ω
$2\theta_{max}$, deg	45	50	50
no. of rflns recorded	3768	3818	3782
no. of nonequiv rflns recorded	3762	3730	3408
R_{merg} (on I)	0.057	0.058	0.025
no. of rflns retained, $I > 2.5\sigma(I)$ or $I > 3.0\sigma(I)$	2827	2380	2387
no. of params refined	132	174	145
R, R_w[a]	0.043, 0.051	0.063, 0.075	0.036, 0.041
goodness of fit[b]	1.55	2.06	1.19
max shift/esd in final least-squares cycle	0.000	0.030	0.004
final max, min $\Delta\rho$, e Å^{-3}	0.740, −0.960	1.780, −1.730	0.620, −0.740

	4	**5**	**6**
mol formula	$C_{32}H_{80}Ga_2P_2Si_4$	$C_{26}H_{62}ClGa_2PSi_2$	$C_{22}H_{62}ClGa_2PSi_6$
fw	778.7	636.8	701.12
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2/n$	$P2_1/n$	$P2_1/n$
a, Å	12.1069(7)	12.355(1)	16.149(5)
b, Å	12.5860(13)	17.257(2)	23.144(5)
c, Å	15.321(2)	17.713(3)	10.700(3)
β, deg	90.148(8)	98.02(1)	90.88(2)
V, Å^3	2334.6(4)	3739.7(6)	3999(1)
Z	2	4	4
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm^{-1}	13.43	16.31	16.4
temp, °C	25	25	−140
D_{calcd}, g cm^{-3}	1.108	1.131	1.16
crystal dimens, mm	0.40 × 0.40 × 0.30	0.30 × 0.30 × 0.40	0.18 × 0.34 × 0.48
T_{max}, T_{min}			0.69, 1.00
scan type	ω	ω	$\omega/2\theta$
$2\theta_{max}$, deg	60	45	50
no. of rflns recorded	6707	7631	8634
no. of nonequiv rflns recorded	5211	4844	7024
R_{merg} (on I)	0.071	0.024	0.072
no. of rflns retained, $I > 2.5\sigma(I)$ or $I > 3.0\sigma(I)$	2126	2654	3589
no. of params refined	182	289	290
R, R_w[a]	0.068, 0.177[c]	0.038, 0.042	0.0805, 0.0806
goodness of fit[b]	0.960	1.00	3.42
max shift/esd in final least-squares cycle	0.000	0.000	0.0006
final max, min $\Delta\rho$, e Å^{-3}	0.551, −0.539	0.36, −0.30	0.89, −0.82

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [b] Goodness of fit $= [\sum w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$. [c] $R(wF^2) = \sum[w(F_o{}^2 - F_c{}^2)^2/\sum(wF_o{}^2)]^{1/2}$.

tors and their anomalous dispersion corrections were taken from ref 10. Interatomic distances and angles are given in Tables 2 and 3. ORTEP[11] diagrams showing the solid-state conformations and atom-numbering schemes of **1**−**3** are presented in Figures 1−3.

Compounds 4 and 5. Colorless crystals of **4** and **5** suitable for X-ray diffraction were mounted in glass capillaries under argon. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° < 2θ < 25°). The structures were solved by direct methods, completed by subsequent difference-Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL PLUS[12] (4.2) and SHELXTL (5.3) program libraries. ORTEP diagrams showing the solid-state conformations and

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Table 2. Selected Bond Distances (Å) for 1−6, with Estimated Standard Deviations in Parentheses

	Compound **1**		
Ga−P(1)	2.534(2)	Ga−Cl(1)	2.258(2)
P(1)−Si(3)	2.275(2)	Ga−C(11)	1.998(5)
P(1)−Si(4)	2.279(2)	Ga−C(21)	1.999(5)
P(1)−Si(5)	2.285(2)		
	Compound **2**		
Ga−P(1)	2.419(2)	Ga−Cl(1)	2.240(2)
Ga−P(1)′	2.424(2)	Ga−C(31)	1.987(8)
P(1)−Si(1)	2.275(3)		
P(1)−Si(2)	2.281(3)		
	Compound **3**		
Ga−P(1)	2.427(2)	Ga−Br(1)	2.372(9)
Ga−P(1)′	2.421(2)	Ga−C(11)	1.979(5)
P(1)−Si(2)	2.272(2)		
P(1)−Si(3)	2.278(2)		
	Compound **4**		
Ga−P(1)	2.512(2)	Ga−C(12)	2.000(7)
Ga−P(2)	2.522(2)		
P(1)−Si(1)	2.267(2)		
P(2)−Si(2)	2.264(2)		
	Compound **5**		
Ga(1)−Cl(1)	2.420(2)	Ga(1)−P(1)	2.446(2)
Ga(1)−C(1)	1.966(6)	Ga(2)−P(1)	2.456(2)
Ga(2)−Cl(1)	2.415(2)	Ga(2)−C(16)	1.976(6)
Ga(2)−C(11)	1.959(6)		
	Compound **6**		
Ga(1)−Cl(1)	2.435(4)	Ga(1)−P(1)	2.414(4)
Ga(1)−C(1)	1.97(1)	Ga(2)−P(1)	2.418(4)
Ga(2)−Cl(1)	2.419(4)	Ga(2)−C(13)	1.97(1)
Ga(2)−C(9)	1.98(1)		

atom-numbering schemes of **4** and **5** are presented in Figures 4 and 5.

Compound 6. A colorless parallelepiped crystal of **6** was mounted in a glass capillary under an argon atmosphere. Cell parameters and an orientation matrix for data collection, obtained from a least-squares analysis of the setting angles of 24 reflections in the range $42.48° < 2\theta < 49.21°$, corresponded to a monoclinic cell. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by standard difference-Fourier techniques and were included in the structure factor calculation at idealized positions based on a riding model. An isotropic group thermal parameter was refined for all of the hydrogens. Structure solution, refinement, and the calculation of derived results were performed using the TEXSAN[13] and SHELXTL[12] packages of computer programs. Neutral atom scattering factors were those of Cromer and Waber,[14] and the real and imaginary anomalous dispersion corrections were those of Cromer.[15] An ORTEP diagram showing the solid-state conformation and atom-numbering scheme of **6** is presented in Figure 6.

Results and Discussion

Tris(trimethylsilyl)phosphine, $(Me_3Si)_3P$, reacts at room temperature with $(Me_3CCH_2)_2GaCl$ in a 1:1 mole ratio to form the simple Lewis acid−base adduct $(Me_3CCH_2)_2(Cl)Ga{\cdot}P(SiMe_3)_3$ (**1**) in a nearly quantitative yield. This result is in accord with that seen when the alkyl/aryl group on the gallium center is phenyl.[4] Compound **1** was characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, partial elemental analysis, and single-crystal X-ray analysis (vide infra).

Table 3. Selected Bond Angles (deg) for 1−6, with Estimated Standard Deviations in Parentheses

	Compound **1**		
Ga−P(1)−Si(3)	110.34(7)	P(1)−Ga−Cl(1)	97.49(6)
Ga−P(1)−Si(4)	114.87(7)	P(1)−Ga−C(11)	101.51(16)
Ga−P(1)−Si(5)	111.80(7)	P(1)−Ga−C(21)	106.23(15)
Si(3)−P(1)−Si(4)	107.14(8)	Cl(1)−Ga−C(11)	110.84(15)
Si(3)−P(1)−Si(5)	107.10(7)	Cl(1)−Ga−C(21)	115.63(15)
Si(4)−P(1)−Si(5)	105.15(7)	C(11)−Ga−C(21)	120.99(21)
	Compound **2**		
Ga(1)−P(1)−Ga(1)′	89.92(8)	P(1)′−Ga(1)−Cl(1)	104.76(8)
Ga(1)−P(1)−Si(1)	113.09(10)	P(1)′−Ga(1) C(31)	121.39(24)
Ga(1)−P(1)−Si(2)	113.09(11)	Ga(1)′−P(1)−Si(1)	113.60(11)
Si(1)−P(1)−Si(2)	108.31(12)	Ga(1)′−P(1)−Si(2)	118.01(10)
P(1)−Ga(1)−P(1)′	90.08(7)		
P(1)−Ga(1)−Cl(1)	105.01(8)		
	Compound **3**		
Ga(1)−P(1)−Ga(1)′	90.32(5)	P(1)′−Ga(1)−Br(1)	104.52(4)
Ga(1)−P(1)−Si(2)	113.96(7)	P(1)′−Ga(1)−C(11)	124.52(16)
Ga(1)−P(1)−Si(3)	112.01(7)	Ga(1)′−P(1)−Si(2)	113.80(7)
Si(2)−P(1)−Si(3)	107.36(8)	Ga(1)′−P(1)−Si(3)	118.85(7)
P(1)−Ga(1)−P(1)′	89.68(5)		
P(1)−Ga(1)−Br(1)	108.14(4)		
	Compound **4**		
Ga(1)−P(2)−Ga(1A)	93.47(8)	C(7)−Ga(1)−P(1)	103.8(2)
Ga(1)−P(1)−Si(1)	118.41(5)	Si(1)−P(1)−Ga(1)	118.41(5)
Si(2)−P(2)−Si(2A)	103.76(14)		
P(1)−Ga(1)−P(2)	86.29(5)		
C(7)−Ga(1)−C(12)	133.0(3)		
	Compound **5**		
Cl(1)−Ga(1)−P(1)	88.4(1)	Cl(1)−Ga(1)−C(1)	109.0(2)
P(1)−Ga(1)−C(1)	112.5(2)	Cl(1)−Ga(1)−C(6)	98.2(2)
P(1)−Ga(1)−C(6)	114.9(2)	Cl(1)−Ga(2)−C(11)	98.1(2)
Cl(1)−Ga(2)−P(1)	88.3(1)	Cl(1)−Ga(2)−C(16)	108.7(2)
P(1)−Ga(2)−C(11)	115.4(2)	Ga(1)−P(1)−Ga(2)	90.9(1)
Ga(1)−Cl(1)−Ga(2)	92.5(1)	Ga(2)−P(1)−Si(1)	120.6(1)
Ga(1)−P(1)−Si(1)	108.9(1)	Ga(2)−P(1)−Si(2)	110.3(1)
Ga(1)−P(1)−Si(2)	120.8(1)		
	Compound **6**		
Cl(1)−Ga(1)−P(1)	87.3(1)	Cl(1)−Ga(1)−C(1	102.7(4)
P(1)−Ga(1)−C(1)	108.7(4)	Cl(1)−Ga(1)−C(5)	102.2(4)
P(1)−Ga(1)−C(5)	119.5(4)	C(1)−Ga(1)−C(5)	126.1(6)
Cl(1)−Ga(2)−P(1)	87.6(1)	Cl(1)−Ga(2)−C(9)	105.1(4)
P(1)−Ga(2)−C(9)	114.2(4)	Cl(1)−Ga(2)−C(13)	104.7(4)
Ga(1)−Cl(1)−Ga(2)	89.9(1)	Ga(1)−P(1)−Ga(2)	90.4(1)
Ga(1)−P(1)−Si(5)	116.0(2)	Ga(2)−P(1)−Si(5)	109.9(2)
Ga(1)−P(1)−Si(6)	110.2(2)	Ga(2)−P(1)−Si(6)	121.3(2)

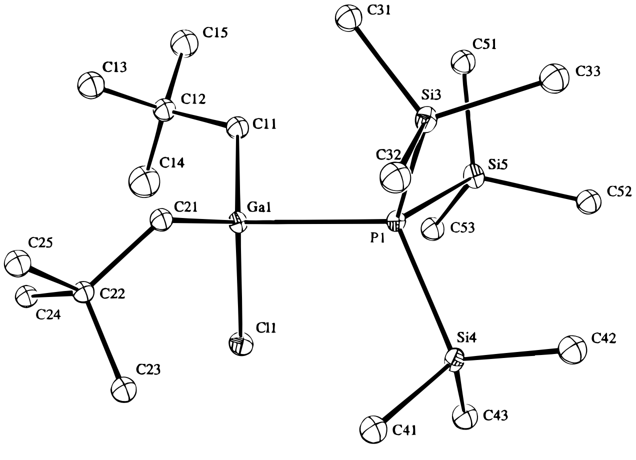

Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of **1**. Hydrogen atoms are omitted for clarity.

The 2:1 reaction of $(Me_3CCH_2)_2GaCl$ and $(Me_3Si)_3P$ does not involve intermolecular dehalosilylation to afford the desired mixed-bridge compound containing a four-membered $\overline{\text{Ga−P−Ga−Cl}}$ ring but yields instead $[(Me_3CCH_2)(Cl)GaP(SiMe_3)_2]_2$ (**2**) as the only isolable product. This is in contrast to the results observed

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(13) Swepston, P. N. TEXSAN Structure Analysis Software, Molecular Structure Corp.: The Woodlands, TX, 1993.

(14) Reference 10, Table 2.2B.

(15) Reference 10, Table 2.3.1.

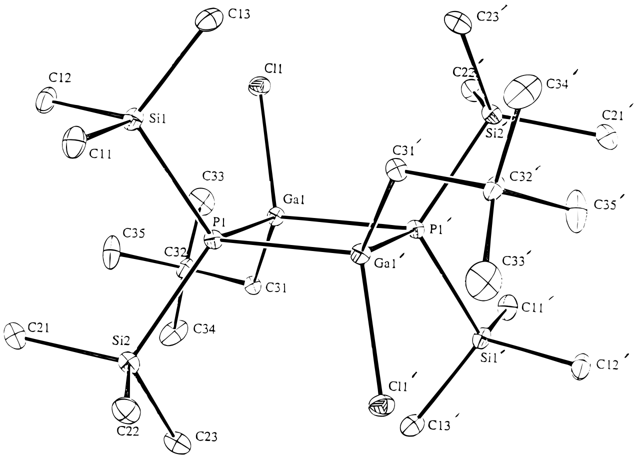

Figure 2. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of **2**. Hydrogen atoms are omitted for clarity. Primed atoms are related to nonprimed atoms by a center of symmetry.

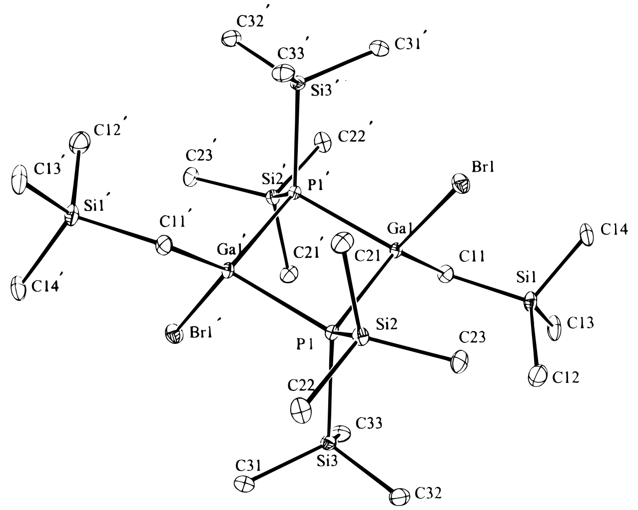

Figure 3. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of **3**. Hydrogen atoms are omitted for clarity. Primed atoms are related to nonprimed atoms by a center of symmetry.

when the substituent on the gallium atom is phenyl, where the mixed-bridge species is formed in moderate yield.[4] Isolation of **2** as the sole product of the reaction is surprising yet plausible. Ligand redistributions of this type are not without precedent in group 13−group 15 systems and can be observed most notably in the aluminum-phosphorus system.[16]

Similarly, $[(Me_3SiCH_2)(Br)GaP(SiMe_3)_2]_2$ (**3**) was the sole product obtained from the 2:1 reaction of $(Me_3SiCH_2)_2GaBr$ with $(Me_3Si)_3P$ and was recovered in a 41% crystalline yield. This compound was characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR, partial elemental analysis, electron impact mass spectrometry, and single-crystal X-ray analysis (vide infra). The formation pathway of **3** is believed to be similar to that of **2**. It is important to note that compounds **2** and **3** are unique in that they are gallium compounds which contain three different substituents on the metal center. As evidenced by Beachley and co-workers,[17] these compounds are difficult to fully characterize in the solid and solution phases. To this end, dimers **2** and **3** represent only the third and fourth examples, in the Ga−P system, of these types of compounds to be characterized by X-ray crys-

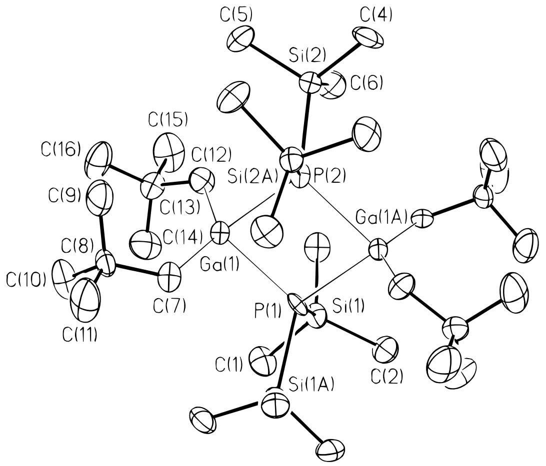

Figure 4. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of **4**. Hydrogen atoms are omitted for clarity.

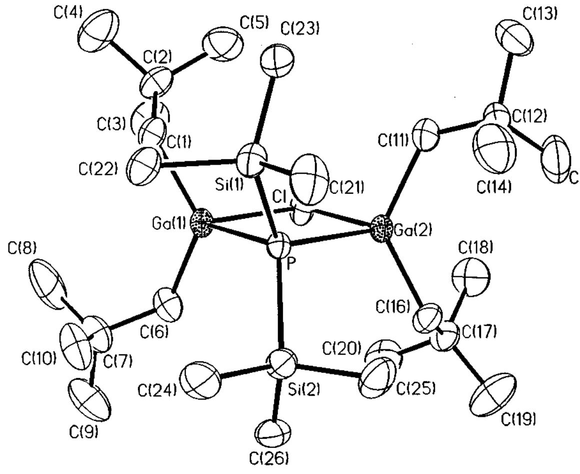

Figure 5. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of **5**. Hydrogen atoms are omitted for clarity.

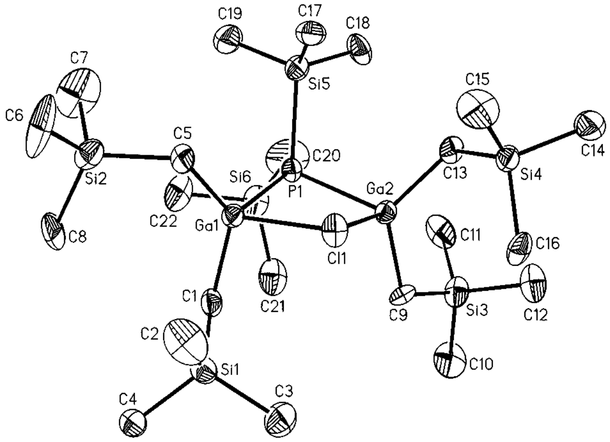

Figure 6. ORTEP diagram (35% probability ellipsoids) showing the solid-state structure and atom-numbering scheme of **6**. Hydrogen atoms are omitted for clarity.

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(16) Wells, R. L.; McPhail, A. T.; Self, M. F.; Laske, J. A. *Organometallics* **1993**, *12*, 3333.

(17) Beachley, O. T., Jr.; Maloney, J. D.; Rogers, R. D.; *J. Organomet. Chem.* **1993**, *449*, 69.

tallographic means. Those whose solid-state structures have been determined are $\{(^tBu)[P(H)(^tBu_3C_6H_2)]GaCl\}_2$ (**11**)[18] and $[(Me_3CCH_2)(Cl)GaPPh_2]_3$ (**12**).[17]

The dimer $[(Me_3CCH_2)_2GaP(SiMe_3)_2]_2$ (**4**) is obtained from the direct 1:1 salt-elimination reaction of $(Me_3CCH_2)_2GaCl$ and $LiP(SiMe_3)_2$ in benzene at room temperature. The solution ^1H NMR data are consistent with the solid-state structure of **4**, as revealed by the single-crystal X-ray analysis. Most notably, the spectrum contains a triplet centered at δ 0.42 ppm which corresponds to virtual coupling between the ring phosphorus atoms and the $SiMe_3$ protons, indicating the dimeric nature of the compound in solution. The absence of a doublet resonance in the ^1H NMR spectrum suggests that **4** does not dissociate in solution to give any monomeric species. Dimeric compounds in the gallium-phosphorus system which contain two alkyl or aryl groups on the metal centers and two trimethylsilyl groups on the pnicogen atoms are scarce; to our knowledge, compound **4** represents only the second example of a structurally characterized species of this type (the other being $[Me_2GaP(SiMe_3)_2]_2$[19] (**13**)).

Equilibration of dimer **4** with 2 molar equiv of $(Me_3CCH_2)_2GaCl$ leads to the mixed-bridge species $(Me_3CCH_2)_2\overline{GaP(SiMe_3)_2Ga(CH_2CMe_3)_2Cl}$ (**5**). As noted above, compound **5** could not be isolated from the direct 2:1 reaction of $(Me_3CCH_2)_2GaCl$ and $(Me_3Si)_3P$. Dimer to mixed-bridge interconversions have been noted in several group 13−group 15 systems.[20] With this in mind, we had hoped to utilize this synthetic method to arrive at our desired mixed-bridge compound.

In contrast to the above, the mixed-bridge species $(Me_3SiCH_2)_2\overline{GaP(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}$ (**6**) is obtained from the direct 2:1 reaction of $(Me_3SiCH_2)_2GaCl$ with $(Me_3Si)_3P$ in pentane at room temperature. This compound was characterized by a variety of methods, including partial elemental analysis, electron impact mass spectrometry, and single-crystal X-ray analysis. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra are consistent with those expected for compounds such as **6**. Most notably, in the ^1H NMR, a doublet resonance at δ 0.34 corresponding to coupling of the ^{31}P nucleus with the methyl protons of the adjacent trimethylsilyl groups and a singlet resonance at δ 0.25 corresponding to the methylene and methyl protons of the (trimethylsilyl)methyl group are observed. The EI mass spectrum shows a fragmentation pattern at *m/z* 697, which corresponds to the molecular ion of **6** minus a proton. Interestingly, halogen mixed-bridge compounds in the gallium−phosphorus system are rare, and **5** and **6** represent only the second and third examples of these species to be characterized in the solution and solid phase. It is important to note that attempted 1:1 reactions of $(Me_3SiCH_2)_2GaCl$ with $(Me_3Si)_3P$ and $LiP(SiMe_3)_2$ did not produce any characterizable compounds, and only the starting materials were recovered in each case.

Crystallographic data and data collection parameters for **1**−**6** are summarized in Table 1. ORTEP diagrams showing the atom-numbering schemes for **1**−**6** are presented in Figures 1−6, respectively. Tables 2 and 3 list selected bond distances and bond angles, while Tables 4 and 5 list selected non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **1**−**3** and **4**−**6**, respectively.

Table 4. Selected Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1−3, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{iso} (Å^2)[a]
		Compound **1**		
Ga(1)	0.71428(4)	0.39355(4)	0.13862(3)	1.19(2)
Cl(1)	0.83862(11)	0.41926(11)	0.23972(6)	1.91(6)
P(1)	0.81451(11)	0.24006(10)	0.09134(6)	1.12(5)
Si(3)	0.75421(12)	0.22521(11)	−0.02645(7)	1.43(6)
Si(4)	1.00269(12)	0.25718(11)	0.11215(7)	1.44(6)
Si(5)	0.78298(13)	0.07649(11)	0.13895(7)	1.53(6)
C(11)	0.5791(4)	0.3177(4)	0.1559(3)	1.81(10)
C(12)	0.4938(4)	0.3760(4)	0.1898(3)	1.99(10)
C(13)	0.4444(5)	0.4722(5)	0.1454(3)	2.65(11)
C(14)	0.5488(6)	0.4160(6)	0.2627(4)	4.05(15)
C(15)	0.4004(5)	0.2968(5)	0.1958(3)	3.19(13)
C(21)	0.7022(4)	0.5143(4)	0.06906(25)	1.53(9)
C(22)	0.7427(4)	0.6312(4)	0.08905(25)	1.37(9)
C(23)	0.8692(4)	0.6345(4)	0.1089(3)	1.77(10)
		Compound **2**		
Ga(1)	0.89428(7)	0.93924(9)	0.05199(5)	1.01(3)
P(1)	1.09586(17)	0.93294(21)	0.06496(11)	1.02(8)
Cl(1)	0.84365(17)	0.73805(20)	0.01196(12)	1.64(8)
Si(1)	0.5346(8)	0.3894(9)	0.1330(5)	6.0(4)
Si(2)	1.16632(19)	1.03857(23)	0.17187(12)	1.28(9)
C(11)	1.16599(20)	0.72490(22)	0.06558(12)	1.23(9)
C(12)	1.1501(7)	0.9296(9)	0.2572(5)	1.9(4)
C(13)	1.3164(7)	1.0746(9)	0.1596(5)	1.9(4)
		Compound **3**		
Ga(1)	0.61904(6)	0.46319(3)	0.13939(5)	1.075(23)
Br(1)	0.49747(6)	0.39270(3)	0.24465(5)	1.966(24)
P(1)	0.48623(14)	0.57379(7)	0.08155(12)	1.03(5)
Si(1)	0.94569(15)	0.39569(8)	0.32154(12)	1.67(6)
Si(2)	0.63588(15)	0.66950(8)	0.11463(13)	1.29(6)
Si(3)	0.33204(15)	0.59174(8)	0.18980(13)	1.25(6)
C(11)	0.8338(5)	0.4733(3)	0.2386(5)	1.61(22)
C(12)	0.9213(7)	0.3235(3)	0.2029(6)	2.6(3)
C(13)	1.1466(6)	0.4185(3)	0.3873(6)	2.6(3)
C(14)	0.8941(6)	0.3658(3)	0.4573(5)	2.2(3)
C(21)	0.7975(6)	0.6520(3)	0.0670(5)	2.0(3)
C(22)	0.7079(6)	0.6909(3)	0.2881(5)	1.98(25)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Adduct **1** crystallizes in the monoclinic system with four molecules occupying the general positions of the centrosymmetric space group $P2_1/c$. In the solid state, this molecule adopts the staggered conformation depicted in Figure 1. The Ga−P bond distance at 2.534(2) Å in **1** is slightly longer than that of 2.459(2) Å found in **10**. This is not surprising, due to the steric bulk of the neopentyl groups in **1** being greater than that of the phenyl ligands in **10**. This trend is also evidenced in the Ga−Cl and mean Ga−C bond lengths (Ga−Cl = 2.258(2) Å in **1** and 2.240(3) Å in **10**; Ga−C(mean) = 1.999 Å in **1** and 1.982 Å in **10**). The Cl−Ga−P angle in **1** at 97.49(6)° is much smaller than that of 101.1(1)° seen in **10**, as is the mean P−Ga−C angle (103.8° in **1**, 111.2° in **10**).

Crystals of dimer **2** belong to the monoclinic system, space group $P2_1/c$, with the P atoms lying on a crystallographic C_2 axis of symmetry, and thus the Ga−P−Ga′−P′ ring is strictly planar. The mean Ga−P bond length of 2.422 Å in **2** is not unusual for dimers of this type. The neopentyl groups and the chlorine atoms

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(18) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G. *Heteroat. Chem.* **1991**, *2*, 11.

(19) Dillingham, M. D. B.; Burns, J. A.; Byers-Hill, J.; Gripper, K. D.; Pennington, W. T.; Robinson, G. H. *Inorg. Chim. Acta* **1994**, *216*, 267.

(20) See for example: Wells, R. L.; McPhail, A. T.; Self, M. F. *Organometallics* **1992**, *11*, 221.

Table 5. Selected Non-Hydrogen Atom Fractional Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 4−6, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	U_{eq}[a]
		Compound **4**		
Ga(1)	8232(1)	7458(1)	1451(1)	41(1)
P(1)	7500	8819(2)	2500	38(1)
P(2)	7500	6084(2)	2500	38(1)
Si(1)	6153(2)	9937(2)	2033(1)	52(1)
Si(2)	6252(2)	4974(2)	1882(1)	48(1)
C(1)	6723(7)	11036(6)	1342(5)	81(3)
C(2)	5428(7)	10589(6)	2987(5)	73(2)
C(3)	5098(7)	9224(6)	1384(5)	71(2)
C(4)	5817(8)	3920(6)	2674(5)	84(3)
C(5)	6832(7)	4272(6)	905(4)	73(2)
		Compound **5**		
Ga(1)	−37.9(6)	1265.9(4)	7058.9(4)	46(1)
Ga(2)	1479.8(6)	2431.0(4)	5982.1(4)	49(1)
Cl(1)	1067(2)	1067(1)	6049(1)	67(1)
P(1)	350(1)	2653(1)	6997(1)	40(1)
Si(1)	−1253(2)	3308(1)	6753(1)	56(1)
Si(2)	1334(2)	3271(1)	7997(1)	57(1)
C(1)	−1568(5)	1018(4)	6673(4)	60(3)
C(2)	−1890(6)	392(4)	6061(5)	69(3)
C(3)	−1214(7)	−331(4)	6225(5)	101(4)
C(4)	−3091(7)	180(5)	6057(5)	121(5)
C(5)	−1739(7)	696(5)	5276(4)	102(4)
		Compound **6**		
Ga(1)	2998(1)	140(1)	6418(2)	26(1)
Ga(2)	2245(1)	1455(1)	5458(1)	26(1)
Cl(1)	3405(2)	855(2)	4877(3)	33(1)
P(1)	2150(2)	881(2)	7338(3)	25(1)
Si(1)	2720(3)	−719(2)	3996(4)	37(2)
Si(2)	4123(3)	−772(2)	8144(4)	39(2)
Si(3)	522(3)	1859(2)	4129(5)	41(2)
Si(4)	3448(3)	2507(2)	4520(4)	31(1)
Si(5)	2721(3)	1362(2)	8964(4)	35(2)
Si(6)	928(3)	501(2)	7951(4)	39(2)
C(1)	2281(8)	−382(6)	5437(13)	32(5)
C(2)	3866(9)	−741(7)	3985(16)	67(8)
C(3)	2329(10)	−309(7)	2588(14)	54(7)
C(4)	2389(10)	−1495(6)	3889(14)	55(7)
C(5)	4057(7)	−61(6)	7206(14)	32(5)

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

adopt a *trans* conformation about the gallium centers, and the coordination geometry about the Ga and P atoms approximates that of a distorted tetrahedron, with the mean Ga−P−Si and P−Ga−Cl angles being 113.1 and 104.9°, respectively. Dimer **3** crystallizes in the centrosymmetric space group $P2_1/c$ with the two molecules in the unit cell lying in general positions. As in **2**, the alkyl groups and the bromine atoms adopt a *trans* conformation about the gallium centers. The mean Ga−P bond length of 2.424 Å in **3** is almost identical with that of 2.422 Å observed in **2**. The Ga−P−Ga′−P′ ring is planar, and the coordination geometry about the Ga and P centers approximates a distorted tetrahedron (mean Ga−P−Si and P−Ga−Cl angles being 112.9 and 106.3°, respectively).

The average Ga−P bond length of 2.517 Å in **4** is slightly longer than those found in dimers **2**, **3**, and **13**. This may be attributed to the added steric bulk of the alkyl substituents on the gallium center. The Ga−P−Ga angle of 93.47(8)° and the P−Ga−P angle of 86.29(5)° evidence the degree of distortion from a perfect square for the four-membered ring. A comprehensive survey of the structural features observed in compound **4** revealed no unusual bond lengths or angles.

Compounds **5** and **6** crystallize in the monoclinic space group $P2_1/n$, with four molecules per unit cell. The asymmetric unit in **5** contains one molecule occupying a general position in the cell, and the four-membered Ga−P−Ga−Cl ring is nearly planar. This is in contrast to the four-membered ring in **6**, where the dihedral angle between the plane defined by Ga(1)−P(1)−Cl(1) and Ga(2)−P(1)−Cl(1) in **6** is 23°. This angle is notably larger than the 6° dihedral angle observed in **7** and may be attributed to steric effects. It is interesting to note that the degree of four-membered-ring planarity observed in **5** and **6** matches closely that observed in the As analogs of these compounds.[21] The As analog of **5** has a mean dihedral angle of 0.05°, while the analog of **6** has a mean dihedral angle of 21.1°. In **6**, the Ga(1)−P−Ga(2) angle at 90.9(1)° and the Ga(1)−Cl−Ga(2) angle at 92.5(1)° evidence a slight degree of distortion for the four-membered ring. The exocyclic Si−P−Si and average C−Ga−C angles of 105.8(1) and 125.75°, respectively, show the distorted-tetrahedral coordination geometry about the phosphorus and gallium atoms. There were no uncharacteristically short intermolecular contacts or other unusual structural features observed in the crystal packing.

Acknowledgment. We wish to thank the Office of Naval Research, the AT&T Bell Laboratories Cooperative Research Fellowship Program, and the Duke Endowment Graduate Fellowship Program for their financial support.

Supporting Information Available: Tables of bond distances and bond angles, anisotropic temperature factor parameters, and hydrogen atom fractional coordinates for **1**−**6** (27 pages). Ordering information is given on any current masthead page.

OM9507641

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