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# Synthesis and Characterization of $[(Me_3SiCH_2)_2GaP(SiMe_3)_2]_2$, an Example of a Gallium-Phosphorus Dimer Obtainable Only Through an Indirect Reaction Pathway

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## ABSTRACT

*The dimeric gallium-phosphorus compound* $[(Me_3SiCH_2)_2GaP(SiMe_3)_2]_2$ *(***1***) was prepared from the 1:1 mole ratio lithium-halide elimination reaction of* $\overline{(Me_3SiCH_2)_2GaP(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}$ *with* $LiP(SiMe_3)_2$ *in benzene solution and has been characterized through multinuclear solution NMR, partial elemental analysis, and single-crystal X-ray analysis. Compound* **1** *could not be obtained from the direct reactions of* $(Me_3SiCH_2)_2GaCl$ *with* $P(SiMe_3)_3$ *or* $LiP(SiMe_3)_2$. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:147–150, 1998

## INTRODUCTION

In our continuing efforts to produce novel potential precursor compounds to group 13–group 15 materials, we have recently reported the synthesis and characterization of several unusual dimeric compounds containing gallium-phosphorus rings. These include compounds containing a four-membered ring core of the form $\overline{\text{Ga-P-Ga-P}}$ [1,2], as well as the mixed-bridge type core $\overline{\text{Ga-P-Ga-Cl}}$ [3]. When the bulky (trimethylsilyl)methyl- and neopentyl- groups were attached to the gallium atom in an effort to influence the oligomerization of the final products, several interesting rearrangements occurred [4]. As a result, the preparation of the dimer $[(Me_3SiCH_2)_2GaP(SiMe_3)_2]_2$ was not possible from the direct reactions. Herein, we report the synthesis and characterization of this compound through an indirect route.

## EXPERIMENTAL

### General Considerations

All manipulations were performed using general Schlenk and/or dry-box techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. Literature methods were used to prepare $\overline{(Me_3SiCH_2)_2GaP(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}$ [4]. $LiP(SiMe_3)_2$ was prepared from the 1:1 reaction of MeLi with $P(SiMe_3)_3$ [5] in THF. All NMR spectra

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Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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**TABLE 1** Crystallographic Data and Measurements for $[(Me_3SiCH_2)_2GaP(SiMe_3)_2]_2$ (**1**)

| | **1** |
|---|---|
| Molecular formula | $C_{28}H_{80}Ga_2P_2Si_8$ |
| Formula weight | 843.02 |
| Crystal system | orthorhombic |
| Space group | *Pbcn* |
| *a*, Å | 12.691 (2) |
| *b*, Å | 20.997 (5) |
| *c*, Å | 18.4259 (14) |
| *V*, Å$^3$ | 4910 (2) |
| *Z* | 4 |
| Radiation (wavelength, Å) | Mo-K$\alpha$ (0.71073) |
| Scan mode | $\omega$ |
| $\mu$, cm$^{-1}$ | 13.75 |
| Temp, K | 246(2) |
| $D_{calcd}$, g cm$^{-3}$ | 1.140 |
| Crystal Dimens., mm | 0.40 × 0.40 × 0.35 |
| Reflections collected | 4043 |
| Independent reflections | 3207 |
| R; $R_w^a$ | 0.0374; 0.0872 |

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

were obtained in septum-sealed 5 mm tubes using dry $d_6$-benzene as the solvent. $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra were obtained on a Varian Unity 400 spectrometer operating at 400, 100.6, and 161.9 MHz, respectively, and referenced to TMS using the residual protons or carbons of deuterated benzene at $\delta$ 7.15 or $\delta$ 128.0. $^{31}P\{^1H\}$ spectra were referenced externally to 80% $H_3PO_4$ at $\delta$ 0.00. Elemental analyses (EA) were performed by E + R Microanalytical Laboratories, Inc., Corona, NY.

*Preparation of* $[(Me_3SiCH_2)_2GaP(SiMe_3)_2]_2$ (1). $(Me_3SiCH_2)_2GaP(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl$ (0.700 g, 1.00 mmol) was dissolved in 20 mL of benzene in a 250 mL round-bottomed flask equipped with a stir bar and a Kontes valve. $LiP(SiMe_3)_2$ (0.256 g, 1.00 mmol) in 20 mL of benzene was added to the flask slowly via pipet. The clear, yellow solution was stirred at room temperature for 24 hours, at which point it had taken on a slightly hazy appearance. The solvent was removed *in vacuo* leaving a yellow/gray solid. Approximately 30 mL of hexane was added via cannula, and the LiCl was allowed to settle out. The clear yellow solution was transferred to a second flask, and the solvent was removed *in vacuo*. The remaining yellow/gray solid was extracted with warm pentane, and the extract was allowed to evaporate at −30°C. Within 24 hours, colorless, prismatic crystals of 1 had formed (0.624 g, 74% yield); mp 120–150°C. Anal. calcd (found) for $C_{14}H_{40}GaPSi_4$: C, 39.89 (39.89); H, 9.58 (9.71). $^1H$ NMR: $\delta$ 0.26 (s, 4H, $Me_3SiCH_2-$), $\delta$ 0.31 (s, 18H, $Me_3SiCH_2-$), $\delta$ 0.48 [bs, 18H, $-P(SiMe_3)_2$]. $^{13}C\{^1H\}$ NMR: $\delta$ 3.75 (s, $Me_3SiCH_2-$), $\delta$ 5.37 (s, $Me_3SiCH_2-$), $\delta$ 6.08 [bs, $-P(SiMe_3)_2$]. $^{31}P\{^1H\}$ NMR: $\delta$ −205.88 (s).

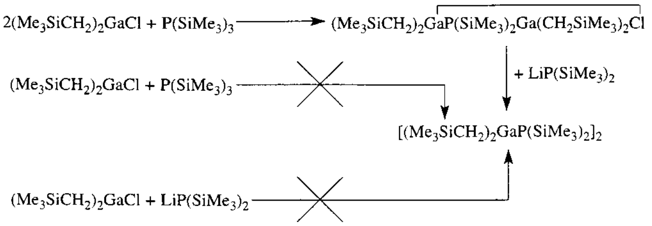
## *X-RAY STRUCTURAL SOLUTION AND REFINEMENT*

X-ray data were collected on a Siemens P4 diffractometer. Colorless crystals of 1 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 ($20° < 2\Theta < 25°$). The structure was solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. All nonhydrogen 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 [6] (4.2) and SHELXTL (5.3) program libraries. An ORTEP diagram showing the solid-state conformation and atom numbering scheme of 1 is shown in Figure 1. Crystallographic data are summarized in Table 1, while selected bond lengths and bond angles are presented in Table 2.

Tables of bond distances and bond angles, anisotropic temperature factor parameters, and fractional coordinates for 1 have been deposited with the Cambridge Crystallographic Data Centre.

## *RESULTS AND DISCUSSION*

When $(Me_3SiCH_2)_2GaCl$ was combined with $P(SiMe_3)_3$ in a 1:1 mole ratio, the anticipated dehalosilylation reaction to form 1 did not take place, and only starting materials were recovered [4]. The 1:1 mole ratio reaction of $(Me_3SiCH_2)_2GaCl$ with $LiP(SiMe_3)_2$ also resulted in the isolation of starting materials [4]. Thus, the preparation of dimeric com-



**SCHEME 1**

**TABLE 2** Selected Bond Distances (Å) and Bond Angles (°) for **1,** with Estimated Standard Deviations in Parentheses

| | | | |
|---|---|---|---|
| | *Bond Lengths* | | |
| Ga(1)-P(1) | 2.4931(11) | Ga(1)-C(4) | 1.976(4) |
| Ga(2)-P(1) | 2.4843(11) | Ga(2)-C(8) | 1.985(4) |
| P(1)-Si(3) | 2.259(2) | | |
| P(1)-Si(4) | 2.266(2) | | |
| | *Bond Angles* | | |
| Ga(1)-P(1)-Ga(2) | 93.00(4) | P(1)-Ga(1)-P(1A) | 86.81(5) |
| P(1)-Ga(2)-P(1A) | 87.19(5) | C(4)-Ga(1)-C(4A) | 121.8(2) |
| C(8)-Ga(2)-C(8A) | 122.6(2) | Si(3)-P(1)-Si(4) | 104.08(6) |
| C(4)-Ga(1)-P(1) | 115.98(14) | C(8)-Ga(2)-P(1) | 113.82(12) |
| Ga(1)-P(1)-Si(3) | 111.55(5) | Ga(1)-P(1)-Si(4) | 120.83(5) |
| Ga(2)-P(1)-Si(3) | 116.27(5) | Ga(2)-P(1)-Si(4) | 111.64(5) |
| P(1)-Ga(1)-C(4A) | 105.59(12) | P(1)-Ga(2)-C(8A) | 106.93(11) |

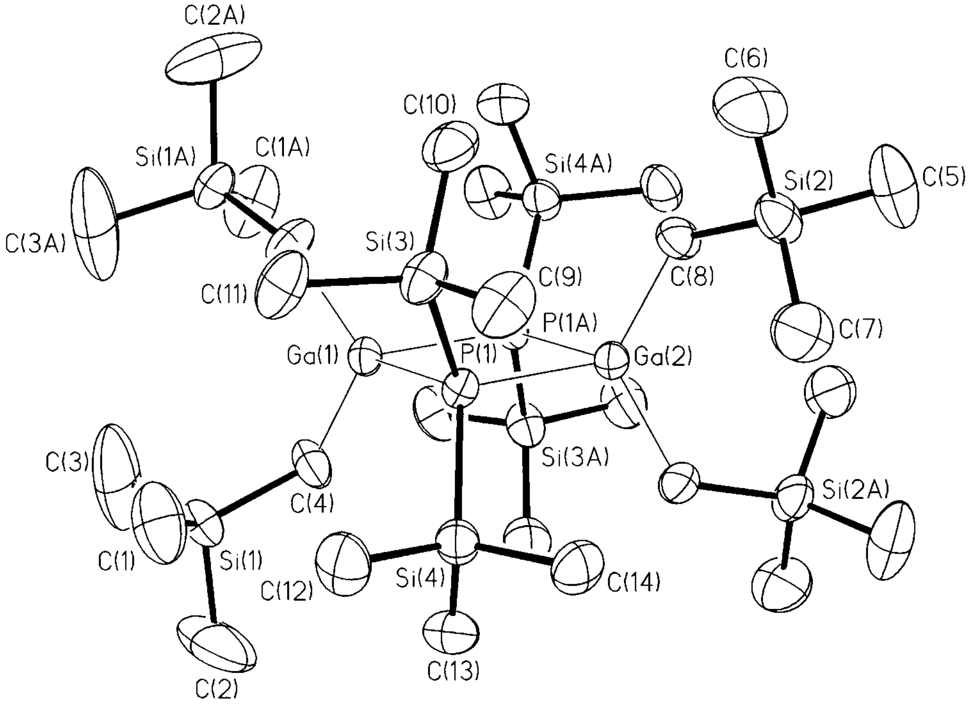


**FIGURE 1** ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme of **1**. Hydrogen atoms are omitted for clarity.

pound 1 needed to be approached through a different series of reactions. Since the mixed-bridge compound $(Me_3SiCH_2)_2\overline{GaP(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}$ could be isolated from the 2:1 mole ratio reaction of $(Me_3SiCH_2)_2GaCl$ with $P(SiMe_3)_3$, this compound was used as the starting material for a metathetical reaction with $LiP(SiMe_3)_2$. This resulted in the isolation of 1 in high yield (see Scheme 1). Compound 1 has been characterized through multinuclear solution NMR, partial EA, and single-crystal X-ray analysis (*vide infra*). An interesting feature of the $^1H$ NMR spectra of 1 is that the expected triplet due to virtual coupling of the $(Me_3Si)_2P$-protons to the ring phosphorus atoms is not present. Instead, the peak is observed as a broad singlet (peak width of approximately 8–10 Hz). A similar phenomena is observed in the $^{13}C$ NMR spectra (peak width approximately 20 Hz). This observation could be explained by a rapid exchange of the trimethylsilyl- groups on the NMR timescale.

Compound 1 crystallizes in the orthorhombic space group *Pbcn,* and the dimeric molecule lies on a $C_2$ axis that passes through the gallium atoms. The average Ga–P bond length of 2.49 Å compares well with the average length found in a similar structure reported by our group, $[(Me_3CCH_2)_2GaP(SiMe_3)_2]_2$ [4], of 2.517 Å. The average endocyclic ring angles of 93.00° for Ga–P–Ga and 87.00° for P–Ga–P also compare well with the analogous angles of 93.47(8)° and 86.29(5)° found in $[(Me_3CCH_2)_2GaP(SiMe_3)_2]_2$. This core Ga-P-Ga-P ring is planar, as is required by the space-group symmetry. There were no other unusual structural features present in this compound.

## *ACKNOWLEDGMENT*

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