and the slurry again was evaporated to dryness (to ensure complete removal of THF). The residue was slurried with ether (50 mL), filtered out, and washed with ether (50 mL). The solid was washed with aqueous HCl (4 N, 2 × 25 mL), H_2O (2 × 10 mL), EtOH (2 × 5 mL), ether (6 × 5 mL), and pentane (2 × 5 mL) and was finally dried under a steam of nitrogen gas. The dark green solid (1.084 g, 34%) was used in this form for hydrogenation. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.79 (d, J = 8.8 Hz, 2 H), 7.45 (pseudo-t, J = 7.7 Hz, 2 H), 7.38 (d, J = 8.7 Hz, 2 H), 7.29 (t, J = 7.4 Hz, 2 H), 6.57 (d, J = 3.2 Hz, 2 H), 5.17 (d, J = 3.1 Hz, 2 H), 3.39–3.34 (m, 2 H), 3.21 (d, J = 16.7 Hz, 2 H), 2.23–2.17 (m, 4 H), 1.75–1.70 (m, 2 H), 1.66–1.60 (m, 2 H).

(*S,S*)-[Ti((1*R*,2*R*)-*trans*-1,2-bis((tetrahydro-1-indenyl)methyl)cyclopentane)Cl_2] (6). A solution of (*S,S*)-[Ti((1*R*,2*R*)-*trans*-1,2-bis(1-indenylmethyl)cyclopentane)Cl_2] (11) (1.071 g, 2.42 mmol) and a suspension of PtO_2 (0.033 g, 0.145 mmol) in CH_2Cl_2 (100 mL) was stirred in a Parr pressure hydrogenator under 60 atm of H_2 gas for 19.5 h. The resulting red solution was filtered through a cotton plug and the solvent removed in vacuo. The red oily residue was extracted with acetone (50 mL), the extract was filtered through Celite, and the solvent was removed in vacuo. A second extraction was performed with boiling hexane (200 mL) and the filtered solution again evaporated to dryness. The red solid residue was chromatographed on a column of silanized silica gel (EM Science, 70-230 mesh, 25 g, 1/9 benzene/hexane eluent) and then crystallized from CH_2Cl_2/hexane (1/6, 35 mL) by gentle warming on a steam bath to remove CH_2Cl_2, followed by cooling to room temperature. An initial crop of 6 (0.293 g) was produced that was washed with pentane (2 × 5 mL). Successive crystallizations of the evaporated supernatant produced further crops that when combined gave a total mass of 6 (0.635 g, 58%) as long red needles. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 6.20 (d, J = 2.9 Hz, 2 H), 5.52 (d, J = 2.9 Hz, 2 H), 3.17–3.11 (m, 2 H), 2.79–2.71 (m, 4 H), 2.55–2.49 (m, 4 H), 2.46–2.40 (m, 2 H), 2.04–1.97 (m, 2 H), 1.87–1.83 (m, 2 H), 1.80–1.73 (m, 2 H), 1.68–1.60 (m, 6 H), 1.58–1.53 (m, 2 H), 1.50–1.43 (m, 2 H). Anal. Calcd for $C_{25}H_{32}Cl_2Ti$: C, 66.53; H, 7.15; Cl, 15.71. Found: C, 66.78; H, 7.05; Cl, 15.72. $[\alpha]^{25}_{436} = -2240°$ (10 cm, c = 2.5 mg/100 mL, $CHCl_3$).

Crystal Structure Determination. Crystallographic data are collected in Table I. A dark red specimen possessed *mmm* Laue symmetry, and systematic absences in the diffraction data uniquely identified the orthorhombic space group $P2_12_12_1$. No correction for absorption was required ($T_{max/min}$ = 1.05). The structure was solved by direct methods and refined with all non-hydrogen atoms anisotropic. Hydrogen atoms were treated as idealized contributions. All computations used Siemens SHELXTL PLUS (VMS) software (G. Sheldrick, Siemens Analytical X-Ray Instruments, Madison, WI). Atomic Coordinates are given in Table II, and selected bond distances and angles are in Table III.

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Supplementary Material Available: Complete listings of crystallographic details, bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for 6 (7 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Structure of Acetylenic Gallium Dialkylphosphides Having the Formula $[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPR_2]_2$ (R = Et, *i*-Pr, *t*-Bu)

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Reactions of the gallium acetylide $[(t\text{-Bu})_2GaC{\equiv}CSiMe_3]_2$ and 2 equiv of the phosphines R_2PH (R = Et, *i*-Pr, *t*-Bu) in toluene at 140 °C give the acetylenic gallium dialkylphosphide dimers $[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPR_2]_2$ (61–81%) as cis and trans isomers. Single-crystal X-ray analysis of colorless cubes obtained from a cold hexane solution of *cis*- and *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPEt_2]_2$ shows the crystals to be *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPEt_2]_2$ (monoclinic, $P2_1/n$ (No. 14); a = 10.023 (6) Å, b = 16.271 (9) Å, c = 12.292 (8) Å, β = 113.91 (5)°, V = 1833 (2) Å^3, Z = 4). Dimer formation occurs via Ga–P bonding in a planar Ga_2P_2 ring. The $^{13}C\{^1H\}$ and ^{13}C NMR spectra of these dimers also give evidence for a gallium–phosphorus bridge.

Introduction

Monomeric, dimeric, and trimeric alkylgallium dialkylphosphides are currently being investigated as potential single-source precursors for the metal–organic chemical vapor deposition (MOCVD) of gallium phosphide (GaP) semiconducting films.[1-4] Source compounds featuring Et, *i*-Pr, and *t*-Bu alkyl groups are of interest since it has been demonstrated that lower film growth temperatures can be achieved with precursors having β-hydrogens which facilitate hydrocarbon elimination.[4] Prior to 1986, the only example of a dimeric alkylgallium dialkylphosphide compound was $[Me_2GaPPh_2]_2$.[5] However, in recent years, many of these dimers have been prepared and several have been structurally characterized.[1,2] In this

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(4) See: Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248 and references therein.

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Table I. IR and Raman Frequencies (cm^{-1}) of Acetylenic Gallium Dialkylphosphide Compounds[a,b]

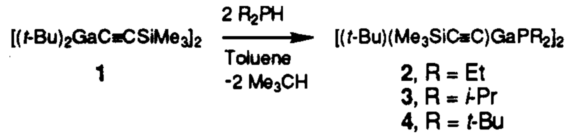
1		*trans*-2		*cis*-/*trans*-3		*trans*-4		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	assignt
	2016 (s)	2070 (m)	2072 (s)	2070 (s)	2072 (s)	2070 (m)	2068 (s)	$\nu_{C\equiv C}$
		970 (w)		920 (w)		940 (w)		ν_{PCC}
850 (s)		845 (s)		855 (s)		845 (s)		ν_{SiC}, $\nu_{SiC\equiv}$
	808 (s)	805 (m)	812 (s)	810 (m)	808 (s)	810 (m)	804 (s)	$\nu_{GaC(CH_3)_3}$
		750 (s)		760 (m)		760 (m)		ν_{PC}
	600 (m)	600 (w)	612 (s)	610 (w)	612 (s)	610 (w)	608 (s)	$\nu_{GaC\equiv}$
	524 (s)		528 (m)		528 (m)		516 (s)	ν_{GaC}
			404 (m)				388 (w)	ν_{GaP}

[a] IR samples were prepared as Nujol mulls; Raman samples were solids. [b] IR $\nu_{C\equiv C}$ peak for 1 in hexane was 2020 cm^{-1} and in THF was 2070 cm^{-1}. IR $\nu_{C\equiv C}$ peak for **2**–**4** in benzene and THF was 2070 cm^{-1}.

paper, we report the synthesis of the alkylgallium acetylide $[(t\text{-Bu})_2GaC{\equiv}CSiMe_3]_2$ and of the series of acetylenic gallium dialkylphosphides *cis*- and *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPR_2]_2$ (R = Et, *i*-Pr, *t*-Bu). The new compounds were characterized by IR, Raman, and NMR spectroscopy. In an effort to ascertain the bridging mode in the acetylenic gallium dialkylphosphide compounds, the crystal structure of *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPEt_2]_2$ was obtained.

Results and Discussion

1. Synthesis of Acetylenic Gallium Dialkylphosphides. The gallium acetylide $[(t\text{-Bu})_2GaC{\equiv}CSiMe_3]_2$ (**1**) and 2 equiv of the phosphines R_2PH (R = Et, *i*-Pr, *t*-Bu) were reacted in toluene at 140 °C for 24–36 h. Workup gave the dimers *cis*- and *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPEt_2]_2$ (**2**), *cis*- and *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaP(i\text{-Pr})_2]_2$ (**3**), and *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaP(t\text{-Bu})_2]_2$ (**4**) in 81%, 62%, and 71% yields, respectively (eq 1). The ^1H NMR spectrum of the distilled toluene solvent showed that 2-methylpropane was the only byproduct. Compounds **1**–**4** were characterized by IR, Raman (Table I), and NMR (^1H, $^{13}C\{^1H\}$, ^{13}C, $^{31}P\{^1H\}$) spectroscopy (Table II and Experimental Section).



$$\underset{\mathbf{1}}{[(t\text{-Bu})_2GaC{\equiv}CSiMe_3]_2} \xrightarrow[\text{Toluene}\\ -2\,Me_3CH]{2\,R_2PH} \underset{\substack{\mathbf{2},\ R = Et\\ \mathbf{3},\ R = i\text{-Pr}\\ \mathbf{4},\ R = t\text{-Bu}}}{[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPR_2]_2} \quad (1)$$

The alkane-elimination method has been employed for many years in the preparation of dimeric and trimeric alkylgallium dialkylphosphides and -arsenides.[1f,3,5,6] Normally, the preparations are carried out by combining the reactants neat and heating in sealed tubes at very high temperatures. For example, Beachley and Coates first prepared $[Me_2GaPEt_2]_3$ from the reaction of trimethylgallium (Me_3Ga) and diethylphosphine in a sealed tube at 150–160 °C for 22 h.[6a] Our analogous reactions demonstrate that the Ga—CMe_3 bond is more reactive than the Ga—C≡$CSiMe_3$ bond.[7] Also, the survival of the reactants at high temperature has been attributed to the formation of an acetylide–phosphine adduct ($R_2HP\cdot Ga(t\text{-Bu})_2(C{\equiv}CSiMe_3)$).[8]

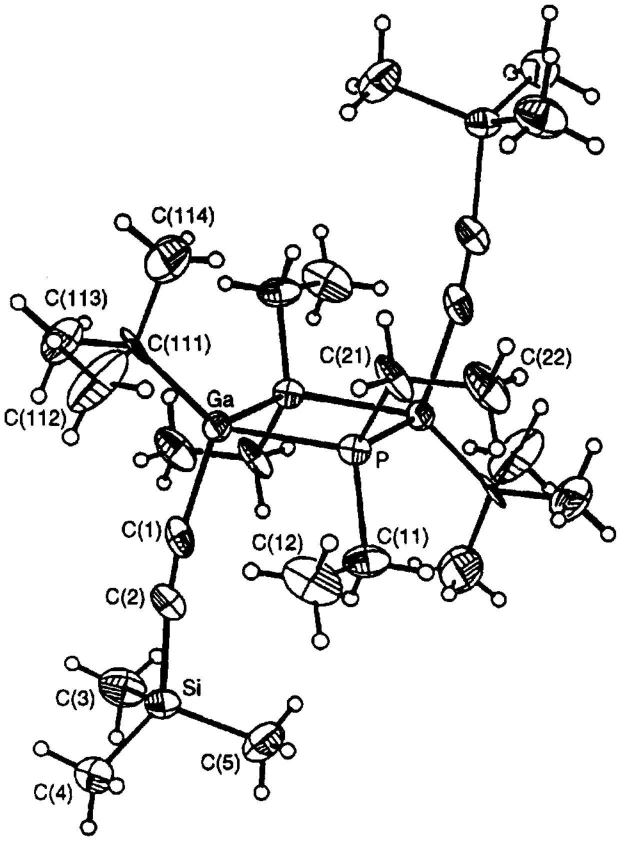


Figure 1. Crystal structure of *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPEt_2]_2$ (**2**).

Acetylide **1** gave a very weak absorption in the IR spectrum for $\nu_{C\equiv C}$ in hexane (2020 cm^{-1}) and a strong $\nu_{C\equiv C}$ band in THF, dioxane, and Et_2O at higher frequency (2070 cm^{-1}). The reaction of **1** and Lewis basic solvents to give base-stabilized monomers has precedent in the work of Jeffery and Mole.[9] The Raman spectrum of **1** gave a strong $\nu_{C\equiv C}$ peak at 2016 cm^{-1} (Table I). Compounds **2**–**4** exhibited strong $\nu_{C\equiv C}$ bands in the IR (2070 cm^{-1} (Nujol, benzene, THF)) and Raman (2068–2072 cm^{-1} (solid)) spectra. Since the acetylenic gallium phosphide dimers **2**–**4** displayed no shift of the IR $\nu_{C\equiv C}$ band in THF versus that found in Nujol or benzene, nothing can be said about the mode of dimer coordination or the stability of **2**–**4** in coordinating solvents. Compounds **2**–**4** exhibited IR ν_{PC}

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(6) (a) Beachley, O. T.; Coates, G. E. *J. Chem. Soc.* **1965**, 3241. (b) Pitt, C. G.; Purdy, A. P.; Higa, K. T.; Wells, R. L. *Organometallics* **1986**, *5*, 1266.

(7) The reactions of phosphines and dimethylgallium acetylides resulted in the formation of the dimethylgallium dialkylphosphide and the corresponding acetylene. Thus, the result can be explained in terms of bond energies where Ga—C≡$CSiMe_3$ bond energy is intermediate between those of Ga—$C(CH_3)_3$ and Ga—CH_3 (63 kcal/mol). For bond energies see: *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; CRC: Boca Raton, FL, 1989; pp F-206–F-209.

(8) The adduct was observed in the ^1H NMR spectrum by a downfield shift of the P–H resonance and an increase in the magnitude of the $^1J_{PH}$ value versus that of the free phosphine. For a discussion of the relationship between the magnitude of the $^1J_{PH}$ value versus coordination at phosphorus see: Brazier, J. F.; Houalla, D.; Loenig, M.; Wolf, R. In *Topics in Phosphorus Chemistry*; Griffith, E. J., Grayson, M., Eds.; Wiley: New York, 1976; pp 99–103.

(9) Jeffery, E. A.; Mole, T. *J. Organomet. Chem.* **1968**, *11*, 393.

Table II. NMR Characterization of Acetylenic Gallium Dialkylphosphide Compounds

compd	^{1}H NMR (ppm)[a,b]	^{13}C{^{1}H} NMR (ppm)[b,c]	^{31}P{^{1}H} NMR (ppm)[d]
cis-**2**[e]	2.09 (heptet of triplets, spacing 7.5, 1.3 Hz, $\mathrm{PC}\mathit{H}_2\mathrm{CH}_3$), 1.79 (heptet, spacing 7.4 Hz, $\mathrm{PC}\mathit{H}_2'\mathrm{CH}_3$), 1.22 (t, $^4J_{\mathrm{PH}}$ = 1.0 Hz, $\mathrm{GaC(CH_3)_3}$), 0.99 (heptet, spacing 7.4 Hz, 2 $\mathrm{PCH_2C}\mathit{H}_3$), 0.21 (s, $^2J_{\mathrm{SiH}}$ = 7.0 Hz, $\mathrm{Si(CH_3)_3}$)	123.2 (t, $^2J_{\mathrm{PC}}$ = 11.7 Hz, GaC$\equiv$), 117.3 (t, $^3J_{\mathrm{PC}}$ = 4.0 Hz, $\equiv$CSi), 31.6 (s, $\mathrm{GaC(}\mathit{C}\mathrm{H_3)_3}$), 24.3 (t, $^2J_{\mathrm{PC}}$ = 9.7 Hz, $\mathrm{Ga}\mathit{C}\mathrm{(CH_3)_3}$), 12.4 (t, spacing 9.4 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 12.2 (t, spacing 2.6 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$), 11.3 (t, spacing 3.4 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$), 10.9 (t, spacing 10.0 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 0.54 (s, J_{SiC} = 56.2 Hz, $\mathrm{Si(CH_3)_3}$)	−37.7
trans-**2**	1.97 (heptet, spacing 7.4 Hz, $\mathrm{PC}\mathit{H}_2\mathrm{CH}_3$), 1.87 (m, $\mathrm{PC}\mathit{H}_2'\mathrm{CH}_3$), 1.26 (t, $^4J_{\mathrm{PH}}$ = 1.0 Hz, $\mathrm{GaC(CH_3)_3}$), 1.14 (heptet, spacing 7.6 Hz, 2 $\mathrm{PCH_2C}\mathit{H}_3$), 0.19 (s, $^2J_{\mathrm{SiH}}$ = 7.1 Hz, $\mathrm{Si(CH_3)_3}$)	121.4 (t, $^2J_{\mathrm{PC}}$ = 12.7 Hz, GaC$\equiv$), 117.8 (t, $^3J_{\mathrm{PC}}$ = 4.1 Hz, J_{SiC} = 81 Hz, $\equiv$CSi),[f] 31.2 (s, $\mathrm{GaC(}\mathit{C}\mathrm{H_3)_3}$), 23.6 (t, $^2J_{\mathrm{PC}}$ = 10.7 Hz, $\mathrm{Ga}\mathit{C}\mathrm{(CH_3)_3}$), 11.8 (t, spacing 2.9 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$), 10.9 (t, spacing 11.4 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 0.47 (s, J_{SiC} = 55.5 Hz, $\mathrm{Si(CH_3)_3}$)	−40.0
cis-**3**[e]	3.09 (heptet of triplets, spacing 7.3, 1.8 Hz, $\mathrm{PC}\mathit{H}\mathrm{(CH_3)_2}$), 2.32 (m, spacing 3.6 Hz, $\mathrm{PC}\mathit{H}\mathrm{(CH_3)_2}$), 1.47 (q, spacing 7.2 Hz, $\mathrm{PCH(C}\mathit{H}_3\mathrm{)_2}$), 1.36 (t, $^4J_{\mathrm{PH}}$ = 1.1 Hz, $\mathrm{GaC(CH_3)_3}$), 1.17 (q, spacing 7.2 Hz, $\mathrm{PCH(C}\mathit{H}_3\mathrm{)_2}$), 0.28 (s, $^2J_{\mathrm{SiH}}$ = 6.9 Hz, $\mathrm{Si(CH_3)_3}$)	117.3 (t, $^3J_{\mathrm{PC}}$ = 4.0 Hz, $\equiv$CSi),[g] 31.7 (t, $\mathrm{GaC(}\mathit{C}\mathrm{H_3)_3}$), 24.5 (t, $^2J_{\mathrm{PC}}$ = 8.5 Hz, $\mathrm{Ga}\mathit{C}\mathrm{(CH_3)_3}$), 24.1 (s, br, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 23.4 (m, $\mathrm{P}\mathit{C}\mathrm{H(CH_3)_2}$), 20.9 (t, spacing 7.9 Hz, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 0.64 (s, J_{SiC} = 55.1 Hz, $\mathrm{Si(CH_3)_3}$)	6.4
trans-**3**[e]	2.60 (heptet of triplets, spacing 7.2 Hz, 2.3 Hz, $\mathrm{PC}\mathit{H}\mathrm{(CH_3)_2}$), 1.48 (q, spacing 7.2 Hz, $\mathrm{PCH(C}\mathit{H}_3\mathrm{)_2}$), 1.39 (t, $^4J_{\mathrm{PH}}$ = 1.1 Hz, $\mathrm{GaC(CH_3)_3}$), 1.38 (q, spacing 7.1 Hz, $\mathrm{PCH(C}\mathit{H}_3\mathrm{)_2}$), 0.20 (s, $^2J_{\mathrm{SiH}}$ = 6.9 Hz, $\mathrm{Si(CH_3)_3}$)	118.1 (t, $^3J_{\mathrm{PC}}$ = 3.5 Hz, $\equiv$CSi),[g] 31.6 (t, $\mathrm{GaC(}\mathit{C}\mathrm{H_3)_3}$), 25.5 (t, $^2J_{\mathrm{PC}}$ = 11.0 Hz, $\mathrm{Ga}\mathit{C}\mathrm{(CH_3)_3}$), 23.9 (s, br, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 23.4 (m, $\mathrm{P}\mathit{C}\mathrm{H(CH_3)_2}$), 22.4 (t, spacing 1.7 Hz, $\mathrm{PCH(}\mathit{C}\mathrm{H_3)_2}$), 0.35 (s, J_{SiC} = 55.6 Hz, $\mathrm{Si(CH_3)_3}$)	1.9
trans-**4**	1.61 (t, spacing 7.0 Hz, 2 $\mathrm{PC(CH_3)_3}$), 1.51 (t, $^4J_{\mathrm{PH}}$ = 1.3 Hz, $\mathrm{GaC(CH_3)_3}$), 0.21 (s, $^2J_{\mathrm{SiH}}$ = 7.0 Hz, $\mathrm{Si(CH_3)_3}$)	133.6 (t, $^2J_{\mathrm{PC}}$ = 11.3 Hz, GaC$\equiv$), 119.3 (t, $^3J_{\mathrm{PC}}$ = 3.7 Hz, $\equiv$CSi),[h] 36.4 (t, spacing 5.8 Hz, $\mathrm{P}\mathit{C}\mathrm{(CH_3)_3}$), 33.1 (s, $\mathrm{PC(}\mathit{C}\mathrm{H_3)_3}$), 32.4 (s, $\mathrm{GaC(}\mathit{C}\mathrm{H_3)_3}$), 26.8 (t, br, $^2J_{\mathrm{PC}}$ = 10.0 Hz, $\mathrm{Ga}\mathit{C}\mathrm{(CH_3)_3}$), 0.07 (s, J_{SiC} = 55.4 Hz, $\mathrm{Si(CH_3)_3}$)	51.5

[a] At 400 MHz and 300 °C in $\mathrm{CD_3C_6D_5}$ and referenced to residual $\mathrm{CD_2HC_6D_5}$ (δ 2.09). [b] "Spacing" refers to the average separation between lines of a virtual multiplet. [c] At 101 MHz and 300 °C in $\mathrm{CD_3C_6D_5}$ and referenced to solvent (20.4 ppm). [d] At 162 MHz and 300 °C in $\mathrm{CD_3C_6D_5}$ and referenced to external 85% $\mathrm{H_3PO_4}$. [e] Data were obtained from a mixture of cis and trans forms. [f] ^{13}C: 121.4 (t, $^2J_{\mathrm{PC}}$ = 12.8 Hz, GaC$\equiv$), 117.8 (tdecet, $^3J_{\mathrm{HC}}$ = 2.2 Hz, $\equiv$CSi). [g] GaC$\equiv$ was obscured by solvent. ^{13}C{^{1}H} ($\mathrm{CD_2Cl_2}$): 125.4 (m, cis-/trans-GaC$\equiv$), 118.0 (t, $^3J_{\mathrm{PC}}$ = 4.0 Hz, trans-$\equiv$CSi), 117.2 (t, $^3J_{\mathrm{PC}}$ = 4.0 Hz, cis-$\equiv$CSi). ^{13}C ($\mathrm{CD_2Cl_2}$): 125.4 (m, cis-/trans-GaC$\equiv$), 118.0 (m, trans-$\equiv$CSi), 117.2 (m, cis-$\equiv$CSi). [h] ^{13}C: 133.6 (t, $^2J_{\mathrm{PC}}$ = 11.4 Hz, GaC$\equiv$), 119.3 (m, $\equiv$CSi).

Table III. Summary of Crystallographic Data for *trans*-[(*t*-Bu)(Me$_3$SiC$\equiv$C)GaPEt$_2$]$_2$ (2)

mol formula	$\mathrm{C_{26}H_{56}Ga_2P_2Si_2}$
mol wt	626.290
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
cell dimens (23 °C)	
a, Å	10.023 (6)
b, Å	16.271 (9)
c, Å	12.292 (8)
β, deg	113.91 (5)
V, Å^3	1833 (2)
Z	4
d_{calc}, g/cm^3 (23 °C)	1.135
cryst dimens, mm	0.16 × 0.38 × 0.52
diffractometer	Siemens R3m/V
radiation (λ, Å)	Mo Kα (0.71073)
data collection method	θ–2θ
scan speed, deg/min	variable, 6.0–15.0
no. of reflns measd	2809
range/indices (hkl)	0–10, 0–17, −13 to +12
scan range, deg	1.20 plus Kα separation
2θ limit, deg	3.5–45.0
total bkgd time/scan time	0.5
no. of reflns between stds	96
total no. of unique data	2414
no. of obsd data, $F > 3\sigma(F)$	882
abs coeff, mm^{-1}	1.627
no. of variables	146
goodness of fit	0.95
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.0827
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.0799
Δ/σ (max)	1.829
$\Delta\rho$ (max), e/Å^3	0.74

Table IV. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for *trans*-[(*t*-Bu)(Me$_3$SiC$\equiv$C)GaPEt$_2$]$_2$ (2)[a]

atom	x	y	z	U(eq), Å^2
Ga	0.0653 (3)	0.0623 (2)	0.9165 (2)	0.046 (1)
P	−0.1272 (6)	0.0694 (4)	0.9849 (4)	0.047 (3)
Si	−0.2183 (7)	−0.0583 (5)	0.5198 (5)	0.064 (3)
C(1)	−0.0364 (27)	0.0293 (13)	0.7518 (20)	0.058 (13)
C(2)	−0.1020 (25)	−0.0033 (13)	0.6586 (21)	0.055 (12)
C(3)	−0.0980 (26)	−0.1404 (15)	0.4963 (20)	0.105 (16)
C(4)	−0.2906 (25)	0.0129 (14)	0.3912 (18)	0.085 (14)
C(5)	−0.3626 (22)	−0.1073 (14)	0.5461 (21)	0.094 (14)
C(11)	−0.3104 (24)	0.0839 (14)	0.8579 (20)	0.078 (13)
C(12)	−0.3291 (28)	0.1624 (14)	0.7977 (20)	0.104 (18)
C(21)	−0.1215 (25)	0.1483 (12)	1.0910 (17)	0.066 (13)
C(22)	−0.2305 (27)	0.1445 (15)	1.1423 (20)	0.098 (16)
C(111)	0.2107 (28)	0.1498 (16)	0.9531 (18)	0.058 (13)
C(112)	0.1396 (30)	0.2256 (15)	0.8831 (29)	0.159 (25)
C(113)	0.3238 (26)	0.1263 (15)	0.9074 (22)	0.106 (17)
C(114)	0.2830 (32)	0.1732 (19)	1.0793 (23)	0.161 (24)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

peaks (750–760 cm^{-1}) not found in the Raman spectra. However, the Raman spectra gave strong peaks at 804–812, 608–612, and 516–528 cm^{-1}, which were assigned to ν_{GaCC}, $\nu_{\mathrm{GaC\equiv}}$, and ν_{GaC}, respectively. The assignment of IR ν_{PC} and Raman ν_{GaC} bands was derived from comparison with known compounds.[1f,6a,10] Weak Raman peaks found at 388–404 cm^{-1} were assigned to a Ga–P stretching mode. Microcrystalline GaP and dimeric alkylgallium dialkylphosphides exhibit Raman Ga–P modes at 384–404 cm^{-1}.[10–12]

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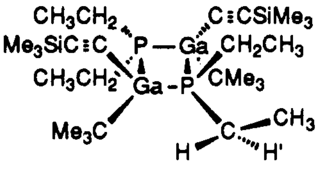
(10) (a) Monteil, Y.; Berthet, M. P.; Favre, R.; Hariss, A.; Bouix, J.; Vaille, M.; Gibart, P. *J. Cryst. Growth* **1986**, *77*, 172. (b) Kvisle, S.; Rytter, E. *Spectrochim. Acta* **1984**, *40A*, 939. (c) Schwering, H.-U.; Jungk, E.; Weidlein, J. *J. Organomet. Chem.* **1975**, *91*, C4. (d) Weidlein, V. J.; Schaible, B. *Z. Anorg. Allg. Chem.* **1971**, *386*, 176.

(11) (a) Hayashi, S. *Solid State Commun.* **1985**, *56* (4), 375. (b) Maury, F.; Combes, M.; Constant, G.; Carles, R.; Renucci, J. B. *J. Phys. (Paris)* **1982**, *43*, C1-347. (c) Hoff, R. M.; Irwin, J. C. *Can. J. Phys.* **1973**, *51*, 63.

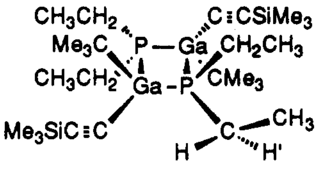
Table V. Bond Lengths (Å) and Bond Angles (deg) for *trans*-[(*t*-Bu)($Me_3SiC{\equiv}C$)$GaPEt_2$]$_2$ (2)

Ga-P	2.399 (7)	Si-C(3)	1.899 (28)
Ga-P′	2.415 (7)	Si-C(4)	1.854 (22)
Ga-C(1)	1.936 (22)	Si-C(5)	1.793 (27)
Ga-C(111)	1.955 (26)	C(11)-C(12)	1.450 (32)
P-C(11)	1.882 (19)	C(21)-C(22)	1.468 (41)
P-C(21)	1.815 (22)	C(111)-C(112)	1.508 (34)
C(1)-C(2)	1.190 (30)	C(111)-C(113)	1.505 (43)
Si-C(2)	1.859 (22)	C(111)-C(114)	1.471 (33)
P-Ga-P′	86.9 (2)	Ga-C(111)-C(112)	109.2 (16)
P-Ga-C(1)	102.8 (9)	Ga-C(111)-C(113)	109.4 (16)
P-Ga-C(111)	121.0 (9)	Ga-C(111)-C(114)	115.7 (21)
C(1)-Ga-C(111)	118.0 (10)	P-C(11)-C(12)	114.5 (16)
C(1)-Ga-P′	101.4 (6)	P-C(21)-C(22)	117.8 (16)
C(111)-Ga-P′	121.0 (7)	C(2)-Si-C(3)	106.1 (10)
Ga-P-Ga′	93.1 (2)	C(2)-Si-C(4)	111.4 (10)
Ga-P-C(11)	111.6 (9)	C(2)-Si-C(5)	107.5 (12)
Ga-P-C(21)	119.4 (9)	C(3)-Si-C(4)	111.3 (12)
C(11)-P-C(21)	104.0 (10)	C(3)-Si-C(5)	108.8 (12)
C(11)-P-Ga′	119.6 (8)	C(4)-Si-C(5)	111.5 (11)
C(21)-P-Ga′	109.9 (7)	C(112)-C(111)-C(113)	104.4 (24)
Ga-C(1)-C(2)	168.8 (21)	C(112)-C(111)-C(114)	107.9 (23)
Si-C(2)-C(1)	173.9 (26)	C(113)-C(111)-C(114)	109.6 (22)

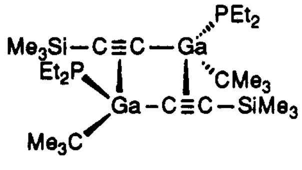
2. Crystal Structure of *trans*-2. In principle, compounds 2–4 can exist as a mixture of cis and trans isomers that are either gallium–phosphorus-bridged (I, II) or gallium–acetylide-bridged (III, IV). In an effort to definitively demonstrate the bridging mode in these compounds, the crystal structure of *trans*-[(*t*-Bu)($Me_3SiC{\equiv}C$)$GaPEt_2$]$_2$ (2) was obtained. X-ray data were collected on colorless cubes of *trans*-2 under the conditions summarized in Table III. Refinement yielded the structure shown in Figure 1. Atomic coordinates, bond distances, and bond angles are summarized in Tables IV and V.



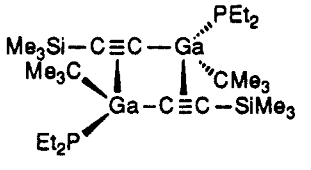
I



II



III



IV

The crystal structure of *trans*-2 exhibited several important features. First, dimer formation occurred through a Ga–P bond (II), complementing the NMR assignment (below). Second, the Ga_2P_2 ring was planar, with the Ga–P bond lengths being nearly equivalent (2.40 (1) and 2.42 (1) Å) and slightly shorter than those found for other dimeric alkylgallium dialkylphosphides [R_2GaPR_2]$_2$ (2.51–2.45 Å, average 2.48 Å; sum of covalent radii 2.35 Å).[13,14] The P–Ga–P (86.9 (2)°) and Ga–P–Ga (93.1 (2)°) angles were close to 90° and similar to the internal angles found for other planar alkylgallium dialkylphosphide compounds (P–Ga–P = 86.5–86.7°, average 86.6°; Ga–P–Ga = 93.1–93.5°, average 93.4°).[1e] The related *trans*-[(*t*-Bu)$_2$GaPH(C_5H_9)]$_2$ was also found to have a planar Ga_2P_2 ring, but the P–Ga–P angle was more compressed (81.8°) and the Ga–P–Ga angle was correspondingly expanded (98.2°).[1c] Third, the Ga—C(*t*-Bu) (1.96 (3) Å), the P—C (1.82–1.88 (2) Å), and the C(1)≡C(2) (1.19 (3) Å) bond lengths were normal and close to the sums of the covalent radii (2.02, 1.87, and 1.20 Å, respectively).[14] Other dimeric alkylgallium dialkylphosphides possess similar Ga—C (2.03–2.00 Å, average 2.01 Å) and P—C (1.92–1.74 Å, average 1.84 Å) bond lengths.[13] Fourth, the Ga—C(acet) bond length (1.94(2) Å) was longer than the sum of the covalent radii (1.85 Å) and shorter than that found for [$Me_2GaC{\equiv}CPh$]$_2$ (2.004 (4) Å).[14,15] Finally, the nonlinear Ga–C(1)–C(2) and C(1)–C(2)–Si angles (168.8 (2) and 173.9 (3)°) indicated that the acetylide group was somewhat bent as the result of steric crowding within the molecule.

3. NMR Properties of 1 and 2–4. The difference between the methylene protons on phosphorus of *cis*- and *trans*-2 is illustrated in I and II. The C_{2v} symmetry of I causes the ethyl groups on phosphorus to have inequivalent magnetic environments, while the methylene protons are equivalent. The ^{1}H and ^{13}C NMR spectra of I would be expected to give separate resonances for the ethyl groups above and below the ring. The C_{2h} symmetry of II causes the ethyl groups to have equivalent magnetic environments, while the methylene protons are inequivalent. Separate resonances are expected for the methylene protons in the ^{1}H NMR spectra, while single resonances are expected for the ethyl groups in the ^{13}C NMR spectra. III and IV are of C_2 and C_i symmetries in which the ethyl groups on the same phosphorus can never have equivalent magnetic environments and NMR spectra would be expected to give separate resonances for each group. ^{1}H and ^{13}C NMR spectra of III and IV would give complicated patterns for GaC(CH_3)$_3$ due to inequivalent coupling of the respective nuclei to the two phosphorus atoms.

The ^{1}H NMR spectrum of 1 (toluene-d_8) gave a singlet for GaC(CH_3)$_3$ and a singlet for Si(CH_3)$_3$ with a $^2J_{SiH}$ value of 7.2 Hz. The resonance for GaC(CH_3)$_3$ was shifted upfield in the coordinating solvent THF-d_8. The ^{1}H NMR spectra of 1 gave no information about the degree of monomer association. However, the ^{1}H NMR spectra (toluene-d_8 +27 to +100 °C) of 2–4 gave triplets for GaC(CH_3)$_3$ with $^4J_{PH}$ values of 1.0–1.3 Hz and singlets for Si(CH_3)$_3$ with $^2J_{SiH}$ values of 6.9–7.1 Hz, indicating the dimeric structures (I, II). In comparison, a $^3J_{PH}$ value of 3.6 Hz was found for the α-protons on the gallium of [(Me_3CCH_2)$_2GaPPh_2$]$_2$.[1b]

For the mixtures *cis*- and *trans*-2 or *cis*- and *trans*-3, up to seven PR_2 ^{1}H NMR resonances are possible. The inequivalent ethyl groups of *cis*-2 gave separate resonances (δ 2.09, 1.79) for the methylene hydrogens but only one resonance (δ 0.99) for the methyl hydrogens. Conversely, the equivalent ethyl groups of *trans*-2 gave one resonance (δ 1.14) for the methyl hydrogens but the methylene hydrogens, which are not equivalent, gave two complex multiplets (δ 1.97, 1.87) due to virtual phosphorus coupling of the type found in $X_nAA'X_n'$ (X = ^{1}H, A = ^{31}P) spin systems.[16] Homonuclear decoupling experiments on *trans*-2 revealed a $^2J_{HH'}$ value of 14.1 Hz and $^2J_{PH}$ values of ~0.0 and 6.0 Hz for the methylene hydrogens. It is likely that the magnitude of the $^2J_{PH}$ value is dependent upon the dihedral angle of the hydrogens to the Ga_2P_2 ring,

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[12] Lee, K. E.; Higa, K. T.; Nissan, R. A. To be submitted for publication.

[13] Bond lengths were averaged from structures of compounds in ref 1a,c,e.

[14] *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985; pp 3-121–3-126.

[15] Tecle, B.; Ilsley, W. H.; Oliver, J. P. *Inorg. Chem.* **1981**, *20*, 2335.

[16] (a) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275. (b) Becker, E. D. *High Resolution NMR*, 2nd ed.; Academic: New York, 1980; pp 163–167. (c) See also ref 1d.

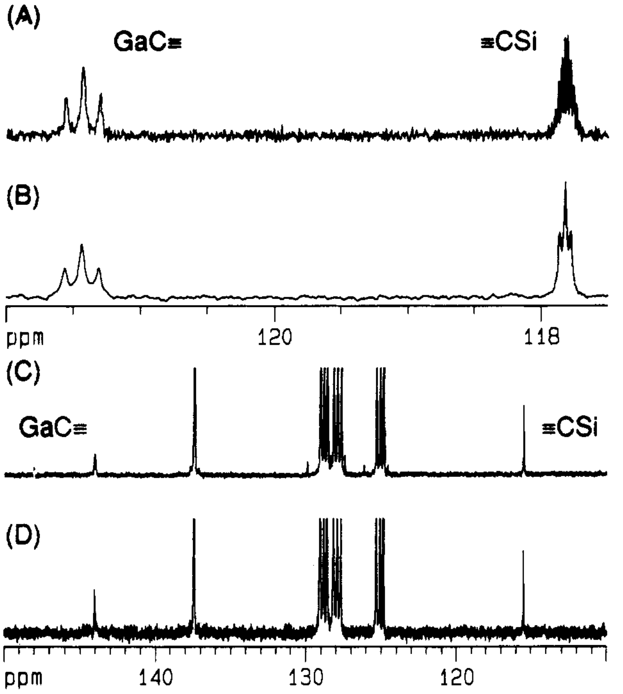

Figure 2. Comparison of the ^{13}C NMR data in the acetylenic carbon region: (A) ^1H coupled and (B) ^1H decoupled for *trans*-[(*t*-Bu)($Me_3SiC{\equiv}C$)$GaPEt_2$]$_2$ (2) (A was enhanced by Gaussian multiplication); (C) ^1H coupled and (D) ^1H decoupled for [(*t*-Bu)$_2GaC{\equiv}CSiMe_3$]$_2$ (1). The resonances centered at 137.5, 128.9, 128.0, and 125.2 ppm are due to $CD_3C_6D_5$.

where the value of J decreases as the angle approaches 90°.[17] Seven resonances were observed for *cis*- and *trans*-3, two each for the methine and methyl groups of the cis isomer and one for the methine and two for the methyl groups of the trans isomer. The +27 °C ^1H NMR spectra of *trans*-2 in THF-d_8 or CD_2Cl_2, *cis*- and *trans*-3 in CD_2Cl_2, and *trans*-4 in THF-d_8 resulted in a change of the relative positions of all peaks, but the multiplicity of each peak remained the same.

The bridging mode of 1 (empty gallium $3p_z$ orbital to carbon–carbon $2p\pi$ orbitals) was evident from the ^{13}C NMR spectrum, which gave broad singlets for both the acetylenic carbons (Figure 2). In contrast, the ^{13}C NMR spectrum of $HC{\equiv}CSiMe_3$ displayed a doublet of decets ($^3J_{HC}$ = 2.7 Hz) for the acetylenic carbon on silicon. Thus, the gallium of a monomer of 1 effectively decouples the $SiMe_3$ protons of the other monomer, giving $^{13}C\{^1H\}$ and ^{13}C NMR spectra that look similar.

The $^{13}C\{^1H\}$ NMR spectra of 2–4 gave broad, downfield triplets or multiplets (2, 123.2, 121.4; 3, 125.4; 4, 133.6 ppm, $^2J_{PC}$ = 11.3–12.7 Hz) for the acetylenic carbon on gallium and upfield triplets (2, 117.8, 117.3; 3, 117.3, 118.1; 4, 119.3 ppm, $^3J_{PC}$ = 3.5–4.1 Hz) for the acetylenic carbon on silicon. Note the downfield progression of the resonances for the acetylenic carbon on gallium as the size of R increases in 2 → 4. The ^{13}C NMR spectra for 2–4 gave a triplet of decets ($^3J_{HC}$ = 2.2 Hz) or multiplets for the acetylenic carbon on silicon, while the acetylenic carbon on gallium remained a triplet (Figure 2). A comparison of the $^{13}C\{^1H\}$ and ^{13}C NMR data with those for 1 demonstrates that dimer formation of 2–4 occurred through a Ga–P bond.

Table VI. Comparison of the $^{31}P\{^1H\}$ NMR Shifts of Monomeric, Dimeric, and Trimeric Alkylgallium Dialkylphosphides

compd	$^{31}P\{^1H\}$ NMR (ppm)
(1) [Me_2GaP(*t*-Bu)$_2$]$_2$	28.4
(2) [Me_2GaP(*i*-Pr)$_2$]$_2$	-11.0
(3) [Me_2GaP(*i*-Pr)$_2$]$_3$	-41.0
(4) [Me_2GaPEt_2]$_3$	-56.8
(5) (*t*-Bu)$_2$GaP(*t*-Bu)$_2$[a]	23.9
(6) [(*t*-Bu)$_2$GaP(*i*-Pr)$_2$]$_2$[a]	17.1
(7) [(*t*-Bu)$_2GaPEt_2$]$_2$[b]	-31.0
(8) [$(Me_3CCH_2)_2GaPPh_2$]$_2$	-25.0
(9) $(Me_3SiCH_2)_2GaPPh_2$	-27.0
(10) [$(Me_3SiCH_2)_2GaPPh_2$]$_2$	-40.0
(11) *cis*- and *trans*-[(*t*-Bu)$_2GaPH(C_5H_9)$]$_2$	-90.3, -94.5

[a] Reference 2. [b] Reference 21.

The $^{31}P\{^1H\}$ NMR spectrum (toluene-d_8) of *cis*- and *trans*-2 displayed two resonances, one at −37.7 ppm and the other at −40.0 ppm. The $^{31}P\{^1H\}$ NMR spectrum of *trans*-2 gave just one resonance at −40.0 ppm and was unchanged up to +100 °C. Similarly, the $^{31}P\{^1H\}$ NMR spectrum (toluene-d_8) of *cis*- and *trans*-3 displayed two resonances (6.4 and 1.9 ppm) in a ratio of 1:2.2.[18] The $^{31}P\{^1H\}$ NMR spectrum (toluene-d_8) of *trans*-4 displayed one resonance at 51.5 ppm and was unchanged up to +100 °C.[19] For 2 → 4, the $^{31}P\{^1H\}$ NMR resonances displayed a downfield progression as the size of R increased.[20] The trend can be compared to that found for other alkylgallium dialkylphosphide compounds (Table VI).[1a–e,2,12,21]

For 2–4, the $^{31}P\{^1H\}$ NMR spectra gave no more than two resonances that were unchanged in either relative intensity or chemical shift under each of the experimental conditions. The ^1H and $^{13}C\{^1H\}$ NMR spectra of 2–4 showed coupling of the $GaC(CH_3)_3$ groups with *two* equivalent phosphorus atoms regardless of solvent (toluene-d_8, THF-d_8, CD_2Cl_2) or temperature (+27 to +100 °C in toluene-d_8), indicating the absence of the monomer under those conditions. In contrast, Beachley has shown that [$(Me_3SiCH_2)_2GaPPh_2$]$_2$ undergoes facile monomer–dimer equilibria at room temperature in C_6D_6.[1d] Thus, the two $^{31}P\{^1H\}$ NMR resonances observed for the mixtures correspond to the cis and trans isomers only. The related *cis*- and *trans*-[(*t*-Bu)$_2GaPH(C_5H_9)$]$_2$ also gave two resonances in the $^{31}P\{^1H\}$ NMR spectrum, but assignment of a chemical shift to a particular isomer was not made.[1c]

4. Conclusion. This study provides a synthetic route to unsymmetrical alkylgallium dialkylphosphide compounds and illustrates the relative reactivity of Ga—CMe_3 versus Ga—$C{\equiv}CSiMe_3$ bonds. The acetylenic compounds may prove to be attractive precursors for the CVD of GaP films due to the weak gallium–carbon bonds that also have the ability to undergo β-hydride elimination. However, the low vapor pressures of these compounds will limit their use to very low pressure chemical vapor deposition systems such as metal–organic molecular beam epitaxy.

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen or argon atmosphere. IR spectra were recorded on a Perkin-Elmer 1300 spectrophotometer. Raman spectra were recorded using a 488.0-nm Ar^+ laser (Lexel Model 95) and double

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[17] For a discussion of the geometrical dependence of P–C–H couplings see: *Annual Reports on NMR Spectroscopy*; Mooney, E. F., Ed.; Academic: London, 1973; Vol. 5B, pp 29–30.

[18] The ^1H NMR spectrum of *cis*- and *trans*-3 gave two singlets for $Si(CH_3)_3$ in a ratio of 1 (cis):2.1 (trans).

[19] No significant amount of *cis*-4 was detected under any conditions.

[20] For a discussion of ^{31}P NMR trends see: (a) Fluck, E.; Heckmann, G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 2. (b) Payne, N. C.; Stephan, D. W. *Can. J. Chem.* **1980**, *58*, 15.

[21] Lee, K. E.; Higa, K. T. To be submitted for publication.

monochromator (Spex Model 1403) coupled to a photomultiplier tube (RCA Model C31034). NMR spectra were recorded on a Bruker AMX 400 spectrometer. Microanalyses were performed by E+R Laboratories. Melting points were determined in capillaries at ambient and reduced pressure.[22]

Toluene, benzene, hexanes, dioxane, Et_2O, and THF were distilled from Na/benzophenone. Deuterated solvents (toluene-d_8, THF-d_8, CD_2Cl_2) were trap-to-trap distilled from Na/benzophenone.

Reagents were obtained as follows: Et_2PH and $i\text{-}Pr_2PH$ (Quantum Design, Inc.), used as purchased; $t\text{-}Bu_2PH$, prepared by literature methods;[23] $t\text{-}Bu_2GaCl$, prepared by a literature method;[10c,24] $LiC{\equiv}CSiMe_3$, prepared from $HC{\equiv}CSiMe_3$ and n-BuLi in hexanes at −78 °C and isolated by filtration.

$[(t\text{-Bu})_2GaC{\equiv}CSiMe_3]_2$ (1). A 50-mL Schlenk flask was charged with $t\text{-}Bu_2GaCl$ (3.90 g, 18.0 mmol), $LiC{\equiv}CSiMe_3$ (1.85 g, 18.0 mmol), benzene (20 mL), and a stirbar. A reflux condenser was attached. The flask was heated at 50 °C for 24 h. The resulting gold solution with a white suspension was filtered through a fritted funnel that had been layered with 1 cm of Celite. The benzene was removed (1 Torr) from the gold filtrate, leaving a light yellow powder. The somewhat heat-sensitive (>130 °C) powder was collected to give 1 (4.46 g, 15.9 mmol, 89%): mp (ambient pressure) 125–135 °C, 135 °C dec; mp (evacuated) 121–124 °C, 133 °C dec. Anal. Calcd for $C_{26}H_{54}Ga_2Si_2$: C, 55.53; H, 9.68; Ga, 24.80. Found: C, 55.42; H, 9.54; Ga, 24.87. ^1H NMR (400 MHz, δ, $CD_3C_6D_5$ referenced to residual $CD_2HC_6D_5$ (δ 2.09)): 1.36 (s, $GaC(CH_3)_3$), 0.12 (s, $^2J_{SiH} = 7.2$ Hz, $Si(CH_3)_3$). ^{13}C NMR (101 MHz, ppm, $CD_3C_6D_5$ referenced to solvent (20.4 ppm)): 144.0 (s, br, $GaC{\equiv}$), 115.5 (s, ${\equiv}CSi$), 31.8 (quartet of septets, $^1J_{HC} =$ 124.2 Hz, $^3J_{HC} = 5.9$ Hz, $GaC(\mathit{C}H_3)_3$), 26.5 (s, br, $Ga\mathit{C}(CH_3)_3$), −0.32 (quartet of septets, $^1J_{HC} = 120.5$ Hz, $^3J_{HC} = 2.0$ Hz, $Si(CH_3)_3$).

***cis*- and *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaPEt_2]_2$ (2).** A 25-mL Teflon-stoppered flask was charged with $[(t\text{-Bu})_2GaC{\equiv}CSiMe_3]_2$ (1; 0.79 g, 2.8 mmol), Et_2PH (0.331 mL, 0.26 g, 2.9 mmol), toluene (2 mL), and a stirbar. The solution was frozen (N_2(l)), and the flask was evacuated. The flask was heated at 140 °C for 36 h. After cooling to 25 °C, the toluene was removed (1 Torr) from the dark yellow solution. The resulting dark yellow residue was sublimed at 110 °C and 0.05 Torr onto a CO_2(s)-cooled probe. *cis*- and *trans*-2 was obtained as colorless needles coated with a yellow oil (0.71 g, 2.3 mmol, 81%). The mixture was crystallized from hexanes at −40 °C. Colorless cubes formed and were collected by cold filtration (−25 °C) and dried in vacuo to give *trans*-2 (0.54 g, 1.7 mmol, 61%): mp (ambient pressure) 110–112 °C, 200–240 °C dec with bubbling; mp (evacuated) 150–220 °C (sublimes). Anal. Calcd for $C_{26}H_{56}Ga_2P_2Si_2$: C, 49.86; H, 9.01; Ga, 22.26; P, 9.89. Found: C, 49.78; H, 9.22; Ga, 22.62; P, 9.72.

***cis*- and *trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaP(i\text{-Pr})_2]_2$ (3).** A 25-mL Teflon-stoppered flask was charged with $[(t\text{-Bu})_2GaC{\equiv}CSiMe_3]_2$ (1; 1.20 g, 4.27 mmol), $i\text{-}Pr_2PH$ (0.730 mL, 0.57 g, 4.82 mmol), toluene (2 mL), and a stirbar. The solution was frozen (N_2(l)), and the flask was evacuated. The flask was heated at 140 °C for 38 h. After cooling to 25 °C, the toluene was removed (1 Torr) from the brown solution. The resulting brown residue was sublimed at 130 °C and 0.05 Torr onto an N_2(l)-cooled probe. *cis*- and *trans*-3 was obtained as a slightly yellow, viscous liquid that upon sitting under N_2(g) for 1 day became a waxy solid (0.91 g, 1.33 mmol, 62%): mp (ambient pressure) 53–55 °C, 205–215 °C dec with bubbling; mp (evacuated): 53–55 °C, 205–215 °C dec with bubbling. Anal. Calcd for $C_{30}H_{64}Ga_2P_2Si_2$: C, 52.80; H, 9.45; Ga, 20.43; P, 9.08. Found: C, 52.74; H, 9.38; Ga, 20.71; P, 8.92.

***trans*-$[(t\text{-Bu})(Me_3SiC{\equiv}C)GaP(t\text{-Bu})_2]_2$ (4).** A 50-mL Teflon-stoppered flask was charged with $[(t\text{-Bu})_2GaC{\equiv}CSiMe_3]_2$ (1; 1.15 g, 4.10 mmol), $t\text{-}Bu_2PH$ (0.754 mL, 0.60 g, 4.12 mmol), toluene (6 mL), and a stirbar. The solution was frozen (N_2(l)), and the flask was evacuated. The flask was heated at 140 °C for 24 h. Upon cooling to 25 °C, colorless white needles began to form. Additional toluene (2 mL) was added to redissolve the needles, and the solution was filtered to remove a solid, gray material. The toluene was removed (1 Torr), and the resulting dark orange residue was crystallized from warm hexanes (60 °C). Colorless cubes and irregularly shaped plates formed and were collected by filtration and dried in vacuo to give *trans*-4 (1.08 g, 2.93 mmol, 71%): mp (ambient pressure) 230–232 °C dec with bubbling; mp (evacuated) 226–234 °C dec with bubbling, remelts 194–198 °C (sublimes). Anal. Calcd for $C_{34}H_{72}Ga_2P_2Si_2$: C, 55.30; H, 9.83; Ga, 18.90; P, 8.39; Si, 7.61. Found: C, 55.31; H, 9.93; Ga, 18.74; P, 8.23; Si, 7.39.

Raman Experiments. The Raman spectrometer consisted of a double monochromator (Spex Model 1403) coupled to a photomultiplier tube (RCA Model C31034) with photon-counting electronics (Stanford Research Systems Model SR400). Spectra were collected in the right-angle scattering mode using 488.0-nm Ar^+ laser (Lexel Model 95) excitation with 200-mW incident power and a beam spot diameter of ∼60 μm. Typical spectral resolution was 4 cm^{-1}.

Crystal Structure of *trans*-2. A colorless cube was grown from a cold hexane solution of *cis*- and *trans*-2. The crystal was sealed in a glass capillary under nitrogen and mounted for data collection on a Siemens R^3m/V diffractometer. Cell constants were obtained (Table III), and the space group was determined from systematic absences ($h0l$, $l = 2n$; $0k0$, $k = 2n$) and subsequent least-squares refinement. Standard reflections showed no decay during data collection.

A total of 2809 reflections was collected. As a check on crystal and electronic stability, four representative reflections were measured every 96 reflections. The intensities of these standards remained constant within experimental error throughout data collection. An absorption correction was not applied, leaving some values in Table III outside of normally accepted ranges.

The structure was solved by the standard heavy-atom techniques using the Siemens SHELXTL PLUS (VMS) package. Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated using the riding model with fixed isotropic U values and added to the structure factor calculations but were not refined. The structure was refined in full-matrix least squares, where the function minimized was $\sum\omega(F_o - F_c)^2$, with a weighting scheme (ω^{-1}) of $\sigma^2(F) + 0.0024F^2$. An extinction correction of $\chi = -0.0003$ (2) ($F^* = F[1 = 0.002\chi F^2/(\sin 2\theta)]^{-1/4}$) was applied. The final refinement cycle converged in R and R_w values given in Table III. The highest peak in the final difference Fourier had a height of 0.74 e/Å^3.

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Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and positional parameters for hydrogen atoms for *trans*-2 (2 pages). Ordering information is given on any current masthead page.

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