Journal of Organometallic Chemistry, *449* (1993) 53–59

JOM 23380

Synthesis, characterization, and reactivity of new alkylgallium acetylides

Kenneth E. Lee and Kelvin T. Higa

Chemistry Division, Research Department, Naval Air Warfare Center, Weapons Division, China Lake, CA 93555 (USA)

(Received August 3, 1992)

Abstract

Reaction of Me_2GaCl and $LiC{\equiv}CSiMe_3$ or R_2GaCl (R = Me, ^tBu) and $LiC{\equiv}CPh$ (benzene, 70°C) gives $[Me_2GaC{\equiv}CSiMe_3]_2$ and $[R_2GaC{\equiv}CPh]_2$ in 62%, 58%, and 71% yields, respectively. The gallium acetylides were characterized by IR, Raman, and NMR (^1H, ^{13}C, $^{13}C\{^1H\}$) spectroscopy. Reactions of the dimethylgallium acetylides and phosphines (R_2PH; R = Et, ^iPr) (toluene, 110–20°C) give $HC{\equiv}CSiMe_3$ or $HC{\equiv}CPh$ and the corresponding dimethylgallium dialkylphosphides $[Me_2GaPR_2]_n$ (R = Et, $n = 3$, ^iPr, $n = 2$).

1. Introduction

The resurgence of interest in Group III–V compounds for the purpose of generating high purity electronic materials from relatively benign sources has resulted in the revival of Group III chemistry. Although alkylgallium acetylides have been known for many years, little data are available about their reactivity [1,2]. The previously reported gallium acetylides $[Me_2GaC{\equiv}CR]_2$ (R = Me, Ph) were shown spectroscopically to react with Lewis basic solvents to give base stabilized monomers [1b,c]. $[Me_2GaC{\equiv}CPh]_2$ has been structurally characterized and was shown to have a gallium–ethynyl bridge [1a]. In an effort to approximate the relative gallium–carbon bond strengths in alkylgallium compounds, we report here the synthesis of the alkylgallium acetylides $[Me_2GaC{\equiv}CSiMe_3]_2$ and $[R_2GaC{\equiv}CPh]_2$ (R = Me, ^tBu) from LiCl elimination reactions and the interaction of the acetylides with secondary phosphines.

2. Results and discussion

2.1. *Synthesis of dimethyl and di-t-butylgallium acetylides*

The gallium chlorides R_2GaCl (R = Me, ^tBu) and the lithium acetylides $LiC{\equiv}CR'$ (R' = $SiMe_3$, Ph) were combined in benzene and heated at 70°C. Workup gave the acetylenic gallium dimers $[R_2GaC{\equiv}CR']_2$ (**1**, R = Me, R' = $SiMe_3$, 62%; **2**, R = Me, R' = Ph, 58%; **3**, R = ^tBu, R' = Ph, 71%) (eqn. (1)). Acetylides **1**–**3** were characterized by elemental analysis, IR, Raman, and NMR (^1H, ^{13}C, and $^{13}C\{^1H\}$) spectroscopy (Experimental section). Previously, **2** had been prepared by reaction of Me_3Ga and $HC{\equiv}CPh$ with a yield of 41% [1c]. The preparation of $[(^tBu)_2GaC{\equiv}CSiMe_3]_2$ has been described previously [3].

$$2\ R_2GaCl + 2\ LiC{\equiv}CR' \xrightarrow[-2\ LiCl]{\text{Benzene}\ 70^\circ C} [R_2GaC{\equiv}CR']_2 \qquad (1)$$

1, R = Me, R' = $SiMe_3$
2, R = Me, R' = Ph
3, R = ^tBu, R' = Ph

The Nujol mull of acetylide **1** gave a weak absorption for ν(C≡C) in the IR spectrum (2050 cm^{-1}) and a strong ν(C≡C) in the Raman spectrum (2040 cm^{-1}) suggesting a symmetric structure. Acetylides **2** and **3** gave strong absorptions for ν(C≡C) (**2**· 2090 and **3**; 2050 cm^{-1}) in the IR spectra suggesting less symmetric structures than for **1**. In comparison, the terminal acetylide groups of the unsymmetrical dialkylgallium dialkylphosphides $[(^tBu)(Me_3SiC{\equiv}C)GaPR_2]_2$ (R = Et, ^iPr, ^tBu) gave strong ν(C≡C) (2068–2072 cm^{-1}) in the IR and Raman spectra [3]. The assignment of IR and Raman ν(Ga*C*C), ν(GaC≡), and ν(GaC) (Experimental section) were derived from comparison with known

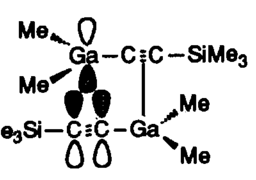
---

Correspondence to: Dr. K.E. Lee

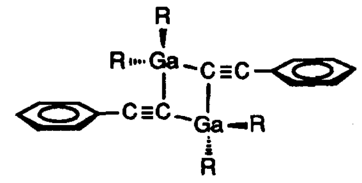
0022-328X/93/$6.00

compounds [4]. The reaction of **1**–**3** and Lewis basic solvents (THF, dioxane, Et_2O) to give base stabilized monomers was evident from the solution IR spectra where the ν(C≡C) was shifted to higher frequency (40–60 cm^{-1}). However, the ^1H NMR spectrum of a THF-d_8 solution of **1** gave three methyl resonances. The ^1H NMR monitored reaction of **1** and THF in C_6D_6 showed that at low concentrations of THF, the monomer/dimer equilibrium was forced more toward the monomer. That was apparent from the observation of an upfield shift of the Me_2Ga resonance and a downfield shift of the Me_3Si resonance. At higher concentrations of THF, the redistribution products THF:$Ga(Me)_2(C{\equiv}CSiMe_3)$, THF:$GaMe_3$, and THF:$Ga(Me)(C{\equiv}CSiMe_3)_2$ were evident from the observation of three peaks in the MeGa region of the ^1H NMR spectrum. Addition of Me_3Ga to the mixture forced the equilibrium towards the THF:$Ga(Me)_2(C{\equiv}CSiMe_3)$ adduct and was evident from the disappearance of one peak in the MeGa region. Similar results were obtained for **2** [1c] and **3** [5].

The π binding mode of **1** (empty gallium $3p_z$ orbital to carbon–carbon $2p\pi$ orbitals, **I**) was evident from the $^{13}C\{^1H\}$ and ^{13}C NMR spectra which gave broad singlets for both of the acetylenic carbons. Broad resonances are expected for carbons attached to gallium and reflects coupling with the two NMR active isotopes of gallium (^{69}Ga and ^{71}Ga; $I = 3/2$). Alternatively, acetylenic carbons attached to trimethylsilyl groups are expected to display a decet in the ^{13}C NMR spectrum (*e.g.*, $HC{\equiv}CSiMe_3$; doublet of decets, $^2J(HC) = 42.0$ Hz, $^3J(HC) = 2.7$ Hz). In addition, the acetylenic carbon attached to the silicon of the terminal acetylenic group in $[(^tBu)(Me_3SiC{\equiv}C)GaPR_2]_2$, which bridges through a Ga–P interaction, appears as a triplet of decets in the ^{13}C NMR spectra [3]. Therefore, the π coordination of the gallium to the triple bond in **I** effectively decouples the $SiMe_3$ protons giving similar $^{13}C\{^1H\}$ and ^{13}C NMR spectra. Thus, the ^{13}C NMR spectra of alkylgallium trimethylsilylacetylides can be used to distinguish between terminal and bridging acetylide groups.



I



II

For the phenyl derivatives **2** and **3**, the $^{13}C\{^1H\}$ NMR spectra gave the expected broad, upfield singlet (**2**, 98.1; **3**, 92.8) for the acetylenic carbon on gallium and a downfield singlet (**2**, 121.5; **3**, 121.5) for the acetylenic carbon on the phenyl group. However, in contrast to the results found for **1**, the ^{13}C NMR spectra of **2** and **3** displayed a triplet ($^3J(HC) = 8.0$ Hz) for the acetylenic carbon on the phenyl group. Observation of a triplet indicates coupling to the phenyl *ortho* protons. In comparison, the ^{13}C NMR spectrum of HC≡CPh displayed a doublet of triplets ($^2J(HC) = 50.2$ Hz, $^3J(HC) = 5.5$ Hz) for the acetylenic carbon on the phenyl group. The following conclusions were inferred from the data. First, the bridging mode of **2** and **3** must be different from that of **1** in that either gallium of the dimer must be an adequate distance from the acetylenic carbon on the phenyl group. The broadening of that carbon resonance in the ^{13}C NMR spectrum would then be precluded. Second, the gallium of the monomer does not couple to the β acetylenic carbon. Thus, the NMR data for **2** and **3** suggest either a monomeric structure or a more likely dimeric structure in which the α acetylenic carbon appears to be five coordinate (**II**). The crystal structure of **2** was drawn in a similar fashion [1a]. An alternative allenic type structure was previously proposed for **2** based upon IR data [1c].

TABLE 1. Bond energies for formation of hydrocarbon free radicals [a]

Bond	H–R → H˙+R˙ D°_{298} (kcal/mol)	Bond	D°_{298} (kcal/mol)
H–C≡CH	132	Ga–C≡CH	?
$H–CH_3$	105	$Ga–CH_3$	63
$H–CH_2CH_3$	100	$Ga–CH_2CH_3$	50
$H–CH(CH_3)_2$	96	$Ga–CH(CH_3)_2$	?
$H–C(CH_3)_3$	93	$Ga–C(CH_3)_3$	?

[a] R.C. Weast (ed.), *CRC Handbook of Chemistry and Physics*, 70th edition, CRC Press, Boca Raton, FL, 1989, pp. F-206–F-209.

2.2. Reactions of 1–3 and secondary phosphines

A consideration of the activation energies of formation of hydrocarbon free radicals allows for the prediction of the gallium–carbon bond strength order shown in Table 1. In order to test the validity of the prediction, acetylides **1** and **2** were reacted with the secondary phosphines R_2PH (R = Et, ^iPr) in toluene-d_8 at 110–120°C for 6–24 h giving dimethylgallium dialkylphosphides $[Me_2GaPR_2]_n$ (**4**, R = Et, $n = 3$; **5**, R = ^iPr, $n = 2$) and $HC{\equiv}CSiMe_3$ or HC≡CPh (eqn. (2)) [6*]. Note that the predicted products from the reaction are the unsymmetrical acetylide $[(Me)(R'C{\equiv}C)GaPR_2]_n$ and methane (CH_4). Authentic samples of **4**

---

* Reference number with asterisk indicates a note in the list of references.

and **5** were prepared by reaction of the phosphines and Me_3Ga (toluene, 130–140°C, 20–96 h) [4f,7]. IR, Raman, and NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra were obtained for **4** and **5** (Experimental section) and matched literature values when available [4f,7]. The reaction results illustrated in eqn. (2) are in contrast to the reaction of the phosphines with $[(^tBu)_2GaC{\equiv}CSiMe_3]_2$ giving the expected unsymmetrical acetylenic gallium dialkylphosphides $[(^tBu)(Me_3SiC{\equiv}C)GaPR_2]_2$ and isobutane (Me_3CH) [3]. Thus, the experimental results suggest that the $Ga-C{\equiv}CSiMe_3$ and $Ga-C{\equiv}CPh$ bond strengths are less than the $Ga-CH_3$ bond strength but greater than the $Ga-C(CH_3)_3$ bond strength. Note that the prediction of reaction products using bond energies for the formation of free radicals does not imply that the reaction proceeds by a free radical mechanism.

$$[Me_2GaC{\equiv}CR']_2 + 2R_2PH \xrightarrow[110-120°C]{\text{Toluene}}$$

$R' = SiMe_3, Ph$

$$[Me_2GaPR_2]_n + 2HC{\equiv}CR' \quad (2)$$

4, $R = Et$, $n = 3$
5, $R = {}^iPr$, $n = 2$

Initial combination of the reactants in eqn. (2) resulted in the formation of an acetylide–phosphine adduct ($R_2HP:Ga(Me)_2(C{\equiv}CR')$). The adduct was observed in ^1H NMR monitored reactions as a downfield shift of the P–H resonance and an increase in the magnitude of the $^1J(PH)$ *versus* that of the free phosphine [8]. To illustrate, the results of reactions involving $^tBu_2PH$ and alkylgallanes are shown in Table 2. Note that the reaction of **1** and **2** with $^tBu_2PH$ (toluene, 110–160°C, 2–4 h) resulted in the decomposition of the acetylides even though the magnitude of the $^1J(PH)$ at room temperature indicated the presence of an adduct. The decomposition of **1** and **2** in this case is due to the fact that the adduct is not maintained at high temperature (see below) and the necessary reaction temperature exceeds the thermal stability of the acetylide. The reaction of Me_3Ga and $^tBu_2PH$ (toluene, 160°C, 240 h) gave only a 17% yield of $[Me_2GaP(^tBu)_2]_2$ (**6**) due to a weak adduct at high temperature and a strong $Ga-CH_3$ bond [9].

TABLE 2. The ^1H NMR $\delta(PH)$ and $^1J(PH)$ of $^tBu_2PH$ alone and in solution with alkylgallanes [a]

Reactants	$\delta(PH)$ (ppm)	$^1J(PH)$ (Hz) [b]	Reaction result [c]
$^tBu_2PH$	3.09	198	
Me_3Ga	3.19	283	Slow
$^tBu_3Ga$	3.08	198	None
$[Me_2GaC{\equiv}CSiMe_3]_2$ (**1**)	3.19	269	Decomposition
$[Me_2GaC{\equiv}CPh]_2$ (**2**)	3.30	305	Decomposition
$[^tBu_2GaC{\equiv}CSiMe_3]_2$ [d]	3.45	265	Fast
$[^tBu_2GaC{\equiv}CPh]_2$ (**3**)	3.37	255	Decomposition

[a] In toluene-d_8 at 24°C. [b] The $^3J(PCCH)$ displayed similar behavior but to a lesser extent. [c] Decomposition refers to that of the acetylide at elevated temperatures. [d] Ref. 3.

^1H NMR monitored reactions of **3** and the secondary phosphines R_2PH ($R = {}^tBu, {}^iPr, Et$) in toluene-d_8 (140°C, 2–24 h) showed that **3** redistributes to $^tBuGa(C{\equiv}CPh)_2$ and $^tBu_3Ga$ (eqn. (3)). Analogous results were observed for $Me_2Ga(C_5H_5)$ in benzene solutions at room temperature [5]. Subsequent reaction of Et_2PH or $^iPr_2PH$ with the $^tBu_3Ga$ gave adducts which then decomposed to either $[(^tBu)_2GaPEt_2]_2$ (**7**) or $[(^tBu)_2GaP(^iPr)_2]_2$ (**8**) (eqn. (3)). Authentic samples of **7** and **8** were prepared by reaction of the phosphines and $^tBu_3Ga$ (toluene, 130°C, 24–96 h). IR, Raman, and NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra were obtained for **7** and **8** (Experimental section) and matched literature values when available [10]. There was no reaction between the $^tBu_2PH$ and the redistribution generated $^tBu_3Ga$. A separate reaction involving $^tBu_2PH$ and $^tBu_3Ga$ (toluene, 130°C, 50 h) resulted in the slow decomposition of $^tBu_3Ga$ (see Table 2). Observation of the ^1H NMR $^1J(PH)$ for a solution of $^tBu_2PH$ and **3** (toluene-d_8, +24 to +100°C) showed that at low temperature, the adduct was present but at high temperature the free phosphine dominated. Thus, these results illustrate the requirement for a strong alkylgallium–phosphine adduct prior to dialkylgallium dialkylphosphide formation.

$$\left[(^tBu)_2GaC{\equiv}CPh\right]_2 \xrightarrow[140°C]{\text{Toluene}}$$

(3)

$$^tBuGa(C{\equiv}CPh)_2 + {}^tBu_3Ga \quad (3)$$

$$\Big\downarrow \begin{array}{l} R_2PH \\ -Me_3CH \end{array}$$

$$1/2[(^t(Bu)_2GaPR_2]_2$$

7, $R = Et$
8, $R = {}^iPr$

Hence, the outcome of the reactions between dialkylgallium acetylides and secondary phosphines is dependent upon the Lewis acidity of the acetylide while the bulkiness of the phosphine is less important. The electron accepting ability of the silyl group of $[(^tBu)_2GaC{\equiv}CSiMe_3]_2$ imparts a high degree of Lewis acidity to the compound resulting in a strong acetylide–phosphine adduct at high temperature [11]. The complex then has time to decompose to the unsymmetrical acetylenic gallium dialkylphosphide $[(^tBu)(Me_3SiC{\equiv}C)GaPR_2]_2$ [3]. The electron donating ability of the phenyl group of $[(^tBu)_2GaC{\equiv}CPh]_2$ decreases the Lewis acidity of the compound resulting in a weak acetylide–phosphine adduct at high temperature and decomposition of the acetylide results.

3. Conclusion

Gallium acetylides have not been considered as appropriate precursors to semiconductor materials like gallium phosphide (GaP) because it was thought that the gallium–acetylide bond strength would be excessive. This study has shown that Ga–C≡CR (R = $SiMe_3$, Ph) bond strengths are likely to be lower than the $Ga{-}CH_3$ bond strength and this has implications for the metal-organic chemical vapor decomposition of gallium containing semiconductor materials. The prudent choice of other electron withdrawing groups for R should further destabilize the gallium–acetylide bond and lead to more easily pyrolized gallium compounds. Finally, the acetylenic gallium dialkylphosphides $[(^tBu)(Me_3SiC{\equiv}C)GaPR_2]_2$ (R = Et, ^{i}Pr, ^{t}Bu) are currently being investigated as single source precursors to GaP.

4. Experimental section

4.1. General

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 monochromator (Spex Model 1403) coupled to a photomultiplier tube (RCA Model C31034). Typical spectral resolution was 4 cm^{-1}. NMR spectra were recorded on a Bruker AMX 400 (27°C) or an IBM NR-80 (24°C) spectrometer. ^1H NMR spectra were obtained in C_6D_6 and were referenced to residual C_6D_5H (δ 7.15). ^1H NMR obtained in $CD_3C_6D_5$ were referenced to residual $CD_2HC_6D_5$ (δ 2.09). ^1H NMR obtained in C_4D_8O (THF-d_8) were referenced to residual C_4D_7HO (δ 3.58). ^{13}C NMR spectra were obtained in C_6D_6 and were referenced to solvent (128.0 ppm). $^{31}P\{^1H\}$ NMR spectra were obtained in C_6D_6 and were referenced to external 85% H_3PO_4. Microanalyses were performed by E + R Laboratories. Melting points were determined in sealed capillaries (N_2 filled or evacuated) [12].

Benzene, toluene, pentane, hexanes, THF, dioxane, and Et_2O were distilled from Na/benzophenone. Deuterated solvents (C_6D_6, $CD_3C_6D_5$, C_4D_8O) were trap-to-trap distilled from Na/benzophenone.

Reagents were obtained as follows: Me_3Ga (Aldrich), used as purchased. Et_2PH and $^iPr_2PH$ (Quantum Design, Inc.), used as purchased or prepared by reduction of Et_2PCl and $^iPr_2PCl$ (Aldrich) using LAH. $^tBu_2PH$ was prepared by literature methods [13]. $^tBu_3Ga$, Me_2GaCl, and $^tBu_2GaCl$ were prepared by literature methods [4d,14]. $LiC{\equiv}CSiMe_3$ and $LiC{\equiv}CPh$ were prepared from $HC{\equiv}CSiMe_3$ or $HC{\equiv}CPh$ and ^nBuLi in hexanes at −78°C and isolated by filtration.

4.2. $[Me_2GaC{\equiv}CSiMe_3]_2$ (1)

A 50 ml Schlenk flask was charged with Me_2GaCl (4.00 g, 30.0 mmol), $LiC{\equiv}CSiMe_3$ (3.10 g, 30.0 mmol), benzene (20 ml), and a stir bar. A reflux condenser was attached. The flask was heated at 70°C for 2 h. The resulting gold solution with 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 an off-white powder. The powder was sublimed at 60°C (0.05 Torr) onto a CO_2/acetone cooled probe. The somewhat heat sensitive (> 110°C), white solid was collected to give **1** (3.61 g, 18.3 mmol, 62%). m.p. (N_2 filled): 76–79°C; m.p. (evacuated): 27–80°C sublimes. Anal. Found: C, 42.51; H, 7.55; Ga, 35.19; Si, 13.94. $C_{14}H_{30}Ga_2Si_2$ calcd.: C, 42.68; H, 7.67; Ga, 35.39; Si, 14.26%. IR (Nujol): ν(C≡C) 2050w, ν(GaC≡) 610m, $\nu(GaCH_3)$ 542m cm^{-1}. Raman (solid): ν(C≡C) 2040s, ν(GaC≡) 604w, $\nu(GaCH_3)$ 544s cm^{-1}. ^1H NMR (400 MHz): δ 0.24 (s, $GaCH_3$); 0.07 (s, $^2J(SiH) = 7.4$ Hz, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (101 MHz): 130.3 (s, br, GaC≡); 126.2 (s, ≡CSi); −0.38 (s, $^1J(SiC) = 56.4$ Hz, $Si(CH_3)_3$); −1.68 (s, br, $GaCH_3$) ppm. ^{13}C NMR: 130.3 (s, vbr, GaC≡); 126.2 (s, br, ≡CSi).

4.3. $[Me_2GaC{\equiv}CPh]_2$ (2)

A 50 ml Schlenk flask was charged with Me_2GaCl (3.07 g, 22.7 mmol), $LiC{\equiv}CPh$ (2.50 g, 23.1 mmol), benzene (15 ml), and a stir bar. A reflux condenser was attached. The flask was heated at 70°C for 2 h. The resulting brown solution with 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 brown filtrate leaving a brown powder that was collected on a fritted funnel and washed with pentane to give **2** (2.63 g, 13.1 mmol, 58%). m.p. (N_2 filled): 95–103°C dec.; m.p. (evacuated): 95–115°C dec. Anal. Found: C, 59.70; H, 5.78; Ga, 34.73. $C_{20}H_{22}Ga_2$ calcd.: C, 59.79; H, 5.52; Ga, 34.70%. IR (Nujol): ν(C≡C) 2090s, ν(PhC≡) 1190m, $\nu(GaCH_3)$ 580w cm^{-1}. Raman (solid): ν(C≡C) 2100s cm^{-1}. ^1H NMR (400 MHZ): δ 7.38 (m, 2H of C_6D_5, *o*); 6.92 (m, 1H of C_6D_5, *p*); 6.85 (m, 2H of C_6D_5, *m*); 0.37 (s, 2 $GaCH_3$). $^{13}C\{^1H\}$ NMR (101 MHz): 133.4 (s, *o*); 130.4 (s, *p*); 128.7 (s, *m*); 127.3 (s, *i*); 121.5 (s, $\equiv CC_6H_5$); 98.1 (s, GaC≡); −2.29 (s, $GaCH_3$) ppm. ^{13}C NMR: 121.5 (t, $^3J(HC) = 8.0$ Hz, $\equiv CC_6H_5$); 98.1 (s, br, GaC≡) [15*].

4.4. [^{t}Bu$_2$GaC$\equiv$CPh]$_2$ (3)

^{t}Bu$_2$GaCl (1.74 g, 7.9 mmol), LiC$\equiv$CPh (0.89 g, 8.2 mmol), and benzene (10 ml) were combined in a procedure analogous to that given for **2**. An identical workup gave a brown powder which was collected to give **3** (1.61 g, 5.6 mmol, 71%). m.p. (N$_2$ filled): 132–137°C, 140°C dec; m.p. (evacuated): 132–137°C, 140°C dec. Anal. Found: C, 67.61; H, 8.09; Ga, 24.50. $C_{32}H_{46}Ga_2$ calcd.: C, 67.41; H, 8.31; Ga, 24.46%. IR (Nujol): ν(C$\equiv$C) 2050s, ν(PhC$\equiv$) 1195w cm^{-1}. Raman (solid): ν(C$\equiv$C) 2060s cm^{-1}. ^{1}H NMR (400 MHz): δ 7.56 (m, 2H of C_6D_5, *o*); 6.91 (m, 3H of C_6D_5, *m*, *p*); 150 (s, 18H, 2 GaC(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (101 MHz): 134.2 (s, *o*); 130.7 (s, *p*); 130.7 (s, *i*); 128.9 (s, *m*); 121.6 (s, $\equiv$CC$_6$H$_5$); 92.8 (s, GaC$\equiv$); 32.2 (s, GaC(CH$_3$)$_3$); 28.3 (s, GaC(CH$_3$)$_3$) ppm. ^{13}C NMR: 121.6 (t, ^3J(HC) = 8.0 Hz, $\equiv$CC$_6$H$_5$); 92.8 (s, br, GaC$\equiv$).

4.5. [Me$_2$GaPEt$_2$]$_3$ (4) [4f]

A 50 ml Teflon stoppered flask was charged with Me$_3$Ga (0.617 ml, 0.71 g, 6.2 mmol), Et$_2$PH (0.700 ml, 0.55 g, 6.1 mmol), toluene (2.5 ml), and a stir bar. The solution was frozen N$_2$(l) and the flask was evacuated. The flask was heated at 130°C for 20 h. After cooling to 25°C, the toluene was removed (1 Torr) from the gray solution. The resulting gray residue was sublimed at 135°C (0.05 Torr) onto a CO$_2$/acetone cooled probe. Trimer **4** was obtained as a colorless, waxy solid (0.60 g, 1.1 mmol, 52%), m.p. (N$_2$ filled): 120–130°C sublimes, m.p. (evacuated): 120–130°C sublimes. Anal. Found: C, 38.26; H, 8.73; Ga, 37.21; P, 16.30. $C_{18}H_{48}Ga_3P_3$ calcd.: C, 38.15; H, 8.54; Ga, 36.91; P, 16.40%. IR (Nujol): ν(PC) 740m cm^{-1}. Raman (solid): ν(GaCH$_3$) 524s, ν(GaP) 420w cm^{-1}. ^{1}H NMR (400 MHz): δ 1.58 (quartet of triplet, spacing = 7.6 Hz, 1.9 Hz, PCH_2CH$_3$), 0.99 (m, PCH$_2$CH_3), −0.04 (q, spacing = 3.0 Hz, GaCH$_3$) [16*]. ^{13}C{^{1}H} NMR (101 MHz): 11.9 (q, spacing = 5.4 Hz, PCH$_2$CH$_3$); 11.2 (q, spacing = 0.7 Hz, PCH$_2$$CH_3$); −7.5 (m, GaCH$_3$) ppm. ^{31}P NMR (163 MHz): −56.8 (s) ppm.

4.6. [Me$_2$GaP(^{i}Pr)$_2$]$_2$ (5) [7]

A 50 ml Teflon stoppered flask was charged with Me$_3$Ga (0.434 ml, 0.50 g, 4.4 mmol), ^{i}Pr$_2$PH (0.649 ml, 0.51 g, 4.3 mmol), toluene (1.0 ml), and a stir bar. The solution was frozen N$_2$(l) and the flask was evacuated. The flask was heated at 140°C for 96 h. After cooling to 25°C, the toluene was removed (1 Torr) from the blue solution. The resulting white solid was sublimed at 110°C (0.05 Torr) onto a CO$_2$/acetone cooled probe leaving a light blue oil behind. Dimer **5** was obtained as a colorless, waxy solid (0.88 g, 2.0 mmol, 94%), m.p. (N$_2$ filled): 43°C glassy, 88–115°C melts; m.p. (evacuated): 43°C glassy, 147–150°C melts and sublimes. Anal. Found: C, 44.39; H, 9.46; Ga, 32.10; P, 14.20. $C_{16}H_{40}Ga_2P_2$ calcd.: C, 44.29; H, 9.29; Ga, 32.14; P, 14.28%. IR (Nujol): ν(PCC) 880m, ν(PC) 745s cm^{-1}. Raman (solid): ν(PCC) 884m, ν(GaCH$_3$) 528s cm^{-1}. ^{1}H NMR (400 MHz): δ 2.16 (septet of triplet, ^3J(HH) = 7.1 Hz, spacing = 2.1 Hz, PCH(CH$_3$)$_2$); 1.16 (q, spacing = 7.1 Hz, PCH(CH_3)$_2$); 0.13 (t, ^3J(PH) = 4.1 Hz, GaCH$_3$). ^{13}C{^{1}H} NMR (101 MHz): 23.1 (s, PCH(CH$_3$)$_2$); 22.5 (t, spacing = 9.5 Hz, PCH(CH$_3$)$_2$); −4.6 (t, ^2J(PC) = 8.8 Hz, GaCH$_3$) ppm. ^{31}P NMR (162 MHZ): −9.0s ppm.

4.7. [Me$_2$GaP(^{t}Bu)$_2$]$_2$ (6) [9]

A 50 ml Teflon stoppered flask was charged with Me$_3$Ga (0.339 ml, 0.39 g, 3.4 mmol), ^{t}Bu$_2$PH (0.625 ml, 0.50 g, 3.4 mmol), toluene (2.0 ml), and a stir bar. The solution was frozen N$_2$(l) and the flask was evacuated. The flask was heated at 160°C for 240 h. After cooling to 25°C, colorless needles formed and were collected by filtration and dried on the fritted funnel. The toluene was removed (1 Torr) and the resulting white residue was crystallized from hexanes. Colorless cubes formed and were collected by filtration and dried on the fritted funnel to give **6** (0.14 g, 0.3 mmol, 17%), m.p. (N$_2$ filled): 225–235°C dec; m.p. (evacuated): 225–235°C sublimes. Anal. Found: C, 48.96; H, 10.11; Ga, 28.71; P, 12.55. $C_{20}H_{48}Ga_2P_2$ calcd.: C, 49.03; H, 9.87; Ga, 28.46; P, 12.64%. IR (Nujol): ν(PCC) 810m, ν(PC) 750s cm^{-1}. Raman (solid): ν(PCC) 812m, ν(GaCH$_3$) 528s, ν(GaP) 400w cm^{-1}. ^{1}H NMR (400 MHz): δ 1.33 (t, spacing = 6.5 Hz, PC(CH_3)$_3$); 0.34 (t, ^3J(PH) = 3.1 Hz, GaCH$_3$). ^{13}C{^{1}H} NMR (101 MHz): 36.1 (t, spacing = 6.3 Hz, PC(CH$_3$)$_3$); 32.9 (s, PC(CH$_3$)$_3$); 2.6 (s, br, GaCH$_3$) ppm. ^{31}P NMR (162 MHz): 29.1s ppm.

4.8. [(^{t}Bu)$_2$GaPEt$_2$]$_2$ (7)

A 25 ml Teflon stoppered flask was charged with ^{t}Bu$_3$Ga (0.68 g, 2.8 mmol), Et$_2$PH (0.318 ml, 0.25 g, 2.8 mmol), toluene (2.0 ml), and a stir bar. The solution was frozen N$_2$(l) and the flask was evacuated. The flask was heated at 130°C for 24 h. After cooling to 25°C, the toluene was removed (1 Torr) and the resulting white solid was crystallized from warm benzene (75°C). Large, colorless cubes and needles formed which were collected by filtration and dried *in vacuo* to give **7** (0.71 g, 1.3 mmol, 93%), m.p. (N$_2$ filled): 150–180°C, 200–220 dec; m.p. (evacuated): 150–180°C sublimes, 200–220°C dec. Anal. Found: C, 52.86; H, 10.16; Ga, 25.58; P, 11.38. $C_{24}H_{56}Ga_2P_2$ calcd.: C, 52.79; H, 10.34; Ga, 25.53; P, 11.34%. IR (Nujol): ν(GaCC) 805s, ν(PC) 760m cm^{-1}. Raman (solid): ν(GaCC) 808s, ν(GaC) 520s, ν(GaP) 384w cm^{-1}. ^{1}H NMR (400 MHz): δ 1.97 (quartet, spacing = 7.4 Hz, PCH_2CH$_3$); 1.28 (s, GaC(CH$_3$)$_3$); 0.99 (pentet, spacing = 7.2 Hz, PCH$_2$

CH_3). $^{13}C\{^1H\}$ NMR (101 MHz): 32.9 (t, $^3J(PC) = 1.6$ Hz, $GaC(CH_3)_3$); 27.2 (t, $^2J(PC) = 8.9$ Hz, $GaC(CH_3)_3$); 12.1 (t, spacing = 8.7 Hz, PCH_2CH_3); 11.9 (t, spacing = 2.9 Hz, PCH_2CH_3) ppm. ^{31}P NMR (162 MHz): −31.0s ppm.

4.9. $[(^{t}Bu)_2GaP(^{i}Pr)_2]_2$ (8) [10]

A 50 ml Teflon stoppered flask was charged with $^{t}Bu_3Ga$ (1.02 g, 4.2 mmol), $^{i}Pr_2PH$ (0.662 ml, 0.52 g, 4.4 mmol), toluene (2.0 ml), and a stir bar. The solution was frozen N_2(l) and the flask was evacuated. The flask was heated at 130°C for 96 h. After cooling to 25°C, the toluene was removed (1 Torr) and the resulting yellow solid was crystallized from warm hexanes (60°C). Fine, colorless cubes and needles formed which were collected by filtration, washed with hexanes, and dried *in vacuo* to give **8** (0.20 g, 0.7 mmol, 16%), m.p. (N_2 filled): 164°C sublimes, 194–197°C dec; m.p. (evacuated): 164°C sublimes. Anal. Found: C, 56.02; H, 10.40; Ga, 23.48; P, 10.22. $C_{28}H_{64}Ga_2P_2$ calcd.: C, 55.85; H, 10.71; Ga, 23.16; P, 10.29%. IR (Nujol): $\nu(PCC)$ 880m, $\nu(GaCC)$ 805s, $\nu(PC)$ 730s cm^{-1}. Raman (solid): $\nu(PCC)$ 880m, $\nu(GaCC)$ 804s, $\nu(GaC)$ 524s, $\nu(GaP)$ 390w cm^{-1}. ^1H NMR (400 MHz): δ 2.68 (septet, $^3J(HH) = 7.2$ Hz, $PCH(CH_3)_2$); 1.48 (q, spacing = 6.5 Hz, $PCH(CH_3)_2$); 1.40 (s, $GaC(CH_3)_3$). $^{13}C\{^1H\}$ NMR (101 MHz): 33.9 (s, $GaC(CH_3)_3$); 28.2 (t, $^2J(PC) = 9.3$ Hz, $GaC(CH_3)_3$); 27.3 (s, $PCH(CH_3)_2$); 26.6 (t, spacing = 5.0 Hz, $PCH(CH_3)_2$) ppm. ^{31}P NMR (162 MHz): 17.2s ppm.

4.10. *Monitoring of reactions by ^1H NMR*

The following experiment is representative. A 5-mm NMR tube (Wilmad/Omnifit equipped with a 5-mm end cap and 2-way valve) was charged with **3** (0.05 g, 0.17 mmol), $^{i}Pr_2PH$ (0.02 g, 0.17 mmol), and toluene-d_8. The solution was frozen N_2(l), the tube was evacuated and sealed, then the solution was slowly warmed to room temperature. A ^1H NMR spectrum was recorded at 25°C and showed adducts of the starting materials. The tube was heated at 140°C for 1 h in an oil bath. After cooling to 25°C, a ^1H NMR spectrum was recorded and a new singlet was observed at 1.25 ppm which corresponds to the adduct $(^{i}Pr)_2(H)P:Ga(^{t}Bu)_3$. After an additional 7 h at 140°C, a ^1H NMR spectrum was recorded and showed that the phenyl region was considerably more complicated, **3** was nearly consumed, a resonance was observed at 1.34 ppm which corresponds to the ^{t}Bu group of $[(^{t}Bu)_2GaP(^{i}Pr)_2]_2$, a new singlet was observed at 1.28 ppm which may correspond to the methyl protons of $^{t}BuGa(C{\equiv}CPh)_2$, the singlet at 1.25 ppm was the most intense peak in the spectrum, and resonances were observed at 0.90 and 0.82 ppm which correspond to isobutane (Me_3CH).

Acknowledgments

We thank the Office of Naval Research for financial support. We thank Drs. R.A. Nissan and L.H. Merwin for collection and manipulation of NMR data. We thank Drs. F.M. Cerio and W.A. Weimer for collection of Raman data. K.E.L. thanks the American Society for Engineering Education for a postdoctoral fellowship.

References and notes

1 (a) B. Tecle, W. H. Ilsley and J. P. Oliver, *Inorg. Chem.*, *20* (1981) 2335. (b) W. Fries, W. Schwarz, H.-D. Hausen and J. Weidlein, *J. Organomet. Chem.*, *159* (1978) 373. (c) E. A. Jeffery and T. Mole, *J. Organomet. Chem.*, *11* (1968) 393.

2 Other related references: (a) V. V. Gavrilenko, V. S. Kolesov and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, *6* (1981) 1374. (b) W. Fries, K. Sille, J. Weidlein and A. Haaland, *Spectrochim. Acta.*, *36A* (1980) 611. (c) M. J. Albright, W. M. Butler, T. J. Anderson, M. D. Glick and J. P. Oliver, *J. Am. Chem. Soc.*, *98* (1976) 3995. (d) G. D. Stucky, A. Mootz-McPherson, W. E. Rhine, J. J. Eisch and J. L. Considine, *J. Am. Chem. Soc.*, *96* (1974) 1941. (e) N. S. Ham, E. A. Jeffery and T. Mole, *Aust. J. Chem.*, *21* (1968) 2687. (f) E. A. Jeffery, T. Mole and J. K. Saunders, *Aust. J. Chem.*, *21* (1968) 649. (g) E. A. Jeffery, T. Mole and J. K. Saunders, *Aust. J. Chem.*, *21* (1968) 137. (h) T. Mole and J. R. Surtees, *Aust. J. Chem.*, *17* (1964) 1229.

3 K. E. Lee, K. T. Higa, R. A. Nissan and R. J. Butcher, *Organometallics*, *11* (1992) 2816.

4 (a) Y. Monteil, M. P. Berthet, R. Favre, A. Hariss, J. Bouix, M. Vaille and P. Gibart, *J. Cryst. Growth*, *77* (1986) 172. (b) S. Kvisle and E. Rytter, *Spectrochim. Acta.*, *40A* (1984) 939. (c) F. Maury and G. Constant, *Polyhedron*, *3* (1984) 581. (d) H.-U. Schwering, E. Jungk and J. Weidlein, *J. Organomet. Chem.*, *91* (1975) C4. (e) Von J. Weidlein and B. Schaible, *Z. Anorg. Allg. Chem.*, *386* (1971) 176. (f) O. T. Beachley and G. E. Coates, *J. Chem. Soc.*, (1965) 3241.

5 Analogous ligand redistribution reactions of $Me_2Ga(C_5H_5)$ and $MeGa(C_5H_5)_2$ have also been studied: O. T. Beachley, Jr., T. L. Royster, Jr., J. R. Arhar, *J. Organomet. Chem.*, *434* (1992) 11.

6 Workup of analogous preparative reaction mixtures gave dimethylgallium diethyl or diisopropylphosphides and a minor, colored impurity that could not be removed either by sublimation or crystallization. ^1H NMR of the mixtures gave peaks for the impurity in the region expected for MeGa (δ 0.29–0.24). Although there was no evidence for phosphine addition to the triple bond in these reactions, diphenylphosphine (Ph_2PH) has been shown to add to alkynes in the presence of a free radical initiator, see: T. N. Mitchell and K. Heesche, *J. Organomet. Chem.*, *409* (1991) 163.

7 A. H. Cowley, R. A. Jones, M. A. Mardones and C. M. Nunn, *Organometallics*, *10* (1991) 1635.

8 For a discussion of the relationship between the magnitude of the $^1J(PH)$ versus coordination at phosphorus see: J. F. Brazier, D. Houalla, M. Loenig and R. Wolf, in E. J. Griffith and M. Grayson (eds.), *Topics in Phosphorus Chemistry*, Wiley, New York, 1976, pp. 99–103.

9 A. M. Arif, B. L. Benac, A. H. Cowley, R. Geerts, R. A. Jones, K. B. Kidd, J. M. Power and S. T. Schwab, *J. Chem. Soc., Chem. Commun.*, (1986) 1543.

10 Compound **8** was first prepared from the reaction of $^{t}Bu_2GaCl$

and LiP(^{i}Pr)$_2$; K. T. Higa and R. E. Cramer, Organometallics, submitted.

11 For a discussion of the activating and directive effects of the Me$_3$Si group see: A. R. Bassindale, P. G. Taylor, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, New York, 1989, Ch. 14. For the phenyl group see: F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 2nd edition, Plenum, New York, 1984, pp. 179–190.

12 G. V. D. Tiers, *J. Chem. Educ.*, *9* (1990) 1351.

13 (a) H. Hoffmann and P. Schellenbeck, *Chem. Ber.*, *99* (1966) 1134. (b) K. Issleib and M. Hoffmann, *Chem. Ber.*, *99* (1966) 1320.

14 R. A. Kovar, H. Derr, D. Brandau and J. O. Callaway, *Inorg. Chem.*, *14*(11) (1975) 2809.

15 ^{13}C NMR of **2** and **3** gave typical sp^2 ^1J(HC) of 161.0–169.0 Hz for the phenyl carbons.

16 "Spacing" refers to the average separation between the lines of a virtual multiplet.