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Synthetic and Structural Studies of Gallium−Phosphorus, Gallium−Arsenic, and Indium−Phosphorus Compounds with Chromophoric Substituents

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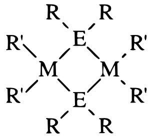
Seven group 13/15 four-membered-ring compounds of the general type $[R_2ME\text{-}t\text{-}Bu_2]_2$ bearing the chromophoric substituents (R) vinyl, allyl, and benzyl have been synthesized by treatment of $t\text{-}Bu_2PLi$ or $t\text{-}Bu_2AsLi$ with the appropriate gallium or indium chloride, R_2MCl (prepared *in situ*), in Et_2O solution: **3** (R = vinyl, M = Ga, E = P); **4** (R = vinyl, M = In, E = P); **5** (R = allyl, M = In, E = P); **6** (R = allyl, M = Ga, E = As); **7** (R = benzyl, M = In, E = P); **8** (R = benzyl, M = Ga, E = As); **10** (R = vinyl, M = Ga, E = As). The partially substituted derivative $[(vinyl)ClGaAs\text{-}t\text{-}Bu_2]_2$ (**9**) was prepared by a similar one-pot procedure. All eight new compounds were characterized by X-ray crystallography, NMR, and mass spectroscopy. Compounds **3**−**8** absorb light at relatively long wavelengths with cutoffs ranging from ∼300 nm for the vinyl-substituted compounds to ∼330 nm for the corresponding allyl- and benzyl-substituted derivatives.

Introduction

The past several years have witnessed an increasingly strong interest in electronic materials based upon 13/15 compound semiconductors.[1] Typically, the production of thin films of these materials involves the organometallic chemical vapor deposition (OMCVD) reaction of a group 13 alkyl, such as Me_3Ga, with a group 15 hydride, such as AsH_3, at relatively high temperatures (∼700 °C) as exemplified by eq 1. Despite its commercial use, several problems are associated with the conventional OMCVD method, such as the safe handling of the pyrophoric and toxic feedstocks. Moreover, the drive toward three-dimensional structures with abrupt interfaces, coupled with the need to minimize impurity migration, has made lower deposition temperatures highly desirable.

$$Me_3Ga + AsH_3 \xrightarrow{\Delta} GaAs + 3CH_4 \tag{1}$$

In an effort to address some of the problems inherent in conventional OMCVD, the development of a single-source precursor approach for 13/15 materials was undertaken beginning in the mid-1980s.[2] From the standpoint of gallium arsenide formation, the two most successful types of precursor are **1** and **2** (M = Ga; E = As) in the sense that epitaxial film growth has been achieved. A key feature of both precursor types is the presence of alkyl groups (R or R′) which are capable of facile β-hydride and/or alkyl radical elimination reactions, thus lowering deposition temperatures into the range 400−590 °C.



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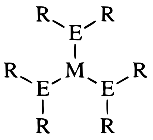

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(M = group 13 element; E = group 15 element)

Insights into the deposition mechanisms of **1** and **2** have been provided by pyrolysis,[3] temperature-programed desorption (TPD),[4] and film growth[5−8] studies. Photoassisted growth represents a viable approach to even further reductions in deposition temperatures yet one that is capable of sustaining reasonable growth rates. The so-called photoepitaxy[9] method has proved effective for the deposition of several 12/16 materials such as CdTe and HgTe.[10] In addition to diminishing thermal budgets, photoassisted growth also offers the possibility of selective or patterned deposition. In this context, it is worth noting that patterned growth of CdTe has been achieved at low temperature by irradiation with 256 nm light.[11] Significantly less is known, however, about the photoassisted growth of 13/15 materials. One of the issues here is that conventional alkylated group 13/15 precursors only absorb radiation in the far-ultraviolet region (∼200 nm)[12,13] thus requiring the use of expensive excimer lasers for deposition. One way of extending

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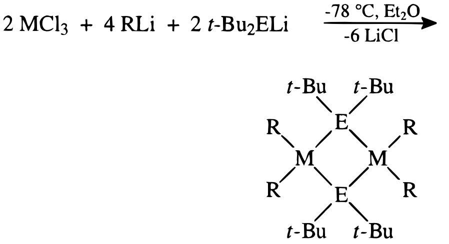
the absorption wavelength into the UV lamp/normal laser range is incorporation of a chromophoric substituent into the 13/15 precursor.

In the present paper, we describe the syntheses and characterization of precursors of type **1** bearing the chromophoric substituents vinyl, allyl, and benzyl. It did not escape our attention that the use of allyl and benzyl substituents was also potentially beneficial from the standpoint of more facile thermal deposition due to the stabilities of the corresponding radicals and the consequent lowering of the element−allyl and element−benzyl homolytic bond dissociation energies.[14] We also note that, while the structure of trivinylgallium has been established by gas-phase electron diffraction,[15] heretofore no single-crystal X-ray structural data were available for allyl- or vinyl-substituted gallium or indium compounds.

Results and Discussion

Synthesis and Characterization. Compounds of structure **1** have been prepared by alkane,[16] silyl halide,[2b] and salt elimination reactions.[17] Given that group 13 organometallics with unsaturated ligands tend to undergo polymerization reactions at elevated temperatures,[18] we opted to use a salt elimination procedure (eq 2) because this can be carried out at lower temperatures. An additional advantage of this procedure is that it is a "one-pot" method, thus obviating the necessity of isolating organometallic halides, R_2MX, which are prone to rearrangement reactions.[19] It was also found that lithium alkyls are the preferred alkylating agents; the use of Grignard reagents results in considerable byproduct formation.



(2)

R = vinyl; M = Ga, E = P (**3**); M = In, E = P (**4**)
R = allyl; M = In, E = P (**5**); M = Ga, E = As (**6**)
R = benzyl; M = In, E = P (**7**); M = Ga, E = As (**8**)

Compounds **3**−**7** are white, crystalline solids which, with the exception of **6**, decompose upon melting. The highest mass peaks in the CI^+ medium resolution mass spectra of **3**−**6** correspond to the dimeric formulation, **1** [either as M^+ or $(M + 1)^+$]. In the case of **7**, the negative-ion mode was employed and the highest mass peak ($m/z = 975$) is attributable to $(M + \text{benzyl})^-$. The gallium isotope patterns for the M^+ or $(M + 1)^+$ peaks of **5** and **6** correspond to digallium species, and for **3**−**7**, the fragmentation patterns are consistent with dimer formation.

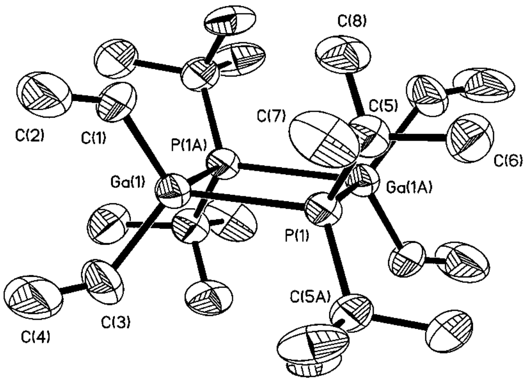


Figure 1. View of $[(\text{vinyl})_2\text{GaP-}t\text{-Bu}_2]_2$ (**3**) showing the atom-labeling scheme for **3**, **4**, and **10**. Thermal ellipsoids are shown at the 30% probability level.

The observation that the ^{31}P NMR signals for **3**−**5** and **7** comprise virtual triplets is consistent with the persistence of the dimeric structures, **1**, in solution. These virtual triplets arise from the coupling of a given ^{31}P nucleus both to the attached *t*-Bu group protons and to the *t*-Bu group protons on the other ring phosphorus atom. The observed spacing of the virtual triplets corresponds to the average of $^3J_{PH}$ and $^5J_{PH}$ and ranges from 6.8 to 7.2 Hz. Virtual triplets were also apparent in the $^{13}C\{^1H\}$ signals of the *t*-Bu carbons. Such virtual couplings would not be anticipated for monomeric or trimeric structures. The observation of only one set of resonances for the vinyl, allyl, or benzyl substituents of **3**−**7** suggests a symmetrical solution structure for each compound.

Compound **8** was prepared *via* a route analogous to that described for **3**−**7** (eq 2). Interestingly, however, the initially formed product (**8a**) is a dark orange oil that solidifies slowly to afford a pale yellow crystalline material (**8b**). Since dimers such as **3**−**7** are typically colorless solids, the possibility that **8a** is a monomer was entertained. Supporting this suspicion is the fact that the monomer, $t\text{-Bu}_2\text{GaAs-}t\text{-Bu}_2$, is reported to be a yellow solid.[20] Confirmation of the monomeric nature of **8a** was provided by a solution molecular weight measurement (calcd for **8a** 441, found 460). The highest peak in the CI^+ mass spectrum of **8b** appeared at *m/z* 691 and could be due to the dimer minus a $t\text{-Bu}_2\text{As}$ fragment or, less likely, to the monomer plus a $(\text{benzyl})_2\text{Ga}$ moiety. A second noteworthy mass spectral feature is that the monomer plus H peak (*m/z* 441) possesses a relative intensity that is an order of magnitude larger than that of the analogous peaks for **6**, **7**, and **10**. The implication of the mass spectral data is that the vapor consists of a monomer/dimer mixture and that the dimer (**8b**) is relatively weakly bonded. The latter surmise was confirmed by a subsequent X-ray crystallographic study (*vide infra*).

X-ray crystallographic studies of **3**−**8** were undertaken both to determine the degree of oligomerization in the solid state and to provide information pertinent to a discussion of the group 13/15 bonding. The X-ray analyses revealed that **3**−**8** are all dimeric molecules with no abnormally short intermolecular contacts. Selected bond distances and angles for the molecules are assembled in Table 1. Compounds **3** and **4** are isomorphic and crystallize in the monoclinic space group *I*2/*m* with two molecules per unit cell (Figure 1). Each molecule possesses an inner core of two group 13 and two phosphorus atoms that have crystallographically imposed planarity. Individual mol-

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Table 1. Selected Bond Distances (Å) and Angles (deg) for [(vinyl)$_2$GaP-*t*-Bu$_2$]$_2$ (**3**), [(vinyl)$_2$InP-*t*-Bu$_2$]$_2$ (**4**), [(allyl)$_2$InP(*t*-Bu)$_2$]$_2$ (**5**), [(allyl)$_2$GaAs(*t*-Bu)$_2$]$_2$ (**6**), [(benzyl)$_2$InP(*t*-Bu)$_2$]$_2$ (**7**), [(benzyl)$_2$GaAs(*t*-Bu)$_2$]$_2$ (**8**), [(vinyl)ClGaAs(*t*-Bu)$_2$]$_2$ (**9**), and [(vinyl)$_2$GaAs(*t*-Bu)$_2$]$_2$ (**10**)

Bond Distances for Compound **3**							
Ga(1)−P(1)	2.462(3)	P(1)−C(5)	1.876(11)	Ga(1)−C(1)	1.96(2)	Ga(1)−C(3)	1.95(2)
Bond Angles for Compound **3**							
Ga(1)−P(1)−Ga(1A)	92.88(12)	C(5)−P(1)−C(5A)	109.8(7)	C(2)−C(1)−Ga(1)	131(2)	C(4)−C(3)−Ga(1)	134(2)
P(1)−Ga(1)−P(1A)	87.12(12)	C(1)−Ga(1)−C(3)	110.8(9)				
Bond Distances for Compound **4**							
In(1)−P(1)	2.6211(8)	P(1)−C(5)	1.894(3)	In(1)−C(1)	2.166(6)	In(1)−C(3)	2.163(6)
Bond Angles for Compound **4**							
In(1)−P(1)−In(1A)	93.58(3)	C(5)−P(1)−C(5A)	112.5(2)	C(2)−C(1)−In(1)	131.1(7)	C(4)−C(3)−In(1)	131.2(7)
P(1)−In(1)−P(1A)	86.42(3)	C(1)−In(1)−C(3)	110.3(3)				
Bond Distances for Compound **5**							
In(1)−P(1)	2.639(1)	In(1)−C(1)	2.204(4)	P(1)−C(7)	1.895(4)	P(1)−C(11)	1.898(4)
In(1)−P(1A)	2.645(1)	In(1)−C(4)	2.218(4)				
Bond Angles for Compound **5**							
In(1)−P(1)−In(1A)	93.66(3)	P(1)−In(1)−P(1A)	86.34(3)	C(1)−In(1)−C(4)	107.3(2)	C(7)−P(1)−C(11)	112.2(2)
Bond Distances for Compound **6**							
Ga(1)−As(1)	2.5377(10)	Ga(1)−C(1)	1.998(6)	As(1)−C(7)	2.020(7)	As(1)−C(11)	2.014(6)
Ga(1)−As(1A)	2.5466(9)	Ga(1)−C(4)	2.017(6)				
Bond Angles for Compound **6**							
Ga(1)−As(1)−Ga(1A)	94.47(3)	As(1)−Ga(1)−As(1A)	85.53(3)	C(1)−Ga(1)−C(4)	109.1(3)	C(7)−As(1)−C(11)	109.6(3)
Bond Distances for Compound **7**							
In(1)−P(1)	2.637(2)	In(1)−C(1)	2.212(7)	P(1)−C(15)	1.889(8)	P(1)−C(19)	1.892(8)
In(1)−P(1A)	2.649(2)	In(1)−C(8)	2.228(7)				
Bond Angles for Compound **7**							
In(1)−P(1)−In(1A)	94.89(6)	C(15)−P(1)−C(19)	112.8(4)	C(8)−In(1)−P(1)	112.7(2)	C(2)−C(1)−In(1)	121.5(5)
P(1)−In(1)−P(1A)	85.11(6)	C(1)−In(1)−P(1)	125.9(2)	C(8)−In(1)−P(1A)	113.8(2)	C(9)−C(8)−In(1)	111.5(5)
C(1)−In(1)−C(8)	105.0(3)	C(1)−In(1)−P(1A)	113.6(2)				
Bond Distances for Compound **8**							
Ga(1)−As(1)	2.5463(10)	Ga(1)−C(1)	2.007(7)	As(1)−C(15)	2.007(7)	As(1)−C(19)	2.018(6)
Ga(1)−As(1A)	2.5746(10)	Ga(1)−C(8)	2.004(6)				
Bond Angles for Compound **8**							
Ga(1)−As(1)−Ga(1A)	95.09(3)	C(15)−As(1)−C(19)	109.1 (3)	C(8)−Ga(1)−As(1)	116.9(2)	C(2)−C(1)−Ga(1)	121.4(5)
As(1)−Ga(1)−As(1A)	84.91(3)	C(1)−Ga(1)−As(1)	121.6(2)	C(8)−Ga(1)−As(1A)	109.3(2)	C(9)−C(8)−Ga(1)	117.1(5)
C(1)−Ga(1)−C(8)	109.6(3)	C(1)−Ga(1)−As(1A)	111.4(2)				
Bond Distances for Compound **9**							
Ga(1)−As(1)	2.512(2)	Ga(2)−As(3)	2.519(2)	Ga(1)−Cl(1)	2.201(6)	Ga(1)−C(1)	1.965(15)
Ga(1)−As(1A)	2.524(3)	Ga(3)−As(2)	2.508(2)	Ga(2)−Cl(2)	2.203(5)	Ga(2)−C(11)	1.957(13)
Ga(2)−As(2)	2.517(2)	Ga(3)−As(3)	2.519(2)	Ga(3)−Cl(3)	2.200(5)	Ga(3)−C(21)	1.952(14)
Bond Angles for Compound **9**							
Ga(1)−As(1)−Ga(1A)	92.7(1)	As(2)−Ga(2)−As(3)	87.5(1)	Cl(3)−Ga(3)−C(21)	107.4(5)	Ga(1)−C(1)−C(2)	117.3(17)
Ga(2)−As(2)−Ga(3)	92.6(1)	As(2)−Ga(3)−As(3)	87.6(1)	C(3)−As(1)−C(7)	112.6(6)	Ga(2)−C(11)−C(12)	120.5(14)
Ga(2)−As(3)−Ga(3)	92.3(1)	Cl(1)−Ga(1)−C(1)	109.3(6)	C(13)−As(2)−C(17)	110.9(7)	Ga(3)−C(21)−C(22)	124.3(18)
As(1)−Ga(1)−As(1A)	87.3(1)	Cl(2)−Ga(2)−C(11)	107.8(5)	C(23)−As(3)−C(27)	112.7(7)		
Bond Distances for Compound **10**							
Ga(1)−As(1)	2.527(1)	As(1)−C(5)	2.021(5)	Ga(1)−C(1)	1.969(8)	Ga(1)−C(3)	1.958(9)
Bond Angles for Compound **10**							
Ga(1)−As(1)−Ga(1A)	94.6(1)	C(5)−As(1)−C(5A)	110.9(3)	Ga(1)−C(1)−C(2)	135.0(10)	Ga(1)−C(3)−C(4)	133.6(9)
As(1)−Ga(1)−As(1A)	85.4(1)	C(1)−Ga(1)−C(3)	111.1(4)				

ecules reside on sites of C_{2h} symmetry such that an inversion center exists at the midpoint of the [MP]$_2$ rhombus; both group 13 atoms and the vinyl carbon atoms lie on the mirror plane, and the phosphorus atoms are located on a 2-fold axis. The Ga−P and In−P bond distances of 2.462(2) and 2.6211(8) Å, respectively, are comparable to those in related dimers[2,21−23] and the group 13 and phosphorus atoms adopt approximately tetrahedral geometries. The M−C═C bond angles of 132(2) and 131.2(7)° for **3** and **4**, respectively, exceed the ideal angle of 120°, and the examination of models reveals that this is due to steric effects.

Compounds **5** and **6** are also isomorphic and crystallize in the monoclinic space group $P2_1/n$ with two molecules per unit cell (Figure 2). Both compounds are dimeric in the solid state, and the basic geometric features of the individual molecules of **5** and **6** are similar to those discussed above for **3** and **4**; *viz.*, there is a four-membered heavy atom kernel and the ligands are arrayed in an approximately tetrahedral fashion. However, because the site symmetry is lower for **5** and **6** (C_i), there are

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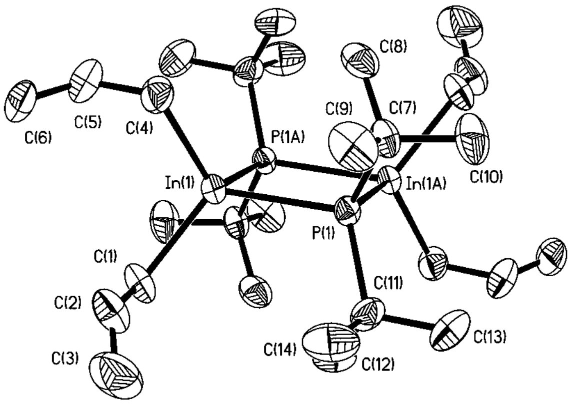


Figure 2. View of [(allyl)$_2$InP-*t*-Bu$_2$]$_2$ (**5**) showing the atom-labeling scheme for **5** and **6**. Thermal ellipsoids are shown at the 30% probability level.

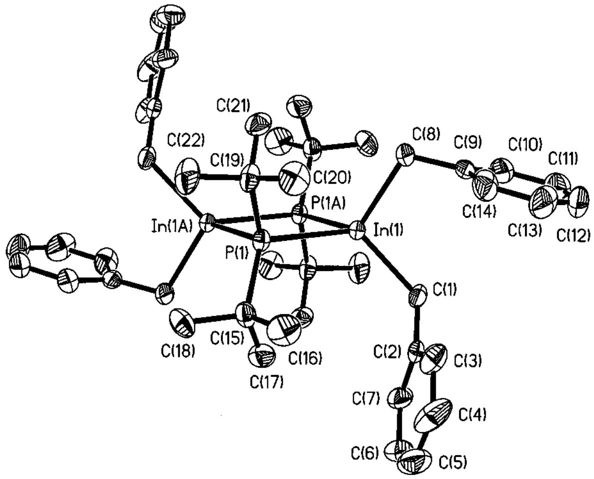


Figure 3. View of [(benzyl)$_2$InP-*t*-Bu$_2$]$_2$ (**7**) showing the atom-labeling scheme for **7** and **8**. Thermal ellipsoids are shown at the 30% probability level.

two independent M−E bond distances in the crystallographically imposed planar [M−E]$_2$ core.

Individual molecules of **7** and **8** are both dimeric (Figure 3) and crystallize in the monoclinic space group $P2_1/c$ with two molecules per unit cell. The overall geometries of the dimers **7** and **8** are similar to those of **3**−**6**. Nevertheless, **7** and **8** possess some distinctive features. A conspicuous difference between the structures of **3**−**7** and that of **8** concerns the fact that the M−E bond distances are inequivalent (2.5463(10) and 2.5746(10) Å). In turn, this suggests that **8** may be on the threshold of division into monomers. Such a suggestion is corroborated by the fact that, omitting As(1A), the geometry at Ga(1) is midway between trigonal planar and tetrahedral (sum of angles = 348.1(4)°). Thus, As(1A) can be thought of as effecting a distortion of the otherwise trigonal planar geometry of the monomer as dimerization takes place. The second noteworthy feature relates to the conformations of the benzyl groups in **7** and **8**. In both compounds, one of the benzyl groups (attached to C(8)) extends straight out from the Ga or In atom and bisects two E-*t*-Bu moieties. This arrangement minimizes steric interactions between the *t*-butyl and benzyl groups; hence the angles subtended at C(8) are close to the ideal tetrahedral values. In the case of the other benzyl group, inter-aryl group repulsion forces a conformation in which it is oriented toward an E-*t*-Bu group. As a consequence of the steric interactions between the *t*-Bu and benzyl groups, the M(1)−C(1)−C(2) angles in **7** (121.5(2)°) and **8** (121.4(2)°) are considerably more obtuse than the ideal tetrahedral value. The arrangement of the benzyl ligands in both **7** and **8** is illustrated in Figure 4.

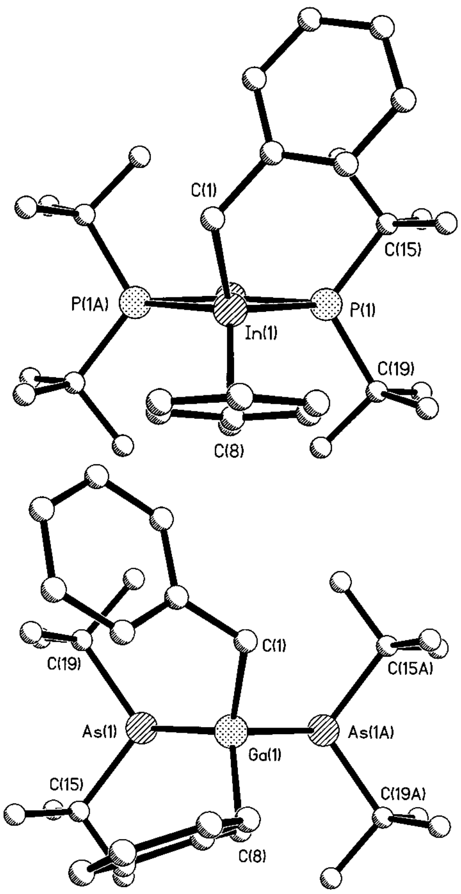
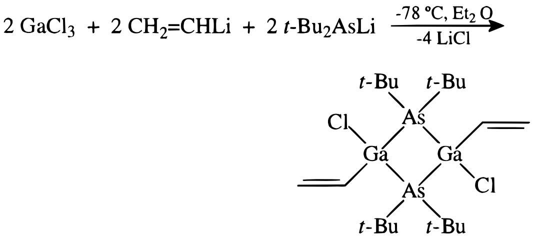


Figure 4. Diagrams of **7** (top) and **8** (bottom) depicting the arrangement of the benzyl ligands. Some atoms have been omitted for clarity.

It was also decided to attempt the synthesis of precursors that are suitable for both photolysis and thermolysis and are thus potential candidates for multiprocessing techniques. The first steps in this direction have been taken by introducing substituents that, in principle, are capable of thermal, β-hydride elimination and photochemical activation. As in the case of **3**−**8**, the preferred synthetic approach was to use the salt elimination methodology.

The reaction of equimolar amounts of gallium trichloride, vinyllithium, and (di-*tert*-butylarsenido)lithium at −78 °C affords [(H$_2$C=CH)ClGaAs-*t*-Bu$_2$]$_2$ (**9**) in modest (25%) yield (eq 3). It was anticipated that **9** would be dimeric, and this



(3)

9

was confirmed by the chemical ionization mass spectrum (positive mode) which exhibits a peak at *m/z* 641 corresponding to the dimer plus one proton. Moreover, the isotope pattern is appropriate for two gallium and two chlorine atoms.

Clearly, **9** is capable of geometrical isomerism in the sense that the vinyl groups can be orientated in a mutually *cis* or *trans*

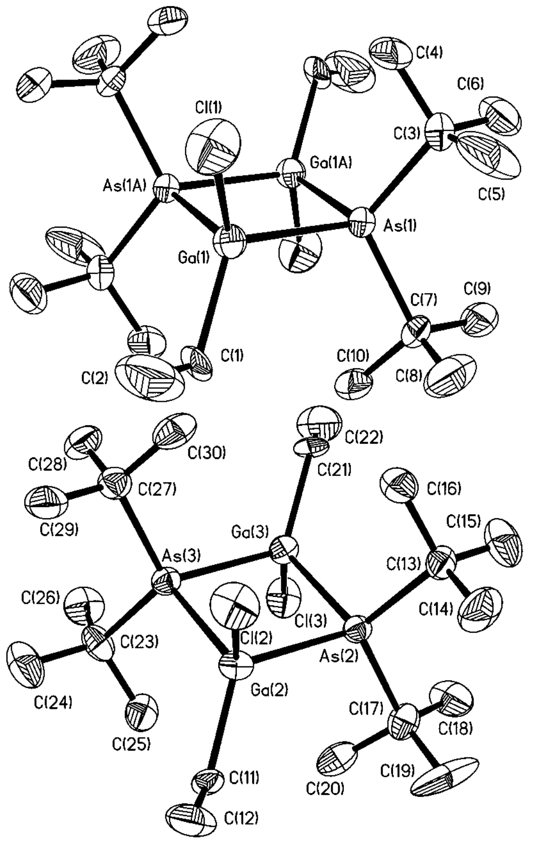


Figure 5. Molecular structures and atom-labeling schemes for both independent molecules of [(vinyl)ClGaP-*t*-Bu_2]$_2$ (**9**). Thermal ellipsoids are shown at the 30% probability level.

fashion. Since the ^{1}H NMR spectrum of **9** exhibits only a single set of resonances for the *t*-butyl and vinyl groups, it was not possible to delineate which isomer had formed and consequently an X-ray crystal structure became necessary.

Compound **9** crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules and a total of six molecules per unit cell (Figure 5). Each of the independent molecules is dimeric, and the vinyl groups are arranged in a mutually *trans* fashion. For the most part, the two independent molecules are very similar; nevertheless, there are some interesting structural differences. Molecule 1 lies on a center of inversion, which imposes planarity upon the [GaAs]$_2$ core, and there are two distinct Ga−As bond distances (2.512(2) and 2.524(3) Å). Molecule 2 has no crystallographically imposed symmetry; however, the [GaAs]$_2$ core is still planar within experimental error (sum of angles = 360.0(2)°) with a maximum deviation from the best mean plane of only 0.006 Å. In this case, there are four independent Ga−As bond distances (2.517(2), 2.519(2), 2.508(2), and 2.519(2) Å). Another interesting feature is that, unlike the cases of **3** and **4**, where the metal atoms and vinyl ligands are strictly coplanar, the vinyl groups of molecule 1 are twisted about the Ga−C bond out of the analogous plane such that the torsion angle defined by Cl(1)Ga(1)−C(1)C(2) is 16(2)°. Interestingly, molecule 2 does not exhibit comparable twisting and the torsion angles defined with respect to Ga(2)−C(11) and Ga(3)−C(21) are only 1(2) and 4(2)°, respectively. Another significant feature relates to the bond angle at the vinyl α-carbon atoms. Because there are no serious steric interactions between the vinyl group and the chlorine atom, the angles are much closer to the ideal value of 120° than those observed in **3**, **4**, and **10** (117.3(17), 120.5(14), and 124.3(18)° for C(1), C(11), and C(21), respectively).

The fully vinyl-substituted derivative [(vinyl)$_2$GaAs-*t*-Bu_2]$_2$ (**10**) was prepared by adding an additional 1 equiv of vinyllithium to a cold diethyl ether solution of **9** (eq 4). The dimeric

$$\underset{\mathbf{9}}{[(\text{vinyl})\text{ClGaAs-}t\text{-Bu}_2]_2} + 2CH_2{=}CHLi \xrightarrow[-2LiCl]{-78\ °C,\ Et_2O} \underset{\mathbf{10}}{[(\text{vinyl})_2\text{GaAs-}t\text{-Bu}_2]_2} \quad (4)$$

nature of **10** was apparent from the presence of a peak at *m/z* 624 in the negative-ion-mode CI mass spectrum, and this was confirmed by single-crystal X-ray diffraction. Compound **10** is isostructural with **3** and **4**, and the same atom-labeling scheme has been employed.

Spectrophotometry of the Precursors. A preliminary survey of the UV−visible spectra of **3**−**8** has been made, and a detailed spectroscopic/materials science study will be the subject of a future publication. All of the compounds containing unsaturated ligands absorb at relatively long wavelengths, with cutoffs ranging from ~300 nm for the vinyl-containing compounds to ~330 nm for the corresponding allyl- and benzyl-substituted derivatives. In contrast, the saturated compound, [Et_2GaAs-*t*-Bu_2]$_2$, only absorbs strongly below 250 nm. In the case of [Bz_2GaAs-*t*-Bu_2] (**8**), the sole colored compound, a broad, continuous absorption commencing at ~500 nm was observed. As pointed out earlier, this may be due to partial dissociation into monomers.

Experimental Section

General Procedures. All reactions were carried out under a dry, oxygen-free argon atmosphere utilizing standard Schlenk manifold techniques or a Vacuum Atmospheres drybox. All solvents were distilled under nitrogen from sodium−benzophenone immediately prior to use. Unless otherwise noted, reagents were obtained from commercial suppliers and used without further purification. Solutions of vinyl-,[24] allyl-,[25] and benzyllithium[26] were prepared by literature methods. The concentrations of the organolithium solutions were determined by quenching measured aliquots with water and titrating with a standardized HCl solution. The compounds *t*-Bu_2PLi[27] and *t*-Bu_2-AsLi[28] were prepared *in situ*, from *t*-Bu_2PH[29,30] and *t*-Bu_2AsH,[28] respectively.

Physical Measurements. NMR spectra were recorded on a GE QE-300 spectrometer (^{1}H, 300.16 MHz; ^{13}C, 75.48 MHz; ^{31}P, 121.50 MHz). ^{1}H and ^{13}C chemical shifts are referenced to the solvent and are reported relative to $Si(CH_3)_4$ ($\delta = 0.00$). ^{31}P chemical shifts are referenced to an external standard (85% H_3PO_4, $\delta = 0.00$). Low-resolution mass spectra were obtained with a Finnigan MAT TSQ-70 triple-stage quadrupole mass spectrometer operating in the chemical ionization mode with CH_4 as the ionizing gas. High-resolution mass spectra were obtained using a VG Analytical ZAB2-E mass spectrometer operating in the chemical ionization mode with isobutane as the ionizing gas. Melting points were obtained in capillaries sealed under argon (1 atm) and are uncorrected. Satisfactory elemental analyses were obtained for all compounds from Atlantic Microlab, Norcross, GA. Molecular weight determinations were made using the method described by Burger and Bercaw[31] with azobenzene as the standard and benzene as the solvent.

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Preparation of Compounds 3−7. Similar procedures were used for the preparation of all five compounds. A representative example for [(vinyl)$_2$InP-*t*-Bu$_2$]$_2$ (**4**) is given below; characterization data for each compound are also presented.

Preparation of [(vinyl)$_2$InP-*t*-Bu$_2$]$_2$ (4). Indium trichloride (1.42 g, 6.42 mmol) was placed in a 250-mL Schlenk flask and suspended in 25 mL of cold (−78 °C) diethyl ether. The flask was placed in a bath of dry ice/2-propanol, and 11.3 mL of a 1.14 M vinyllithium solution (12.9 mmol) was added dropwise over a period of 1.5 h to the InCl$_3$ solution. The reaction mixture was allowed to stir for an additional 30 min, and then a −78 °C solution of 6.43 mmol of *t*-Bu$_2$PLi in 14 mL of THF was added slowly over 1 h. The stirred reaction mixture was allowed to warm slowly to room temperature overnight. The resulting tan solution containing a white precipitate was pumped down and extracted with toluene (3 × 25 mL), and the extract was filtered through a glass frit covered with diatomaceous earth. The solvent was removed under vacuum, giving crude **4** as a pale yellow gummy solid. This solid was redissolved in warm (45 °C) toluene, and the solution was cooled slowly to −20 °C overnight to give **4** as analytically pure colorless crystals in two batches (0.634 g, 31% yield). Mp: 227−9 °C dec. ^{1}H NMR (C$_6$D$_6$): δ 1.35 (t, 36 H, $J_{\rm P-H}$ = 7.1 Hz, *t*-Bu), 6.08 (dd, 4 H, J_{trans} = 21.0 Hz, J_{gem} = 4.0 Hz, vinylic *cis* to In), 6.51 (dq, 4 H, J_{cis} = 14.2 Hz, J_{gem} = 4.0 Hz, vinylic *trans* to In), 7.07 (dd, 4 H, J_{trans} = 21.0 Hz, J_{cis} = 14.2 Hz, vinylic *gem* to In). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 32.97 (t, $J_{\rm P-C}$ = 2.3 Hz, C(*C*H$_3$)$_3$), 36.00 (t, $J_{\rm P-C}$ = 3.6 Hz, *C*(CH$_3$)$_3$), 134.00 (t, $^3J_{\rm P-C}$ = 2.3 Hz, CH═*C*H$_2$), 153.44 (br, *C*H═CH$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ +44.97. MS (CI$^-$): *m/z* 628 (M, 100.0), 571 (M − *t*-Bu, 25.6), 483 (M − *t*-Bu$_2$P, 7.7), 341 ($^1/_2$M + Vi, 3.2), 314 ($^1/_2$M, 0.8). MS (CI$^+$): *m/z* 629 (M + H, 3.8), 601 (M − Vi, 100.0), 483 (M − *t*-Bu$_2$P, 12.7), 432 (M − Vi$_3$In, 8.0), 287 ($^1/_2$M − Vi, 0.8). 147 (*t*-Bu$_2$PH + H, 10.5), 169 (Vi$_2$In, 0.4). HRMS (CI$^-$), *m/z*: calculated for C$_{24}$H$_{48}$In$_2$P$_2$ (M$^-$), 628.130 879; found, 628.130 004. Anal. Calcd for C$_{24}$H$_{48}$In$_2$P$_2$: C, 45.88; H, 7.70. Found: C, 45.72; H, 7.66.

Characterization of [(vinyl)$_2$GaP-*t*-Bu$_2$]$_2$ (3). Mp: 175−8 °C dec. ^{1}H NMR (C$_6$D$_6$): δ 1.38 (t, 36 H, $J_{\rm P-H}$ = 6.8 Hz, *t*-Bu), 6.04 (dd, 4 H, J_{trans} = 21 Hz, J_{gem} = 4.2 Hz, vinylic *cis* to Ga), 6.38 (dd, 4 H, J_{cis} = 12 Hz, J_{gem} = 4.2 Hz, vinylic *trans* to Ga), 7.00 (dd, 4 H, J_{trans} = 21 Hz, J_{cis} = 12 Hz, vinylic *gem* to Ga). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 32.65 (t, $J_{\rm P-C}$ = 2 Hz, C(*C*H$_3$)$_3$), 36.36 (t, $J_{\rm P-C}$ = 6 Hz, *C*(CH$_3$)$_3$), 132.28 (t, $^3J_{\rm P-C}$ = 3 Hz, CH═*C*H$_2$), 149.34 (br, *C*H═CH$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 31.43. MS (CI$^+$): *m/z* 537* (M + H, 0.4), 509* (M − Vi, 1.7), 391* (M − *t*-Bu$_2$P, 0.7), 269* ($^1/_2$M + H, 0.5), 241* ($^1/_2$M − Vi, 0.9), 147 (*t*-Bu$_2$PH + H, 100), 145 (*t*-Bu$_2$P, 13.2), 131 (*t*-Bu$_2$P − Me, 5.2), 123* (Vi$_2$Ga, 0.6) (* indicates presence of appropriate Ga$_x$ isotope pattern). HRMS (CI$^+$), *m/z*: calculated for C$_{24}$H$_{48}$Ga$_2$P$_2$ (M$^+$), 536.174 291; found, 536.174 030. Anal. Calcd for C$_{24}$H$_{48}$Ga$_2$P$_2$: C, 53.58; H, 8.99. Found: C, 53.20; H, 9.05.

Characterization of [(allyl)$_2$InP-*t*-Bu$_2$]$_2$ (5). Mp: 160−73 °C dec. ^{1}H NMR (C$_6$D$_6$): δ 1.24 (t, 36 H, $J_{\rm P-H}$ = 7.2 Hz, *t*-Bu), 2.14 (d, 8 H, J = 8.7 Hz, InCH$_2$), 4.88 (dd, 4 H, J_{cis} = 9.9 Hz, J_{gem} = 2.1 Hz, CH═C(*H*)H), 5.07 (dd, 4 H, J_{trans} = 17.7 Hz, J_{gem} = 1.8 Hz, CH═C(H)*H*), 6.42 (m, 4 H, C*H*═CH$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 26.04 (br, InCH$_2$), 33.22 (t, $J_{\rm P-C}$ = 2.1 Hz, C(*C*H$_3$)$_3$), 35.79 (t, $J_{\rm P-C}$ = 2.6 Hz, *C*(CH$_3$)$_3$), 107.52 (CH═*C*H$_2$), 140.74 (*C*H═CH$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 53.81. MS (CI$^+$, isobutane): *m/z* 685 (M + H, 3.0), 643 (M − allyl, 100), 561 (M − 3allyl, 12.2), 539 (M − *t*-Bu$_2$P, 2.5), 301 ($^1/_2$M − allyl, 5.2). 187 (*t*-Bu$_2$P(allyl) + H, 18.9), 147 (*t*-Bu$_2$PH + H, 52.3), 145 (*t*-Bu$_2$P, 7.3), 130 (*t*-Bu$_2$P − Me, 11.3). MS (CI$^-$, CH$_4$): *m/z* 725 (M + allyl, 1.2), 684 (M, 2.0), 643 (M − allyl, 34.2), 627 (M − *t*-Bu, 3.6), 487 (M − (allyl)$_2$In, 32.6), 383 ($^1/_2$M + allyl, 100), 342 ($^1/_2$M, 3.6), 301 ($^1/_2$M − allyl, 5.9). HRMS (CI$^+$), *m/z:* calculated for C$_{28}$H$_{56}$In$_2$P$_2$ (M$^+$); 684.193 479; found 684.193 291. Anal. Calcd for C$_{28}$H$_{56}$In$_2$P$_2$: C, 49.14; H, 8.25. Found: C, 48.88; H, 8.15.

Characterization of [(allyl)$_2$GaAs-*t*-Bu$_2$]$_2$ (6). Mp: 157−65 °C. ^{1}H NMR (C$_6$D$_6$): δ 1.34 (s, 36 H, *t*-Bu), 2.14 (dt, 8 H, ^3J = 8.4, ^4J = 1.1 Hz, GaCH$_2$), 4.98 (ddt, 4 H, J_{cis} = 10.0 Hz, J_{gem} = 2.3 Hz, ^4J = 1.1 Hz, CH═C(*H*)H), 5.13 (ddt, 4 H, J_{trans} = 16.8 Hz, J_{gem} = 2.3 Hz, ^4J = 1.1 Hz, CH═C(H)*H*), 6.31 (m, 4 H, C*H*═CH$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 24.33 (GaCH$_2$), 33.06 (C(*C*H$_3$)$_3$), 40.50 (*C*(CH$_3$)$_3$), 110.23 (CH═*C*H$_2$), 139.28 (*C*H═CH$_2$). MS (CI$^+$): *m/z* 680* (M, 11.4), 639* (M − allyl, 100), 491* (M − *t*-Bu$_2$As, 10.8), 381* ($^1/_2$M + allyl, 7.4), 341* ($^1/_2$M + H, 4.8), 299* ($^1/_2$M − allyl, 16.1), 231 (*t*-Bu$_2$As(allyl) + H, 20.7), 191 (*t*-Bu$_2$AsH + H, 13.7), 189 (*t*-Bu$_2$As, 8.9) (* indicates presence of appropriate Ga$_x$ isotope pattern). Anal. Calcd for C$_{28}$H$_{56}$Ga$_2$As$_2$: C, 49.31; H, 8.28. Found: C, 48.77; H, 8.10.

Characterization of [(benzyl)$_2$InP-*t*-Bu$_2$]$_2$ (7). Mp 225−8 °C dec. ^{1}H NMR (C$_6$D$_6$): δ 1.12 (t, 36 H, $J_{\rm P-H}$ = 7.1 Hz, *t*-Bu), 2.62 (s, 8 H, InCH$_2$), 6.8−7.5 (br m, 20H, aromatic). ^{13}C{^{1}H} APT NMR (C$_6$D$_6$): δ 28.18 (InCH$_2$), 33.07 (C(*C*H$_3$)$_3$), 35.79 (*C*(CH$_3$)$_3$), 122.89 (*para* ring CH), 128.17 (ring CH), 128.66 (ring CH), 146.48 (*ipso* ring C). ^{13}C{^{1}H} NMR (THF-*d*$_8$): δ 28.28 (br, InCH$_2$), 33.50 (C(*C*H$_3$)$_3$), 36.50 (t, $J_{\rm P-C}$ = 2.1 Hz, *C*(CH$_3$)$_3$), 123.02 (*para* ring CH), 128.53 (ring CH), 128.85 (ring CH), 147.02 (*ipso* ring C). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 60.84. MS (CI$^-$): *m/z* 975 (M + benzyl, 23.1), 884 (M, 2.1), 827 (M − *t*-Bu, 63.2), 793 (M − benzyl, 55.1), 739 (M − *t*-Bu$_2$P, 100), 587 (M − (benzyl)$_2$In, 12.9), 533 ($^1/_2$M + benzyl, 14.6), 442 ($^1/_2$M, 3.5), 297 ((benzyl)$_2$In, 1.0). HRMS (CI$^-$), *m/z*: calculated for C$_{22}$H$_{32}$InP ($^1/_2$M$^-$), 442.128 040; found, 442.127 759. Anal. Calcd for C$_{44}$H$_{64}$In$_2$P$_2$: C, 59.74; H, 7.29. Found: C, 59.55; H, 7.17.

Preparation of [(benzyl)$_2$GaAs-*t*-Bu$_2$]$_n$ (8). Gallium trichloride (1.03 g, 5.8 mmol) was placed in a 250-mL Schlenk flask and dissolved in 25 mL of cold (−78 °C) diethyl ether. The flask was placed in a bath of dry ice/2-propanol, and 27.9 mL of a 0.42 M benzyllithium solution (11.7 mmol) was added dropwise over a period of 1 h to the GaCl$_3$ solution. The reaction mixture was allowed to stir for an additional 1 h, and then a −78 °C solution of 5.8 mmol of *t*-Bu$_2$AsLi in 14 mL of THF was added slowly over a 1 h period. The stirred reaction mixture was allowed to warm slowly to room temperature overnight. The resulting orange solution containing a white precipitate was pumped down and extracted with toluene (3 × 35 mL), and the extract was filtered through a glass frit covered with diatomaceous earth. The clear orange solution was pumped down to give a viscous dark orange liquid that was identified as the monomer [(benzyl)$_2$GaAs-*t*-Bu$_2$]. ^{1}H NMR (C$_6$D$_6$): δ 1.44 (s, 18 H, *t*-Bu), 2.72 (s, 4 H, GaCH$_2$), 6.94 (t, J = 7.2 Hz, 2 H, *para*), 7.20 (t, J = 6.9 Hz, 4 H, *meta*), 7.43 (d, J = 6.9 Hz, 4 H, *ortho*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 26.10 (GaCH$_2$), 33.11 (C(*C*H$_3$)$_3$), 38.18 (*C*(CH$_3$)$_3$), 126.16 (*para* ring CH), 128.73 (ring CH), 128.99 (ring CH), 141.86 (*ipso* ring C). Molecular weight determination (C$_6$D$_6$): found, 460(30); calcd, 441.14.

Upon standing, the orange liquid crystallized to give yellow parallelepipeds which were identified as the dimer [(benzyl)$_2$GaAs-*t*-Bu$_2$]$_2$. Mp: 153−8 °C. ^{1}H NMR (C$_6$D$_6$): δ 1.26 (s, 36 H, *t*-Bu), 2.71 (s, 8 H, GaCH$_2$), 6.96 (t, J = 7.4 Hz, 4 H, *para*), 7.14 (t, J = 7.7 Hz, 8 H, *meta*), 7.26 (d, J = 8.0 Hz, 4 H, *ortho*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 26.48 (GaCH$_2$), 32.96 (C(*C*H$_3$)$_3$), 40.73 (*C*(CH$_3$)$_3$), 123.82 (*para* ring CH), 128.50 (ring CH), 129.35 (ring CH), 144.79 (*ipso* ring C). MS (CI$^+$): *m/z* 691* (M − *t*-Bu$_2$As, 7.0.), 531* ($^1/_2$M + benzyl, 21.7), 441* ($^1/_2$M + H, 56.5), 281 (*t*-Bu$_2$As(benzyl) + H. 10.3), 251* ((benzyl)$_2$Ga, 4.0), 191 (*t*-Bu$_2$AsH + H, 100), 189 (*t*-Bu$_2$As, 12.0). HRMS (CI$^+$), *m/z*: calculated for C$_{22}$H$_{33}$GaAs ($^1/_2$M + H), 441.105 403; found, 441.103 959. Anal. Calcd for C$_{44}$H$_{64}$Ga$_2$As$_2$: C, 59.90; H, 7.31. Found: C, 59.70; H, 7.13.

Preparation of [(vinyl)(Cl)GaAs-*t*-Bu$_2$]$_2$ (9). Gallium trichloride (1.02 g, 5.78 mmol) was placed in a 250-mL flask and dissolved in 25 mL of cold (−78 °C) diethyl ether. The flask was placed in a bath of dry ice/2-propanol, and 5.1 mL of a 1.14 M vinyllithium solution (5.8 mmol) was added dropwise over a period of 45 min to the GaCl$_3$ solution. The reaction mixture was allowed to stir for an additional 40 min, and then a 0 °C solution of 5.78 mmol of *t*-Bu$_2$AsLi in 10 mL of THF was added slowly over a 2 h period. The stirred reaction mixture was allowed to warm slowly to room temperature overnight. The resulting pale yellow solution containing a white precipitate was pumped down and extracted with toluene (3 × 15 mL), and the extract was filtered through a glass frit covered with diatomaceous earth. The solvent was removed under vacuum, giving crude **9** as a pale yellow powder. This solid was recrystallized from toluene to give **9** as analytically pure colorless crystals in three batches (0.466 g, 25% yield). Mp: 192−6 °C dec. ^{1}H NMR (C$_6$D$_6$): δ 1.46 (s, 36 H, *t*-Bu), 6.30 (dd, 2 H, J_{cis} = 13.5 Hz, J_{gem} = 3.5 Hz, vinylic *trans* to Ga), 6.46 (dd, 2 H, J_{trans} = 20.1 Hz, J_{gem} = 3.6 Hz, vinylic *cis* to Ga), 6.76 (dd, 2 H, J_{trans} = 20.1 Hz, J_{cis} = 13.6 Hz, vinylic *gem* to Ga). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 32.43 (C(*C*H$_3$)$_3$), 44.93 (*C*(CH$_3$)$_3$), 134.11 (CH═*C*H$_2$), 144.53 (*C*H═CH$_2$). MS (CI$^+$): *m/z* 641* (M + H, 2.0), 613* (M − Vi, 38.6),

Table 2. Crystal Data for [(vinyl)$_2$GaP(t-Bu)$_2$]$_2$ (**3**), [(vinyl)$_2$InP(t-Bu)$_2$]$_2$ (**4**), [(allyl)$_2$InP(t-Bu)$_2$]$_2$ (**5**), and [(allyl)$_2$GaAs(t-Bu)$_2$]$_2$ (**6**)

	3	**4**	**5**	**6**
emp formula	$C_{24}H_{48}Ga_2P_2$	$C_{24}H_{48}In_2P_2$	$C_{28}H_{56}In_2P_2$	$C_{28}H_{56}Ga_2As_2$
fw	538.00	628.20	684.31	682.01
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$I2/m$	$I2/m$	$P2_1/n$	$P2_1/n$
a, Å	8.771(1)	8.933(1)	11.4704(7)	11.482(2)
b, Å	11.484(1)	11.666(1)	11.2284(9)	11.120(2)
c, Å	14.321(3)	14.570(1)	13.2773(8)	13.122(3)
β, deg	90.27(2)	90.25(1)	98.234(7)	97.21(3)
V, Å^3	1442.5(4)	1518.4(2)	1692.4(2)	1662.2(6)
Z	2	2	2	2
d(calc), g cm^{-3}	1.239	1.374	1.343	1.363
μ, cm^{-1}	19.86	16.31	14.70	36.09
cryst size, mm^3	0.5 × 0.4 x 0.1	0.7 × 0.4 × 0.3	0.4 × 0.4 × 0.2	0.6 × 0.6 × 0.3
no. of tot. reflns	1140	1362	3815	3825
no. of ind reflns	896	1231	2954	2919
R(int)	0.0399	0.0233	0.0183	0.0561
abs cor	SHELXA	XABS	semi-empirical	none
max/min tansm	0.862 79/0.335 39	n/a	0.8900/0.7103	n/a
param/restr	79/0	79/0	174/12	174/12
R1/wR2	0.0686/0.1654	0.0236/0.0638	0.0293/0.0714	0.0581/0.1533
refined on	F^2	F^2	F^2	F^2
ext coeff, χ^a	0.0051(11)	0.0019(4)	n/a	n/a

[a] $F^* = F[1 + 0.001\chi F^2\lambda^3/(\sin 2\theta)]^{-1/4}$.

Table 3. Crystal Data for [(benzyl)$_2$InP(t-Bu)$_2$]$_2$ (**7**), [(benzyl)$_2$GaAs(t-Bu)$_2$]$_2$ (**8**), [(vinyl)ClGaAs(t-Bu)$_2$]$_2$ (**9**), and [(vinyl)$_2$GaAs(t-Bu)$_2$]$_2$ (**10**)

	7	**8**	**9**	**10**
emp formula	$C_{44}H_{64}In_2P_2$	$C_{44}H_{64}Ga_2As_2$	$C_{20}H_{42}Cl_2Ga_2As_2$	$C_{24}H_{48}Ga_2As_2$
fw	884.53	882.23	642.7	625.9
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$I2/m$
a, Å	10.431(2)	10.862(1)	9.447(2)	8.838(1)
b, Å	17.070(1)	15.691(3)	28.030(8)	11.625(2)
c, Å	12.686(1)	13.393(3)	16.417(4)	14.425(4)
β, deg.	108.19(1)	110.02(1)	105.07(1)	90.68(2)
V, Å^3	2146.0(5)	2144.7(7)	4198(2)	1481.8(7)
Z	2	2	6	2
d(calc), g cm^{-3}	1.369	1.366	1.525	1.403
μ, cm^{-1}	11.77	28.15	44.67	40.42
cryst size, mm^3	0.3 × 0.3 × 0.1	0.6 × 0.6 × 0.2	0.5 × 0. 5 × 0.5	0.2 × 0.2 × 0.4
no. of tot reflns	3987	4751	6764	1825
no. of ind reflns	3768	3763	5221	1372
R(int)	0.0364	0.0372	0.0140	0.0219
abs cor	none	semiempirical	semiempirical	none
max/min transm	n/a	0.999/0.440	0.8340/0.7080	n/a
no. of params	226	226	356	73
R/R_W			0.0533/0.0601	0.0381/0.0452
R1/wR2	0.0518/0.1037	0.0641/0.1274		
refined on	F^2	F^2	F	F

605* (M − Cl, 100), 583* (M − t-Bu, 5.3), 451* (M − t-Bu$_2$As, 7.2), 321* ($^1/_2$M + H, 0.5), 293* ($^1/_2$M − Vi, 3.8), 285* ($^1/_2$M − Cl, 6.2), 191 (t-Bu$_2$AsH + H, 12.5), 189 (t-Bu$_2$As, 7.6), 175 (t-Bu$_2$As − Me, 5.6) (* indicates presence of appropriate Ga$_x$Cl$_y$ isotope pattern). HRMS (CI$^+$), m/z: calculated for $C_{20}H_{43}Ga_2As_2$ (M + H), 640.967 036; found, 640.968 535. Anal. Calcd for $C_{20}H_{42}Cl_2Ga_2As_2$: C, 37.37; H, 6.59; Cl, 11.03. Found: C, 37.08; H, 6.60; Cl, 11.45.

Preparation of [(vinyl)$_2$GaAs-t-Bu$_2$]$_2$ (10). Vinyllithium (0.4 mL, 1.14 M, 0.5 mmol) was added by syringe to a cold (−78 °C) solution of **9** (0.116 g, 0.36 mmol) dissolved in 15 mL of diethyl ether. The stirred reaction mixture was allowed to warm slowly to room temperature overnight. The resulting colorless solution containing a white precipitate was pumped down and extracted with toluene (3 × 8 mL), and the extract was filtered through a glass frit covered with diatomaceous earth. After the volume was reduced under vacuum, the resulting solution was cooled to −20 °C overnight. Colorless crystals of **10** were obtained. Mp: 207−12 °C dec. ^{1}H NMR (C_6D_6): δ 1.43 (s, 36 H, t-Bu), 6.07 (dd, 4 H, J_{trans} = 20.7 Hz, J_{gem} = 4.1 Hz, vinylic *cis* to Ga), 6.38 (dd, 4 H, J_{cis} = 14.3 Hz, J_{gem} = 4.1 Hz, vinylic *trans* to Ga), 7.04 (dd, 4 H, J_{trans} = 20.7 Hz, J_{cis} = 14.4 Hz, vinylic *gem* to Ga). MS (CI$^+$): m/z 625* (M + H, 24.5), 597* (M − Vi, 73.3), 435* (M − t-Bu$_2$As, 56.1), 312* ($^1/_2$M + H, 8.4), 285* ($^1/_2$M − Vi, 12.3), 191 (t-Bu$_2$AsH + H, 100.), 189 (t-Bu$_2$As, 63.6), 175 (t-Bu$_2$As − Me, 14.9) 123* (Vi$_2$Ga, 54.8). MS (CI$^-$): m/z 624* (M, 1.0), 567* (M − t-Bu, 100) (* indicates presence of appropriate Ga$_x$ isotope pattern). HRMS (CI$^+$), m/z: calculated for $C_{24}H_{49}{}^{69}Ga^{71}GaAs_2$ (M + H), 627.076 899; found, 627.075 113. Anal. Calcd for $C_{24}H_{48}Ga_2As_2$: C, 46.05; H, 7.73. Found: C, 45.62; H, 7.56.

X-ray Crystallography. X-ray-quality crystals of all compounds except **8** and **9** were grown from toluene solutions stored at −20 °C. Crystals of **8** were obtained from the slow solidification of the monomeric oil. Crystals of **9** were grown by slow evaporation of a benzene solution in an NMR tube with a needle-pierced septum. Suitable crystals of all compounds were mounted inside thin-walled glass capillaries and sealed under argon (1 atm). Data for **3**−**5** and **9** were collected on a Siemens R2m/V diffractometer, while data for **6**−**8** and **10** were collected on an Enraf-Nonius CAD4 diffractometer. In all cases, the data were collected at room temperature in the 2θ−θ scan mode utilizing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods and refined using full-matrix least-squares calculations on F^2 (all except **9** and **10**) by the Siemens SHELXTL PLUS 5.0 (PC) software package[32] or on F

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(32) Sheldrick, G. M. *SHELXTL PC Version 5.0*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.

(**9** and **10**) using the SHELXTL PLUS 4.2 (PC) software package.[33] All non-hydrogen atoms were refined with anisotropic thermal parameters in the later stages of refinement. All hydrogen atoms except those of the methyl groups in the structures refined on F^2 were placed in idealized positions and refined using the riding model with general isotropic temperature factors. The methyl hydrogens in **3**−**8** were placed by using a difference electron density synthesis to set the initial torsion angle and then refined as a riding−rotating model with general isotropic temperature factors. In each of the allyl-containing compounds, **5** and **6**, one of the allyl groups is disordered, and atoms C(5) and C(6) were refined with restrained anisotropic displacement parameters over two sites with occupation factors of 0.65(3)/0.35(3) and 0.71(4)/0.29(4), respectively. Details of the crystal data and summaries of intensity data collection parameters are given in Tables 2 and 3.

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Supporting Information Available: Listings of structure refinement details, bond distances, bond angles, atomic coordinates, and thermal parameters (45 pages). Ordering information is given on any current masthead page.

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(33) Sheldrick, G. M. *SHELXTL PC Version 4.2*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.