Organometallics **1996,** *15,* 5179−5184

Synthesis and Characterization of Monomeric Amide, Phosphide, and Thiolate Complexes of Gallium and Indium

Wing-Por Leung,* Candy M. Y. Chan, Bo-Mu Wu, and Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong,
Shatin, New Territories, Hong Kong

Received June 14, 1996⊗

Monomeric gallium and indium compounds $ArGaN(SiMe_3)_2Cl$ (**1**), $ArIn\{N(SiMe_3)_2\}_2$ (**2**), $ArGa\{P(H)Ar\}_2$ (**3**), $ArIn\{P(H)Ar\}_2$(**4**), and $ArGa(SAr)_2$ (**5**) [Ar = 2,4,6-$Bu^t{}_3C_6H_2$] have been synthesized by the reaction of $ArMCl_2$ (M = Ga and In) with corresponding lithium amide, phosphide, or thiolate compounds and characterized by elemental analysis and NMR and mass spectroscopy. For compounds **1**−**3**, the single-crystal X-ray structures have been determined. The metal center adopts a trigonal planar geometry with metal to group 15 atoms at distances of 1.867(10) Å (Ga−N), 2.099(av) Å (In−N), and 2.388(av) Å (Ga−P), respectively . The energy barrier of the dynamic processes involved in these compounds as estimated by variable-temperature NMR lies in the range 14.2−17.8 kcal mol^{-1}.

Introduction

Organometallic compounds featuring σ-bonding between group 13 (M) and 15 (E) elements have attracted the attention of material scientists for their uses as single-source precursors for the production of electronic materials such as InP, GaAs, and GaN. Compounds with substituents which are capable of facile thermal elimination during the fabrication process to produce solids containing ME components have been reported to be more favorable for use as potential precursors. The synthesis of this type of compounds can be achieved by alkane elimination, salt elimination, and dehalosilylation.[1] For example, compounds of the type $[Me_2MER_2]_n$ (M = Ga, In; E = P, As; R = Me, Et, Ph), have been prepared *via* the alkane elimination method. The degree of aggregation of these compounds is primarily dependent on ring size, conformation, and valence angle strain, as well as substituent steric requirements. The dimeric form would be more favorable for compounds of small metal and donor atoms. The valence angle strain in dimers is crucial, but this is tolerated more readily by heavier elements than those of the first period.[2] Thus, for example, $[Me_2MEPh_2]_2$ (M = Ga, In; E = P, As) are dimeric while $[Me_2MER_2]_n$ (R = Me, Et) are polymeric in the condensed phase but trimeric in solution. Dimeric compounds $[Me_2InNEt_2]_2$ and $[Me_2GaPBu^t{}_2]_2$ have been prepared by reacting $RnMCl_{3-n}$ (M = Ga, In; n = 0, 1, 2) with appropriate equivalents of lithium reagents R_2ELi (E = N, P, As).[3−5]

The use of dehalosilylation (with elimination of $SiMe_3Cl$) in the preparation of some compounds containing a gallium−arsenic bond has been reported.[6] This type of reaction has been used in the synthesis of $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$.

In spite of the extensive work on the organometallic chemistry of these group 13 metal compounds, monomeric three-coordinate indium amides and phosphides are scarcely found. So far, the only examples that have been reported are $Bu^t{}_2InN(Dipp)SiPh_3$, $In\{N(SiMe_3)_2\}_3$, and $In(PBut_2)_3$.[7,8]

For group 13 metal thiolate compounds, very few examples are known due to the formation of polymers which causes difficulties in structural characterization. Nevertheless, this problem has been overcome by using large substituents on chalcogens. For example, the monomeric gallium compounds $Ga(SEAr)_3$ (E = S, Se) have been structurally characterized.[9,10]

In this paper, we report the synthesis and structural characterization of compounds containing covalent bonds between some group 13 and 15 elements. A highly sterically hindered substituent, the tri-*tert*-butylphenyl (Ar) group, is employed in the anticipation of synthesizing monomeric compounds. $ArGaCl_2$ and $ArInCl_2$ have been used as starting compounds to react with appropriate reagents of $LiER_2$ [ER_2 = $N(SiMe_3)_2$, P(H)Ar, or SAr].

In addition, we have carried out variable-temperature NMR spectroscopy experiments to estimate the energy barrier of the dynamic process involving the MER_2 moiety.

Results and Discussion

Synthesis of Gallium(III) and Indium(III) Amides. Group 13 metal amides $ArGaN(SiMe_3)_2Cl$ (**1**) and ArIn-

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⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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$\{N(SiMe_3)_2\}_2$ (**2**) were prepared by the reaction of $ArMCl_2$ with $LiN(SiMe_3)_2(Et_2O)$ (eq 1). It was found

$$ArMCl_2 + LiN(SiMe_3)_2(Et_2O) \longrightarrow ArMN(SiMe_3)_nCl_{2-n} \tag{1}$$

$$\begin{array}{l}\text{M = Ga; n = 1, } (\mathbf{1})\\ \text{M = In; n = 2, } (\mathbf{2})\end{array}$$

that compound **1** was the dominant product in the reaction with $ArGaCl_2$, even when 2 equiv of $LiN(SiMe_3)_2(Et_2O)$ was used. In contrast, in the reaction of $LiN(SiMe_3)_2(Et_2O)$ with $ArInCl_2$, compound **2** was the exclusive product. This is probably due to the difference in size between Ga and In (covalent radii of Ga = 1.25 Å, In = 1.40 Å), such that substitution of two bulky $N(SiMe_3)_2$ groups is not sterically favorable for gallium . For the larger size of In, stabilization by two $N(SiMe_3)_2$ group is the more favorable. Both compounds have been characterized by elemental analyses, mass spectra, NMR spectra, and X-ray structure analysis.

Synthesis of Gallium(III) and Indium(III) Phosphides. Treatment of $ArMCl_2$ with 1 or 2 equiv of lithium organophosphide LiP(H)Ar afforded bis(phosphido) complexes $ArGa\{P(H)Ar\}_2$ (**3**) and $ArIn\{P(H)Ar\}_2$ (**4**) (eq 2). The mono(phosphido) compounds have not

$$ArMCl_2 + LiPAr(H) \longrightarrow ArM\{PAr(H)\}_2 \tag{2}$$

$$\begin{array}{l}\text{M = Ga } (\mathbf{3})\\ \text{M = In } (\mathbf{4})\end{array}$$

been isolated. Compounds **3** and **4** have been characterized by elemental analyses, mass spectra, and NMR spectra, and for the former a single-crystal X-ray structure has been determined. The readily loss of solvent from the crystals of **4** has rendered the structure determination by X-ray crystallography. The phosphido ligand ArPH is probably less sterically demanding than the amido ligand $N(SiMe_3)_2$, as two phosphido ligands can be incorporated into the coordination sphere of the metals.

Synthesis of Gallium(III) Thiolate. Treatment of 2 equiv of LiSAr to $ArGaCl_2$ afforded the dithiolate compound $ArGa(SAr)_2$ (**5**) (eq 3). Compound **5** has been

$$ArGaCl_2 + LiSAr \longrightarrow ArGa(SAr)_2\ (\mathbf{5}) \tag{3}$$

characterized by elemental analysis and NMR and mass spectroscopy. The related compounds $Ga(SAr)_3$ and $BuGa(SAr)_2$, reported by Power and co-workers, were found to be a three-coordinate monomeric gallium thiolate compounds.[9] Therefore, it is not unreasonable to predict that the structure of compound **5** is also monomeric.

NMR Spectra. The ^{1}H NMR spectrum of compound **1** at 298 K displayed two singlet signals due to two different groups of $SiMe_3$ protons. The different environments of the $SiMe_3$ groups is caused by a restricted rotation about the Ga−N bond with respect to the NMR time scale. The coalescence of the $SiMe_3$ peaks was not observed in the ^{1}H NMR spectrum at temperature up to 368 K. Only broadening of the peaks was shown in the spectrum.

The variable-temperature ^{1}H NMR spectra for compound **2** is shown in Figure 1. A broad singlet peak was observed for the two $SiMe_3$ protons in the ^{1}H NMR spectrum recorded at 298 K. This is obviously due to a relatively faster rotation of the $N(SiMe_3)_2$ groups as compared to compound **1**. The spectrum at 246 K displayed two well-resolved singlets due to different $SiMe_3$ group resonances as a result of restricted rotation along the In−N bond. Increasing the temperature resulted in broadening and eventual coalescence of the peaks at 286 K. The energy barrier ($\Delta G^{\ddagger}$) calculated for the dynamic process using Eyring equation[11] is 13.3 kcal mol^{-1}.

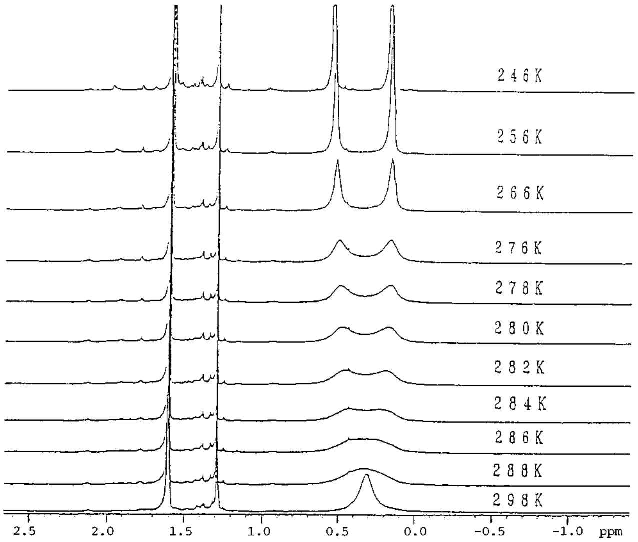

Figure 1. Variable-temperature NMR spectra for compound **2** in the region of δ −1.0 to 2.5 ppm.

The ^{1}H NMR spectra of compounds **3** and **4** at 308 K displayed broad signals due to the *ortho*-*tert*-butyl group and the *meta*-aromatic protons of the Ar group in [ArPH]. Similar broadening of peaks was also observed for the thiolate compound **5**.

The ^{1}H NMR spectra of compounds **3** and **4** at 283 K showed two well-resolved peaks due to the *ortho*-Bu^t groups and also for the aromatic protons of the ArPH groups. Coalescence temperatures of 303 and 295 K were observed respectively for **3** and **4**, and the same energy barriers of 14.2 kcal mol^{-1} were estimated for both compounds. The similar values obtained suggest that same dynamic process is operative, regardless of the nature of the metal center.

The variable-temperature ^{1}H NMR spectra of compound **5** was also recorded. The coalescence temperature of the *ortho*-Bu^t groups and also the aromatic protons resonances of the SAr group occurred around 299 K, and the energy barrier was estimated to be 13.6 kcal mol^{-1}. The similarity of the magnitude of energy barrier as in **3** and **4** suggests that a similar process may occur in **5**.

The ^{31}P and ^{31}P{^{1}H} NMR spectra were also obtained for compounds **3** and **4**. The data were compared with those of some related compounds in Table 1. In the ^{31}P{^{1}H} NMR spectra, singlet signals were observed for both compounds while, in the ^{1}H-coupled ^{31}P NMR spectra, the signals split into doublets in accordance with the monomeric structure of the phosphido complexes where the phosphorus atom is coupled to one proton only to give the expected doublet.

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Table 1. ^{31}P NMR Data for 3 and 4 and Related Compounds[a]

compds	δ (ppm)	$^1J_{P-H}$ (Hz)	ref
ArGa{P(H)Ar}$_2$ (**3**)	−95.7	221.6	this work
ArIn{P(H)Ar}$_2$ (**4**)	−114.3	207.5	this work
Ga{P(H)Ar}$_3$	−91.6	215.6	4
Bu^{t}Ga{P(H)Ar}$_2$	−113.1	203.0	17
ArPH$_2$	−134.3	208.5	24

[a] Chemical shifts measured are referenced externally to 85% H_3PO_4 (δ 0.00 ppm).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 1−3

Compound **1** [ArGaN(SiMe$_3$)$_2$Cl]

Ga(1)−Cl(1)	2.228(4)	Ga(1)···H(9A)	2.335
Ga(1)−C(6)	1.953(12)	Ga(1)···H(16B)	2.297
Ga(1)−N(1)	1.867(10)	N(1)−Si(1)	1.751(10)
N(1)−Si(2)	1.751(12)		
Cl(1)−Ga(1)−N(1)	115.1(3)	Ga(1)−N(1)−Si(2)	117.6(5)
N(1)−Ga(1)−C(6)	133.4(4)	Si(1)−N(1)−Si(2)	120.9(6)
Cl(1)−Ga(1)−C(6)	111.5(3)	Ga(1)−N(1)−Si(1)	121.5(6)

dihedral angle: Ga(1)−N(1) 3.1

Compound **2** [ArIn{N(SiMe$_3$)$_2$}$_2$]

In(1)−N(1)	2.103(6)	N(1)−Si(1)	1.739(5)
In(1)−N(2)	2.094(4)	N(1)−Si(2)	1.726(5)
In(1)−C(6)	2.188(6)	N(2)−Si(3)	1.731(5)
In(1)···H(8B)	2.310	N(2)−Si(4)	1.738(5)
In(1)···H(18B)	2.427		
N(1)−In(1)−N(2)	119.4(2)	In(1)−N(1) −Si(1)	119.4(2)
N(1)−In(1)−C(6)	118.3(2)	In(1)−N(1)−Si(2)	119.0(3)
N(2)−In(1)−C(6)	122.2(2)	Si(1)−N(1)−Si(2)	121.5(3)
In(1)−N(2)−Si(3)	119.8(3)	Si(3)−N(2)−Si(4)	119.9(2)
In(1)−N(2)−Si(4)	120.3(2)		

dihedral angles: In(1)−N(1) 47.2; In(1)−N(2) 44.4

Compound **3** [ArGa{P(H)Ar}$_2$]

Ga(1)−P(1)	2.384(2)	P(1)−C(6)	1.862(5)
Ga(1)−P(2)	2.392(2)	P(1)−H(1p)	1.129
Ga(1)−C(42)	1.996(6)	P(2)−C(24)	1.856(5)
Ga(1)···(44C)	2.372	P(2)−H(2p)	1.106
Ga(1)···H(54A)	2.374		
P(1)−Ga(1)−P(2)	111.2(1)	Ga(1)−P(1) −C(6)	106.7(2)
P(1)−Ga(1)−C(42)	125.6(2)	Ga(1)−P(1)−H(1p)	80.2
P(2)−Ga(1)−C(42)	123.1(2)	C(6)−P(1)−H(1p)	100.0
Ga(1)−P(2)−C(24)	108.6(2)	C(24)−P(2)−H(2p)	115.6
Ga(1)−P(2)−H(2p)	83.5		

The restricted rotation along the M−N bonds is probably due to steric hindrance of the bulky SiMe$_3$ and *ortho*-Bu^t groups. These are different from the multiple bonding in some examples of B−P and B−As species, which involves pπ−pπ interaction between the two elements.[12−14]

X-ray Structures. Selected bond distances and angles of compounds **1**−**3** are shown in Table 2.

Molecular Structure of [ArGaN(SiMe$_3$)$_2$Cl] (1). The molecular structure of **1** with the atom-numbering scheme is shown in Figure 2. The gallium atom is surrounded in a distorted trigonal planar manner (∑° Ga = 360.0°), by Ar, Cl, and N(SiMe$_3$)$_2$ ligands. The largest angle is that of N(1)−Ga(1)−C(6) [133.4(4)°]. This is due to the steric congestion of both bulky Ar and N(SiMe$_3$)$_2$ ligands. The plane of the Ar ring is oriented almost perpendicular (86.9°) to the coordination plane at gallium so as to minimize the steric repulsion between the two bulky ligands. A special feature of this conformation is that there are close approaches between hydrogens from the *ortho*-Bu^t group and the gallium metal. The Ga(1)···H(9A) and the Ga(1)···H(16B) distances are 2.335 and 2.297 Å, which are shorter than the sum of the van der Waals radii for Ga and H.[15] This interaction may help to stabilize the monomeric monoamide complex. The coordination at nitrogen is also planar (∑°N = 360.0°) with fairly regular interligand angles (all within *ca.* 3° of 120°). The Ga−N, Ga−C, and Ga−Cl bond lengths are 1.867(10), 1.953(12), and 2.228(4) Å, respectively. These distances are comparable to corresponding distances of 1.868 Å (Ga−N) in Ga{N(SiMe$_3$)$_2$}$_3$ and 1.844 Å (Ga−N) and 2.130 Å (Ga−Cl) in Ga{N(SiMe$_3$)$_2$}$_2$Cl.[16] There is a dihedral angle of 3.1° between the perpendiculars to the coordination planes at the gallium and nitrogen centers in compound **1**.

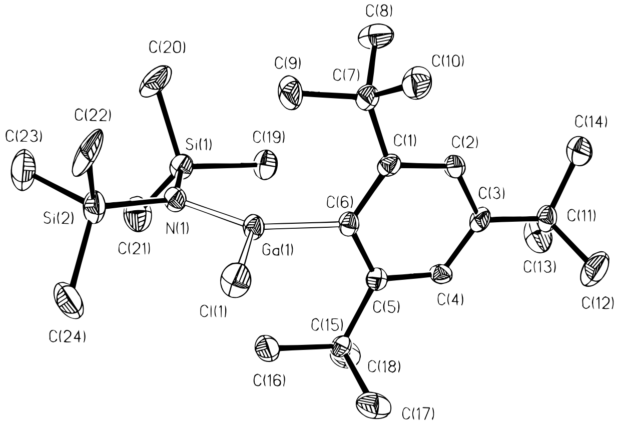

Figure 2. Molecular structure of [ArGaN(SiMe$_3$)$_2$Cl] (**1**) with the atomic labeling scheme. Hydrogen atoms have been omitted, and the thermal ellipsoids are drawn at the 35% probability level.

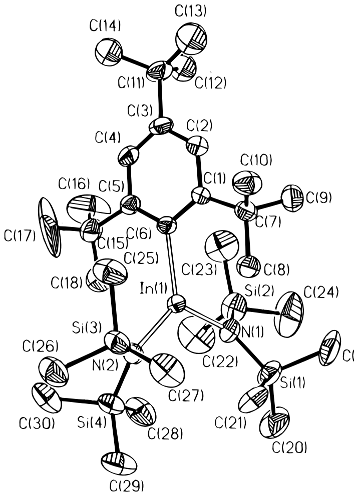

Figure 3. Molecular structure of [ArIn{N(SiMe$_3$)$_2$}$_2$] (**2**) with the atomic labeling scheme. Hydrogen atoms have been omitted, and the thermal ellipsoids are drawn at the 35% probability level.

Molecular Structure of [ArIn{N(SiMe$_3$)$_2$}$_2$] (2). The molecular structure of **2** as shown in Figure 3 is one of the rare examples of a monomeric three-coordinate organoindium bis(amido) complex that has

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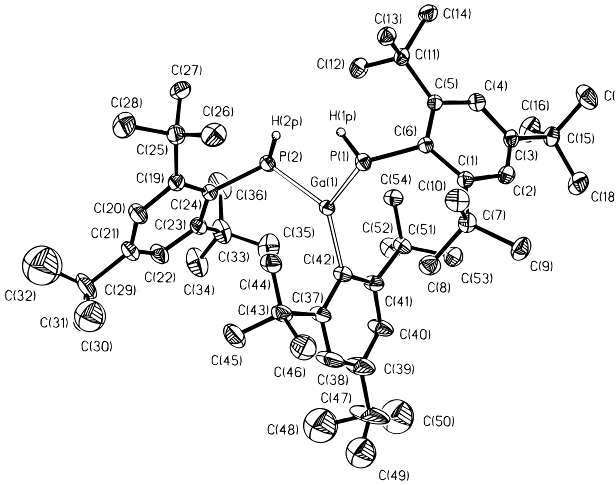

Figure 4. Molecular structure of [ArGa{P(H)Ar}$_2$] (**3**) with the atomic labeling scheme. Hydrogen atoms have been omitted, and the thermal ellipsoids are drawn at the 35% probability level.

been structurally characterized. The indium and nitrogen centers each has essentially a planar coordination geometry ($\sum$°In = 359.9°) with only minor distortions from idealized 120° bond angles. The In−N bond distances are 2.094(4) and 2.103(6) Å. The shortest In···H distances are found to be 2.310 Å (In(1)···H(8B)) and 2.427 Å (In(1)···H(18B)). The In(1)−C(6) bond length is 2.188(6) Å. The dihedral angles between the planes at indium and the two nitrogen atoms are 47.2 and 44.2°, respectively. The *para*-*tert*-butyl groups of the Ar ligand on indium metal is disordered, and it was refined with equal probability for its two possible orientations.

Molecular Structure of [ArGa{P(H)Ar}$_2$] (3). The molecular structure of 3 in its crystalline hexane solvate is shown in Figure 4. A similar compound Bu$^t_2$Ga{P(H)Ar}$_2$ has been structurally characterized.[17] Compound 3 is monomeric, with the gallium atom in a trigonal-planar configuration ($\sum$°Ga = 359.9°) while the three-coordinate phosphorus atoms are both pyramidal. Obviously, the substituents on the phosphorus atoms are not bulky enough to induce flattening of the pyramidal geometry. This is undoubtedly attributed to the presence of protons on the phosphorus centers. The Ga−P bond lengths are 2.384(2) and 2.392(2) Å, which are somewhat longer than those found in other three-coordinate organogallium phosphides including Ga{P(H)Ar}$_3$ [2.34(1) Å], Bu^{t}Ga{P(H)Ar}$_2$ [2.295(3) Å], and {(Trip)$_2$Ga}$_2$PMes·Et$_2$O [2.256(3) Å] (Trip = 2,4,6-Bu$^i_3$C$_6$H$_2$).[4,17,18] In addition, two hydrogens are found at close distances of 2.372 Å [H(44c)] and 2.374 Å [H(54A)] to the gallium metal center. There are dihedral angles of 45.0° (for P(1)) and 41.2° (for P(2)) between the perpendiculars to the CGaP$_2$ and GaPHC planes, respectively. The corresponding angle for the Ar aromatic plane and the gallium coordination plane is 95°. Thus the aromatic ring is oriented almost orthogonal to the Ga trigonal plane in order to reduce the steric crowding of the ligands. The values for the angle ϕ, which is a measure of pyramidicity of the phosphorus atoms, are 75.4° [P(1)] and 73.3° [P(2)].

Taking the sum of the covalent radii of gallium (1.25 Å) or indium (1.40 Å) and sp^2-hydridized nitrogen (0.7 Å) with consideration of ionic character due to electronegativity differences, the calculated bond distances for Ga−N and In−N are 1.84 and 1.96 Å, respectively.[19] The Ga−N distance of 1.867(10) Å observed in compound **1** is comparable to the calculated value, but the In−N bond of 2.103(6) Å in compound **2** is longer than the calculated value. Comparison of the data for **1** and **2** with other similar compounds shows that deviation from the predicted M−N distances is most significant in highly crowded molecules such as Bu$^t_2$GaN(Bu^t)SiPh$_3$ and Bu$^t_2$GaN(1-Ad)SiPh$_3$ where steric effects are believed to be responsible for the induction of some elongation of the M−N bond.[20]

The bis(phosphido) complex **3** is not believed to involve significant multiple bond character owing to the pyramidal coordination retained at the phosphorus atoms. In addition, the large dihedral angles between the PCH plane and the GaCP$_2$ plane (ϕ = 73.3, 75.4°) preclude good interaction between the phosphorus lone pair and the empty metal p-orbitals. Significantly, the large inversion barrier observed in the trivalent phosphorus compounds represent a formidable obstacle to multiple bonding.[17]

Since the same energy barrier of 14.2 kcal mol^{-1} is obtained for both compounds **3** and **4**, it is suggested that the dynamic process is primarily due to flipping of the Ar groups of the phosphido ligands rather than restriction in rotation around the M−P bond. The fact that no splitting of the *para*-Bu^t signals of the ArPH groups can be observed in both compounds further supports the proposed ring flipping mechanism, which is slow on the NMR time scale at low temperature. On the basis of these observations, there is little evidence of dative π bonding from phosphorus lone pairs to the formally vacant p orbitals on gallium or indium.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques or in a dinitrogen glovebox. Solvents were dried over and distilled from CaH$_2$ (hexane) and/or Na (Et$_2$O and thf). GaCl$_3$ and InCl$_3$ were purchased from Aldrich Chemical Ltd. and used as received without further purification. ArGaCl$_2$,[21,22] ArInCl$_2$,[22] LiN(SiMe$_3$)$_2$(Et$_2$O),[23] and ArPH$_2$[24] were prepared according to literature methods.

Physical Measurements. ^{1}H and ^{13}C NMR spectra were recorded at 250 and 62.90 MHz, respectively, using a Bruker WM-250 spectrometer or at 500 and 125.8 MHz, respectively, using a Bruker ARX-500 spectrometer. All spectra were recorded in benzene-d_6, and the chemical shifts δ are relative to SiMe$_4$. Mass spectral data were obtained either on a VG 7070F mass spectrometer or performed at Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, China. In all cases, signals were reported as m/z. Elemental analyses were performed at MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, U.K.

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Table 3. Selected X-ray Data Collection and Structure Analysis Parameters for Compounds 1−3

	1	2	3
molecular formula	$C_{24}H_{47}N_2Si_2GaCl$	$C_{30}H_{65}N_2Si_4In$	$C_{54}H_{89}P_2Ga.C_6H_{14}$
M_r	511	681.0	956.1
color and habit	colorless prism	colorless prism	colorless plate
cryst size, mm	0.12 × 0.16 × 0.28	0.10 × 0.20 × 0.50	0.16 × 0.48 × 0.42
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No.2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.637(2)	17.815(1)	22.783(5)
b, Å	12.472(2)	11.206(1)	16.423(3)
c, Å	13.858(3	20.939(1)	18.773(3)
β, deg	101.37(3)	105.50(1)	111.06(3)
V, Å^3	1536.8(8)	4028(2)	6553(3)
Z	2	4	4
F(000)	548	1456	2096
density, g cm^{-3}	1.104	1.123	0.969
abs coeff, mm^{-1}	1.070	0.724	0.50
$2\theta_{max}$, deg	55	55	55
unique data measd	5015	11779	12961
no. of obsd reflecns	2064	5158	6763
no. of variables	263	332	569
R	0.071	0.051	0.064
wR	0.096	0.061	0.010

The energy barrier ($\Delta G^{\ddagger}$) of the dynamic process described is calculated using the Eyring equation:

$$\Delta G^{\ddagger} = (4.575 \times 10^{-3})T_c[9.972 + \log(T_c/\delta\nu)]$$

The coalescence temperatures T_c and $\delta\nu$ were measured from the variable-temperature ^{1}H NMR spectra.

[ArGaN(SiMe$_3$)$_2$Cl] (1). To a solution of $ArGaCl_2$ (1.07 g, 2.78 mmol) in Et_2O was added dropwise a solution of LiN(SiMe$_3$)$_2$(Et$_2$O) (0.60 g, 2.67 mmol) in Et_2O. A white cloudy solution was formed. After being stirred for 12 h, the reaction mixture was filtered, concentrated, and cooled. Upon standing of the concentrated filtrate at room temperature for 18 h, colorless crystals of **1** were formed: yield 0.63 g (46%), mp 147−149 °C. Anal. Found: C, 56.01; H, 9.16; N, 2.60. Calc for $C_{24}H_{47}NSi_2GaCl$: C, 56.41; H, 9.27; N, 2.74. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.10 (s, 9H), 0.59 (s, 9H), 1.25 (s, 9H), 1.54 (s, 18H), 7.48 (s, 2H). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz): δ 5.38, 5.58, 31.35, 33.19, 34.87, 37.86, 123.00, 151.52, 154.04. Mass spectrum (CI): m/z 509 (P$^+$), 496 (P − CH$_3{}^+$), 474 (P − Cl$^+$).

[ArIn{N(SiMe$_3$)$_2$}$_2$] (2). A stirring ethereal solution of $ArInCl_2$ (1.51 g, 3.49 mmol) was added dropwise to a solution of LiN(SiMe$_3$)$_2$(Et$_2$O) (0.84 g, 3.48 mmol) in Et_2O. The white cloudy solution formed was allowed to stir for a further 10 h. The reaction mixture was filtered, concentrated, and stored at −30 °C to afford colorless crystals of **2**: yield 0.31 g (27%), mp 145−148 °C. Anal. Found: C, 52.87; H, 9.62; N, 4.01. Calc for $C_{30}H_{65}N_2Si_4In$: C, 52.91; H, 9.62; N, 4.11. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.31 (br s, 36H), 1.26 (s, 9H,), 1.58 (s, 18H,), 7.54 (s, 2H). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz): δ 6.39, 31.25, 33.79, 34.65, 37.42, 123.28, 150.24, 154.28. EI mass spectrum: m/z 665 (P − CH$_3{}^+$), 520 (P − N(SiMe$_3$)$_2{}^+$), 435 (P − Ar$^+$), 360 (ArIn$^+$).

[ArGa{P(H)Ar}$_2$] (3). A solution of ArP(H)Li freshly prepared from $ArPH_2$ (0.27 g, 0.95 mmol) and n-BuLi (0.6 mL, 0.96 mmol, 1.6 M solution in n-hexane) was added slowly to $ArGaCl_2$ (0.21 g, 0.54 mmol) at room temperature. After the mixture was stirred for 8 h, all the solvent was removed *in vacuo* and the residue was extracted with n-hexane. The off-white solid was removed by filtration, and the filtrate was concentrated and kept at ambient temperature. Upon standing at room temperature for 3 days, colorless crystals of **3** were obtained: yield 0.22 g (53%), mp 201−207 °C (dec). Anal. Found: C, 74.32; H, 10.34. Calc for $C_{54}H_{89}P_2Ga$: C, 74.55; H, 10.31. ^{1}H NMR (C_6D_6, 250 MHz): δ 1.08 (s, 18H), 1.22 (s, 9H), 1.31 (s, 18H), 1.41−1.73 (br s, 36H), 5.16 (2H, d, ^1J(P−H) = 221.63 Hz), 7.40 (s, 2H), 7.53 (br s, 4H). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz): δ 30.86, 31.30, 31.90, 32.81, 33.59, 34.88, 37.72, 38.42, 122.54, 122.88, 147.56, 150.05, 153.97, 155.02. ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz, 85% H_3PO_4 ext): δ −95.74. ^{31}P NMR (C_6D_6, 202.5 MHz, 85% H_3PO_4 ext): δ −97.19 (d, ^1J(P−H) = 231.61 Hz). Mass spectrum (CI): m/z 868 (P$^+$), 591 (P − ArPH$^+$), 534 (P − ArPH − Bu^{t+}), 347 (GaP(H)Ar$^+$ + 1), 314 (GaAr$^+$).

ArIn{P(H)Ar}$_2$ (4). A freshly prepared solution of ArP(H)Li from $ArPH_2$ (0.23 g 0.83 mmol) and n-BuLi (0.52 mL, 0.83 mmol, 1.6 M solution in n-hexane) was added slowly to $ArInCl_2$ (0.36 g, 0.83 mmol) in Et_2O at room temperature. The pale yellow turbid solution was filtered through a Celite-padded glass frit. The filtrate was concentrated and stored at −30 °C for 24 h to afford pale yellow crystals of **4**: yield 0.26 g (69% based on $ArPH_2$), mp 158−160 °C (dec). Anal. Found: C, 70.95; H, 9.99. Calc for $C_{54}H_{89}P_2In$: C, 70.88; H, 9.80. ^{1}H NMR (C_6D_6, 250 MHz): δ 1.01 (s, 18H), 1.23 (s, 9H), 1.32 (s, 18H), 1.66 (br s, 36H), 5.02 (2H, d, ^1J(P−H) = 207.63 Hz), 7.39 (s, 2H), 7.46 (br s, 4H). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 31.04, 31.35, 31.61, 31.75, 32.31, 33.25, 33.81, 37.47, 119.66, 122.32, 122.91, 147.18. ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz, 85% H_3PO_4 ext): δ −114.25. ^{31}P NMR (C_6D_6, 202.5 MHz, 85% H_3PO_4 ext): δ −114.25 (d, ^1J(P−H) = 204.48 Hz). CI mass spectrum: m/z 669 (P − Ar$^+$), 637 (P − ArPH$^+$), 360 (ArIn$^+$).

ArGa(SAr)$_2$ (5). A suspension of freshly prepared LiSAr from ArSH (0.40 g, 1.44 mmol) was added slowly to a solution of $ArGaCl_2$ (0.26 g, 0.68 mmol) in toluene at room temperature. A turbid white solution was formed was filtered through Celite, and all the solvent was removed *in vacuo*. The residue was extracted with pentane and kept at −20 °C. A colorless crystalline solid of **5** was obtained: yield 0.23 g (39%), mp 228−230 °C. ^{1}H NMR (C_6D_6, 250 MHz): δ 1.18 (s, 18H), 1.20 (s, 9H), 1.29 (s, 18H), 1.60 (br s, 36H), 7.29 (s, 2H), 7.47 (br s, 4H). ^{13}C{^{1}H} NMR (C_6D_6, 62.9 MHz): δ 31.24, 31.65, 32.73, 32.98, 34.91, 36.80, 37.78, 38.78, 122.74, 123.06, 148.06, 150.63, 154.31, 155.26. FAB mass spectrum: m/z 811 (P − Bu^{t+}), 591 (P − SAr$^+$), 534 (P − ArPH − Bu^{t+}), 314 (GaAr$^+$).

X-ray Structure Determination of Compounds 1−3. Selected single crystals were sealed in a Lindemann glass capillaries under dinitrogen. X-ray intensities were measured on a MSC/Rigaku RAXIS-IIC imaging plate using monochromatized Mo Kα radiation (λ = 0.710 73 Å, 50 kV, 150 mA) from a rotating-anode generator. N unique reflections were measured, and N_o “observed” reflections with $|F_o| \geq 8\sigma(|F_o|)$ for **1** and **2** and $|F_o| \geq 6\sigma(|F_o|)$ for **3** were used in the structure solution and refinement. The weighting schemes $w = [\sigma^2|F_o|^{-1} + 0.0005|F_o|^2]^{-1}$ for **1**, $w = [\sigma^2|F_o| + 0.0001|F_o|^2]^{-1}$ for **2**, and $w = [\sigma^2|F_o|^{-1}$ for **3** were used. Computations were performed using the computer program SHELXTL-PLUS program package (Sheldrick, 1985, 1990) on a PC 486 computer and refined by full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1974) . The crystal data and structure analysis parameters are summarized in Table 3. Atomic coordinated of **1**−**3** are given in the Supporting Information.

Acknowledgment. This research was supported by Hong Kong Research Grants Council Earmarked Grant CUHK 22/91. We thank the Hong Kong Croucher Foundation for a studentship for C.M.-Y.C.

Supporting Information Available: Tables giving data collection and processing parameters, atomic coordinates, bond distances and angles, thermal parameters, and solution and refinement details and ORTEP diagrams (23 pages). Ordering information is given on any current masthead page.

OM960479X