

Synthesis and characterization of rings with the atom combination Ga/As and In/As

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Abstract—The organogallium arsenide $[Pr^{i}(Cl)GaAsBu_{2}^{i}]_{2}$ (1) and the organoindium arsenide $[(PhCH_{2})_{2} InAs Bu_{2}^{i}]_{2}$ (2) have been prepared by the reaction of the corresponding halides $Pr^{i}GaCl_{2}$ and $(PhCH_{2})_{2}InCl$ with $Bu_{2}^{i}AsLi$ in THF and $Et_{2}O$, respectively. 1 and 2 have been fully characterized by elemental analysis and IR, NMR, and MS techniques as well as by X-ray diffraction. According to cryoscopic molecular weight determinations in benzene, 1 and 2 are present as dimers in solution. The structures of 1 and 2 display rhombic distorted four-membered rings $M_{2}As_{2}$ (M = Ga, In). © 1998 Elsevier Science Ltd. All rights reserved

Keywords: gallium arsenide; indium arsenide; crystal structures.

During the last ten years the synthesis and characterization of compounds possessing the element combination group 13/group 15 has developed into one of the most exciting areas in main group chemistry. The predominant important driving force for the research in this field is the potential employment of such compounds in MOCVD processes generating layers and thin films of group 13/15 semiconductor materials [1– 3]. Nitrogen and phosphorus derivatives have been studied intensively, whereas arsenic and especially antimony compounds have not been investigated in great detail [1–4].

One approach to the better understanding of this class of compounds involves basic investigations such as optimizing the synthesis and studying the structural features of the compounds which often display rings and cages.

In this paper we report the reaction of an organogallium dichloride and a diorganoindium chloride with Bu¹₂AsLi to yield species with R(Cl)GaAsBu¹₂and $R_2InAsBu¹₂$. The structural features of the products have been studied in solution and the solid state. Compounds of the type $R(Cl)GaAsR'_2$ have been investigated already by Wells *et al.* who reported a dimer-trimer equilibrium in solution. A crystal structure analysis was not carried out [5]. However, not only the degree of association is of interest in this case, but also, whether Cl or As in μ_2 -bridging. One should expect As as a bridging atom, nevertheless, under certain conditions the chlorine atom can occupy this position [6,7].

EXPERIMENTAL

Instruments and materials

All experiments were carried out under an atmosphere of argon. Purification and drying of the solvents were done, using standard methods [8]. $Pr^{i}GaCl_{2}$ [34], (PhCH₂)₂InCl [10,11], and Bu^t₂AsLi [35] were prepared by literature procedures.

The ¹H and ¹³C NMR spectra were recorded on a Bruker AC-300 spectrometer (¹H, 300.134 MHz; ¹³C, 75.469 MHz). The standard was TMS (external) with $\delta = 0.0$ ppm. The IR spectra were obtained using a Bruker IFS-88 instrument (Nujol mulls, CsI disks for the range 4000–500 cm⁻¹; polyethylene disks for the range 500–100 cm⁻¹). For the EI mass spectra a Varian CH7a mass spectrometer (70 eV) was used. The melting points were measured with a Dr Tottoli (Büchi) melting point apparatus in sealed capillaries under argon (values not corrected). The cryoscopic measurements were performed using a Normag molecular weight determination apparatus combined with a Beckmann thermometer.

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[†] Dedicated to Prof. Dr Manfred Weidenbruch on the occasion of his 60th birthday.

Synthesis of the compounds

Preparation of $[Pr^{i}(Cl)GaAsBu_{2}^{t}]_{2}$ (1). A solution of 1.81 g (9.25 mmol) of Bu₂AsLi in 10 ml of THF was added at -78° C to a solution of 1.70 g (9.25 mmol) of Pr'GaCl₂ in 10 ml of THF. The green solution was stirred for 12 h until 20°C was reached. The color turned to yellow during this process. The solvent was removed under vacuum and the residue was treated with 10 ml of toluene. The suspension was filtered and the filtrate was reduced to dryness under vacuum. Recrystallization from toluene gives colorless crystals $(2.69 \text{ g}; 78.3\%); \text{m.p. } 180^{\circ}\text{C.}$ ¹H NMR $(C_6D_6; \text{ppm}):$ 1.38 [d, 6H, CH (CH₃)₂], 1.39 (m, 1H, CH(CH₃)₂, AB₆ spin system), 1.41 [s, 18H, $C(CH_3)_3$]. ¹³C NMR (C_6D_6 ; ppm): 20.2 $[CH(CH_3)_2]$, 21.0 $[CH(CH_3)_2]$, 32.6 $[C(CH_3)_3]$, 43.8 $[C(CH_3)_3]$. Molecular weight determination (cryoscopic, benzene, c = 0.0288 mol/l): 703; n = 2.1. EI-MS: m/z (%) 190 (4) [As(C₄H₉)₂]⁺, 179 (1) (ClGaAs)⁺, 132 (2) (AsC₄H₉)⁺, 105 (2) $(HGaC_{3}H_{7})^{+}$, 75 (1) (As)⁺, 69 (2) (Ga)⁺, 57 (100) $(C_4H_9)^+$, 43 (14) $(C_3H_7)^+$. IR (cm^{-1}) : 2719 w, 1198 w, 1160 vs, 1071 w, 1024 m, 977 m, 939 m, 918 m, 870 s, 845 m, 806 w, 654 vw, 522 m (vGaC), 395 m (vGaCl), 349 m (sh, vGa₂As₂), 327 m (vGa₂As₂), 266 m (br). Anal. calc. for $C_{22}H_{50}As_2Cl_2Ga_2$ (*M*, 674.82) C, 39.16; H, 7.47; As, 22.20; Ga, 20.66. Found: C, 38.92; H, 7.34; As, 22.45; Ga, 20.36.

Preparation of $[(PhCH_2)_2InAsBu_2^t]_2$ (2). A solution of 0.64 g (3.26 mmol) of Bu^t₂AsLi in 15 ml of Et₂O was added to a solution of 1.04 g (3.13 mmol) of $(PhCH_2)_2$ InCl in 35 ml of Et₂O at 20°C. The mixture was stirred for 18 h while a voluminous colorless solid was formed. The solvent was removed under vacuum and the residue was extracted with four portions of 25 ml of boiling toluene. The filtrate was dried under vacuum and the colorless solid was recrystallized from *n*-pentane (1.10 g, 73% calculated from $(PhCH_2)_2$ InCl; mp 210°C dec). ¹H NMR (C_6D_6 ; ppm): 1.14 [s, 18 H, C(CH₃)₃], 2.56 (s, 4 H, CH₂Ph), 6.82–7.06 (m, 10 H, Ph—H). ¹³C NMR (C₆D₆; ppm): 26.8 (CH₂Ph), 33.4 $[C(CH_3)_3]$, 40.2 $[C(CH_3)_3]$, 122.9 (C^4) , 127.5 $(C^{3,5})$, 128.8 $(C^{2.6})$, 146.4 (C^{1}) . Molecular weight determination (cryoscopic, benzene, c = 0.0255mol/l): 895; n = 1.8. EI-MS: m/z (%) 190 (5) $(InAs)^+$, 132 (2) $(AsC_4H_9)^+$, 115 (1) $(In)^+$, 91 (66) $(CH_2Ph)^+$, 57 (100) $(C_4H_9)^+$. IR (cm^{-1}) : 2720 w, 1594 m, 1302 w, 1262 m, 1206 m, 1154 m, 1069 m, 1036 m, 996 w, 936 w, 895 w, 880 m, 866 m, 795 s, 747 s, 695 s, 681 m, 660 m, 621 s, 534 s, 484 w (v_{as}InC₂), 447 w (v_sInC₂), 411 w, 329 w, 284 w (vIn₂As₂), 267 vw (vIn₂As₂), 209 vw, 167 vw, 119 vw. Anal. calc. for $C_{44}H_{64}As_{2}In_{2}$ (*M*, 972.47): C, 54.34; H, 6.63; As, 15.41. Found: C, 54.07; H, 6.59; As, 15.19.

X-ray measurements and structure determination

The crystals were covered with a high-boiling paraffin oil and mounted on the top of a glass capillary under the flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections on a four-circle diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 71.073$ pm; Siemens P4). The final cell parameters were determined from 25 high-angle reflections.

The intensities were corrected for Lorentz and polarization effects (for cell parameters and collection of the intensities, see Table 1). Both structures were solved with the program SHELXTL-Plus [36] (1: direct methods; 2: Patterson method) and refined against F^2 by full-matrix least-squares using SHELXTL [37] (1) and SHELXL-93 [38] (2). The positions of the hydrogen atoms for 1 were calculated for ideal positions and refined with a common displacement parameter. The hydrogen atoms for 2 have been free refined. The calculation of the bond lengths, bond angles, and U_{eq} values was performed using the program PLATON [39]. Selected bond lengths and angles are listed in Table 2.

A comparison of M—As bond lengths is compiled in Table 3.

Table 1. Crystallographic data for $[Pr^{i}(Cl)GaAsBu_{2}^{t}]_{2}$ (1) and $[(PhCH_{2})_{2}InAsBu_{2}^{t}]_{2}$ (2)

	1	2
Formula	C22H50As2Cl2Ga2	$C_{44}H_{64}As_2In_2$
Formula weight	674.82	972.47
a (pm)	963.9(4)	1028.4(1)
b (pm)	1691.9(4)	1032.1(1)
c (pm)	1832.7(4)	1220.3(1)
α (°)		100.63(1)
β (°)		113.70(1)
γ (°)		107.77(1)
$V (pm^3 \cdot 10^6)$	2989(2)	1057.0(2)
Z	4	1
$D_{\rm calc}$ (g/cm ³)	1.500	1.528
Temp. (K)	223	223
Space group	Pbca (no. 61) [41]	PI (no. 2)
2θ range (°)	2-50	2-50
h	-1 to 11	-1 to 11
k	-1 to 20	-11 to 11
1	-21 to 21	-14 to 13
Absorpt. corr.	numerical	no
μ (cm ⁻¹)	41.9	26.7
Collected data	7013	4344
Unique data	2634	3644
Data with $F_{o} > 4\sigma(F_{o})$	1458	3006
Refined parameter	128	345
$R_1 \left[F_{\rm o} > 4\sigma(F_{\rm o}) \right]^a$	0.0475	0.0212
wR_2^{b}	0.0942	0.0470
Weight factor a ^c	0.0324	0.0287
$\Delta ho_{ m max}/\Delta ho_{ m min}$	1.02 / -0.67	0.59 / -0.72
$(e/pm^3 \cdot 10^6)$		

^{*a*} $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

 ${}^{b} w R_{2} = \left\{ \left[\Sigma (F_{o}^{2} - F_{c}^{2})^{2} \right] / \left[w (F_{o}^{2})^{2} \right] \right\}^{1/2}.$

 $^{c}w = 1/[\sigma^{2}(F_{o}^{2}) + (aP)^{2}]$ and $P = [Max(F_{o}^{2}, 0) + 2F_{c}^{2}]/3$.

		1	
Gal—Asl	252.9(1)	As1-Ga1-Asla	88.16(3)
Gal—Asla	252.0(1)	Gal—Asl—Gala	91.84(3)
Gal-Cll	223.0(2)	As1Ga1Cl1	106.68(6)
Gal—Cl	198.7(7)	As1a-Ga1-Cl1	108.34(6)
As1—C2	200.8(7)	As1-Ga1-C1	124.8(2)
As1-C3	201.6(7)	Cl1—Ga1—Cl	106.2(3)
		Asla—Gal—Cl	120.9(3)
		Ga1—As1—C2	112.7(2)
		Ga1—As1—C3	114.0(2)
		C2—As1—C3	111.4(3)
		C2-Asl-Gala	111.8(2)
		C3-As1-Gala	113.8(2)
		2	
In1—Asl	271.64(4)	As1—In1—As1a	83.18(1)
In1—Asla	271.21(5)	In1—As1—In1a	96.82(2)
In1—C1	221.1(3)	As1-In1-C1	114.2(1)
In1–C2	223.0(3)	As1-In1-C2	113.76(8)
As1–C3	200.9(3)	C1—In1—C2	106.6(1)
As1C4	201.3(3)	C1—In1—Asla	123.4(1)
		C2-In1-Asla	114.4(1)
		In1—As1—C3	112.60(9)
		In1—As1—C4	108.74(8)
		C3-As1-C4	111.7(1)
		C3-As1-Inla	117.80(9)
		C4-As1-Inla	108.1(1)

Table 2. Selected atomic distances (pm) and bond angles (°) in 1 and 2

Compound	M—As	Ref.
1	250.0(1), 252.9(1)	a
$[Ph_2GaAs(SiMe_3)_2]_2$	251.8(1), 253.0(1)	16
[Me ₂ GaAsBu ¹ ₂] ₂	254.1(1), 255.8(1)	17
[Bu ⁿ ₂ GaAsBu ^t ₂] ₂	254.8(3)-255.7(3)	17
$[Bu_2^t GaAs(SiMe_3)_2]_2$	263.0(1)	42
Bu ¹ ₂ GaAsBu ¹ ₂	246.6(3)	18
$[({(Me_3Si)_2CH},Ga)_2(Cl){As(SiMe_3)_2}]$	250.3(1), 250.5(1)	43
$[{Bu_{2}^{1}Ga}_{2}(Cl){As(SiMe_{3})_{2}}]$	257.7(1)	42
(Mes*Ga),AsPh ^b	240.1(1), 241.8(1)	44
$Bu_{3}^{1}GaAs(SiPh_{3})[CH(SiMe_{3})_{2}]$	245.8(1)	19
[Me ₂ GaAsPr ¹ ₂]	249.8(2)-253.1(2)	45
$[(\{(Me_3Si)_2CH\}_2Ga)_3Ga_2(AsPh_2)(AsPh)\{(H)AsPh\}]$	245.0(1)-255.3(1)	46
2	271.21(5), 271.64(4)	а
[Me ₂ InAsMe ₂] ₃	265.7(3)-267.9(2)	29
$[Ph_2InAs(SiMe_3)_2]_2$	268.2(1)-268.9(1)	30
$[(Me_3CCH_2)_2InAs(SiMe_3)_2]_2$	275.2(1)	31
$[\{(Me_3CCH_2)_2In\}_2(Cl)\{As(SiMe_3)_2\}]$	269.4(3)	31
$[(\mathbf{Ph})\{(\mathbf{Me}_{3}\mathbf{Si})_{3}\mathbf{C}\}\mathbf{InAs}(\mathbf{SiMe}_{3})_{2}]_{2}$	267.8(1), 268.0(1)	47

Table 3. M—As bond lengths (M=Ga, In) for selected metal-arsenic compounds (pm)

"This work.

 ${}^{\flat}\operatorname{Mes}^{*}=\operatorname{Pr}_{3}^{i}\operatorname{C}_{6}\operatorname{H}_{2}.$

RESULTS AND DISCUSSION

Addition of Bu_2^tAsLi to Pr^iGaCl_2 in THF at $-78^{\circ}C$ gives the organogallium arsenide $[Pr^i(Cl)GaAsBu_2^t]_2$ (1).

$$\begin{array}{c} Pr^{i}GaCl_{2}+LiAsBu_{2}^{t}\rightarrow1/2[Pr^{i}(Cl)GaAsBu_{2}^{t}]_{2}+LiCl\\ 1\end{array} \tag{1}$$

In a similar metathesis reaction $(PhCH_2)_2InCl$ reacts with Bu_2^tAsLi in Et_2O at room temperature to $[(PhCH_2)_2InAsBu_2^t]_2$ (2).

$$(PhCH_2)_2 InCl + LiAsBu_2^t \rightarrow 1/2[(PhCH_2)_2 InAsBu_2^t]_2 + LiCl \quad (2)$$
2

1 and 2 are air-sensitive colorless solids and soluble in non-polar solvents like n-pentane or toluene. According to cryoscopic measurements, 1 and 2 both possess a dimeric character in benzene.

A solution of 1 in C_6D_6 shows the typical AB₆ spin system for the Prⁱ group [6–9]. Here the multiplet for the methine proton is partly covered by the singlet of the Bu^t groups at 1.41 ppm. The signal for the methylene protons in 2 at 2.56 exhibits a distinct low field shift in comparison to In(CH₂Ph)₃ [10,11] (1.81 ppm), [(PhCH₂)₂InN(H)Bu¹₂ [7] (transoid derivative, AB spin system : 2.08, 2.28 ppm, ²J(HH) = 11.1 Hz) and [(PhCH₂)₂InPPh₂]₃ [12] (2.26 ppm). Higher values of 2.60 and 2.72 ppm have been observed for the bromides (PhCH₂)₂InBr and [PhCH₂InBr₂(THF)₂] [13].

1 and 2 possess C_r -symmetry leading to only two observal M₂As₂ ring vibrations caused by the rule of mutual exclusion [14]. We assign the two bands at 349, 327 cm⁻¹ (1) and 284, 267 cm⁻¹ (2), respectively, to those asymmetric ring vibrations. The absorption at 395 is caused by the terminal Ga—Cl bond [15]. For the M—C vibrations in 1 and in 2 the signals at 522 (1), 484 ($v_{as}InC_2$) and 447 cm⁻¹ (v_sInC_2) have been found. Both compounds are not very stable under EI mass spectra conditions. Prominent peaks of 1 are observed for m/z = 57 (C₄H₉)⁺ and m/z = 43(C₃H₇)⁺. The spectrum of 2 exhibits peaks for (InAs)⁺ (m/z = 190), for (CH₂Ph)⁺ (m/z = 91) and for (C₄H₉)⁺.

Description of the structures

Figure 1 shows the centrosymmetric dimer 1 with a planar rhombic distorted Ga2As2 four-membered ring. The Ga-As distances of 252.0(1) and 252.9(1) pm can be compared to 251.8(1) and 253.0(1) pm in $[Ph_2GaAs(SiMe_3)_2]_2$ [16]. The dimers $[Me_2GaAsBu_2^t]_2$ and [Buⁿ₂GaAsBu^t₂]₂ [17] possess longer bond lengths of 255 pm (average) whereas the 263.0(1) pm in $[Bu_2^tGaAs(SiMe_3)_2]_2$ can be attributed mainly to the bulk of eight large substituents. The values for the first mentioned examples are due to the exchange of the electronegative Cl atom in 1 against an organic group. For gallium centers with the coordination number (CN) three, a shortening of the Ga-As bond should be observed such as the 246.6(3) pm for Bu^t $GaAsBu_2^t$ [18] and the 245.8(1) pm in Bu_2^tGaAs (SiPh₃) [CH(SiMe₃)₂] [19]. The rhombic distortion of M_2E_2 rings with group 13 metals is a generally observed feature. An angle larger than 90° can be found in almost all cases at the electronegative heteroelement E. Angles of 90° for M and E have been observed for the amid [Me₂InN(SiMe₃)₂]₂ [20]. There exist only few examples in which the group 15 element



Fig. 1. Molecular structure of 1 (without H atoms). The thermal ellipsoids have a probability level of 50%.



Fig. 2. Stereoscopic view of the unit cell of 1 (ORTEP) [40].



Fig. 3. Molecular structure of 2 (without H atoms).

does not occupy the μ_2 -bridging position. In the case of $[Mes(Cl)InN(SiMe_3)_2]_2$ [7] this can be explained by the well-known low basicity of the N(SiMe₃)₂ group and in $[Bu^t(Cl)GaP(H)Mes']_2$ $[Mes' = 2,4,6-Bu_3^t]_2$ C_6H_2 [21] the bulky aryl substituent is responsible for this behavior. In both cases the Cl atoms occupy the bridging position. The Ga-Cl bond length of 223.0(2) pm is typical for a terminal Cl atom attached to a Ga center with CN four. 221.1(3) pm has been found for [Mes*GaCl₂(THF)] [22]. The shortening to 212.4(4) pm for [Cp*GaCl₂]₂ [23], 215.1(2) pm for $[Bu'GaCl_2]_2$ [24], 216 pm (average) for $[MesGaCl_2]_n$ [25] and to 218 pm (average) in [GaCl₂(NPPh₃)]₂ [26] are due to the two or more electronegative ligands coordinating the metal center. A low CN in combination with bulky substituents leads to Ga-Cl dis-

tances in the same range (Mes^{*}₂GaCl: 222.0(5) pm [22]; Mes'GaCl₂: 215.7(1) pm) [22,27]. The gallium atom in 1 shows no tendency to extend the coordination sphere to CN5 by intermolecular Ga \cdots Cl contacts (Fig. 2), a characteristic behavior of Ga. Exceptions were observed if effects like intramolecular stabilization forces a higher CN, e.g. in [2,6-(Me₂N-CH₂)₂C₆H₃Ga(N₃)₂] [28].

The centrosymmetric four-membered ring In_2As_2 in **2** exhibits in principle the same rhombic distortion as the Ga analogue in **1** (Fig. 3). The In—As distances of 271.21(5) and 271.64(4) pm are at the upper limit for this bond. [Me₂InAsMe₂]₃ [29] [265.7(3)–267.9(2) pm] and [Ph₂InAs(SiMe₃)₃]₂ [30] [268.2(1)–268.9(1) pm] have more typical bond lengths. A longer In—As bond of 275.2(1) pm [31] was found only in the steri-

cally crowded indium arsenide $[(Me_3CCH_2)_2$ InAs(SiMe_3)₂]₂. An indicator of the sterical situation is the In--C bonds, which are relatively long [221.1(3); 223.0(3) pm] in comparison to In(CH₂Ph)₃ [218.6(7)-220.5(6) pm] [11] and $[(PhCH_2)_2InPPh_2]_3$ [218.5(4)-220.3(4) pm] [12].

1 possesses $Ga \cdots Ga$ contacts [362.7(1) pm] which are somewhat shorter than the sum of the van der Waals radii (380 pm). Recently, theoretical studies dealing with diamond shaped four-membered rings, like the ones present in 1 and 2, verified that there is no evidence for a metal-metal bond. The contacts are rather forced by the ring geometry [32].

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