*Journal of Organometallic Chemistry*, 341 (1988) C1–C5
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

**Preliminary communication**

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# The conformations of six-membered indium-arsenic and gallium-antimony rings *

**Alan H. Cowley*, Richard A. Jones*, Kenneth B. Kidd, Christine M. Nunn and Donald L. Westmoreland**

*Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 (U.S.A.)*

(Received September 8th, 1987)

## Abstract

An X-ray diffraction study reveals that the solid state of $[Me_2InAsMe_2]_3$ contains two independent molecules per asymmetric unit: one has a planar $In_3As_3$ ring while the other is puckered. The $Ga_3Sb_3$ ring of $[Cl_2GaSb(t\text{-}Bu)_2]_3$ (**2**) is basically boat-shaped, with one Sb atom and one Ga atom 0.938 Å and 0.620 Å respectively above the central $Ga_2Sb_2$ plane of the molecule.

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There is a rapidly growing interest in the chemistry of compounds containing bonds between the heavier group 13 and 15 elements. One reason for this is their potential as useful precursors to semiconductors such as GaAs and InP [1]. Pioneering work by Beachley and Coates [2] demonstrated that compounds of the general type $[Me_2MEMe_2]_x$ (M = Al, Ga, In; E = P, As) can be prepared by the thermal reaction of $Me_3M$ with $Me_2EH$. Although cryoscopic molecular weight measurements indicated a trimeric formulation, definitive structural information has been lacking since the original report indicated that these compounds are glassy solids. More recent studies have shown that compounds of empirical composition $R_2MER'_2$ (R,R′ = alkyl, aryl) exist as dimers or trimers depending on the steric demands of the substituents. Thus $[(Me_3SiCH_2)_2AsGaPh_2]_2$ [3], $[R_2ME(t\text{-}Bu)_2]_2$ (R = Me, n-Bu; M = Ga, In; E = P, As [4], and $[(Me_3SiCH_3)_2InPPh_2]_2$ [5] have been shown to be dimeric by X-ray analysis while mass spectral data indicate that compounds of empirical formula $Et_2MPEt_2$ (M = Ga, In) are trimeric [6]. A very recent gas phase electron diffraction study of $[Me_2InPMe_2]_3$ [7] is based on the premise that the $In_3P_3$ ring adopts a chair conformation. This publication prompts us to report details of our recently completed X-ray structure determination of

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* This paper is dedicated to Professor Colin Eaborn, F.R.S. in recognition of his outstanding contributions to organometallic chemistry.

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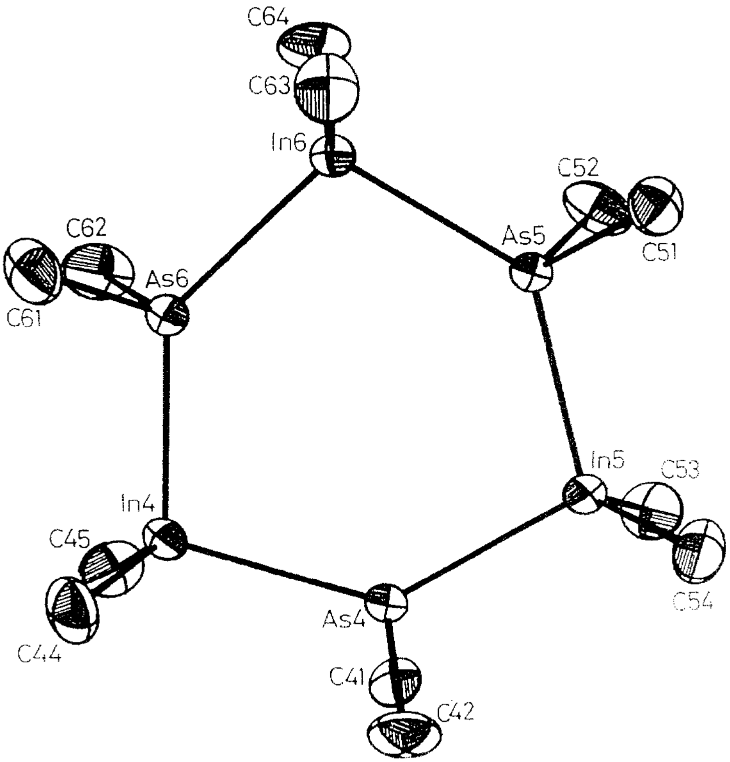

Fig. 1. Molecular structure of planar conformer of $[Me_2InAsMe_2]_3$, (**1**). Typical bond lengths and angles: In(4)–As(4) 2.674(2), In(5)–As(4) 2.673(2), In(5)–As(5) 2.678(2), In(6)–As(5) 2.679(2), In(6)–As(6) 2.673(2), In(4)–As(6) 2.677(2) Å. C(64)–In(6)–C(63) 124(1), C(52)–As(5)–C(51) 99.2(8)°.

$[Me_2InAsMe_2]_3$ (**1**). Although this compound was originally reported to be a glass [2], we have found that slow cooling of concentrated toluene solutions to −20 °C affords colorless crystals of X-ray quality.

*Crystal data:* $C_{12}H_{36}As_3In_3$, $M = 749.65$, triclinic, space group $P\bar{1}$ (No. 2), *a* 10.601(3), *b* 13.921(3), *c* 17.961(4) Å, $\alpha$ 76.07(2), $\beta$ 85.38(2), $\gamma$ 76.48(2)°, *U* 2500.4 Å$^3$, $D_c$ 1.991 g cm$^{-3}$, $Z = 4$, $\lambda$(Mo-$K_\alpha$) 0.71073 Å, $\mu$(Mo-$K_\alpha$) 66.28 cm$^{-1}$. A total of 8307 unique reflections was collected on an Enraf–Nonius CAD4 diffractometer at 23 ± 2 °C. The structure was solved by direct methods and refined (difference Fourier, full-matrix least-squares) using 3904 reflections with $I > 3\sigma(I)$. The final $R$ and $R_w$ values were 0.041 and 0.052, respectively.

The most interesting structural feature is the presence of two independent molecules in the asymmetric unit. One molecule (Fig. 1) is approximately planar, the deviations from the least squares $In_3As_3$ plane ranging from 0.097(4) to −0.139(3) Å. The other molecule (Fig. 2) possesses a puckered $In_3As_3$ ring. The three In atoms and As(3) are virtually coplanar. One As atom (As(2)) lies above this plane by 1.037(4) Å while the other (As(1)) lies below it by 1.252(3) Å. Clearly, this molecule has neither the classic chair nor the boat conformation of cyclohexane. Interestingly, the overall geometry of the $In_3As_3$ core resembles those of some *d*-block phosphido derivatives such as $[Co(\mu\text{-}P(C_6H_{11})_2)(CO)_2]_3$ [8].

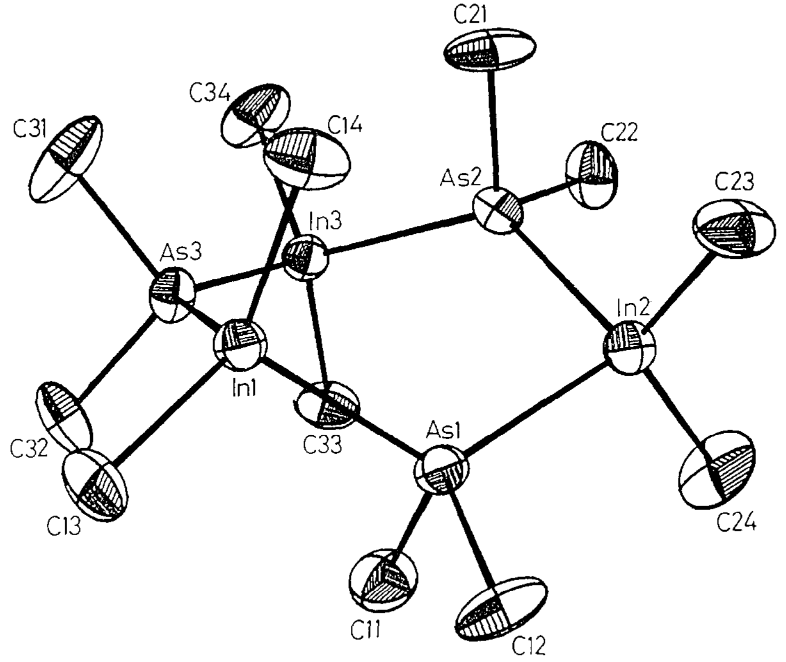

Fig. 2. Molecular structure of puckered conformer of $[Me_2InAsMe_2]_3$, (**1**). Typical bond lengths and angles: In(1)–As(1) 2.657(3), In(2)–As(1) 2.662(2), In(2)–As(2) 2.674(2), In(3)–As(2) 2.661(2), In(3)–As(3) 2.677(2), In(1)–As(3) 2.688(2) Å. C(11)–As(1)–C(12) 99(1), C(13)–In(1)–C(14) 126(1)°.

Dynamic $^1H$ NMR data indicate that equivalent In–Me and As–Me environments persist in solution down to $-80\,°C$. This suggests either a rapid interconversion of the planar and nonplanar forms of **1** on the NMR timescale or the existence of the planar form in solution.

The foregoing results imply that six-membered rings of alternating heavier group 13 and 15 elements are rather flexible. With a view to further exploration of this idea, the new compound $[Cl_2GaSb(t\text{-}Bu)_2]_3$ (**2**) was synthesized from the reaction of $t\text{-}Bu_2SbSiMe_3$ [9] and $GaCl_3$ [10]. An X-ray structure determination revealed a boat-type conformation for the $Ga_3Sb_3$ ring (Fig. 3). Note, however, that the "bow" (Sb(2)) is higher than the "stern" (Ga(2)). The molecule possesses a mirror plane passing through Ga(2) and Sb(2). Thus Sb(2) and Ga(2) lie 0.938 Å and 0.620 Å above the Sb(1)–Sb(1)′–Ga(1)–Ga(1)′ plane.

*Crystal data:* $C_{24}H_{54}Cl_6Ga_3Sb_3$, $M = 1129.83$, monoclinic, space group $P2_1/m$ (No. 11), $a$ 8.871(1), $b$ 23.630(2), $c$ 11.861(2) Å, $\beta$ 106.56(1)°, $U$ 2383.2 Å$^3$, $D_c$ 1.574 g cm$^{-3}$, $Z = 2$, $\lambda$(Mo-$K_\alpha$) 0.71073 Å, $\mu$(Mo-$K_\alpha$) 37.08 cm$^{-1}$. A total of 4290 unique reflections was collected as described above for **1**. Solution and refinement of the structure as per **1** but using 3009 reflections with $I > 3\sigma(I)$ afforded final $R$ and $R_w$ values of 0.0853 and 0.1022 respectively. We attribute these relatively high $R$ values to thermal motion of the t-butyl groups.

There is a paucity of structural data for In–As and Ga–Sb bonds. However, the average In–As bond lengths for **1** (planar form, 2.679(2); puckered form, 2.669(3) Å) are slightly longer than the sum of covalent radii (2.64 Å) or the bond distance in

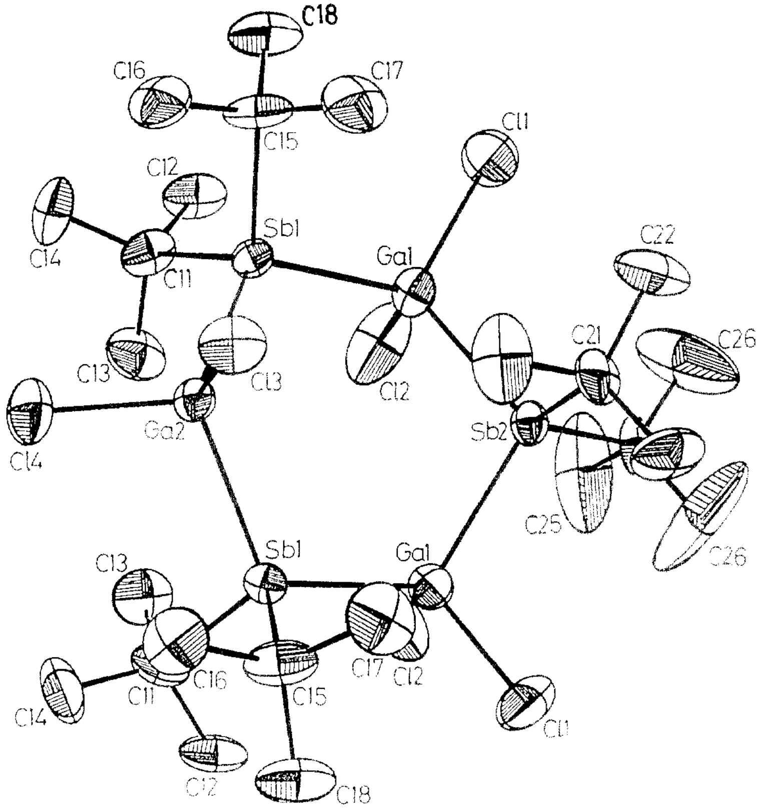

Fig. 3. Molecular structure of $[Cl_2GaSb(t\text{-}Bu)_2]_3$ (**2**). Typical bond lengths and angles: Ga(1)–Sb(1) 23.659(2), Ga(1)–Sb(2), 2.662(2), Ga(2)–Sb(1) 2.659(2) Å. Cl(1)–Ga(1)–Cl(2) 108.4(4), C(11)–Sb(1)–C(15) 109.8(9)°.

InAs (2.614 Å) [10 *]. The average Ga–Sb bond length for **2** (2.661(2) Å) is the same as the sum of covalent radii (2.66 Å) and similar to the bond distance in GaSb (2.649 Å) [11].

**Acknowledgements**. We thank the Robert A. Welch Foundation, the National Science Foundation and the Texas Advanced Technology Research Program for support. R.A.J. also thanks the Alfred P. Sloan Foundation for a fellowship (1985-87).

## References

1 See, for example, D.C. Bradley, M.M. Faktor, M. Scott and E.A.D. White, J. Crystal Growth, 75 (1986) 101; F. Maury, A.E. Hammadi and G. Constant, ibid., 68 (1986) 88.
2 O.T. Beachley and G.E. Coates, J. Chem. Soc., (1955) 3241.
3 R.L. Wells, A.P. Purdy, A.T. McPhail and C.G. Pitt, J. Organomet. Chem., 308 (1986) 281.
4 A.M. Arif, B.L. Benac, A.H. Cowley, R.L. Geerts, R.A. Jones, K.B. Kidd, J.M. Power and S.T. Schwab, J. Chem. Soc., Chem. Commun., (1986) 1543.

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* A reference number with an asterisk indicates a note in the list of references.

5 O.T. Beachley, J.P. Kopasz, H. Zhang, W.E. Hunter and J.L. Atwood, J. Organomet. Chem., 325 (1987) 69.

6 F. Maury and G. Constant, Polyhedron, 3 (1984) 581.

7 A. Haaland, J. Hougen, H.V. Volden, G. Hanika and H.H. Karsch, J. Organomet. Chem., 322 (1987) C24.

8 T.A. Albright, A.M. Arif, A.J. Bard, R.A. Jones, S.K. Kang, J.K. Leland and S.T. Schwab, Inorg. Chem., in press.

9 H.J. Breunig and T. Sevenergiz, Z. Naturforsch. B, 37 (1987) 395.

10 (**2**) M.p. 120–122 °C (dec.), $^1$H NMR ($C_6D_6$, 300 M Hz); $\delta$ 1.69 s ppm. $^{13}C\{^1H\}$ NMR ($C_6D_6$); 75.47 MHz, $\delta$ 33.63 ppm; $^{71}$Ga NMR ($C_6D_6$, 72.04 MHz, rel. $[Ga(H_2O)_6]^{3+}$ $3(NO_3)^-$); $\delta$ 237 ppm, $w_{1/2}$ 1400 Hz. IR (KBr): 2900 vs, br 1497 m, sh, 1396 m, sh, 1369 m, sh, 1366 s,sh, 1263 m, 1210 w, 1148 s,br, 1096 m, br, 1022 s, 938 w,sh, 870 w, 804 m, br, 737 s,sh, 699 m,sh, 504 w,sh, 497 m, 467 m,sh cm$^{-1}$. Deviations (Å) from the least squares plane through Sb(1), Ga(1), Sb(1)′ and Ga(1)′ are as follows: Sb(1) 0.079(3), Ga(1) −0.079(3), Sb(1)′ −0.079(3), and Ga(1)′ −0.079(3).

11 R.W.G. Wyckoff, Crystal Structures, 2nd edit., Wiley, New York, 1963, (a) Vol. 1, p. 108–111; (b) Vol. 4, p. 531.