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Final Report

THE SYNTHESIS AND CHARACTERIZATION OF GALLIUM-ARSENIC  
MONOMERS, CHAINS, CYCLES, AND CLUSTERS

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July 8, 1991

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**Final Report for Contract # N00014-83-K0572, R&T Project Code  
# 4135008 (August 1, 1983 - December 31, 1988) entitled:  
"THE SYNTHESIS AND CHARACTERIZATION OF GALLIUM-ARSENIC  
MONOMERS, CHAINS, CYCLES, AND CLUSTERS"**

### **1.0 Summary**

Although gallium arsenide is widely studied because of its importance in semiconductor technology, and there is the expectation that the gallium arsenic bond in polymeric form will exhibit interesting electronic properties, there had been a paucity of knowledge regarding even the most simple gallium-arsenic compounds. The latter is exemplified by the fact that when we initiated our program in organogallium-arsenic chemistry in 1983, the latest report of any activity in this area was in 1965. During the time this contract was active, we prepared a number of new gallium-arsenic compounds using the method of Coates (*i.e.*, "alkane" elimination) and also applied two new methods of synthesis. These methods are dehalosilylation between a silylarsine and a halogallane, and coupling using a lithium arsenide and a halogallane. Among the compounds prepared are the first examples of bis- and tris(arsino)gallanes, a novel gallium-arsenic cluster, and the first monomeric tricoordinate tris(arsino)gallane, the first gallium-arsenic compound containing a single  $\text{Ga}_3\text{As}$  unit, and the first organogallium four-membered ring compound with arsenic, halogen mixed-bridging. Dynamic NMR studies of two of the bis(arsino)gallanes showed they have novel fluxional properties. In addition, we successfully used dehalosilylation reactions to prepare gallium arsenide and indium arsenide.

## 2.0 Publications and Presentations Describing Results Obtained

### 2.0.1 Publications

1. C. G. Pitt, K. T. Higa, A. T. McPhail, and R. L. Wells, "Synthesis and Crystal Structure of Tris(dimesitylarsino)gallane, a Monomeric Tricoordinate Gallium-Arsenic Compound", *Inorg. Chem.*, 25, 2483 (1986).
2. R. L. Wells, A. P. Purdy, A. T. McPhail, and C. G. Pitt, "Isolation and Characterization of an Organogallium-Arsenic Cluster: Crystal Structure of  $[(\text{PhAsH})(\text{R}_2\text{Ga})(\text{PhAs})_6(\text{RGa})_4]$  ( $\text{R} = \text{Me}_3\text{SiCH}_2$ )", *J. Chem. Soc., Chem. Commun.*, 487 (1986).
3. R. L. Wells, A. P. Purdy, A. T. McPhail, and C. G. Pitt, "Synthesis and Crystal Structure of the Dimer Bis{bis(trimethylsilylmethyl)arsino}diphenylgallane", *J. Organomet. Chem.*, 308, 281 (1986).
4. C. G. Pitt, A. P. Purdy, K. T. Higa, and R. L. Wells, "Synthesis of Some Arsinogallanes and the Novel Rearrangement of a Dimeric Bis(arsino)gallane, Bis{bis[bis(trimethylsilyl)methyl]arsino}chlorogallane", *Organometallics*, 5, 1266 (1986).
5. R. L. Wells, A. P. Purdy, K. T. Higa, A. T. McPhail, and C. G. Pitt, "Synthesis and Characterization of a Dimeric Tris(arsino)gallane Containing a Nonplanar (Ga-As)<sub>2</sub> Ring: Crystal Structure of  $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_3\text{Ga}_2\}$ ", *J. Organomet. Chem.*, 325, C7 (1987).
6. A. P. Purdy, R. L. Wells, A. T. McPhail, and C. G. Pitt, "Reactions of  $(\text{Me}_3\text{SiCH}_2)_2\text{AsSiMe}_3$  with Gallium Halides; Crystal Structure and Dynamic NMR Study of the Dimer  $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_2\text{GaBr}\}_2$ ", *Organometallics*, 6, 2099 (1987).

7. R. L. Wells, S. Shafieezad, A. T. McPhail, and C. G. Pitt, "The First Gallium-Arsenic Compound Containing a Single Ga<sub>3</sub>As Unit: Isolation and Crystal Structure of [(thf)Br<sub>2</sub>Ga]<sub>3</sub>As (thf = tetrahydrofuran)", J. Chem. Soc., Chem. Commun., 1987, 1823.
8. R. L. Wells, A. P. Purdy, A. T. McPhail, and C. G. Pitt, "The Twist-Boat Conformation in a Gallium-Arsenic Six-Membered Ring: Crystal Structure of [(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>AsGaBr<sub>2</sub>]<sub>3</sub>", J. Organomet. Chem., 354, 287 (1988).
9. R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Shafieezad, and R. B. Hallock, "Use of Tris(trimethylsilyl)arsine to Prepare Gallium Arsenide and Indium Arsenide", Chemistry of Materials, 1, 4 (1989).
10. R. L. Wells, W. K. Holley, S. Shafieezad, A. T. McPhail, and C. G. Pitt, "The First Organogallium Four-Membered Ring Compound with Arsenic, Halogen Mixed Bridging: Synthesis and Crystal Structure of Ph<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>Ga(Ph)<sub>2</sub>Cl", Phosphorus, Sulfur, and Silicon, 41, 15 (1989).
11. R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Shafieezad, and R. B. Hallock, "The Use of Tris(trimethylsilyl)arsine to Prepare AlAs, GaAs and InAs. The X-Ray Crystal Structure of (Me<sub>3</sub>Si)<sub>3</sub>AsAlCl<sub>3</sub>•C<sub>7</sub>H<sub>8</sub>", Materials Research Society Symposium Proceedings, 131, 45 (1989).

### 2.0.2 Papers Presented at Meetings

1. R. L. Wells, A. P. Purdy, A. T. McPhail, and C. G. Pitt, "Synthesis and Characterization of Some Organogallium-arsenic Compounds", ACS Meeting, Miami Beach, FL, 1985, INOR 26.
2. C. G. Pitt, K. T. Higa, A. T. McPhail, and R. L. Wells, "Synthesis and Crystal Structure of Tris(dimesitylarsino)gallane, a Monomeric Tricoordinate Gallium-Arsenic Compound", 191st National Meeting of the American Chemical Society, New York, NY, 1986, INOR 347.

3. C. G. Pitt, A. P. Purdy, K. T. Higa, and R. L. Wells, "The Use of Silylarsines to Synthesize Arsinogallanes", presented by A. P. Purdy (graduate student), XX Organosilicon Symposium, Tarrytown, NY, 1986, P-2.27.
4. A. P. Purdy, R. L. Wells, A. T. McPhail, and C. G. Pitt, "Reactions of  $(\text{Me}_3\text{SiCH}_2)_2\text{AsSiMe}_3$  with Gallium Halides; Crystal Structure and Dynamic NMR Study of the Dimer  $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_2\text{GaBr}\}_2$ ", paper presented by A. P. Purdy (graduate student) at Meeting-in-Miniature, North Carolina Section, American Chemical Society, Duke University, Durham, NC, 1987.
5. R. L. Wells, A. P. Purdy, K. T. Higa, A. T. McPhail, and C. G. Pitt, "Synthesis of a Dimeric Tris(arsino)gallane Containing a  $(\text{Ga-As})_2$  Ring, and a Trimeric Mono(arsino)gallane Containing a  $(\text{Ga-As})_3$  Ring in the Twist-Boat Conformation; Crystal Structures of  $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_3\text{Ga}\}_2$  and  $\{[(\text{Me}_3\text{SiCH}_2)_2\text{AsGaBr}_2]_3\}$ ", Meeting-in-Miniature, North Carolina Section, American Chemical Society, Duke University, Durham, NC, 1987.
6. R. L. Wells, S. Shafieezad, A. P. Purdy, and C. G. Pitt, "The Use of  $\text{As}(\text{SiMe}_3)_3$  and  $\text{RAs}(\text{SiMe}_3)_2$  ( $\text{R} = \text{Me}_3\text{SiCH}_2$  and Mesityl) to Synthesize Organogallium-Arsenic Compounds", paper presented by S. Shafieezad, (post-doctoral research associate) at Meeting-in-Miniature, North Carolina Section, American Chemical Society, Duke University, Durham, NC, 1987.
7. R. L. Wells, A. P. Purdy, S. Shafieezad, A. T. McPhail, and C. G. Pitt, "Use of Silylarsines to Prepare Gallium-Arsenic Compounds with Unique Structures", 39th Southeast Regional Meeting, American Chemical Society, Orlando, FL, 1987, 28.

8. R. L. Wells, C. J. Benjock, M. L. Stanley, A. P. Purdy, W. K. Holley, and C. G. Pitt, "Kinetic Study of the Reaction of  $(\text{Me}_3\text{SiCH}_2)_2\text{AsH}$  with  $\text{Ph}_3\text{Ga}$  via  $^1\text{H}$  NMR Spectroscopy", Meeting-in-Miniature, North Carolina Section, American Chemical Society, North Carolina State University, Raleigh, NC, 1988 (paper presented by M. L. Stanley, undergraduate student).
9. R. L. Wells, W. K. Holley, A. T. McPhail, and C. G. Pitt, "The First Organogallium Four-Membered Ring Compound with Arsenic, Halogen Mixed Bridging: Synthesis and Crystal Structure of  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}$ ", Meeting-in-Miniature, North Carolina Section, American Chemical Society, North Carolina State University, Raleigh, NC, 1988 (paper presented by W. K. Holley, post-doctoral research associate).
10. R. L. Wells, C.-Y. Kwag, A. T. McPhail, and C. G. Pitt, "Isolation and Crystal Structure of  $(\text{Me}_3\text{SiCH}_2\text{As})_5$ ", Meeting-in-Miniature, North Carolina Section, American Chemical Society, North Carolina State University, Raleigh, NC, 1988 (paper presented by C.-Y. Kwag, graduate student).
11. R. L. Wells, W. K. Holley, S. Shafieezad, A. T. McPhail, and C. G. Pitt, "The First Organogallium Four-Membered Ring Compound with Arsenic, Halogen Mixed Bridging: Synthesis and Crystal Structure of  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}$ ", Fifth International Symposium on Inorganic Ring Systems, Amherst, MA, 1988 (paper presented by W. K. Holley, post-doctoral research associate).
12. R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Shafieezad, W. K. Holley, and R. B. Hallock, "The Use of  $(\text{Me}_3\text{Si})_3\text{As}$  to Prepare Gallium Arsenide Precursors and Gallium Arsenide", Workshop on Group III-V Chemistry and Semiconductors, Grand Island, NY, 1988.

13. R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, K. T. Higa, and S. Shafieezad, "Gallium-Arsenic Assemblages: Synthesis and Coordinate Structure", Symposium on Novel Main Group Element Ligands: Main Group Materials with Unusual Properties, Third Chemical Congress of North America, Toronto, Canada, 1988, INOR 50.
14. R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Shafieezad, and R. B. Hallock, "The Use of Tris(trimethylsilyl)arsine to Prepare Gallium Arsenide", 2nd Annual North Carolina ACS Section Symposium: Chemistry at Surfaces and Interfaces, Duke University, Durham, NC, 1988, poster D2.
15. R. L. Wells, C. G. Pitt, A. T. McPhail, A. P. Purdy, S. Shafieezad, and R. B. Hallock, "The Use of Tris(trimethylsilyl)arsine to Prepare AlAs, GaAs and InAs. The Crystal Structure of  $(\text{Me}_3\text{Si})_3\text{AsAlCl}_3 \cdot \text{C}_7\text{H}_8$ ", Symposium E: Chemical Perspectives of Microelectronic Materials, Materials Research Society Meeting, Boston, MA, 1988, E2.2.

### 2.0.3 Seminars and Special Lectures Presented

1. Naval Research Laboratory, Washington, D.C., Polymeric Materials Chemistry Division Seminar, 1984.
2. Davidson College Chemistry Department Seminar, 1985.
3. Morgan Semiconductor Division of the Ethyl Corporation, Garland, Texas, 1985.
4. E.I. du Pont de Nemours & Company, Inc., Central Research & Development Department Seminar, Wilmington, Delaware, 1986.
5. Shippensburg University of Pennsylvania Chemistry Department Seminar, 1986.
6. UNC-Asheville Chemistry Department Seminar, 1986.

7. AT&T Bell Lab., Murray Hill, New Jersey (Local New Jersey Section of the ACS meeting), 1987.
8. Akzo Corporate Research America, Inc., Dobbs Ferry, NY, 1988.

### **3.0 Patent Filed**

1. a. R. L. Wells, C. G. Pitt, and R. B. Hallock, "Preparation of Compound Semiconductors", pending, filed on May 27, 1988.  
  
b. R. L. Wells, C. G. Pitt, and R. B. Hallock, Continuation-In-Part Patent Application of Prior Serial No. 199,615, filed on May 27, 1988 and Entitled "Preparation of Compound Semiconductors", November 29, 1988.