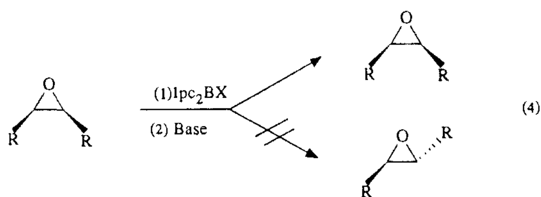

highly valuable difunctionalized compounds in good to excellent enantiomeric purity from simple olefins. Synthesis of optically active halohydrins is but one of the many possible applications that we are currently exploring.

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Organometallic Chemical Vapor Deposition of III/V Compound Semiconductors with Novel Organometallic Precursors

Alan H. Cowley,*,† Brian L. Benac,† John G. Ekerdt,*,‡ Richard A. Jones,*,† Kenneth B. Kidd,† James Y. Lee,‡ and James E. Miller‡

Departments of Chemistry and Chemical Engineering
The University of Texas at Austin
Austin, Texas 78712

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Compound semiconductors such as gallium arsenide (GaAs) and indium phosphide (InP) are important materials used in the fabrication of microelectronic and optoelectronic devices. Several techniques have been employed for the preparation of thin films of these materials, including organometallic chemical vapor deposition (OMCVD) and molecular beam epitaxy (MBE).[1] The OMCVD method is often preferred for larger scale processes and typically involves the reaction of a group III trialkyl such as Me_3Ga, with AsH_3 or PH_3 at elevated temperatures (600–700 °C) (eq 1).[2]

$$Me_3Ga + AsH_3 \rightarrow GaAs + 3CH_4\uparrow \quad (1)$$

Apart from the potential environmental, safety, and health hazards of handling pyrophoric and toxic reagents under these conditions, the conventional OMCVD methodology also suffers from stoichiometry control problems, impurity incorporation (particularly carbon), and unwanted side reactions. Moreover, the high temperatures involved can promote interdiffusion of layers which prevents sharp heterojunctions from being achieved.

Attempts to grow superior films by modifications of the OMCVD process include low-pressure OMCVD,[3] plasma-enhanced OMCVD,[4] rapid thermal OMCVD,[5] and hybrid MBE–OMCVD systems.[6] Several groups of workers have investigated the use of alternative sources of both the group III and group V components, e.g., Me_3P, Et_3P, t-$BuPH_2$,[7,8] t-$BuAsH_2$,[9] Et_2AsH,[10] and group III triethyl derivatives.[11,12] The use of adducts such as $Me_3In{\cdot}PEt_3$ and $Me_3In{\cdot}NMe_3$ has also been explored.[13] Adducts are less air sensitive than their components and are thus easier to handle and purify. However, the donor–acceptor bonds in the adducts are generally considered to be relatively weak compared to the other bonds present (such as Ga–C or As–H).[14] Ultimately these bonds have to be broken in order to form the III/V material. Dissociation of the adduct and loss of stoichiometry can occur, and typically excess PH_3 or AsH_3 is required for the production of good quality films.[15]

The ideal chemical solution to the problem is to cause the III–V bond to be as strong as, or stronger than, the other bonds in the molecule such that under film growth conditions the bonds between the group III and group V elements remain intact while the other bonds are broken. The obvious way to strengthen the III–V interaction is to replace the donor–acceptor linkage by a two-center, two-electron bond. Our initial studies have therefore focussed on the design and synthesis of organometallic molecules which feature σ bonding between the group III and group V elements.[16] A further objective was to lower the deposition temperature by employing substituents that undergo facile hydrocarbon elimination.

We have found that compounds of type **1** are excellent single source precursors for the preparation of III/V compound semiconductor materials such as GaAs and InP under relatively mild conditions. A typical example is the use of $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$ as the single source for the production of GaAs films. Film growth conditions involve the use of a cold-wall reactor, H_2 or He as the carrier gas, maintenance of the saturator containing the organometallic source at 130 °C, substrate temperatures of 450 to 700 °C, and a total system pressure of 1×10^{-4} to 10 Torr.

† Department of Chemistry.
‡ Department of Chemical Engineering.

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(16) Arif, A. M.; Benac, B. L.; Cowley, A. H.; Geerts, R. L.; Jones, R. A.; Kidd, K. B.; Power, J. M.; Schwab, S. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1543. Arif, A. M.; Benac, B. L.; Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M. *New J. Chem.*, accepted for publication. There are few other examples of compounds of these types. Pioneering work by Coates et al. established that compounds of the type $(Me_2EMMe_2)_3$ may be produced from the interaction of Me_3M and HEM_2 (M = Ga, In; E = P, As): Coates, G. E.; Graham, J. *J. Chem. Soc.* **1963**, 233. Beachley, O. T.; Coates, G. E. *J. Chem. Soc.* **1965**, 3241. More recently Wells and Beachley have reported compounds of similar stoichiometry that are dinuclear as well as related compounds. See, for example: Wells, R. L.; Purdy, A. P.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.* **1986**, *308*, 281. Beachley, O. T.; Kopasz, J. P.; Zhang, H.; Hunter, W. E.; Atwood, J. L. *J. Organomet. Chem.* **1987**, *325*, 69. Pitt, C. G.; Purdy, A. P.; Higa, K. T.; Wells, R. L. *Organometallics* **1986**, *5*, 1266. Pitt, C. G.; Higa, K. T.; McPhail, A. T.; Wells, R. L. *Inorg. Chem.* **1986**, *25*, 2483. Wells, R. L.; Purdy, A. P.; Higa, K. T.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.* **1987**, *325*, C7. Purdy, A. P.; Wells, R. L.; McPhail, A. T.; Pitt, C. G. *Organometallics* **1987**, *6*, 2099–2105. To our knowledge there has been only one report of a III/V OMCVD study involving a σ-bonded precursor. $[Et_2Ga\text{–}PEt_2]_3$ has been used as a precursor for GaP: Maury, F.; Combes, M.; Constant, G.; Carles, R.; Renucci, J. B. *J. Phys., Colloq.* **1982**, *(C1)*, 347. Maury, F.; Constant, G. *Polyhedron* **1984**, *3*, 581.

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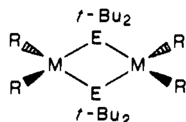
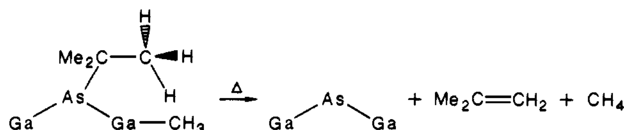
Cr-doped and Si-doped GaAs(100), As-doped Si(100) 3° off (100) toward (011), and quartz have been used as substrates[17] and film composition has been established with XPS. The Ga 3d, As 3d, and C 1s signals at 18.8, 40.9, and 284.6 eV, respectively, reveal the films to be 1:1 Ga:As and void of carbon. (The carbon levels are less than 1000 ppm, which is approximately equal to 2.2×10^{19} atoms cm^{-3}.) Growth rates (determined by Dektak) of 0.7 to 1.0 μm/h are found when the source is maintained at 130 °C. X-ray diffraction and SEM results suggest polycrystalline GaAs on quartz and epitaxial GaAs on GaAs(100) and Si(100). Films of indium phosphide have been grown in a similar manner with $[Me_2In(\mu\text{-}t\text{-}Bu_2P)]_2$ as the precursor.[18]



1: R = Me, M = Ga, E = As, M = Al, Ga, In; E = P, As (ref 16)

The use of precursor compounds of type **1** is attractive because they possess the advantages of being much more stable toward air and moisture than either adducts or mixtures of group III and V compounds. They are also sufficiently volatile for OMCVD processes, hydrocarbon soluble, and not appreciably toxic.

A possible mechanism for the deposition of the III/V thin films involves interaction of the group III metal with a C–H bond of a *t*-Bu group followed by elimination of methane. Pyrolysis of **1** under vacuum produces isobutylene and methane as the major hydrocarbons in addition to smaller quantities of isobutane. Further support for the proposed mechanism comes from the solid-state X-ray structure of $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$.[16] The H atoms were not located in this study; however, by placing them in idealized positions, we find that there is a "close" Ga···H interaction of 2.62 Å between the Ga atom and a hydrogen atom of a *t*-Bu–As group. Cleavage of the group V–carbon bond would then produce isobutylene. There is precedent for the analogous step in transition-metal chemistry in the formation of arsenidene (AsR^{2-}) complexes from diorganoarsenide (R_2As^-) species.[19]



Other mechanisms are, of course, possible and we are currently carrying out labeling studies and characterization of the volatile products in order to address this point. Further characterization of the grown films by low-temperature photoluminescence, Hall effect, and DLTS (deep level transient spectroscopy) is in progress.

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the Texas Advanced Technology Research Program for support and J. A. Cook for XPS analyses. R.A.J. also thanks the Alfred P. Sloan Foundation for a fellowship (1985–1989). We thank Professor B. G. Streetman (U.T. Department of Electrical Engineering) for helpful advice.

(17) The GaAs substrates were cleaned by degreasing in tetrachloroethylene, rinsed with methanol and deionized water, and finally etched in a 8:1:1 solution of H_2SO_4, H_2O_2, and H_2O, rinsed with deionized water and dried under a stream of nitrogen at room temperature. GaAs substrates were heated to 580 °C under vacuum prior to deposition to remove any oxides. The silicon substrates were degreased and rinsed in the same manner, dipped in a 25% HF solution rinsed with deionized water, and dried under a stream of nitrogen. The quartz substrates were degreased and dried as for GaAs and Si but not etched.

(18) Professor D. C. Bradley and co-workers have independently synthesized this precursor and described its conversion to InP. For the vapor pressure of $[Me_2In(\mu\text{-}t\text{-}Bu_2P)]_2$, see: Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; Young, K. V. *Chemtronics* **1988**, *3*, 50. For the deposition of InP, see: Bradley, D. C.; Faktor, M. M.; White, E. A. D.; Frigo, D. M. UK patent No. 8703227. Andrews, D.; Davies, G. J.; Bradley, D. C.; Frigo, D. M.; White, E. A. *Appl. Phys. Lett.*, in press.

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A Novel Synthesis of Tetrahydrofurans via a Synthetic Equivalent to a Carbonyl Ylide

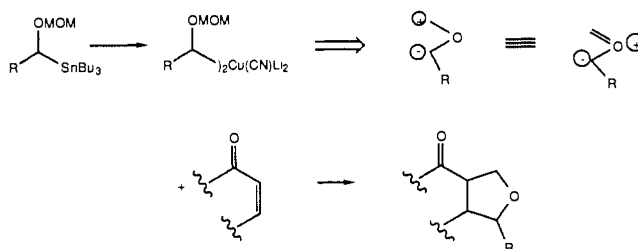
Russell J. Linderman* and Alex Godfrey

Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27695-8204

Received May 13, 1988

α-Alkoxyorganostannanes have enjoyed considerable attention recently as precursors to the corresponding α-alkoxyorganolithium species.[1] Recently the development of α-alkoxyorganocuprates has extended the potential synthetic utility of this class of functionalized carbanions.[2] We would now like to report that α-alkoxyorganostannanes can also function as synthetic equivalents to a carbonyl ylide, providing direct access to highly substituted tetrahydrofurans from enones.

Carbonyl ylides are extremely reactive transient species that have been generated from oxiranes,[3] or by carbene additions to carbonyl compounds.[4] The carbonyl ylides are typically only generated from precursors bearing several stabilizing groups and regiochemical control in subsequent reactions of these 1,3-dipoles is not readily achieved. Due to these constraints, the potential synthetic utility of carbonyl ylides for the construction of oxacyclic compounds has not been realized. We envisioned a potential answer to these problems by the sequential formation of the anionic and cationic components of the carbonyl ylide. This approach required an α-alkoxy anion that would bear the necessary functionality for subsequent formation of an oxonium ion. α-Alkoxystannanes provided ready accessibility to the anionic portion by facile transmetalation. Regiocontrol in additions to electron deficient olefins could then be obtained via the derived organocuprate. The oxonium ion would then be generated by Lewis acid activation of the acetal protecting group present in the initial stannane. In this fashion, the overall reaction would be equivalent to a regiocontrolled tetrahydrofuran synthesis by means of a carbonyl ylide addition reaction.



Carbon–carbon bond-forming reactions for the synthesis of oxacyclic compounds have been rare until recently.[5] In particular,

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