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**Design and Construction of Main Group
Element-Containing Molecules and
Molecule-Derived Materials With
Unusual Electronic, Optical, and
Magnetic Properties**

**Research Grant
No. DE-FG02-96ER45603**

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DOE Patent Clearance Granted

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DOE Chicago Operations Office

Final Report

**For
The Department of Energy**

MRI Project No. 101438

August 4, 2004

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**For
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MRI Project No. 101438

August 4, 2004

Preface

This report describes results and accomplishments from the Midwest Research Institute's (MRI) program for the *"Design and Construction of Main Group Element-Containing Molecules and Molecule-Derived Materials with Unusual Electronic, Optical and Magnetic Properties,"* under Grant No. DE-FG02-96ER45603 from the Department of Energy, Division of Materials Research, Office of Basic Energy Sciences.

This program was successful in achieving its primary objectives. Namely, we succeeded in the development of multiple synthetic routes to a wide variety of new candidate CVD precursor compounds. These new precursors incorporated the following principles:

- i) A broadly applicable synthetic strategy was developed and implemented, thus enabling **greater predictability** across the entire collection of molecular precursor compounds developed, with respect to their decomposition kinetics and mechanism;
- ii) Substituent **fluorination** was used to provide for or enhance volatility; and
- iii) The molecular structures developed provided a **low-energy pathway for decomposition** that is "inherently clean" and minimizes incorporation of impurities in the product thin films.

MIDWEST RESEARCH INSTITUTE

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Section 1. Introduction

1.1 Program Objectives

The objective for this research program was the development of new source compounds for the Metal Organic Chemical Vapor Deposition (MOCVD) of thin films, especially those which incorporate the Group 13 and 15¹ elements, and which are known to have utility as sensors in the automobile industry. New source compounds were characterized, and evaluated with regard to their volatility, thermal lability, and for their thin film-forming tendencies. Source compounds that appeared promising were to be examined further for epitaxial growth of, for instance, InSb (indium antimonide),² and subjected to more sophisticated film characterization including surface morphology, SEM, EDS, XRD, XPS, and electronic transport measurements. This vertically integrated program was organized to yield a wide variety of new and useful precursor molecules for the preparation of thin films for energy conversion materials (electronic ↔ optical, electronic ↔ magnetic), and optimization of the corresponding materials performance and processing characteristics.

The project team for this program was assembled to ensure that, in the case of the short-term objectives, there was a focused transition of the technology from MOCVD precursor design and development, through material growth and process development, to device fabrication. Because the proposal for this grant was originally submitted (in 1996) in response to Program Notice 96-05: "Research for Improving Vehicular Transportation and Reducing Energy Consumption and Pollution from Manufacturing Processes," we enlisted the support and collaboration of the General Motors Research and Development Center staff. The GM Research and Development Center provided a letter of endorsement in support of our original grant application, and to further their commitment they actively collaborated in the project to ensure that it remained relevant to their long-term goals.

The key project team members include:

- Dr. Bruce N. Diel, *Principal Investigator*, Section Manager—Chemical Sciences Division, Midwest Research Institute, Kansas City Missouri
- Dr. Catherine M. Zelenski, Post-Doctoral Chemist—Chemical Sciences Division, Midwest Research Institute, Kansas City Missouri
- Dr. Dale L. Partin and Dr. Joseph P. Heremans—General Motors Research and Development Center

The project responsibilities were defined as follows:

¹ Group 13 = Group IIIA, Group 15 = Group VA.

² GM uses InSb in magnetoresistive sensors to diagnose engine misfire.

Midwest Research Institute

- Precursor (source molecule) design, synthesis and characterization
- Evaluation of vapor deposition chemistry, mechanistic studies, film-forming tendencies, and film purity profiles
- Determination of MOCVD surface-selectivity and surface chemistry, as it relates to thin film deposition

General Motors Research And Development Center

- Investigation of electronic transport properties of InSb and other materials

1.2 Work Accomplished Under the Contract

1.2.1 Research Strategy

The objectives for this research program were the development of new source compounds for the Metal Organic Chemical Vapor Deposition (MOCVD) of thin films. New source compounds were developed, characterized, and evaluated with regard to their volatility, thermal lability, and for their thin film-forming tendencies.

The strategy for the development of new and improved MOCVD precursor compounds incorporated the following four principles:

- i) Development of a broadly applicable synthetic strategy to enable greater predictability across the entire collection of molecular precursor compounds to be developed, with respect to decomposition kinetics and mechanism, and thin film purity profile
- ii) Minimization of intermolecular interactions by encapsulating the Main Group element(s)³ (or metals) of interest in a sterically saturating, nonpolar ligand or chelate-ring structural environment
- iii) Substituent fluorination to enhance volatility
- iv) The molecular structure should provide a low-energy pathway for decomposition that is "inherently clean" and minimizes incorporation of impurities in the product thin films

Significant progress was made toward the achievement of each of these objectives over the term of this contract. Several examples of volatile precursor compounds were prepared and evaluated. These novel compounds were evaluated and show promise as

³ Referred to as "the element to be delivered" to the thin film.

source compounds for the deposition of nanocrystalline thin films via thermolysis under relatively mild conditions and with a clean decomposition profile.

1.3 Results and Discussion

1.3.1 Synthetic Approaches to MOCVD Precursor Molecules

We have developed multiple synthetic routes to several novel α -diimines (diazabutadienes), which are in turn utilized for the construction of Main Group element-containing heterocycles of the general structure 1 (the 1,3,2-diazaheteroles).

E = the "delivered" atom; Main Group element, transition metal, alkali metal

X = $-\text{NH}_2$, $-\text{NR}_2$, $-\text{N}(\text{R}_\text{F})_2$, Etc.

R = Perfluoroalkyl, perfluoroaryl

Heterocycle construction involves a ring-closure reaction between the α -diimine and a polyhaloelement compound (eq. 1), taking advantage of either HX or Me_3SiX elimination to drive the reactions, and thereby encapsulating the heteroatom (E) in a chelate-ring structural environment.

For the purposes of CVD precursor (1,3,2-diazaheterole) design, we developed and optimized two convenient, high-yield synthetic approaches to the required α -diimines:

1. Reaction of α -Diones with Lithium bis(trimethylsilylamide)

The first synthetic route (eq. 2) involves the reaction of an α -dione (cannot possess enolizable protons) with lithium bis(trimethylsilyl)amide, $\text{Li}[\text{N}(\text{SiMe}_3)_2]$, followed by quenching with ClSiMe_3 to yield the corresponding N,N' -bis(trimethylsilyl)- α -diimines.^{1a,b}

R = Alkyl, Aryl, Perfluoroalkyl, Perfluoroaryl, Etc.

This is a very general synthetic route to α -diimines possessing a wide variety of substituents (R), ranging from extensively conjugated π -systems^{1a} to electron-withdrawing perfluoroalkyl and perfluoroaryl substituents,^{1b} and is derived from a synthesis first reported by Tüchtenhagen and Rühlmann.²

2. Reductive-Coupling of Perfluoroalkyl (or -aryl) Nitriles

Recognizing that the presence of Si in starting materials [i.e., the N,N' -bis(trimethylsilyl)- α -diimines] used to synthesize CVD source compounds (1) could lead to unacceptable levels of Si-contamination in the CVD source compounds, and ultimately deleterious levels of Si-incorporation in the product thin films, we developed a parallel synthetic route to these same α -diimines that does not use Si-containing reagents,^{1c} as depicted below (Scheme 1). This approach involves an organometallic-based reductive coupling of a perfluoroalkyl- or perfluoroarylnitrile to give the desired N,N' -dihydro- α -diimines. Subsequent hydrogen halide elimination (eq. 1, Y = H; using amine HX-scavengers) provides a second synthetic route to the 1,3,2-diazaheterole ring compounds (1).^{1c}

Scheme 1

As illustrated, the HCl/Et₂O cleavage of the diimine also produces Cp₂TiCl₂, which can be recovered and recycled/reduced back to [Cp₂TiCl]₂, in 75% overall yield (based on the initial [Cp₂TiCl]₂).

Thus, reaction of the α-diimines (i.e., 2a/b, Y = -SiMe₃ or -H, where R = -CF₃) with the appropriate polyhaloelement species (EX_n), as depicted in equation 1, and subsequent derivatization (at the remaining E-X bond, where applicable) provides access to a wide variety of new, volatile, and reactive 4,5-bis(trifluoromethyl)-1,3,2-diazaheteroles (i.e., 1, where R = CF₃, E = Ga, In, As, Sb, Bi, Se, Te).

1.3.2 Synthesis of Main Group Element-Containing Diazaheteroles

Group 15 Elements (As, Sb, Bi)

In general, reactions of either 2a, or 2b with added HCl-scavenger (e.g., 1-methylpyrrolidone),^{1c} with AsCl₃, SbCl₃ or BiCl₃ proceed readily and in high yield to produce the corresponding 2-chloro-4,5-bis(trifluoromethyl)-1,3,2-diazaheteroles (i.e., 1; E = As, Sb, Bi; X = Cl; R = -CF₃) as volatile crystalline solids. For example, compound 3 is isolated/purified obtained by room temperature sublimation to yield the red-orange crystalline product, and 4 is obtained by recrystallization from THF.

The 2-halo-4,5-perfluoroalkyl-1,3,2-diazaheteroles (i.e., 3, or 4) can be easily derivatized at the remaining E-X bond by, e.g., reaction with LiNR_2 as exemplified by 5. Alternatively, one can start with an already functionalized Main Group element halide, e.g., R_2NECl_2 (E = As, Sb, Bi), and react this directly with either 2a or 2b to obtain the corresponding 2-amido-1,3,2-diazaheterole.³ In addition, a second equivalent of diimine (in this instance 2b) can be added to provide compounds such as 6,⁴ molecules in which a second element (e.g., from Group III) could potentially be tethered to provide single-source precursors (*vide infra*).

Group 16 Elements (Se, Te)

Reaction of 2a with TeBr_4 produces the spiro-*bi*(diazatellurole) 7. Compound 7 [Te(IV)] is labile (eq. 3) and under pyrolysis conditions (120°C, under Ar-flow) undergoes quantitative exothermic (as evidenced by DSC) oxidative decoupling (see

⁴ In 6, although the terminal hydrogen atom of the η^1 -diimine could not be located from the difference map, the As(1)-N(4) distance of 2.496(5) Å suggests strong hydrogen bonding.

Section 4.1.1.4) of one of the chelate rings, yielding **8** plus two equivalents of trifluoroacetonitrile (CF_3CN ; confirmed via TGA-mass spectrometry). Compound **8**, 4,5-bis(trifluoromethyl)-1,3,2-diazatellurole, can be sublimed as large single crystals at room temperature.

In contrast, reaction of **2a** with SeBr_4 produces only the Se(II) analogue of **8**, 4,5-bis(trifluoromethyl)-1,3,2-diazaselenole **9**, which also sublimes readily at room temperature as large single crystals. Presumably, under the reaction conditions SeBr_4 reacts with **2a** to form the Se-analogue of **7**, which rapidly eliminates 2 equivalents of CF_3CN to yield **9**. We are studying these reactions further under low temperature conditions, and with analysis of evolved gas(es). Both **8** and **9** have been structurally characterized (see below), but we have not yet succeeded in growing x-ray quality single crystals of **7**.

Group 13 Elements (Ga, In)

Reactions of 2a with either GaBr₃ or InI₃ (eq. 4) proceed, in a stepwise manner, to formation of the desired 1,3,2-diazagallole or 1,3,2-diazaindole.

These reactions proceed rapidly at 0°C to eliminate the first equivalent of XSiMe₃ to yield 10 or 11. Presumably there is initial coordination of the imine-N to the Lewis Acid Ga or In, with essentially free rotation about the Ga-N or In-N bond to achieve the optimum geometry (4-centered transition state) for rapid dehalosilylation at 0°C. However, this intermediate, as shown below for 10, is now locked into a configuration for which the activation energy, i.e., the energy required to distort the ring to achieve a comparable 4-centered transition state, is significantly higher due to hindered rotation about the E-N (E = Ga, In) coordinate covalent bond. Thermal analysis techniques, i.e., Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC), are invaluable for probing this second dehalosilylation step. For both 10 and 11 there is a weight-loss, which by TGA corresponds to the loss of the second equivalent XSiMe₃, and this weight loss is exothermic.⁵ By interfacing a mass spectrometer⁶ with the TGA, the identity of the byproduct gas has been confirmed as BrSiMe₃ (for 10) or ISiMe₃ (for 11) by TGA-mass spectrometry.

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⁵ The exotherms are approximately 69 kcal·mol⁻¹ for 10, and approximately 56 kcal·mol⁻¹ for 11, which correspond well with Br-Si (74 kcal·mol⁻¹) and I-Si (56 kcal·mol⁻¹) bond energies. However, the precision is low (±10%) on these numbers, given the sample size (5 to 15 mg) in the DSC cell.

⁶ A Fisons MD-S00 quadrupole mass spectrometer using full scan analysis.

To reiterate, the CVD source compound research program developed under this contract and described herein offers the following advantages over existing technology:

1. A generally applicable synthetic approach that is anticipated to result in greater predictability of the chemical and physical properties of the resultant (CVD) source compounds, as well as greater predictability regarding the resultant CVD-produced films, coatings, etc.;
2. A low energy pathway for decomposition which is expected to provide access to thin films at lower temperatures than conventional precursors, and therefore cleaner film deposition processes;
3. The lack of element-to-carbon bonds, as is prevalent in many currently employed CVD precursors, with the attendant reduction of deleterious carbon contamination in the CVD-produced films; and
4. The synthetic approach(es) claimed herein provide the opportunity for construction of single-source compounds (Schemes 2, 3, 4) in which each delivered atom (E, E') is incorporated into a diazaheterole ring structure.

1.3.3 Chemical and Physical Properties of Main Group Element-Containing Diazaheteroles

When this program was initiated, one of the more important attributes that we sought to provide in the various classes of new source compounds proposed for development and evaluation was a low energy pathway for decomposition that might be inherently clean. That is, one pathway which predominates over other possible fragmentation pathways, is facile at low temperatures (< 200° to 250°C), and gives rise to gaseous byproducts that are relatively inert to secondary reactions (homogeneous or heterogeneous) that could lead to incorporation of impurities in the product thin films.

We have examined the pyrolysis chemistry of the 1,3,2-diazaheteroles described herein (E = Ga, In, As, Sb, Bi, Se, Te), using a combination of TGA/DSC (e.g., Figure 1) and TGA-mass spectrometry to characterize the nature (exothermic/endothermic, % mass loss) of the decomposition reactions and the identity of the by-product gas(es). In addition, we have conducted sealed-vessel solution-phase (solvothermal) pyrolyses, with subsequent mass spectrometric analysis of the headspace gases.

Figure 1. (a) TGA of 2-chloro-4,5-bis(trifluoromethyl)-1,3,2-diazastibole
(b) DSC of 2-chloro-4,5-bis(trifluoromethyl)-1,3,2-diazastibole (31.8 kcal·mol⁻¹ evolved in exotherm)

The picture that has emerged with regard to decomposition of the diazaheterole ring itself, and is common to all of the Main Group element heterocycles synthesized thus far and described herein, involves oxidative decoupling of the ring, with liberation of two equivalents of CF₃CN, and concomitant reduction at the metal center (eq. 5).

Although the oxidative decoupling process is depicted above as a concerted process (primarily for the purpose of visualization), according to results obtained thus far from computational chemistry this is not the case.⁷ In fact, a nonsynchronous pathway (below) is currently under investigation.

Our computational study began with optimization of the geometry of the 2-chloro-4,5-bis(trifluoromethyl)-1,3,2-diazastibole using the AM1 method, with the following criteria. The energy was minimized at the restricted Hartree-Fock level, using extensive configuration interaction, to account for the radical nature of the system. Once the output geometry was obtained, it was verified to be the minimum energy configuration by frequency analysis. The enthalpy of formation of the stibole was determined to be -259.40 kcal/mol.

⁷ All thermochemical data are the result of AM1 calculations as implemented in AMPAC® (Semichem). Diel, B. N.; Holder, A.; Andreasen, K., unpublished results.

The concerted mechanism (eq. 5) was examined using the GRID algorithm in AMPAC. The potential energy surface that was generated contained two saddle points. Each of the points was investigated to identify a transition state. The potential transition states were identified by performing a gradient minimization, followed by a frequency calculation. Neither of the saddle points yielded a transition state; the first yielded no negative eigenvalues, and the second was a complex point not corresponding to the reaction path being investigated. Our computational research efforts continue and are now focusing on identifying a nonsynchronous pathway that yields the known products of the reaction. Currently, the mechanism shown below is the favored path. It yields the desired products, with an activation barrier that seems reasonable [E_a (loss of 1st CF₃CN) = 30 kcal·mol⁻¹; ΔH_{rxn} = 10 kcal·mol⁻¹]. This reaction is being examined further to refine the transition state and continues the study of the path.

1.3.4 Chemical Vapor Deposition Studies

Metal Organic Chemical Vapor Deposition (MOCVD) is a standard technique for depositing coatings or growing thin film-layers on a substrate. In conventional MOCVD, gaseous compounds, which typically do not react at room temperature, are passed over a substrate (e.g., Si) heated to a temperature at which either the reactants decompose or combine with other constituents to form a layer on the substrate. In a typical MOCVD process, the reactant gases (often diluted in a carrier gas) at room temperature enter the reaction chamber. The gas mixture is heated as it approaches the deposition surface, heated radiatively, or placed on a heated substrate. Depending on the process and operating conditions, the reactant gases may undergo homogeneous chemical reactions in the gas phase before striking the surface. Heterogeneous reactions of the source gas(es) or reactive intermediate species (formed via homogeneous pyrolysis) occur at the deposition surface forming the deposited material. Gaseous reaction by-products are then transported out of the reaction zone.

In this research program, chemical vapor deposition reactions were examined in one of two CVD reactors. Depositions were accomplished in either (i) an inductively (Ameritherm Nova 3.0 RF generator) heated quartz cold-wall reactor (Figure 2) with infrared thermometer/temperature controller (IRCON Modline 3), or (ii) a horizontal or vertical quartz hot-walled tube reactor (Lindberg tube furnace). CVD experiments were conducted at 25°C to 600°C, both under vacuum and in the presence of H₂ (or other reactant gases as required), and over a variety of substrates (e.g., Si, glass, GaAs, etc.,

supported on ceramic stage). Product films were characterized using, at a minimum, XRD, EDS, and SEM. Precursors were introduced neat or diluted with hydrogen via a mass flow controller. Heating was accomplished using the tube furnace and temperature controller.

(a)
**Figure 2. (a) Cold-wall CVD Reactor; Graphite Stage (Susceptor)
 Surrounded by RF Coil**
 (b)
**(b) Close-Up of Reactor; Graphite Stage With Recessed Substrate Well, and
 Reactor "Throat" Where Entry Ports are Tangential to Throat Walls, Inducing a
 Vortex in Gas Flow to Ensure Uniform Deposition on Substrate Surface**

In work completed thus far, we employed experimental conditions that favored the growth of nanocrystalline (heteroepitaxial) films by using (i) higher temperatures (350°C) and (ii) lower growth rates, such that surface diffusion was fast relative to the incoming flux. Illustrated below are results (Figure 3) obtained very early in the growth process, from one arsenic precursor [2-chloro-4,5-bis(trifluoromethyl)-1,3,2-diazaarsole] deposited on glass (pyrex) and Si (100). As seen in the SEM photomicrographs, nucleation is occurring at many different points on the surface. In this type of three-dimensional island growth,⁸ these small clusters ultimately grow into islands of the film material, which eventually coalesce to form a continuous film. This growth mode occurs when the film atoms (As in this case, similarly with Sb) are more strongly bound to each other than to the substrate. These As particles appear to be crystalline; EDS shows them to be arsenic (Figure 4), and the crystals were defined by the SEM prior to XRF analysis.⁹ We are examining thicker film samples by XRD to define the crystalline form.

⁸ Referred to as Volmer-Weber growth.

⁹ That is to say they were not formed under the subsequent vacuum of the XRF instrument, nor from the mild heating ($\leq 50^\circ\text{C}$) which results from irradiation with x-rays.

**Figure 3. (a) SEM Photomicrograph of As Grains on Glass (Pyrex); Grains are Approximately 1 μm in Diameter, Image Magnification is 5000x
(b) SEM Photomicrograph of As Grains on Si(100); Image Magnification is 5000x**

**Figure 4. EDS Spectrum of Crystalline Grain (of Figure 3b) on Silicon Substrate;
Note Proportionately Strong As Peak**

Similar grains are observed for Sb-growth on glass (pyrex) substrates (Figure 5). We are also observing surface selectivity in the single-element films derived from these new precursors. In general, growth rates under identical conditions are approximately 2.5

times greater for As on glass than on Si (100), and approximately 4 times greater for Sb on glass than on Si.

**Figure 5. SEM Photomicrograph of Crystalline Sb Grain on Glass (Pyrex);
Image Magnification is 500x**

A situation that is often encountered during MOCVD operations, and has been observed/described in this research, is the presence of two or more surfaces with different reactivities towards the precursor(s). If the precursor reacts more slowly on one surface (substrate) than on another, selective CVD can occur—the different reaction rates can result from different rate-determining steps. There are numerous examples of such behavior. Although the qualitative aspects of this selectivity have been identified, no quantitative data exist for the rates of the various reactions on the initial growth and nongrowth surfaces.

1.4 Summary

To reiterate, our objectives for this research program were to develop new source compounds for the Metal Organic Chemical Vapor Deposition (MOCVD) of thin films. This includes new precursors to III-V, II-VI, Group III-nitride, metal nitride and metal phosphide, and metallic thin films. Our strategy for developing these new and improved MOCVD precursors incorporated the following four principles:

- i) A broadly applicable synthetic strategy will provide for greater predictability across the entire collection of molecular precursor compounds to be developed, with respect to decomposition kinetics and mechanism, and thin film purity profile

- ii) **Minimization of intermolecular interactions by encapsulating the Main Group element (or metal) in a sterically saturating, nonpolar ligand or chelate-ring structural environment**
- iii) **Substituent fluorination to enhance volatility**
- iv) **The molecular structure should provide a low-energy pathway for decomposition that is "inherently clean" and minimizes incorporation of impurities in the product thin films**

As we have shown through the results described herein, significant progress was made over the term of the contract toward accomplishing each of these objectives.

1.4.1 Publications/Presentations

Publication of research results was postponed initially to enable MRI to file a patent application for the research described herein. The application, entitled "Compounds for Use as Chemical Vapor Deposition Precursors, Thermochromic Materials, Light-Emitting Diodes, and Molecular Charge-Transfer Salts and Methods of Making These Compounds," was filed March 10, 1999. The subsequent patent, with 23 claims, issued August 15, 2000.

Manuscripts published, in press, submitted for publication, or in preparation include:

1. "Synthesis and Characterization of the First Examples of 1,3,2-Diazastibole and 1,3,2-Diazabismole Ring Compounds," Diel, B. N.; Hubler, T. L.; Ambacher, W. G. *Heteroatom Chemistry* 1999, 10, 423-429.
2. "Synthesis of New 2,3-Perfluoroalkyl- and 2,3-Perfluoroaryl-1,4-Diazabutadienes (α -Diimines)," Diel, B. N.; Deardorff, P. J.; Zelenski, C. M. *Tetrahedron Letters* 1999, 40, 8523-8527.
3. "Carbon-Carbon Bond Formation in the Reductive Coupling of Trifluoroacetonitrile and Pentafluorobenzonitrile. Synthetic Routes to New Perfluoroalkyl- and Perfluoroaryl-Substituted α -Diimines," Diel, B. N.; Deardorff, P. J.; Zelenski, C. M. *Inorganica Chimica Acta*, manuscript accepted for publication (November 2004).
4. "Synthesis, Characterization and Properties of Novel Main Group Element-Containing Heterocycles: 4,5-Bis(trifluoromethyl)-1,3,2-diazaheteroles Containing Ga, In, As, Sb, Bi, Se and Te," Diel, B. N.; Deardorff, P. J.; Zelenski, C. M. *Inorganic Chemistry*, manuscript submitted for publication.
5. "A New Class of Pnictogen-Containing Source Compounds for Chemical Vapor Deposition - The 4,5-Bis(trifluoromethyl)-1,4,5-pnictadiazoles," Diel, B. N.; Deardorff, P. J.; Zelenski, C. M., manuscript in preparation, to be submitted to *Chemistry of Materials*.

Presentations at professional society meetings include:

1. "Synthesis, Characterization and Application of Main Group Element-Containing Heterocycles in Materials Synthesis," Diel, B. N.; Deardorff, P. J.; Zelenski, C. M.; 217th ACS National Meeting, Anaheim, CA, March 21-25, 1999; INOR-639.
2. "Synthesis, Structure and Physical Properties of Novel Main Group Element-Containing Heterocycles: The 1,5,2-Diazaheteroles," Diel, B. N.; Deardorff, P. J.; Zelenski, C. M.; 217th ACS National Meeting, Anaheim, CA, March 21-25, 1999; INOR-508.
3. "Synthesis, Characterization and Application of Main Group Element-Containing 1,3,2-Diazaheteroles in Materials Chemistry," Diel, B. N.; Deardorff, P. J.; 216th ACS National Meeting, Boston, MA, August 23-27, 1998; INOR-545.
4. "Synthesis and Characterization of the First Examples of 1,3,2-Diazaheterole Ring Compounds," Diel, B. N.; Taylor, G. R.; Grisham, C. C. 215th ACS National Meeting, Dallas, TX, March 29-April 2, 1998; INOR-529.

1.4.2 References

1. "Synthesis and Characterization of the First Examples of 1,3,2-Diazastibole and 1,3,2-Diazabismole Ring Compounds," Diel, B. N.; Hubler, T. L.; Ambacher, W. G. *Heteroatom Chemistry* 1999, 10, 423-429; (b) "Synthesis of New 2,3-Perfluoroalkyl- and Perfluoroaryl-1,4-Diazabutadienes (α -Diimines)," Diel, B. N.; Deardorff, P. J.; Zelenski, C. M. *Tetrahedron Letters* 1999, 40, 8523-8527; (c) "Carbon-Carbon Bond Formation in the Reductive Coupling of Trifluoroacetonitrile and Pentafluorobenzonitrile. Synthetic Routes to New Perfluoroalkyl- and Perfluoroaryl-Substituted α -Diimines: Versatile Synthons for Main Group Element-Containing Heterocycle Synthesis," Diel, B. N.; Deardorff, P. J.; Zelenski, C. M. *Inorganica Chimica Acta*, manuscript accepted for publication.
2. Tuchtenhagen, G.; Rühlmann, K. Liebig's *Ann. Chem.* 1968, 711, 174; (b) Buchwald, H.; Rühlmann, K. *J. Organomet. Chem.* 1979, 166, 25. (c) Krüger, C.; Rochow, E. G.; Wannagat, U. *Chem. Ber.* 1963, 96, 2132. (d) Matsuda, I.; Takahashi, T.; Ishii, Y. *Chem. Lett.* 1977, 1457.
3. "Synthesis, Characterization and Properties of Novel Main Group Element-Containing Heterocycles: 4,5-Bis(trifluoromethyl)-1,3,2-diazaheteroles Containing Ga, In, As, Sb, Bi, Se and Te," Diel, B. N.; Deardorff, P. J.; Zelenski, C. M. *Inorganic Chemistry*, submitted for publication.
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FINANCIAL STATUS REPORT

(Short Form)

(Follow instructions on the back)

1. Federal Agency and Organizational Element to Which Report is Submitted U.S. Department of Energy		2. Federal Grant or Other Identifying Number Assigned By Federal Agency DE-FG02-96ER45603		OMB Approval No. 0348-0038	Page of pages
3. Recipient Organization (Name and complete address, including ZIP code) Midwest Research Institute 425 Volker Blvd., Kansas City, MO 64110					
4. Employer Identification Number 44-0545878		5. Recipient Account Number or Identifying Number		6. Final Report ☒ Yes ☐ No	7. Basis ☐ Cash ☒ Accrual
8. Funding/Grant Period (See instructions) From: (Month, Day, Year) 09/15/1996		To: (Month, Day, Year) 02/29/2000		9. Period Covered by this Report From: (Month, Day, Year) 09/15/1996	
				To: (Month, Day, Year) 02/29/2000	
10. Transactions:		I Previously Reported		II This Period	
				III Cumulative	
a. Total outlays				0 \$586,491.45	
b. Recipient share of outlays				0	
c. Federal share of outlays				0 \$586,491.45	
d. Total unliquidated obligations				0	
e. Recipient share of unliquidated obligations				0	
f. Federal share of unliquidated obligations				0	
g. Total Federal share (Sum of lines c and f)				\$586,491.45	
h. Total Federal funds authorized for this funding period				\$600,000.00	
i. Unobligated balance of Federal funds (Line h minus line g)				\$13,508.55	
11. Indirect Expenses		a. Type of Rate (Place "X" in appropriate box) ☐ Provisional ☐ Predetermined ☒ Final ☐ Fixed			
b. Rate See Attached		c. Base		d. Total Amount \$254,302.67	
				e. Federal Share	
12. Remarks: Attach any explanations deemed necessary or information required by Federal sponsoring agency in compliance with governing legislation.					
13. Certification: I certify to the best of my knowledge and belief that this report is correct and complete and that all outlays and unliquidated obligations are for the purposes set forth in the award documents.					
Typed or Printed Name and Title Jeanette Tombaugh, Sr. Contract Administrator				Telephone (Area code, number and extension) (816) 753-7600 ext. 1748	
Signature of Authorized Certifying Official				Date Report Submitted 6/30/04	