FOUNDED 1898
NORTHEASTERN SECTION • AMERICAN CHEMICAL SOCIETY
NESACS

THE NUCLEUS

April 2010 *Vol. LXXXVIII, No. 8*

Monthly Meeting

Esselen Award Meeting at Harvard
Award to Stephen L. Buchwald of MIT

Summer Scholar Report

By Elizabeth Neuhardt, Keene State College

ACS Scholars

By Mindy Levine

Developing Leaders

By Stefan Koenig

ACS Scholars

By Mindy Levine, Massachusetts Institute of Technology, Department of Chemistry, Cambridge, MA 02139

Shaymus Hudson is a self-proclaimed science nerd. Growing up, he watched "Bill Nye the Science Guy" on television. He studied math and science at a Governor's School for Science and Technology in rural Virginia, and did a science project at a local community college during his junior year of high school. When it was time for him to apply to college, he applied to a variety of science and technology schools, including Virginia Polytechnic Institute and Rochester Institute of Technology. Although he applied to MIT, it seemed like a stretch, both geographically and financially. Then he received a scholarship from the American Chemical Society through the ACS Scholars program, which helped him join the MIT class of 2012. "I'm very, very grateful to the American Chemical Society," Mr. Hudson said. "Every little bit helps."

Many of the Scholars interviewed agreed with Mr. Hudson that the ACS Scholars program helped them attend a university that would have been otherwise inaccessible. Merricka Livingstone was planning on attending the University of Florida. Alden Williams thought she would go to Columbia University. Thanks in part to the ACS Scholars program, both of them are currently freshmen at MIT. "I really appreciate being here, and the opportunities I have," Ms. Williams said.

Program Structure

The ACS Scholars program was established in 1995 to provide scholarships to college students from historically under-represented minority groups. "The goal is to have the students enter the chemical sciences, and to change the face of a field that historically has been dominated by white males," said Mr. Robert Hughes, manager of the ACS Scholars program since 1998.

Each year the program receives approximately 600 scholarship applications, from which 100-120 scholarships are awarded. The 20 members of the selection committee award the scholarships based solely on academic merit, with awards ranging from $1,000-$5,000 per year. Students, who are selected either during their senior year of high school or during college, major in a chemistry-related field - for example, chemistry, chemical engineering or biochemistry.

Funding Sources

The majority of the funding for the ACS Scholars program comes from the ACS itself, although some corporate and private donors contribute. More recently, the current economic climate has made it difficult to attract potential donors. Because the ACS covers all administrative and overhead costs, all donations are used directly for student scholarships.

Mentoring

Mr. Hughes partners with mentoring consultant Ms. Zaida Morales-Martinez, emeriti professors at Florida International University, to identify mentors for the program participants. "I look for people who have the three C's – committed, caring, and con-

continued on page 12

The Northeastern Section of the American Chemical Society, Inc.

Office: Anna Singer, 12 Corcoran Road, Burlington, MA 01803, 1-800-872-2054 (Voice or FAX) or 781-272-1966.
e-mail: secretary@nesacs.org
Any Section business may be conducted via the business office above.
NESACS Homepage:
http://www.NESACS.org
ACS Hotline, Washington, D.C.:
1-800-227-5558

Contents

ACS Scholars ____ 2
By Mindy Levine

Developing Leaders ____ 4
By Stefan Koenig

Monthly Meeting ____ 5
Esselen Award Meeting at Harvard.
Award to Stephen L. Buchwald, MIT

Announcements ____ 6,13
6th Annual NESACS Golf Tournament, 2010 Theodore William Richards Award for Excellence in Teaching Secondary School Chemistry, NERM 2010

Advances in Chemical Sciences Symposium ____ 7
April 9, 2010 at the Royal Sonesta, Cambridge, MA

Summer Scholar Report ____ 8
By Elizabeth Neuhardt, Keene State College, Keene, NH

Cover: *Professor Stephen L. Buchwald of the Massachusetts Institute of Technology, 2010 recipient of the Esselen Award for Chemistry in the Public Interest singing karaoke with post-doctoral fellow Tom Maimone at a group holiday party. (Photo by Xiaoxing Wu)*

Deadlines: *Summer 2010 Issue: June 15, 2010*
September 2010 Issue: July 15, 2010

THE NUCLEUS

The Nucleus is published monthly, except June and August, by the Northeastern Section of the American Chemical Society, Inc. Forms close for advertising on the 1st of the month of the preceding issue. Text must be received by the editor six weeks before the date of issue.

Editor:	Michael P. Filosa, Ph.D., ZINK Imaging, Inc., 16 Crosby Drive, Building 4G, Bedford, MA 01730 Email: Michael.filosa(at)zink.com; Tel: 508-843-9070
Associate Editors:	Myron S. Simon, 20 Somerset Rd., W. Newton, MA 02465, Tel: 617-332-5273, Sheila E Rodman, Konarka Technologies, Inc., 116 John St. Suite 12, Lowell, MA 01852 Email: srodman(at)konarka.com tel 978-569-1414, Mindy Levine, 516-697-9688 (c), 617-258-6536(w), mindy.levine(at)gmail.com
Assistant Editors:	Stefan G. Koenig, Sonia Taktak
Board of Publications:	Vivian K. Walworth (Chair), Mindy Levine, Mary Mahaney
Business Manager:	Karen Piper, 19 Mill Rd., Harvard, MA 01451, Tel: 978-456-8622
Advertising Manager:	Vincent J. Gale, P.O. Box 1150, Marshfield, MA 02050, Email: Manager-vincegale@mboservices.net; Tel: 781-837-0424
Contributing Editors:	Morton Hoffman, Feature Editor; Dennis Sardella, Book Reviews
Calendar Coordinator:	Sheila Rodman, email: srodman(at)konarka.com
Photographers:	Morton Z. Hoffman and James Phillips
Proofreaders:	Donald O. Rickter, Vivian K. Walworth, Mindy Levine
Webmaster:	Position currently open

Developing Leaders

by Stefan G. Koenig, Ph.D.

In January I had the privilege of participating in the American Chemical Society's 2010 Leadership Development Institute (LDI) in Fort Worth, TX. The invitation to partake in the Younger Chemists Committee (YCC) Leadership Development Workshop afforded me a glimpse into the efforts that ACS officials make on behalf of their membership and the chemistry enterprise as a whole. The number of programs available to benefit members is substantial, and many are geared toward adapting members to a changing global marketplace by growing their leadership capabilities. Given the current economic realities, chemists should consider these training opportunities when contemplating volunteer roles and their professional development.

The history of ACS training programs dates back 45 years and has evolved to more effectively coordinate Society activities. In recent years, local, regional, and national officers – the vast majority of whom are volunteers with full-time careers – have gathered at LDI to discuss how best to serve the membership. For 2010, this event focused on creating successful leaders by enhancing management and communication skills, demonstrating the value of volunteerism to employers, and sharing best practices. The weekend included networking events, coaching in organizational skills, and keynote lectures by the ACS presidential succession.

A newly created Leadership Development System (www.acs.org/leaderdevelopment) offers a curriculum for vocational and volunteer advancement. This comprehensive set of 17 courses is available at scheduled local, regional, and national gatherings or in a self-paced format online, anytime. Importantly, members benefit from taking courses at a discounted rate. Seven of the modules are of the online variety; the remaining ten are composed of 4-hour facilitated sessions and one advanced 8-hour capstone course. "The Extraordinary Leader" class, based on research by John H. Zenger and Joseph Folkman, described in a book of the same title, addresses key findings: (1) leaders can, in fact, be created, and (2) superior ones make an enormous difference, while (3) building strengths and (4) fixing flaws are critical.

The Younger Chemists Committee was created by ACS to address the particular needs of early-stage chemists, with a vision to foster successful careers, as well as active roles within the Society. Since 2002, YCC has selected a group of promising chemists, 35 years and younger, for the Leadership Development Award (http://membership.acs.org/y/ycc/awards/ldw.htm). Participants invited to attend the LDI explore the attributes of effective leaders, learn how to become part of the ACS hierarchy, and network with current officers. This is an excit-

continued on page 12

Corporate Patrons ($2000+)

Abbott Bioresearch
Genzyme
Lyophilization Service of New England
Merck
Novartis Institutes for Biomedical Research
Schering Corporation
Sepracor
Serono Reproductive Institute
Vertex Pharmaceuticals
Wyeth Pharmaceuticals

Patrons ($1000-$1999)

Aptuit
Broad Institute
Creagen Biosciences
Estate of Wallace Gleekman
Irix Pharmaceuticals
PCI Synthesis
Shasun USA
Sirtris Pharmaceuticals
Strem Chemicals

Donors ($300-$999)

Cambridge-Major Laboratories
Medicilon Inc
Organix
Peptech Corp
SAPA-NE

Monthly Meeting

The 905th Meeting of the Northeastern Section of the American Chemical Society

Esselen Award Meeting
Thursday, April 8, 2010

Harvard University, Cambridge, MA
Harvard Faculty Club, 20 Quincy Street

5:30 pm Social Hour

6:30 pm Dinner

8:15 pm **Award Meeting**, Mallinckrodt Building, 12 Oxford Street
Pfizer Lecture Hall (MB23), Ground Floor

Dr. John McKew, NESACS Chair, presiding

Welcome - Dr. Charles Kolb, Chair, Esselen Award Committee

The Esselen Award – Dr. Myron S. Simon, Founding Member of the Esselen Award Committee

Introduction of the Award Recipient - Dr. Timothy M. Swager, John D. MacArthur Professor of Chemistry and Department Head, Massachusetts Institute of Technology.

Presentation of the Award - Gustavus J. Esselen, IV

Palladium- and Copper-Catalyzed Processes for the Synthesis of Pharmaceutically-Relevant Molecules - Dr. Stephen L. Buchwald, Camille Dreyfus Professor of Chemistry, Massachusetts Institute of Technology.

Dinner reservations should be made no later than noon, Friday, April 2. Please call Anna Singer at (800) 872-2054 or e-mail at secretary@nesacs.org . Reservations not cancelled at least 24 hours in advance must be paid. Members, $30.00; Non-members, $35; Retirees, $20; Students, $10.

THE PUBLIC IS INVITED

Anyone who needs special services or transportation, please call Anna Singer a few days in advance so that suitable arrangements can be made.

Free Parking in the Broadway Street Garage (3rd level or higher), enter from Cambridge Street via Felton Street. Directions to the Harvard Faculty Club can be found at http://www.hfc.harvard.edu/ .

Abstract

Palladium- and Copper-Catalyzed Processes for the Synthesis of Pharmaceutically-Relevant Molecules

Cross-coupling methodology is an indispensable part of the everyday repertoire of synthetic organic chemists. In recent years, the creation of new ligands has opened the way for the discovery of catalysts with ever-increasing activity and scope. Crucial to our success in the development of new and more generally applicable methods has been the use of a new class of monodentate biaryl phosphine ligands. This lecture will detail our progress in formation of carbon-carbon, carbon-heteroatom and carbon-halogen bonds. Included will be: 1) Studies on structure-reactivity relationships of biaryl phosphine ligands and the catalyst systems based on them. 2) Mechanistic studies of both catalytic processes and stoichiometric model systems. 3) Our latest progress in the discovery of new catalysts and transformations of interest. ◇

Biography

Stephen L. Buchwald was born (1955) in Bloomington, Indiana. He received his Sc.B. degree from Brown University in 1977, where he worked with Kathlyn A. Parker and David E. Cane at Brown University, as well as Professor Gilbert Stork at Columbia University. He entered Harvard University as a National Science Foundation Predoctoral Fellow in 1977, and received his Ph.D. in 1982. His thesis work, with Jeremy R. Knowles, concerned the mechanism of phosphoryl transfer reactions in chemistry and biochemistry. He then was a Myron A. Bantrell postdoctoral fellow at Caltech with Professor Robert H. Grubbs. There he studied titanocene methylenes as reagents in organic synthesis and the mechanism of Ziegler-Natta polymerization. In 1984, he began as an assistant professor of chemistry at MIT. He was promoted to associate professor (1989) and to professor (1993) and was named the Camille Dreyfus Professor in 1997. During his time at MIT he has received numerous honors, including the Harold Edgerton Faculty Achievement Award of MIT, an Arthur C. Cope Scholar Award, the 2000 Award in Organometallic Chemistry from the American Chemical Society, and a MERIT award from the National Institutes of Health. He has also been the recipient of the Bristol-Myers Squibb Distinguished Achievement Award and the CAS Science Spotlight Award, both received in 2005, and the American Chemical Society's Award for Creative Work in Synthetic Organic Chemistry, as well as the Siegfried Medal Award in Chemical Methods which Impact Process Chemistry, both received in 2006. In 2000 he was elected as a fellow of the American Academy of Arts and Sciences, and in 2008, he was elected as a member of the National Academy of Science. He is the co-author of over 330 published or accepted papers and 41 issued patents. He was the most cited chemist in the world (per paper) during the period January 1999-June 2009. He also serves as a consultant to a number of companies. ◇

SAVE THE DATE

6th Annual

Northeastern Section of the American Chemical Society

Golf Tournament

All proceeds support NESACS programs

Wedgewood Pines Country Club

http://www.wedgewoodpines.com
Stow, MA

June 22, 2010

Shot Gun Start at 1 PM

BOX LUNCH WILL BE INCLUDED BEFORE GOLF

BBQ Dinner and Awards Immediately Following

Check our website www.nesacs.org for updates

Contact Amy Tapper (amytap@gmail.com)
to reserve a single or a foursome

Announcement

The 2010 Theodore William Richards Award for Excellence in Teaching Secondary School Chemistry

The Richards Award for excellence in teaching high school chemistry is the most prestigious award the Northeastern Section offers in recognition of outstanding, innovative, and inspired teaching at the secondary level. It is intended to honor a teacher in the Northeastern Section who, through innovation and dedication, has inspired potential chemists, has communicated chemistry to non-chemists, or has influenced other teachers of chemistry.

The criteria for excellence correspond broadly to the effectiveness with which the teacher conveys chemistry, the innovative techniques used to help students comprehend chemical concepts, his/her interaction with students, both academic and extra-curricular, and the influence a teacher has had on other teachers for promoting new approaches to teaching and learning.

The selected teacher will be officially honored and will receive both a $1,500 prize and a Certificate of Recognition at the NESACS High School Night ceremony in May, 2010.

A complete description of the award, the nomination criteria, and nomination forms can be obtained from the NESACS website at: <http://www.nesacs.org/awards_richards.htm> Nominations are due no later than April 16, 2010. Nomination forms are to be returned to

Richards Award Committee
Attention: Steve Lantos
Science Department
Brookline High School
115 Greenough Street
Brookline MA 02445

SURPRISE

our editor by calling and saying you appreciate the quality and content of our newsletter. Our editor works hard to maintain a publication of interest to our membership. Oh, and by the way you could also give credit to our advertisers who financially support us.

Fourth Annual

Advances In Chemical Sciences Symposium

sponsored by

NESACS and The Royal Society of Chemistry-US

Royal Sonesta Hotel, Cambridge, MA

9:00 a.m. April 9, 2010

This day long scientific conference will focus on
Medicinal Chemistry
Organic Synthesis
Methodology

Eminent scientists from industry and academia will deliver plenary lectures.
Confirmed Lecturers include:

Viresh Rawal, University of Chicago
Simple, Chiral Hydrogen Bond Donors as Enantioselective Catalysts

Daniel Kahne, Harvard University
How Do Cells Fold Proteins Into Membranes?.

Sarah O'Connor, MIT
Engineering and Understanding Alkaloid Biosynthesis

Mark Flanagan, Pfizer
Discovery of tasocitinib (CP-690,550): A Potent and Selective JAK Inhibitor for the Treatment of Autoimmune Diseases and Renal Allograft Rejection

Melissa Ashlock, Cystic Fibrosis Foundation Therapeutics
Peter Grootenhuis Vertex
Public Private Partnerships for Drug Development

Preliminary Announcement
The symposium will be followed by a networking reception and vendor exhibition

Symposium registration fee: $50 or $25 for Students
Vendors please contact the Organizing Committee
Attendance is Limited – Advanced Registration is REQUIRED
Please send your full contact information along with your check for $50 made payable to NESACS to
Anna Singer
Administrative Secretary, NESACS, 12 Corcoran Rd, Burlington, MA 01803

For additional details, including sponsorship and exhibition opportunities contact any of the Organizing Committee:

Chorghade@comcast.net
Scott.Cowen@Astrazeneca.com
Gurmit.Grewal@Astrazeneca.com
Gabriel.Martinez-Botella@Astrazeneca.com
Kristin.Rosner@SPcorp.com
John.McKew@gmail.com
ralphscannell@comcast.net
jamedio@seasidetherapeutics.com
rrajur@creagenbio.com
Leslie.McQuire@Novartis.com
Yanhong.Li@Pfizer.com
Bayard.Huck@EMDSerono.com
m.pollastri@neu.edu
katherinelee@yahoo/com

Summer Scholar Report

Norris-Richards Undergraduate Summer Research Scholarship Research Report

Elizabeth A. Neuhardt, Keene State College, Keene, NH 03435

Objectives: The objective of the summer research project was the investigation of the reactions of two germylene compounds with Lewis acidic vanadium chlorides in the hope of preparing the first characterized germylene complexes of an early transition metal.

Background: Germylenes are compounds that contain a divalent germanium atom.[1] Since germanium is in group 14 of the periodic table, germylene molecules are isoelectronic to carbenes (Figure 1). N-heterocyclic carbenes (NHCs) have an extensive and rich coordination chemistry; there are reports of NHC complexes of almost all of the metallic and metalloid elements in the periodic table.[2] In addition, NHCs are used extensively as ligands to support transition-metal based catalysts that effect synthetically important carbon-carbon bond-forming reactions; for example, the second generation Grubbs olefin metathesis catalyst.[3] Accordingly, the synthesis and characterization of new complexes containing NHC ligands is an expanding field of research.

Figure 1. *N-Heterocyclic Germylene (1) and N-heterocyclic Carbene (2)*

In contrast to the abundance of complexes with NHC ligands reported in the literature, the coordination chemistry of N-heterocyclic germylenes (NHGes) is severely limited. In fact, a recent search of the Cambridge Crystallographic Database for transition-metal NHGe complexes revealed that such complexes have only been characterized for the elements nickel,[4] copper,[5] silver,[6] and molybdenum.[7,8] In view of the importance of NHC complexes as efficient transition-metal catalysts for a variety of important reactions, the paucity of characterized NHGe transition-metal complexes is truly surprising.

The differences in size and nucleophilicity between the $C_{carbene}$ of an NHC and the $Ge_{germylene}$ of an NHGe may impart significant differences in both stability and reactivity to their respective complexes. It follows that NHGe complexes may have important catalytic applications complementary to their NHC analogs. The synthesis and characterization of new transition-metal complexes featuring NHGe ligands, together with a thorough investigation of their chemical properties, is therefore an important research project.

For this project it was decided to attempt the synthesis of NHGe complexes of a group 5 metal, vanadium. The starting materials chosen were: the vanadium(V) compound, vanadium oxytrichloride, $VOCl_3$, which is a viscous yellow liquid; and, the vanadium(IV) compound, vanadium tetrachloride, VCl_4, which is a viscous purple liquid. These compounds are Lewis acidic, meaning that they will readily accept lone-pairs of electrons from a donor molecule (Lewis base) to form a complex with a new coordinate covalent bond, as illustrated in Scheme 1.

Scheme 1. *The reaction of a Lewis basic molecule with the Lewis acidic VCl_4 to form an adduct complex.*

It was expected that the germylene molecules used in this study would donate the lone pairs of electrons on their germanium to the strongly Lewis acidic transition metal chloride compounds employed, thus forming new germanium-metal bonds and yielding the desired germylene complexes.

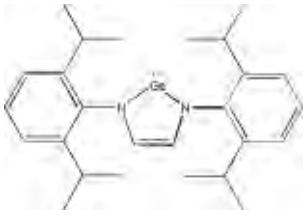
Techniques for the Manipulation of Air-sensitive Compounds

Both the germylene compounds and the transition metal halides employed react with the moisture present in the air. The reactions described below involving these species were, therefore, all conducted in dried and degassed organic solvents under argon. Solids were manipulated in an MBraun drybox filled with dry argon gas, while solutions were manipulated in Schlenk-type glassware attached to inert atmosphere/vacuum lines. Liquids were transferred between Schlenk flasks via either glass syringes or metal cannula.

Results and Discussion

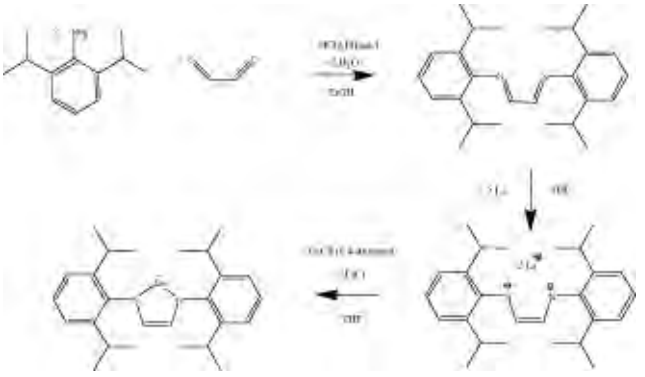
Reactions of Dipp-DAB germylene with Lewis acidic vanadium chloride compounds

Figure 2. *Dipp-DAB germylene, **1**.*



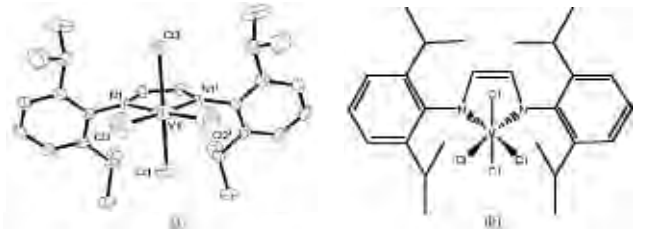
One of the easiest NHGe compounds to prepare is N,N´-bis(2,6-diisopropylphenyl)diazabutadiene germylene (Dipp-DAB germylene, **1**, Figure 2). This was synthesized by the sequence of reactions based on the published procedure (Scheme 2).[2]

Scheme 2. *Synthesis of Dipp-DAB Germylene, **1**.*



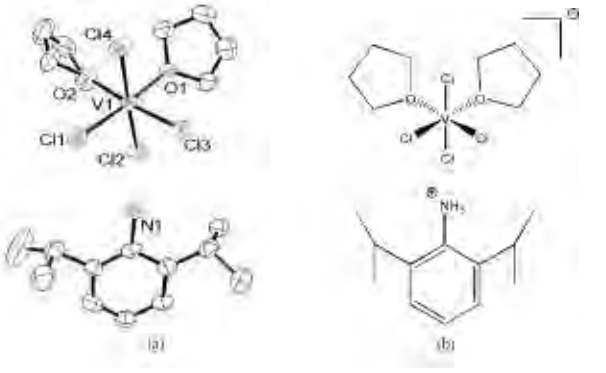
The reaction of 1 with VCl_4 in hexane.
An equimolar amount of VCl_4 was added dropwise via a syringe to an orange solution of **1** in hexane. On addition, a dark solid immediately precipitated from solution. This solid was then collected by filtration and dried under vacuum. Addition of toluene to this solid resulted in the formation of a dark purple solution with a grey precipitate, which was separated by filtration. The grey powder was insoluble in both tetrahydrofuran and chloroform and is, therefore, presumed to be elemental germanium. When the purple solution in toluene was set aside for several days, large quantities of purple crystals formed (approx. 50 % yield). The ^1H NMR spectrum ($CDCl_3$) of this material consisted of very broad overlapping resonances, consistent with the spectrum of a paramagnetic material; as expected for a vanadium(IV) containing compound. Single-crystal X-ray diffraction revealed the structure shown in Figure 3, in which the N,N´-bis(2,6-diisopropylphenyl)-diazabutadiene (Dipp-DAB) fragment of **1** has coordinated to the vanadium center through its two nitrogen atoms, forming the new distorted octahedral vanadium(IV) complex, (Dipp-DAB)VCl_4, **2**.

Figure 3. ***(a)** ORTEP drawing of **2** with 50 % probability ellipsoids for non-hydrogen atoms. **(b)** Chemdraw representation of **2**.*



The reaction of 1 with VCl_4 in toluene.
When VCl_4 was added dropwise to a toluene solution of **1**, a large amount of dark solid precipitated. This was collected by filtration and dried under vacuum. When tetrahydrofuran was added, a purple/red solution formed, leaving a grey powder, which was removed by filtration. Again, this insoluble grey material is believed to be elemental germanium. The THF solution was layered with hexane and set aside at room temperature for several days, after which time red crystals of the new ionic compound 2,6-diisopropylanilinium [*cis*-$VCl_4(thf)_2]^-$, **3,** formed (Figure 4) in approx. 30 % yield.

Figure 4. ***(a)** ORTEP drawing of **3** with 50 % probability ellipsoids for non-hydrogen atoms. **(b)** Chemdraw representation of **3**.*

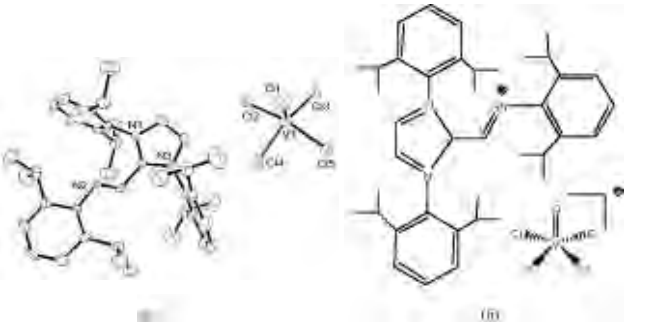


In this reaction, one of the C-N bonds of the Dipp-DAB has been cleaved and the nitrogen atom of the 2,6-diisopropylaniline fragment was produced then protonated to form the cationic species. The vanadium(IV) center of the starting material was reduced during the reaction to vanadium(III), which was coordinated by two THF molecules to afford the observed distorted octahedral complex anion, [*cis*-$VCl_4(THF)_2]^-$. This result shows that the reactions of Dipp-DAB germylenes with vanadium chlorides can be far from straightforward. Clues to the question, "What happened to the other fragment of the cleaved Dipp-DAB?" were given by the product isolated from the reaction of Dipp-DAB germylene with $VOCl_3$ described below.

The reaction of 1 with $VOCl_3$ in toluene
When $VOCl_3$ was added dropwise to a solution of **1** in toluene, a dark red solution and a grey precipitate of germanium were formed. The germanium was removed by filtration and the toluene solution was concentrated under vacuum. After standing for several days at room temperature, large quantities of bright red crystals formed. X-ray diffraction studies revealed that these crystals were an unusual and unexpected ionic product, **4** (Figure 5).

continued on page 10

Figure 5. ***(a)** ORTEP drawing of **4** with 50 % probability ellipsoids for non-hydrogen atoms. **(b)** Chemdraw representation of **4**.*



Summer Scholar

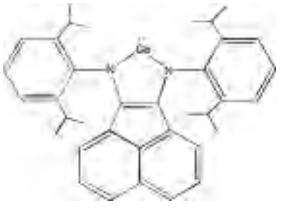
Continued from page 9

The cation in **4** is the product of the loss of germanium from **1** and cleavage of a C-N bond in the Dipp-DAB moiety. This cleavage results in the formation of a carbocation in the larger fragment, which is stabilized by the coordination of both of the nitrogen atoms of a second Dipp-DAB moiety. The formation of this 2-substituted imidazolium cation by such C-N bond cleavage in one diazabutadiene together with coordination by a second diazabutadiene is unprecedented and probably involves participation of the vanadium center. The square-pyramidal vanadium(V) anion in **4** is the product of the addition of a chloride ligand to the vanadium starting material, $VOCl_3$. This chloride must originate from the decomposition of a different $VOCl_3$ molecule; one that is, perhaps, involved in the formation of the cation described above.

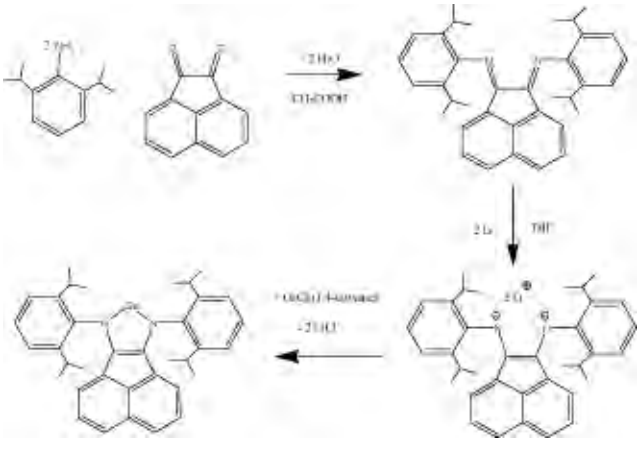
Reactions of Dipp-BIAN Germylene with Lewis acidic vanadium chloride compounds

Since the reactions described above indicated that the Dipp-DAB germylene is unstable in the presence of both VCl_4 and $VOCl_3$, a more robust germylene was then used to continue the study. A germylene based on a bis(imino)-acenaphthene (BIAN) framework, N,N´-bis(2,6-diisopropylphenylimino)acenaphthene germylene, **5** (Dipp-BIAN germylene, Figure 6), was prepared according to literature procedures (scheme 2),[9]

Figure 6. *Dipp-BIAN germylene, **5**.*



Scheme 2. *Synthesis of Dipp-BIAN germylene, **5**.*



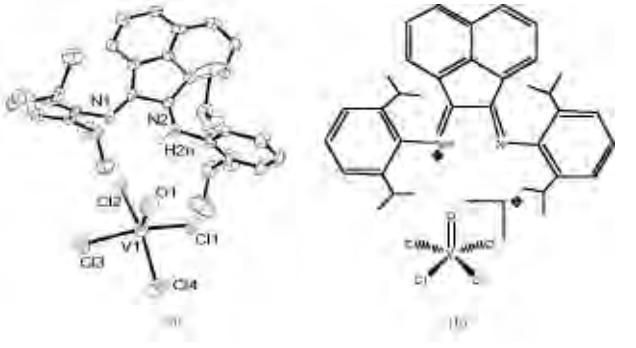
The reaction of 5 with VCl_4.

When VCl_4 was added dropwise to solutions of **5** in either toluene or hexane, intractable purple/black oily solids formed in both cases.

The reaction of 5 with $VOCl_3$ in toluene.

When $VOCl_3$ was added to a solution of **5** in toluene, a dark red solution with a grey precipitate formed. The germanium precipitate was removed by filtration and the solution was set aside at room temperature for two weeks. In that time, large quantities of dark red crystals grew. The supernatant solution was removed via cannula and the crystals dried under vacuum. X-ray diffraction analysis showed the product, **6**, to be ionic, with the structure illustrated in Figure 7. In addition to the resonances expected for the protons in the Dipp-BIAN moiety, the ^1H NMR spectrum ($CDCl_3$) of these crystals also showed a small broad resonance at 10.3 ppm consistent with the additional proton observed in the crystal structure on one of the imine nitrogens of the cation. The square-planar vanadium(V) complex anion of **5** is the same as that of **6** with very similar bond lengths and angles. In this reaction, not only was the Dipp-BIAN moiety protonated, but the $VOCl_3$ acquired an additional chloride ligand. It is possible that this was a consequence of the presence of traces of water in the toluene used as a solvent in this reaction; the presence of water would cause the formation of HCl due to hydrolysis of some of the $VOCl_3$. Such HCl present in the reaction mixture would account for both the protonation of the Dipp-BIAN and the formation of the $[VOCl_4]^-$. This reaction is still under investigation.

Figure 7. ***(a)** ORTEP drawing of **6** with 50 % probability ellipsoids for non-hydrogen atoms. **(b)** Chemdraw representation of **6**.*



Conclusions

Unfortunately, in all of the attempted reactions of NHGe molecules with Lewis acidic vanadium chloride compounds the germylene molecule decomposed with the elimination of germanium from its ligand backbone. In the case of the Dipp-DAB germylene two types of product were characterized: firstly, a molecular product where the DAB framework remained intact, which then acted as a bidentate ligand coordinating to a VCl_4 moiety; secondly, ionic products were observed in which the cations were formed from the fragmentation of the DAB framework and the anions were formed by the addition of additional chloride ligands to the vanadium center.

continued on page 11

Summer Scholar

Continued from page 10

In the case of the Dipp-BIAN reaction, the ionic product may be the result of reaction with HCl formed by the hydrolysis of some of the very moisture-sensitive $VOCl_3$ starting material.

These results seem to indicate that NHGe compounds are unstable in the presence of high-oxidation-state metal centers. It is therefore suggested that if NHGe complexes of early transition metals are to be prepared, then NHGes should be reacted with compounds in which the metal exists in a low oxidation state, for instance metal carbonyl compounds.

Acknowledgements

I am grateful to my supervisor, Dr Colin D. Abernethy (Keene State College), and to Professor Alan H. Cowley (University of Texas at Austin), for their advice and encouragement. I would also like to thank my laboratory coworkers this summer, Ms. Katherine Edes and Mr. Jeremy Zolan. Special thanks are also due to Dr. Kalyan Vasudevan (University of Texas at Austin) for collecting X-ray diffraction data and solving the structures presented in this report.

References

1) Kuhl, O. *Coord. Chem. Rev.* **2004**, *248*, 411.
2) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.
3) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.
4) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed.* **1992**, *31*, 1485.
5) York, J. T.; Young, V. G.; Tolman, W. B. *Inorg. Chem.* **2006**, *45*, 4191.
6) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3890.
7) Kuhl, O.; Lonnecke, P.; Heinicke, J. *Inorg. Chem.* **2003**, *42*, 2836.
8) Zabula, A. V.; Hahn, F. E.; Pape, T.; Hepp, A. *Organometallics* **2007**, *26*, 1972.
9) Fedushkin, I. L.; Khvoinova, N. M.; Baurin, A. Y.; Kukin, G. K.; Cherkasov, V. K.; Bubnov, M. P. *Inorg. Chem.* **2004**, *43*, 7807. ◇

ACS Scholars

Continued from page 2

cerned," said Ms. Morales-Martinez, or "Mama Z," as she is known to program participants. "I am like a mother to the students," Ms. Morales-Martinez said. "Sometimes my own kids get jealous."

Ms. Morales-Martinez is extraordinarily successful in finding mentors for the Scholars by the time they graduate from college. Of the Scholars who graduated in 2008, for example, 91% had mentors by the time of graduation. Most of the mentors are faculty members at the Scholar's college, although there are some corporate mentors as well. "The mentors are not necessarily from under-represented groups." She believes that "You don't have to be a minority to mentor a minority."

Follow-up

A key component of the Scholars program is the detailed set of records Mr. Hughes maintains on all alumni of the Scholars program. Currently, Mr. Hughes has information on 89% of the program alumni. Of the approximately 2,200 alumni, 70 have received Ph.D.s in chemistry-related fields, and an additional 180 students are enrolled in Ph.D.-granting programs. Dr. Robert Lichter, of Merrimack Consultants, LLC, who has been heavily involved in the ACS Scholars program since its inception, reported that 9 alumni are currently faculty members in the chemical sciences. This detailed information allows Mr. Hughes and Ms. Morales-Martinez to facilitate networking and communication between current and former ACS Scholars.

Event Planning

There is a limited amount of formal programming for ACS Scholars, although the Scholars are invited to attend national ACS meetings. The program provides the Scholars with a free first-year membership in the ACS, which includes a subscription to *Chemical and Engineering News*. Several of the ACS Scholars talked about how interesting they find the publication. "I read it," said Ms. Williams, "and it's so much fun."

Dr. Harry Bermudez, assistant professor of chemical engineering at the University of Massachusetts Amherst and alumnus of the ACS Scholars program, spoke about the advantages of being a member of the ACS. "There were a bunch of doors that opened just by being a member of ACS," Dr. Bermudez said. "It got me on the road to thinking about research opportunities."

All of the local ACS Scholars interviewed attended the NESACS-NIBR Town Hall Forum entitled, "The Prospects for Chemistry in the Future U.S. Economy," on February 18th. For the college freshmen, it was their first experience at a local ACS event. Nathan Nakatsuka, Harvard class of 2012, has had more opportunities to interact with the local ACS section during his almost two years as an ACS Scholar. "The Northeastern Section of ACS is amazing," Mr. Nakatsuka said. "The ACS Scholars program gives us lots of opportunities."

Many ACS Scholars expressed an interest in more programming and networking events. "I would be interested in having people from companies come and talk about what they do," said Ms. Livingstone. "Talking to people in graduate school would be helpful. So would a mixer with local ACS Scholars."

Anniversary Celebration

The ACS Scholars program will mark its 15-year anniversary in 2010. There will be anniversary events at both the spring ACS meeting in San Francisco and the fall ACS meeting in Boston. A technical symposium in San Francisco will include scientific presentations by alumni and current participants of the ACS Scholars program. In Boston, there will be a symposium that focuses on the success of the ACS Scholars program.

Future Directions

The ACS Scholars program had hoped to double the number of participants over the next five years, explained Dr. Hughes, but that plan was derailed by the difficult economic climate. "Right now the goal is just to maintain current participation," said Mr. Hughes. "Hopefully, as the economy improves, we can reevaluate things."

Dr. Bermudez is hoping to implement a research component to the program. "Now that I'm in a faculty position, I have the resources to open doors in my own research laboratories," said Dr. Bermudez, "and to invite ACS Scholars and other minority students."

"There is a long way to go until minority groups are adequately represented," Dr. Bermudez said. "Until the time that ACS decides that we've done all that we can do, there will continue to be a need for the Scholars program." ◇

Developing Leaders

Continued from page 4

ing window into the mechanism by which representatives develop the Society. Interested individuals need letters of support for their applications.

ACS is a congressionally chartered, non-profit organization with a mission "to advance the broader chemistry enterprise and its practitioners for the benefit of Earth and its people" and a vision to improve "people's lives through the transforming power of chemistry." It recognizes the evolving global chemical enterprise and, as the largest scientific society, is an authority for chemistry-related professions in the U.S. and around the world. By providing leadership training opportunities, ACS encourages members to adapt to changing times by updating their skill sets. Pursuing this available training, participating in Society volunteer roles, and using our voices to give the chemist's perspective on pertinent social, political, and business matters, will further ensure that the chemical sciences remain relevant and respected. ◇

Q. Exactly, how many awards and scholarships does NESACS sponsor?

A) One b) Two c) Many

www.nesacs.org/awards

BUSINESS DIRECTORY

Announcement

NERM2010

June 2-5, 2010

Potsdam, NY

The 2010 American Chemical Society Northeast Regional Meeting, NERM2010, will be held June 2-5, at the SUNY Potsdam campus, New York. The theme of our event is "Chemistry for a Sustainable World". Our keynote speakers, including Dr. Catherine T. Hunt (2007 ACS president) from Dow Chemical, Prof. Paul T. Anastas from Yale University and Prof. Vicki L. Colvin from Rice University, will elaborate on this theme, headlining our technical sessions on green and environmental chemistry. The meeting features 25 special symposia with particularly strong programming in physical chemistry and nanotechnology; biomedical and biochemistry; analytical chemistry; organic/medicinal chemistry; and chemical education. There will be a strong program for K-12 educators on Saturday, June 5. ACS regional meetings provide a high level of scientific discourse, excellent networking opportunities, and are a great value for the money. We invite you to visit our website: www.nerm2010.org, to learn more about our special symposia, our many distinguished invited speakers, and the wonderful social and networking events planned for this meeting. We also invite you to present your research: the meeting is open for abstract submission until April 20. ◇

Looking for seminars in the Boston area?

Check out the NESACS Calendar

www.nesacs.org/seminars

SERVICES

SERVICES

BUSINESS DIRECTORY

SERVICES

BUSINESS DIRECTORY

SERVICES

SERVICES

CAREER SERVICES

Index of Advertisers

Arendt & Associates IP Group 14
Cambrex Corporation 11
Columbia Analytical Services .13
CreaGen Biosciences 13
Eastern Scientific Co. 4
EMD.....15
Front Run OrganX, Inc. 14
Huffman Laboratories, Inc.....14
Mass Spec Services.....14
Mass-Vac, Inc. 11
Micron Inc.....14
Nacalai USA, Inc. 2
New Era Enterprises, Inc. 14
NuMega Resonance Labs 14
Organix, Inc. 14
PCI Synthesis 13
PolyOrg, Inc.....15
Rilas Technologies 13
Robertson Microlit Labs. 14
Vacuubrand, Inc. 6
Waters Corporation 15

THE NUCLEUS
19 Mill Road
Harvard, MA 01451

NONPROFIT ORG.
U.S. POSTAGE PAID
NORTHEASTERN
SECTION
AMERICAN CHEMICAL
SOCIETY

Calendar

Check the NESACS home page for late Calendar additions: http://www.NESACS.org

Note also the Chemistry Department web pages for travel directions and updates.
These include:
http://chemserv.bc.edu/seminar.html
http://www.bu.edu/chemistry/events/
http://www.chem.brandeis.edu/colloquium.shtml
http://www-chem.harvard.edu/events/
http://web.mit.edu/chemistry/
www.chem.neu.edu/web/calendar/index.html
http://chem.tufts.edu/seminars.html [CHEM.]
http://ase.tufts.edu/chemical/seminar.htm
[CHEM. ENGG.]
http://www.chem.umb.edu/
www.umassd.edu/cas/chemistry/seminars.cfm
www.uml.edu/Dept/Chemistry/speakers.html
http://www.unh.edu/chemistry/seminars.html

April 1
Dr. Lucinda Buhse (Food and Drug Administration)
Univ. New Hampshire, Room L103 11:10 am

April 5
Francois Diederich (ETH Zurich)
Harvard, Pfizer Lecture Hall 4:00 pm

April 6
Prof. Francois Diederich (ETH Zurich)
"Optoelectronic Organic Materials by New Acetylene Chemistry"
Boston College, Merkert 130 4:00 pm

Prof. Kurt Pennell, (Tufts University)
Tufts Univ., Pearson Chemistry Building, Room P-106 4:30 pm

Tom Rovis (Colorado State University)
Univ. New Hampshire,Room L103
11:10 am

April 7
Dr. Terri Camesano (Worcester Polytechnic Institute)
"Actions of Cranberry Against Uropathogenic E. coli"
UMass Dartmouth, Building Group II, Room 115 4:00 pm

Frank H. Westheimer Prize and Prize Lecture
Peter Dervan (California Institute of Technology)
Harvard, Pfizer Lecture Hall 4:00 pm

Prof. James Leighton (Columbia University)
Brandeis Univ., Gerstenzang 122 3:45 pm

Dr. Terri Camesano (Worcester Polytechnic Institute)
"Actions of Cranberry Against Uropathogenic E. coli"
UMass Dartmouth, Building Group II, Room 115 4:00 pm

April 8
Prof. Sergio Granados-Focil (Clark University)
Univ. New Hampshire, Room L103
11:10 am

April 12
Prof. Sunny Xie (Harvard University)
Brandeis Univ. Gerstenzang 122
3:45 pm

William Shih (Dana Farber Cancer Institute)
Harvard, Pfizer Lecture Hall
4:00 pm

April 13
Prof. Neil Marsh (University of Michigan)
"From frying pans to frogs: adventures with fluorinated proteins and peptides"
Boston College, Merkert 130 4:00 pm

Prof. Daniel Chiu (University of Washington)
"Physical Tools for Probing Biological Complexity at the Single-Cell Level"
Tufts Univ., Pearson Chemistry Building, Room P-106 4:30 pm

William C. Shakespear (ARIAD Pharmaceuticals, Inc.)
"AP24534, a Potent, Orally Active Multi-Targeted Kinase Inhibitor for the treatment of Chronic Myeloid Leukemia (CML)"
Univ. New Hampshire, Room L103 11:10 am

April 14
Dr. Wei Cao (Harvard Medical School/MGH)
UMass Dartmouth, Building Group II, Room 115 4:00 pm

Dr. Wei Cao (Harvard Medical School/MGH)
"Toll-like receptor 2 contributes to cardiac dysfunction and high mortality during polymicrobial sepsis."
UMass Dartmouth, Building Group II, Room 115 4:00 pm

April 15
Prof. Bruce Parkinson (University of Wyoming)
"Sensitization of TiO2 crystals to visible light using molecular dyes and quantum dot sensitizers"
Boston College, Merkert 130 4:00 pm

David Chandler (University of California, Berkeley)
"The glass transition: Order-disorder in space-time"
MIT, Room 6-120 4:00 pm

Prof. Louis Kirschenbaum (U. of Rhode Island)
Univ. New Hampshire, Room L103
11:10 am

April 16
Bristol-Myers Squibb Sponsored Lecturer
Professor Dr. Alois Fürstner (Max-Planck-Institut für Kohlenforschung)
"Tinkering with Nature's Macrolides"
Boston College, Merkert 127
4:00 pm

April 17
Bristol-Myers Squibb sponsored lecture series
Dr. Martin Eastgate (Bristol-Myers Squibb)
"Mechanistic Insight and Ligand Design in the 1,4-Oxidation of 1,3- Dienes"
Boston College, Merkert 127
10:00 am

Professor Dr. Alois Fürstner (Max-Planck-Institut für Kohlenforschung)
"A Cheap Metal for a Noble Task: Progress in Iron Catalysis"
Boston College, Merkert 127
11:15 am

April 21
Kim Dunbar (Texas A&M University)
Harvard, Pfizer Lecture Hall
4:00 pm

April 22
Chemistry and Sustainability Lecture Series
Professor Richard Eisenberg (Rochester University)
Univ. New Hampshire, Room L103
11:10 am

April 27
Professor Sir Harold Kroto (Florida State University)
"Architecture in NanoSpace"
Boston College, Merkert 127
4:00 pm

Prof. Vincent LaBella (SUNY-Albany)
Tufts Univ., Pearson Chemistry Building, Room P-106
4:30 pm

Iddles Lecture Series
Kim Janda (Scripps Research Institute)
Univ. New Hampshire, Room L103
11:10 am

April 28
Alan Heyduk (University of California, Irvine)
MIT, Room 6-120
4:00 pm

April 29
Professor Teri Odom (Northwestern University)
"Pyramidal Shells: A Platform for Designing Multifunctional Plasmonic Particles"
Boston College, Merkert 130
4:00 pm

David Walt (Tufts University)
Harvard, Pfizer Lecture Hall
4:00 pm

James Whitten (UMass Lowell)
Univ. New Hampshire, Room L103
11:10 am

Notices for The Nucleus Calendar of Seminars should be sent to:

Sheila E Rodman
Konarka Technologies, Inc.
116 John St. Suite 12,
Lowell, MA 01852
email: srodman(at)konarka.com ◇