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Phosphinosilanes and phosphino(halo)silanes [e.g. $MeSi(PH_2)_3$ and $MeSi(PH_2)Cl_2$] have been obtained which can condense with amine and borazane N-H bonds to form Si-N and B-N bonds cleanly. Polyborazane, polysilazane, and polyborosilazane 1,3,2-borodiazole [$C_6H_4(NH)_2BPh$] and 1,3,2-siladiazole [$C_6H_4(NH)_2R$, R = Me, Ph] precursors and the new $C_6H_4(NHSiPh_2)_2O$ heterocycle have been synthesized. $C_6H_4(NH)_2BPh$ and $C_6H_4(NHSiPh_2)_2O$ were analyzed by X-ray crystallography; $C_6H_4(NH)_2BPh$ has a novel structure of stacked planar molecules. Reactions of phosphinosilanes and phosphino(halo)silanes with ammonia and 1,3,2-borodiazoles to form polysilazane, polyborazane, and polyborosilazane precursors to Si_3N_4, BN, and B/Si/N ceramics have been studied.

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NEW POLYMER PRECURSORS TO BORON AND SILICON NITRIDES

Principal Investigator:
Professor Arlan D. Norman
Department of Chemistry
University of Colorado
Boulder, Colorado 80309
(303) 492-7366 office
(303) 499-9124 home

Scientific Program Officer:
Dr. Kenneth J. Wynne
Polymer and Organic Chemistry Division
Office of Naval Research, Code 1113PO
800 North Quincy Street
Arlington, VA 22217-5000
(202) 696-4409

TABLE OF CONTENTS

II. RESEARCH REPORT

I. SUMMARY

Phosphinosilanes and phosphino(halo)silanes [e.g. $MeSi(PH_2)_3$ and $MeSi(PH_2)Cl_2$] have been obtained which can condense with amine and borazane N-H bonds to form Si-N and B-N bonds cleanly. Polyborazane, polysilazane, and polyborosilazane 1,3,2-borodiazole [$C_6H_4(NH)_2BPh$] and 1,3,2-siladiazole [$C_6H_4(NH)_2R$, R = Me, Ph] precursors and the new $C_6H_4(NHSiPh_2)_2O$ heterocycle have been synthesized. $C_6H_4(NH)_2BPh$ and $C_6H_4(NHSiPh_2)_2O$ were analyzed by x-ray crystallography; $C_6H_4(NH)_2BPh$ has a novel structure of stacked planar molecules. Reactions of phosphinosilanes and phosphino(halo)silanes with ammonia and 1,3,2-borodiazoles to form polysilazane, polyborazane, and polyborosilazane precursors to Si_3N_4, BN, and B/Si/N ceramics have been studied.

II. RESEARCH REPORT

A. Introduction

The successful development of new high-technology initiatives requires the increased availability of new and improved materials,[1-3] especially ones which are highly refractory, physically and thermally shock resistant, and passive to chemical, thermal, and photochemical degradation. Clearly, future commercial and military advantage could rest with those who possess the technology to meet these stringent materials requirements.[3,4] Of the materials needed, ceramics such as BN, Si_3N_4, AlN, and SiC appear destined to play a major role.[1,5,6] Two of these, BN and Si_3N_4, have been the object of this research program.

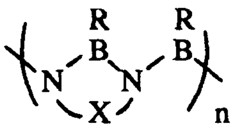
Polymeric borazanes, silazanes, and borosilazanes can be useful precusors to BN, Si_3N_4, and B/Si/N whiskers, coatings, and binders.[7-10] Although in some cases it has been possible to obtain these polymers with viscoelastic, depolymerization, and compositional properties suitable for efficient conversion to BN and Si_3N_4 ceramics,[7-10] the varieties of systems available and their application are still limited. Consequently, it is of considerable interest to examine new polymers and polymer syntheses which might lead to improved ceramic products.

The general goals of this research have been to : (1) examine new precursors to borazane, silazane and borosilazane polymers and (2) identify new polymers for conversion to BN and Si_3N_4 ceramics. To achieve these goals we have examined novel precursor systhesis, new condensation monomers, and the selective catalysis of condensation reactions. Since the project was defined as a feasibility study, approaches studied were often speculative in nature and were examined to the point of determining feasibility but were not necessarily carried to problem completion.

B. Research Conducted

1. Polymer Precursors

From the outset we have been interesed in synthesizing new cyclo-linear[11] polyborazanes, polysilazanes, and polyborosilazanes. We have sought generally one- and two-dimensional polymers and specifically skeletally stabilized systems[12,13] such as 1 - 4 (X = bridging group).



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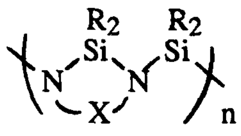

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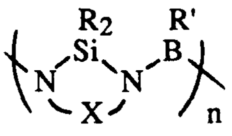

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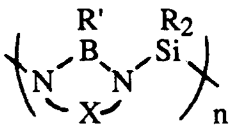

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To achieve these ends we sought new condensation reaction moieties (individual boron and/or silicon containing units) and to achieve greater insight into B-N and Si-N condensation reactions.

We have studied new classes of reactive silanes which might be used instead of halosilanes to obtain especially pure silazanes and borosilazanes. We have discovered that phosphinosilanes and phosphino(halo)silanes can be prepared and, in selected systems, appear functionally useful for synthesis of new silazanes and borosilazanes.

Several potentially important new phosphinosilanes have been made. Reactions of $LiAl(PH_2)_4$[14] with $MeSiCl_3$ and $SiCl_4$ yield the tris- and tetra-(phosphino)silanes $MeSi(PH_2)_3$[15] and $Si(PH_2)_4$ as:

$$4\,MeSiCl_3 + 3\,LiAl(PH_2)_4 \longrightarrow 3\,LiCl + 3\,AlCl_3 + 4\,MeSi(PH_2)_3 \qquad (1)$$

$$SiCl_4 + LiAl(PH_2)_4 \longrightarrow LiCl + AlCl_3 + Si(PH_2)_4 \qquad (2)$$

Secondly, from reactions of $MeSiCl_3$ and Me_2SiCl_2 with a deficiency of $LiAl(PH_2)_4$ we were suprised to find that mixed phosphino(halo) silanes (e.g. 5 and 6) can be obtained.

$$4\ \mathrm{MeSiCl_3} \xrightarrow[\text{- LiCl, AlCl}_3]{<3\ \mathrm{LiAl(PH_2)_4}} \underset{5}{\mathrm{MeSi(PH_2)Cl_2}},\ \underset{6}{\mathrm{MeSi(PH_2)_2Cl}},\ \mathrm{MeSi(PH_2)_3} \qquad (3)$$

Typically $\mathrm{MeSi(PH_2)_3}$ and $\mathrm{Si(PH_2)_4}$ form in 40 - 55 % yield. **5** and **6**, depending on reactant ratios, can be obtained in 25 - 45 % yields. Finally, from reactions of phosphido-bridged phosphinating agents (**7**) prepared by removal of $\mathrm{PH_3}$ from $\mathrm{LiAl(PH_2)_4}$ solutions,

$$2\ \mathrm{LiAl(PH_2)_4} \longrightarrow \mathrm{PH_3} + \underset{7}{\mathrm{Li_2[(PH_2)_3AlPHAl(PH_2)_3]}} \qquad (4)$$

good yields of the bis(silyl)phosphine $\mathrm{(Me_3Si)_2PH}$ have been achieved.

$$2\ \mathrm{Me_3SiCl} \xrightarrow{7} \mathrm{(Me_3Si)_2PH} \qquad (5)$$

Although many interesting reactant combinations using the new phosphinosilanes can be envisaged, only selected systems have been studied so far in order to best establish the feasibility of general use in polymer synthesis. In general, phosphinosilanes react with N-H bond functionality[16] to eliminate $\mathrm{PH_3}$ and form Si-N bonds as:

$$\geqq\mathrm{Si{-}PH_2} + \geq\mathrm{N{-}H} \longrightarrow \geqq\mathrm{Si{-}N}\leq + \mathrm{PH_3} \qquad (6)$$

This reaction produces a very clean silazane product, compared to that obtained from halosilane or aminosilane transamination reactions with amines, because the condensation elimination product $\mathrm{PH_3}$ is a highly volatile low reactivity gas which is easily completely removed from the system. We find that $\mathrm{MeSi(PH_2)_3}$ with $\mathrm{NH_3}$ proceeds at room temperature to the unstable **8**.

$$\mathrm{MeSi(PH_2)_3} + 3\ \mathrm{NH_3} \longrightarrow 3\ \mathrm{PH_3} + \underset{8}{[\mathrm{MeSi(NH_2)_3}]} \qquad (7)$$

$$\mathrm{MeSi(NH_2)_3} \xrightarrow{-\mathrm{NH_3}} \underset{9a}{\mathrm{MeSi(NH_2)_a(NH)_b}} \xrightarrow{-\mathrm{NH_3}} \underset{9b}{\{\mathrm{MeSi(NH)_c(N)_d}\}} \qquad (8)$$

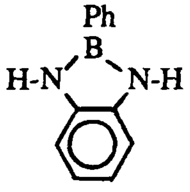
8 loses NH_3 slowly under vacuum forming gelatinous amide/imide products (**9a** , 9b) which could have potential for use in sol-gel formation of Si_3N_4. Interestingly, in the analogous $Si(PH_2)_4/NH_3$ system, there exists a unique, carbon and halide free, route to Si_3N_4 as:

$$Si(PH_2)_4 + 4\,NH_3 \longrightarrow 4\,PH_3 + [Si(NH_2)_4] \qquad (9)$$

$$3\,[Si(NH_2)_4] \longrightarrow 8\,NH_3 + Si_3N_4 \qquad (10)$$

These discoveries merit further investigation in connection with Si_3N_4 ceramic synthesis.

Although precursor 1,3,2-borodiazole **10**[17] and 1,3,2-siladiazole **11**[18] and **12**, species essential to our studies, had been reported previously they had not been unambiguously structurally characterized. Hence, **10** [from $PhB(OH)_2/1,2\text{-}(NH_2)_2C_6H_4$ reaction] was studied by single crystal x-ray analysis. Because 11 had been inadequately reported[18] and 12 was unknown, their syntheses were examined in detail.



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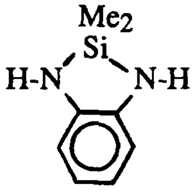

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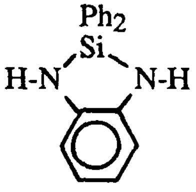

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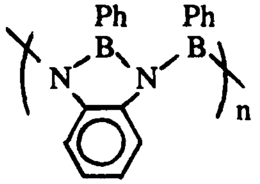
X-ray analysis of **10** reveals an interesting structure in which within experimental error the phenyl ring and the C_6N_2B ring are coplanar. In addition, in the solid the molecules are arranged in layers such that the planar units are stacked approximately parallel as a result of weak interaction between B and N atoms in adjacent layers. This packing is unique and different from what is expected by the skeletally stabilized borazanes reported recently by Neilson and coworkers.[13] This layer/stacking tendency could have a profound influence on the structures of borazane polymers which are based on a system of repeating 1,3,2-borodiazole units, e.g. as **13**. One can imagine borazane chains orienting in planar stacked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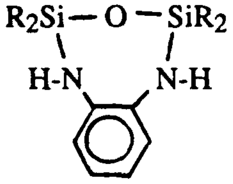
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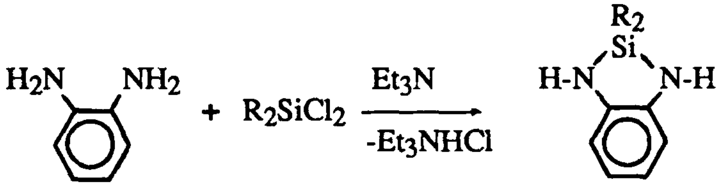
fashion in the condensed phase and in so doing producing polymers with a high degree of order. How this would affect polymer properties, especially properties necessary to make the polymer useful as a BN ceramic precursor awaits study.

The formation of 1,3,2-siladiazoles from $R_2SiCl_2/1,2-(NH_2)_2C_6H_4$ (R = Me, Ph) reactions was examined and found to be potentially more complex than recognized in the earlier reports.[18] In both cases (R = Me, Ph), reaction occurs to form the desired siladiazoles (**14**, **15**), but in competiton with formation of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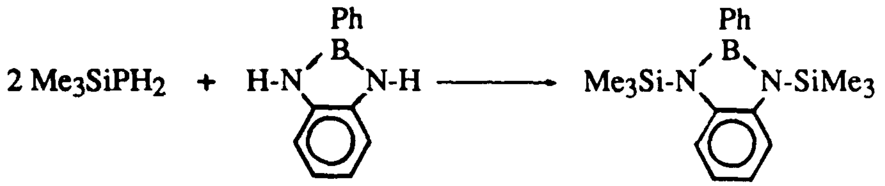
(11)

skeletally stabilized silazoxanes (**16**). The latter results when the $1,2-(NH_2)_2C_6H_4$ is not scrupulously dry. **16** (R = Ph), which we have characterized unambiguously by x-ray analysis is itself a potentially useful precursor in oxynitride ceramic synthesis, however, it was not studied further during this project.

B. Polymer Formation

Selected reactions to determine the feasibility of obtaining new skeletally stabilized polyborazanes, polysilazanes, and polyborosilazanes and to couple/bridge other systems were examined.

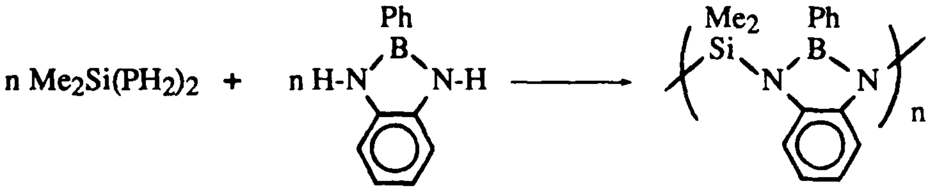
Phosphinosilanes react with 1,3,2-borodiazoles to from products tentatively characterized as borosilazanes. Me_3SiPH_2 and **10** react as:



10 **17**

(12)

The reaction in equation 13 appears tentatively to yield skeletally stabilized polyborosilazanes (**18**) as:



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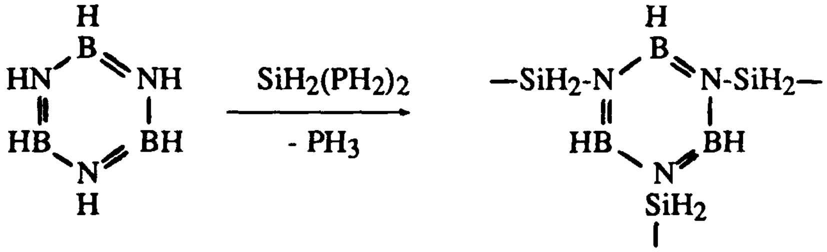
(13)

These reactions appeared catalyzed by the presence of Me_3SiCl. By extrapolation, it seems possible that phosphinosilanes could be used to bridge/couple borazines, and in so doing form cyclolinear polyborosilazanes (**19**), e.g. as:



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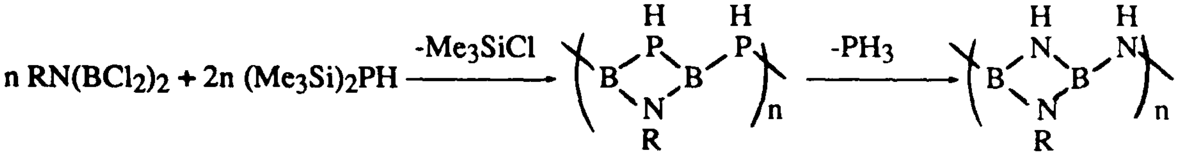
(14)

Such reactions could produce polymers free of carbon or halogen, making them unique precursors to especailly high purity B/Si/N materials.

We find that $(Me_3Si)_2PH$ reacts with boron halides upon mild heating to eliminate Me_3SiCl;

$$3n\,(Me_3Si)_2PH + 2n\,BCl_3 \longrightarrow 6n\,Me_3SiCl + [(PH)_3B_2]_n \qquad (15)$$

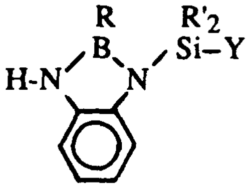
and thus is a potentially valuable reactant for the coupling of haloborane molecules in polymer formation. For example, reaction of a dihaloboryl amine with $(Me_3Si)_2PH$ could yield oligomers of type 20, which upon subsequent treatment with NH_3 might be converted to borazane oligomer/polymer precursors (21).



(16)

20 21

Polyborosilazanes of the types shown above (3 and 4) might be synthesized directly by reactions of appropriately selected diamines and difunctional boron or silicon reagents, however, they might be obtained in higher molecular weight from reactions of A-B type[19] monomers (22 and 23), species which have both moieties needed for condensation polymerization in the same molecule.



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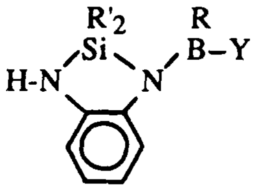


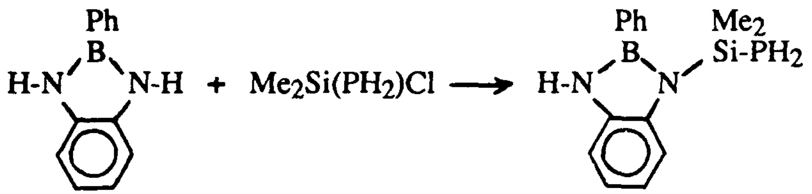
23

To this end we have studied a synthetic approach using our newly discovered phosphino-(halo)silanes. Reaction of $Me_2Si(PH_2)Cl$ with bulky alcohols and amines proceed selectively first at the Si-Cl bond and subsequently at the Si-P bond, to form products stepwise as:

$$Me_2Si(PH_2)Cl + R_2NH \longrightarrow HCl + Me_2Si(PH_2)NR_2 \qquad (17)$$

$$Me_2Si(PH_2)NR_2 + R_2NH \longrightarrow PH_3 + Me_2Si(NR_2)_2 \qquad (18)$$

In the reaction of $C_6H_4(NH)_2BPh$ (10) with $Me_2Si(PH_2)Cl$ analogous reaction occurs, to produce a product tentatively characterized as the phosphino A-B monomer 24.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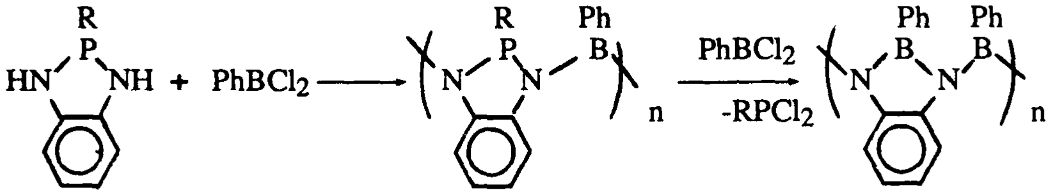
(19)

Complete characterization of **24** and its use in polymerization reactions is in progress.

Finally, a novel route to polyborazane synthesis based on haloborane/phosphadiazole exchange has been examined. Since it is known that reactions of $RBCl_2$ with 1,3,2-borodiazoles yields polymers of type **13** only with difficulty, it was thought that an alternate approach using 1,3,2-phosphadiazoles as initial skeleton forming units might have merit. Thus 1,3,2-phosphadiazoles, prepared first in our laboratories,[20] were allowed to react with $PhBCl_2$, in the expectation that initially a polyborophosphazane (**25**) might form, and then subsequently in a slower reaction step the $PhBCl_2$ units could displace the RP units as $RPCl_2$.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26

Reaction of $C_6H_4(NH)_2PMe$ with $PhBCl_2$ showed promise. Initially a high molecular weight product forms which from ^{31}P NMR still contains the phosphorus moieties in the diazole rings. Upon standing in the presence of excess $PhBCl_2$, MeP moieties appear to be displaced. Although our results are still tentative, the reaction warrants further investigation.

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20. E. G. Bent, R. Schaeffer, R. C. Haltiwanger, A. D. Norman, *Inorg. Chem.*, submitted for publication.

III. PUBLICATIONS FROM CURRENT GRANT

The following publications result (wholly or in part) from work supported by the above grant.

A. Refereed Journal Articles Published

M. L. J. Hackney, R. C. Haltiwanger, P. F. Brandt, and A. D. Norman, "A New Class of Silicon Phosphorus Heterocycles: 4-Silaphosphorinanes," *J. Organometal. Chem.*, 359, C36 (1989). Other support: National Science Foundation and Colorado Advanced Materials Institute.

B. Refereed Journal Articles Submitted

E. G. Bent, R. Schaeffer, R. C. Haltiwanger, and A. D. Norman, "Synthesis of Mono- and Di-Phosphorus Phosphazane Oligomer/Polymer Precursors", submitted for publication. Other support: National Science Foundation and Colorado Advanced Materials Institute.

P. F. Brandt, M. L. J. Hackney, and A. D. Norman, "Bis(Trimethylsilyl)Phosphine; A Synthon for Synthesis of Primary Phosphines", submitted for publication. Other support: National Science Foundation.

C. Refereed Journal Articles In Preparation

Two papers dealing with studies of synthesis and structure of 1,3,2-boradiazoles and 1,3,2-siladiazoles and studies of silylphosphine reactivity are in preparation.

D. Contibuted Presentations at Professional Meetings

P. F. Brandt, M. L. J. Hackney, D. M. Schubert, A. D. Norman, "Trimethylsilylphosphines Reaction Selectivity Towards Olefins", 196th National American Chemical Society Meeting (Fall), Los Angeles, CA; Sept 25 - 30, 1988. Other support: National Science Foundation.

IV. PROJECT MANAGEMENT

Research in connection with this research project was carried by the personnel listed in Section VI, below. Although it was originally intended that a major part of the research effort would be conducted by a postdoctoral research associate, it became clear early on that because the project was largely a feasibility study of limited duration, maximium impact could be achieved by involvement of several persons for shorter periods of time. Hence, the research effort was largely carried out by senior graduate students.

V. PERSONNEL SUPPORTED

The following persons received research support, in the form described below, from this research grant.

A. Principal Investigator : Arlan D. Norman

Partial summer salary and materials support.

B. Visiting Fellow

Professor Martin L. Thompson, Lake Forest College, Lake Forest, Illinois; faculty 1988.

C. Research Associates

Persons below recieved whole or partial stipend and/or materials support during the period 9/1/87 - 12/31/89.

1. Paul Brandt; senior Ph.D. graduate student.
2. Elizabeth Bent; senior Ph.D. graduate student.
3. Timothy Prout; senior Ph.D. graduate student.

VI. PERSONNEL CONTRIBUTING TO THE PROGRAM

1. Professor Arlan D. Norman; Principal Investigator.
2. Professor Martin L. Thompson, Lake Forest College, summer 1988 faculty research associate.
3. Professor Riley Schaeffer, University of New Mexico, sabbatical associate during 1987- 88.
4. Paul Brandt; Ph.D. degree student, Research Associate.
5. Elizabeth Bent; Ph.D. student, Research Associate.
6. Timothy Prout; Ph.D. student, Research Associate.
7. R. Curtis Haltiwanger; Chemistry Department staff x-ray crystallographer.