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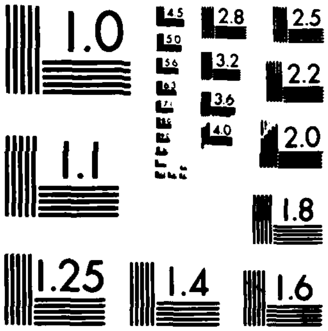

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Final Report

for

Contract N00014-78-C-0562

Task No. NR 053-686

Inorganic Polymers and the Elimination-Condensation Reaction

O. T. Beachley, Jr.
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Summary of Research Accomplishments

During the course of our research a number of new organo-aluminum, -gallium and -indium compounds have been prepared and fully characterized by elemental analyses, cryoscopic molecular weight measurements, physical properties, chemical properties, infrared and NMR spectroscopy as well as X-ray structural studies. In addition, the kinetics and mechanism of the elimination-condensation reaction, a reaction of fundamental significance to the chemistry of group 13-15 compounds, have been eludicated for several pairs of aluminum-nitrogen and -phosphorus compounds. semiconductor materials

Our synthetic studies have provided a variety of new types of compounds as well as new compounds of significance to the formation of semiconductor materials by ORGANO MOLECULAR CRYSTAL VAPOR DISPOSITION ~~OMCVD~~ and potentially by LIQUID CRYSTAL VAPORIZATION ~~LCV.~~ The first examples of transition metal derivatives of amphoteric ligands were $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$, $MesGa[MesCr(CO)_3]_2$ and $Mes_2Ga[MesCr(CO)_3]$ $Cr(CO)_5[PPh_2C_4H_8OAlR_2]$ (R=Me, Et, CH_2SiMe_3). The compounds $Al(CH_2CMe_3)_3$, $Al(CH_2CMe_3)_2H$, $Ga(CH_2CMe_3)_3$, $In(CH_2CMe_3)_3$ and $In(CH_2CMe_3)_2Me$ have been prepared and have been proposed as starting materials for MOCVD applications. A patent has been awarded for the preparation of the first four compounds in the above list. The last compound is the subject of a current patent application. The compounds of the type, R_2MPPh_2 and $R_2MPMePh$, (R=CH_2CMe_3, CH_2SiMe_3) are unique because monomeric species have been observed in solution and might be useful for LCD applications. Other new compounds are included in the attached "End-of-the-year Reports" and submitted "Technical Reports".

Our kinetic studies of the reactions of Me_2AlH with NMePhH, $N(CH_2Ph)H_2$ and PMePhH have lead to a general mechanism for the elimination of H_2 and the formation of oligomers. The important step in the mechanism of the elimination reaction involves the reaction between monomeric Me_2AlH and the Lewis base with the appropriate orientation. Before our research was

$$HMe_2Al + YMePhH \longrightarrow Me_2AlYMePh + H_{2(g)}$$

published, most chemists had assumed incorrectly that the elimination reaction was a reaction of the performed adduct.

The eight previously issued "End-of-the-Year Reports" contain appropriate lists of all Technical Reports and journal articles which have been issued during the course of our work as well as the names of all graduate students, who have participated in the research project.

End of Year Report

Inorganic Polymers and the Elimination-Condensation Reaction

Task No. NR-053-686

Contract N00014-78-C-0562

Principal Investigator: O. T. Beachley, Jr.
Department of Chemistry
State University of New York at Buffalo

Funding History:		
	July 1, 1978-February 28, 1979	$27,000
	March 1, 1979-February 28, 1980	$35,000

Description of the Project

The general objective of the project is the development of reactions for the synthesis of inorganic polymers which incorporate Group III elements and have useful electronic properties. The elimination-condensation reaction sequence should provide a route into the desired system of polymers but until the present time only small molecules (dimers) have been observed as products. Thus, the mechanism of the fundamental elimination-condensation reaction sequence for Lewis acid-base adducts will be elucidated through kinetics experiments in order to determine (1) why the dimer is the preferred product and (2) how the dimerization reaction can be prevented to permit the formation of higher polymers. The second goal of the research program is directed toward the synthesis of novel compounds which incorporate a M_T-V-M_M atom sequence (M_T-transition metal carbonyl, V-Group V main-group element derivative, M_M-main group metal derivative). These types of compounds can be envisioned to incorporate the proposed intermediate from the elimination-condensation reaction sequence, and to serve as possible catalysts and/or reactants for the formation of the desired inorganic polymers.

Significant Results

In the past year great strides have been taken toward achieving our goals of understanding the mechanism of the elimination-condensation reaction sequence for Lewis acid-base adducts and in synthesizing novel compounds with a M_T-V-M_M backbone. A specific working hypothesis for the synthesis of the desired inorganic polymers has been formulated on the basis of our experimental results. The elimination reaction occurs as a bimolecular reaction between a monomeric Lewis acid and a Lewis base. Then, two monomeric intermediates from the elimination reaction combine in a concerted cycloaddition reaction to form the observed dimeric product. Thus, the nature of the cycloaddition reaction precludes the formation of higher polymers. These conclusions suggest that high polymers might be formed if one end of the monomeric intermediate from the elimination reaction undergoes a sequential reaction instead of the observed concerted cycloaddition reaction.

Our synthetic experiments have produced the first examples of the proposed model compounds which might react sequentially with only one end of the intermediate from the elimination reaction. Preliminary characterization data have been obtained for $(CO)_5CrP(C_6H_5)_2AlBr_2$ and $(CO)_5CrP(C_6H_5)_2Al(CH_2SiMe_3)_2$. Other experiments have lead to the synthesis of a novel class of main-group, potentially nucleophilic, low oxidation state, organometallic compounds. Representative examples of this new class of compounds include $NaGa(CH_2SiMe_3)_2$ and $NaIn(CH_2SiMe_3)_2$.

Plans for Next Year's Work

Research will continue on both our kinetic studies of the elimination-condensation reaction sequence and the syntheses of model compounds with the M_T-V-M_M backbone. The kinetics experiments will be directed toward gaining a more complete understanding of the nature of the fundamental reaction sequence for a variety of Lewis acids and bases. Experiments using HMe_2Al with $N(CH_2C_6H_5)H_2$, $N(C_6H_5)H_2$ and $PMe(C_6H_5)H$ are planned.

The synthetic experiments will fully explore compounds with the M_T-V-M_M backbone. Our immediate goal is the detailed and complete characterizations of $(CO)_5M_TP(C_6H_5)_2AlBr_2$ and $(CO)_5M_TP(C_6H_5)_2Al(CH_2SiMe_3)_2$ (M_T = Cr, Mo, W). We must know the effects of the transition metal carbonyl moiety on the Lewis acidity of the terminal aluminum atom. The preparative reaction will also be extended to other transition metal and main-group metal derivatives.

The chemistry of the novel nucleophilic, organometallic anions, $Ga(CH_2SiMe_3)_2^-$ and $In(CH_2SiMe_3)_2^-$, will be explored fully. These unusual compounds have the potential to open an entirely new area of organometallic chemistry. They might even hold an important key for the eventual synthesis of a mixed oxidation state, covalent organometallic polymer.

Persons Doing Experimental Work on the Project

1. O. T. Beachley, Jr. - Principal Investigator
2. Claire Tessier-Youngs - Graduate assistant
3. Robert N. Rusinko - Graduate assistant
4. Randall G. Simmons - Graduate assistant
5. Shaun Clancy - Undergraduate assistant
6. Robert J. Bianchini - Undergraduate assistant
7. John P. Kopasz - Undergraduate assistant

List of Technical Reports and Publications

1. O. T. Beachley, Jr. and Claire Tessier-Youngs, "Kinetics and Mechanism for the Elimination of Hydrogen between Dimethylaluminum Hydride and N-Methylaniline". Technical Report; Inorg. Chem., 1979, 18, 3188.
2. O. T. Beachley, Jr. and R. G. Simmons, "The Structure of $HGaCl_2$ - A Chlorine Bridged Dimer". Technical Report; Accepted for publication in Inorganic Chemistry.
3. O. T. Beachley, Jr., and R. G. Simmons, "Preparation and Properties of ((Trimethylsilyl)methyl) gallium(III) Compounds". Technical Report; Accepted for publication in Inorganic Chemsitry.

End of Year Report

Inorganic Polymers and the Elimination-Condensation Reaction

Task No. NR-053-686

Contract N00014-78-C-0562

Principal Investigator: O. T. Beachley, Jr.
Department of Chemistry
State University of New York at Buffalo

Funding History:	July 1, 1978-February 28, 1979	$27,000
	March 1, 1979-February 28, 1980	$35,000

Description of the Project

The general objective of the project is to develop reactions which will ultimately yield inorganic polymers incorporating both main-group and transition metal elements. The elimination-condensation reaction sequence for Lewis acid-base adducts of Groups IIIB and VB should provide a route into the system of desired polymers. Therefore, the first goal in our research is to understand the nature of the mechanism of the fundamental elimination-condensation reaction for a variety of Lewis acid-base pairs. The second aspect of our experimental studies is directed toward understanding of the mode of synthesis and the nature of compounds with the atom sequence M_T-V-M_M (M_T-transition metal carbonyl, V-Group VB atom and M_M-main-group metal derivative) such as $(CO)_5M_T$-PR_2-$M_MR'_2$. The proposed synthetic routes to this type of compound will involve the addition of the main-group species to the transition-metal carbonyl-phosphorus unit or the reaction of the transition metal center with the main-group element sequence R_2P-$M_MR'_2$. All new compounds will be fully characterized by available techniques.

Significant Results

Significant progress has been made in the investigation of the mechanism of the elimination reaction and in the synthesis of compounds with the desired M_T-V-M_M atom sequence. The results of the kinetic experiments involving the Lewis acid-base pair, $HMe_2Al{-}{-}NMe\phi H$, suggest the following mechanism for the elimination reaction. The elimination of H_2 occurs as a second order reaction in which a monomeric HMe_2Al species and $NMe\phi H$ come together with the appropriate orientation. Elimination is not a unimolecular reaction of a performed adduct. The

$$1/3\ (HMe_2Al)_3 \longrightarrow HMe_2Al$$

$$HMe_2Al + NMe\phi H \underset{}{\overset{K}{\rightleftharpoons}} HMe_2AlNMe\phi H$$

$$HMe_2Al + NMe\phi H \xrightarrow{k} H_2 + Me_2AlNMe\phi \quad \text{(Rate Determining)}$$

$$Me_2AlNMe\phi \longrightarrow 1/2\ (Me_2AlNMe\phi)_2$$

$$\frac{d[H_2]}{dt} = \left(\frac{k}{1 + K\,[NMe\phi H]}\right)\ [HMe_2Al]_T[NMe\phi H]$$

$$K \sim 150\ M^{-1}$$

$$k \sim 8 \times 10^{-3}\ M^{-1}\ sec^{-1}$$

rate law is consistent with all of our kinetic observations. However, the numerical values for K and k are only preliminary and will be refined by additional experiments.

The first example of a compound of the type $Li^+(CO)_5Cr{-}P\phi_2{-}AlMe_3^-$ has been prepared from $Li^+(CO)_5P\phi_2^-$ and $(AlMe_3)_2$. Even though $Li^+(CO)_5CrP\phi_2^-$ was a known compound, we had to develop better preparative techniques than those in the literature[1] before we could study its chemistry. The nature of the interaction between this anion and $(AlMe_3)_2$ has been investigated in a variety of basic ether solvents including tetrahydrofuran, diethylether, diglyme and dimethoxyethane. Our ^1H nmr and infrared data suggest that the compound $Li^+(CO)_5CrP\emptyset_2AlMe_3^-$ exists in all of these solvents, even THF. (THF is the best solvent for the compound but THF is also the strongest Lewis base). The infrared spectral data do not suggest any bonding between aluminum and an oxygen of a CO unit. All data suggest that the aluminum is bound to the phosphorus. The atom sequence Cr-P-Al will be most interesting for further study.

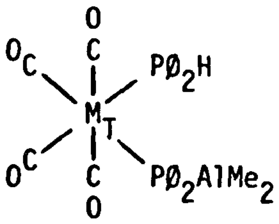
References

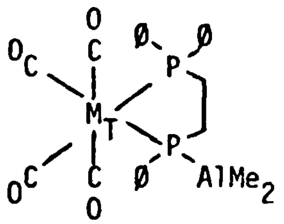
1. Treichel, P. M., Douglas, W. M., Dean, W. K., Inorg. Chem. 1972 11, 1615.

Plans for Next Year's Work

Research will continue on both major aspects of the current proposal, kinetic studies of the elimination reaction and syntheses of compounds with the M_T-V-M_M atom sequence (M_T-transition element, V-Group VB element, M_M-main-group metal derivative). The kinetic experiments will be directed toward a more complete understanding of the nature of the transition state for the elimination reaction and of the factors which influence the rate of the elimination reaction. We plan to study the rate of elimination of H_2 from HMe_2Al with $NEt\phi H$, $N\phi H_2$ and $N(CH_2\phi)H_2$. Future experiments might also include $PMe\phi H$. If time and manpower permit, we want to study the elimination reaction of other Group IIIB-VB elements pairs, particularly gallium and arsenic.

Our synthetic experiments will continue to explore compounds with the M_T-V-M_M atom sequence. Our first goal will be to learn more about the nature of $(CO)_5Cr-P\phi_2-AlMe_3^-$ and particularly $(CO)_5Cr-P\phi_2-AlMe_2$. It is important to study the Lewis acidity of the aluminum and the extended π-bonding in the Cr-P-Al atom sequence. Derivatives which incorporate gallium and/or molybdenum will also be prepared. Additional experiments will attempt to prepare and fully characterize the following compounds.





M_T = Cr, Mo

The di-substituted derivatives might have increased stability at the transition metal center.

Persons Doing Experimental Work on the Project

1. Claire T. Youngs - Graduate Student, Synthetic Chemistry, $Li^+(CO)_5Cr\text{-}P\phi_2\text{-}AlMe_3^-$
2. O. T. Beachley, Jr. - Principal Investigator, Kinetics of elimination reaction

We are currently searching for a postdoctoral associate to work on the project.

List of Technical Reports and Publications

There have been no technical reports or publications issued up to the current time. It must be realized that we were not notified that the contract had been finalized until the beginning of October, 1978.

End of Year Report 1980-81

Inorganic Polymers and the Elimination-Condensation Reaction

Task No. NR-053-686

Contract N00014-78-C-0562

Principal Investigator: O. T. Beachley, Jr.
Department of Chemistry
State University of New York at Buffalo

Funding History:	March 1, 1980 - February 28, 1981	$40,000
	March 1, 1981 - February 28, 1982	$43,000

Description of the Project

The general objective of the project is the development of reactions which might lead to the syntheses of inorganic polymers which incorporate Group III elements and have useful electronic properties. The elimination-condensation reaction sequence should provide a route into a system of polymers but small molecules (dimers) are the typical products. Thus, the mechanism of the fundamental elimination-condensation reaction sequence for Lewis acids and bases will be elucidated through kinetic experiments in order to determine (1) why the dimer is the typical product and (2) how the dimerization reaction can be prevented to permit the formation of higher polymers. The second goal of the research program is directed toward the syntheses of novel compounds. Compounds which incorporate a M_T-V-M_M and M_T-M_M-V atom sequence (M_T-transition metal carbonyl, V-Group V main-group element derivative, M_M-main-group metal derivative) can be envisioned to incorporate the proposed intermediate from the elimination-condensation reaction sequence. Low oxidation state compounds, which incorporate Group III elements in the +1 state, will also be investigated as novel reagents for the synthesis of inorganic polymers.

Significant Results

Our kinetic-mechanistic and synthetic investigations of Group III-V compounds are providing new insights into the origin of the formation of dimers, their properties in solution and their potential for the formation of inorganic polymers. Our recent kinetic studies (HMe_2Al - $N(CH_2C_6H_5)H_2$) and the earlier literature are consistent with our conclusion that the elimination reaction occurs as a bimolecular reaction between the monomeric Lewis acid and the Lewis base. The elimination reaction is not a reaction of an adduct. The adduct must first dissociate. Elimination occurs as the Lewis acid and base recombine. Our ^1H NMR studies suggest that $[Me_2AlNMe(C_6H_5)]_2$ dimers are formed by a concerted π-cycloaddition reaction but the gallium- and indium-nitrogen analogs are formed by a series of metal-nitrogen bond forming reactions.

A goal of the research program is the synthesis of compounds which incorporate a transition metal-Group V element-main-group element atom sequence (M_T-V-M_M). The first example of this class of compounds, $(CO)_5Cr-(C_6H_5)_2P-Al(CH_2SiMe_3)_2-NMe_3$ has been synthesized and fully characterized, including an X-ray crystal study. The compound is formed in quantitative yields from $Cr(CO)_5NMe_3$ and $(Me_3SiCH_2)_2AlP(C_6H_5)_2$. The synthetic key to the preparative reaction is the monomer-dimer equilibrium observed for $(Me_3SiCH_2)_2AlP(C_6H_5)_2$ in benzene solution.

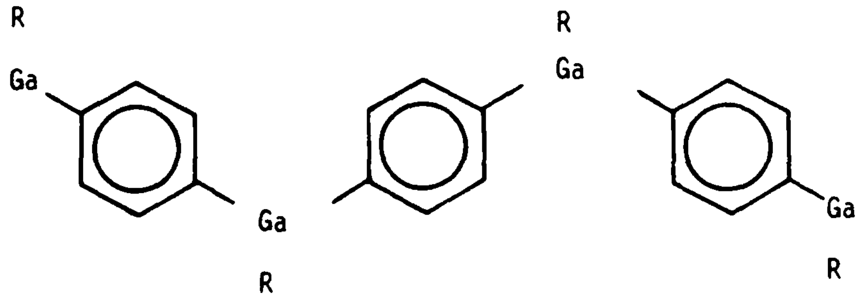
The low oxidation state main-group organometallic compound, $KGa(CH_2SiMe_3)_2$, is proving to be a novel and exceedingly useful reagent for the synthesis of unusual compounds. New compounds with Ga-Ga, Ga-Si and Ga-Ge bonds have been prepared. Many of the reactions will have utility for the proposed synthesis of an inorganic polymer.

Plans for Next Year's Work

The kinetic-mechanistic and synthetic studies will continue to explore potential routes to polymer systems. The kinetics experiments will be directed toward expanding our understanding of the effects and role of the different Lewis base atoms in the elimination reaction. Studies of reactions of $PMe(C_6H_5)H$ and alcohols with Me_2AlH or other organoaluminum hydrides will be explored. The kinetics experiments require unusual attention to the choice of reagents and reaction variables.

The goal of our synthetic work will be the synthesis and complete characterization of $(Me_3Si\text{-}CH_2)_2GaP(C_6H_5)_2$ and $(CO)_5M_T\text{-}(C_6H_5)_2P\text{-}Ga(CH_2SiMe_3)_2$ (M_T = Cr, Mo, W). We will be anxious to compare the chemistry of this Cr-P-Ga compound with the analogous Cr-P-Al derivative. These compounds are very important intermediates in our overall research plan. Consequently, their reaction chemistry will be thoroughly studied.

The chemistry of the novel main-group metal, low oxidation state anions will be explored. The characterizations of the novel compounds with unusual bonded atoms will be completed. The reaction of $KGa(CH_2SiMe_3)_2$ with phenyl iodide and p-diiodobenzene will be explored as a possible route to a polymer system of the following type.



Persons Doing Experimental Work on the Project

1. O. T. Beachley, Jr. - Principal Investigator
2. Claire Tessier-Youngs - Graduate Assistant
3. Robert N. Rusinko - Graduate Assistant
4. Randall G. Simmons - Graduate Assistant
5. Robert B. Hallock - Graduate Assistant
6. John P. Kopasz - Graduate Assistant
7. Rein N. Kirss - Undergraduate Assistant
8. Thomas D. Getman - Undergraduate Assistant

List of Technical Reports, Manuscripts and Publications.

Technical Reports

1. O. T. Beachley, Jr. and R. N. Rusinko, "Low Oxidation State, Sigma Bonded Organometallic Derivatives of Indium(I)" Inorg. Chem. 20, 1367-1370 (1981).

2. O. T. Beachley, Jr., "Kinetics and Mechanism for the Elimination of Hydrogen between Dimethylaluminum Hydride and Benzylamine". Accepted for publication in Inorganic Chemistry.

3. O. T. Beachley, Jr., C. Bueno, M. R. Churchill, R. B. Hallock and R. G. Simmons, "The Nature of the Dimethyl-aluminum, (-gallium and -indium) Methylphenylamide Dimers and the Molecular Structure of $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$". Accepted for publication in Inorganic Chemistry.

The following manuscripts have been submitted for publication but Technical Reports have not been issued

1. O. T. Beachley, Jr., C. Tessier-Youngs, R. G. Simmons and R. B. Hallock, "The Attempted Syntheses of Low Oxidation State, Organometallic Derivatives of Aluminum, Gallium and Indium, A New Synthesis of $Al(CH_2SiMe_3)_3$".

The following presentations have been given at various conferences

Gordon Conference in Inorganic Chemistry, August 2-7, 1981

"The Chemistry of Organometallic Derivatives of Main-Group Elements in Their Low Oxidation States".

X International Conference on Organometallic Chemistry, August 9-14, 1981

"Reactivity Patterns of Potassium Bis((trimethylsilyl)methyl) gallium(I), A Metal Centered Nucleophile or a Lewis Base".
O. T. Beachley, Jr., R. G. Simmons and R. B. Hallock.

End of Year Report 1981-82

Inorganic Polymers and the Elimination-Condensation Reaction

Task No. NR-053-686

Contract N00014-78-C-0562

Principal Investigator: O. T. Beachley, Jr.
Department of Chemistry
State University of New York at Buffalo

Funding History:

Funding History:	March 1, 1981 - February 28, 1982	$43,000
	March 1, 1982 - February 28, 1983	$47,000

Description of the Project

The general objective of the project is the development of reactions which might lead to the syntheses of inorganic polymers which incorporate Group III elements and have useful electronic properties. The elimination-condensation reaction sequence should provide a route into a system of polymers but small molecules (dimers) are the typical products. Thus, the mechanism of the fundamental elimination-condensation reaction sequence for Lewis acids and bases will be elucidated through kinetic experiments in order to determine (1) why the dimer is the typical product and (2) how the dimerization reaction can be prevented to permit the formation of higher polymers. The second goal of the research program is directed toward the syntheses of novel compounds. Compounds which incorporate a M_T-V-M_M and M_T-M_M-V atom sequence (M_T-transition metal carbonyl, V-Group V main-group element derivative, M_M-main-group metal derivative) can be envisioned to incorporate the proposed intermediate from the elimination-condensation reaction sequence.

Significant Results

Our understanding of the nature of the elimination-condensation reactions which occur between Group III Lewis acids and Group V Lewis bases is being enhanced by our kinetic, spectral and synthetic investigations. During the past year our efforts have concentrated on Group III-phosphorus compounds. The reaction between Me_2AlH and PMePhH in benzene at 55°C leads to the stoichiometric formation of H_2 and a tetramer $(Me_2AlPMePh)_4$. The observation of a tetramer might be significant in our search for an inorganic polymer because in every system in which a polymer has been prepared, a tetramer has been observed as a simple associated cyclic system, i.e. Me_3SiO, Cl_2PN, H_2BPMe_2, H_2BAsMe_2, SN. These observations suggest that thermodynamic effects such as bond strengths, steric effects and entropy changes will be major factors influencing association if there is a single type of kinetic process for elimination. The observed formation of the tetramer, $(Me_2AlPMePh)_4$, prompted us to study the kinetics of the elimination-condensation reactions. The preliminary initial rate data show that the elimination reaction is first order in Me_2AlH and first order in PMePhH, which suggests that the mechanism will be similar to that of our previously described Al-N systems but complicated by a variety of equilibria.

The synthetic studies have produced two fully characterized new compounds $(Me_3SiCH_2)_2GaPPh_2$ and $(Me_3SiCH_2)_2InPPh_2$, which exist as monomer-dimer equilibrium mixtures in benzene solution. These compounds, which are examples of amphoteric ligands, are being reacted with transition metal carbonyl compounds to form new types of main-group compounds.

Plans for Next Year's Work

Our plans for next year include the extensions of both our kinetic studies and the synthesis of new compounds. The investigations of the kinetics of the HMe_2Al-PMePhH system will continue because this system holds the promise of unraveling the key factors required for the formation of an inorganic polymer. Our preliminary experiments suggest that the reaction between $In(CH_2SiMe_3)_3$ and PPh_2H might be ameniable to a kinetic study so that we can determine whether the second order kinetics observed between a monomeric alane and a nitrogen or phosphorus base is applicable to the Group III derivatives of gallium and indium.

The synthetic chemistry aspects of our research will probe the variety of reactions which occur between $M(CO)_5NMe_3$ and $M(CO)_6$ (M=Cr,W) and the amphoteric ligands $(Me_3SiCH_2)_2GaPPh_2$ and $(Me_3SiCH_2)_2InPPh_2$. Our previous work has suggested that the desired compounds, such as $Cr(CO)_5PPh_2In(CH_2SiMe_3)_2 \cdot NMe_3$ are formed initially but this compound rearranges to produce a different final product. A potential route for rearrangement involves dissociation at the In-P bond, then reaction of the PPh_2^- nucleophile with a cis CO molecule. The reaction of $(Me_3SiCH_2)_2InPPh_2$ with $M(CO)_6$ (M=Cr,W) will help to define this nucleophile reaction path. Further reactions of $(Me_3SiCH_2)_2MPPh_2$ (M=Al,Ga,In) with other transition metal carbonyls such as $C_5H_5Mn(CO)_3$ or $[(C_5H_5)Mo(CO)_3]_2$ are also being planned. What appeared to be a very simple reaction in the case of preparing $Cr(CO)_5PPh_2Al(CH_2SiMe_3)_2NMe_3$ is turning out to be unusual and complicated chemistry in the cases of gallium and indium.

Persons Doing Experimental Work on the Project

1. O. T. Beachley, Jr. - Principal Investigator
2. Luis Victoriano - Postdoctoral Associate
3. Claire Tessier-Youngs - Graduate Assistant
4. Robert B. Hallock - Graduate Assistant
5. John P. Kopasz - Graduate Assistant
6. Rein N. Kirss - Graduate Assistant

List of Technical Reports, Manuscripts, Dissertations and Publications

Technical Reports

1. O. T. Beachley, Jr., C. Tessier-Youngs, R. G. Simmons and R. B. Hallock, "The Attempted Syntheses of Low Oxidation State, Organometallic Derivatives of Aluminum, Gallium and Indium, A New Synthesis of $Al(CH_2SiMe_3)_3$".

Manuscripts Submitted for Publication

1. C. Tessier-Youngs, C. Bueno, O. T. Beachley, Jr. and M. R. Churchill, "Transition Metal Complexes of Organoaluminum-Phosphides. The Synthesis, Characterization and Crystal and Molecular Structure of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$".

Publications

1. O. T. Beachley, Jr., "Kinetics and Mechanism for the Elimination of Hydrogen between Dimethylaluminum Hydride and Benzylamine". Inorg. Chem. 1981, 20, 2825.
2. O. T. Beachley, Jr., C. Bueno, M. R. Churchill, R. B. Hallock and R. G. Simmons, "The Nature of Dimethyl-aluminum, (-gallium and indium) Methylphenylamide Dimers and the Molecular Structure of $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$". Inorg. Chem. 1981, 20, 2423.
3. O. T. Beachley, Jr., C. Tessier-Youngs, R. G. Simmons and R. B. Hallock, "The Attempted Syntheses of Low Oxidation State, Organometallic Derivatives of Aluminum, Gallium and Indium, A New Synthesis of $Al(CH_2SiMe_3)_3$". Inorg. Chem. 1982, 21, 1970.

Ph.D. Dissertations

1. R. N. Rusinko, "The Syntheses of Novel Organoindium(I) Compounds and Their ((Trimethylsilyl)methyl)indium(III) Precursors". SUNY-Buffalo 1981.

2. C. Tessier-Youngs, "Transition-Metal Complexes of Organoaluminum Phosphides", SUNY-Buffalo 1981.

M.A. Dissertations

1. R. N. Kirss, "The Alkylation of Gallium by an Alkyl Cobalt Complex", SUNY-Buffalo 1982.

End of Year Report 1982-83

Inorganic Polymers and the Elimination-Condensation Reaction

Task No. NR-053-686

Contract N00014-78-C-0562

Principal Investigator: O. T. Beachley, Jr.
Department of Chemistry
State University of New York at Buffalo

Funding History:	March 1, 1982 - February 28, 1983	$47,000
	March 1, 1983 - February 28, 1984	$45,000

Description of the Project

The general objective of the project is the development of reactions which might lead to the syntheses of inorganic polymers which incorporate Group III elements and have useful electronic properties. The elimination-condensation reaction sequence should provide a route into a system of polymers but small molecules (dimers) are the typical products. Thus, the mechanism of the fundamental elimination-condensation reaction sequence for Lewis acids and bases will be elucidated through kinetic experiments in order to determine (1) why the dimer is the typical product and (2) how the dimerization reaction can be prevented to permit the formation of higher polymers. The second goal of the research program is directed toward the syntheses of novel compounds. Compounds which incorporate a M_T-V-M_M and M_T-M_M-V atom sequence (M_T-transition metal carbonyl, V-Group V main-group element derivative, M_M-main-group metal derivative) can be envisioned to incorporate the proposed intermediate from the elimination-condensation reaction sequence.

Significant Results

Significant results have been achieved in two major areas of our research. We have gained a much better understanding of the nature of the elimination and resultant condensation reactions of Group III Lewis acids with Group V Lewis bases. Secondly, our research with the initial product from the elimination reaction, $R_2III-PPh_2$, has shown this type of compound to have a varied and interesting reaction chemistry as an amphoteric ligand with transition metal compounds. The chemistry of amphoteric ligands is a fertile new area of organometallic chemistry with potentially important applications for the catalysis of olefin polymerization as well as CO, CO_2 and organic carbonyl group activation.

The elimination and condensation reactions between Me_2AlH and PMePhH in aromatic solvents have been examined in detail. The stoichiometry of the general reaction, the formulation of the product and the important mechanistic steps and kinetic constants have been identified. The experimental results are consistent with the hypothesis

$$(HAlMe_2)_3 + 3PMePhH \xrightarrow{C_6H_6} 3H_2 + (Me_2AlPMePh)_3$$

Mechanism

$$1/3\ (HAlMe_2)_3 + PMePhH \rightarrow HMe_2Al\text{-}PMePhH$$

$$HMe_2Al\text{-}PMePhH \overset{K_d}{\rightleftarrows} HMe_2Al + PMePhH$$

$$HMe_2Al + PMePhH \xrightarrow{k} H_2 + Me_2AlPMePh$$

$$Me_2AlPMePh \rightarrow \rightarrow \rightarrow (Me_2AlPMePh)_3$$

$K_d = 0.389$ M

$K_a = 2.57\ M^{-1}$

$k = 1.15 \times 10^{-4}\ M^{-1}\ s^{-1}$ at 22°C.

that dissociation of an adduct is required for elimination. These conclusions suggest that the formation of semiconductor materials such as GaAs from GaR_3 and AsH_3 might be aided by the use of more sterically demanding substituents on the gallium alkyl. Our experimental observations also suggest that the degree of association of the final product $[Me_2AlPMePh]_n$ is controlled by a balance between the change in entropy and enthalpy of the system and the kinetic stability of a given associated species is determined by the rates of dissociative reactions at the donor-acceptor bond sites. The material $[Me_2AlPMePh]$ has been observed as a trimer in benzene solution and as a higher polymer (a glass) after sublimation at 170°C. Benzene at 150°C is required to convert the polymeric glass to the trimer.

The chemistry of $(Me_3SiCH_2)_2GaPPh_2$ and $(Me_3SiCH_2)_2InPPh_2$ as amphoteric ligands to transition metal carbonyl moieties has been investigated. The reactions of these new ligands with $Cr(CO)_5NMe_3$ was attempted in order to extend our work which led to the formation of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$. However, neither $(Me_3SiCH_2)_2MPPh_2$ (M=Ga,In) reacted, surprising results. When the amphoteric ligands are combined in benzene with $Et_4NM_T(CO)_5Cl$ (which is insoluble), all components dissolve within 5 minutes. Available data suggest $Et_4NM_T(CO)_5[PPh_2M(CH_2SiMe_3)_2Cl]$ (M_T=Cr,Mo,W; M=Ga,In) are formed. The ^{31}P NMR chemical shifts and M_T-P coupling constants confirm the formation of a M_T-P bond. The origin of this unusual reactivity pattern of the amphoteric ligands and the reaction chemistry of the compounds which incorporate both main-group and transition metals is under investigation.

Plans for Next Year's Work

During the next year our plans are to continue our research on the syntheses of new compounds which might be used for making semiconductors, for studying the chemistry of amphoteric ligands and for investigating the nature of compounds which incorporate both main-group and transition metal moieties. Our kinetic studies of the elimination reaction will involve the reaction of an organoindium compound with a phosphine. The system, $InMe_3$-PMePhH, would be ideal. We will be able to compare our proposed mechanism for an aluminum-phosphorus system with the heavier Group III element, indium.

The synthetic chemistry aspects of our research will be directed toward the synthesis of $Al(CH_2CMe_3)_3$, $Al(CH_2CMe_3)_2H$, $Al(CH_2CMe_3)_2Br$, $(Me_3CCH_2)_2AlPPh_2$, $(Me_3CCH_2)_2AlPMePh$, $In(CH_2CMe_3)_3$, $In(CH_2CMe_3)_2Cl$, $(Me_3CCH_2)_2InPPh_2$, $Ga(C_5H_5)Me_2$, $Ga(C_5H_5)_2Me$ and possibly $(Me_3SiCH_2)_2$-$GaCH_2PPh_2$. These compounds can be viewed as either starting materials for preparing semiconductors or as potential amphoteric ligands. Our research on amphoteric ligand chemistry will be involved with completing studies in progress as well as starting new reactions. Our studies of the chemistry of R_2MPPh_2 (M=Al,Ga,In) with transition metal carbonyl moieties will continue. A new direction in this research will involve attempts to use main-group compounds such as $(C_5H_5)GaMe_2$ and/or $R_2MNMePh$ as amphoteric π-bonded ligands. The transition metal can be potentially bonded to double bonds or the aromatic rings in these main-group compounds. We are anticipating a very exciting year with many new results, new compounds and novel ideals for additional research.

Persons Doing Experimental Work on Project

1. O. T. Beachley, Jr. - Principal Investigator
2. Luis Victoriano - Postdoctoral Associate
3. John P. Kopasz - Graduate Assistant
4. Tommie L. Royster - Graduate Assistant

List of Technical Reports, Manuscripts, Dissertations and Publications

Technical Reports

1. C. Tessier-Youngs, C. Bueno, O. T. Beachley, Jr. and M. R. Churchill, "Transition-Metal Complexes of Organoaluminum-Phosphides. The Synthesis, Characterization and Crystal and Molecular Structure of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$".

2. O. T. Beachley, Jr. and C. Tessier-Youngs, "Synthesis and Characterization of Organoaluminum Compounds Containing the Trimethylsilylmethyl Substituent, $Al(CH_2SiMe_3)_2Br$, $Al(CH_2SiMe_3)_2H$ and $(Me_3SiCH_2)_2AlPPh_2$ and a Reinvestigation of the Chemistry of Me_2AlPPh_2 and Et_2AlPPh_2".

3. C. Tessier-Youngs, W. Youngs, O. T. Beachley, Jr. and M. R. Churchill, "The Reaction Chemistry of Transition Metal Diphenylphosphorus Complexes with Organoaluminum Compounds. The Synthesis, Characterization and Crystal and Molecular Structure of $Cr(CO)_5[PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]$, An Example of THF Cleavage".

Publications

1. C. Tessier-Youngs, C. Bueno, O. T. Beachley, Jr. and M. R. Churchill, "Transition Metal Complexes of Organoaluminum-Phosphides. The Synthesis, Characterization and Crystal and Molecular Structure of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2 \cdot NMe_3]$, Inorg. Chem. 1983, 22, 1054.

2. O. T. Beachley, Jr. and C. Tessier-Youngs, "Synthesis and Characterization of Organoaluminum Compounds Containing the Trimethylsilylmethyl Substituent, $Al(CH_2SiMe_3)_2Br$, $Al(CH_2SiMe_3)_2H$ and $(Me_3SiCH_2)_2AlPPh_2$ and a Reinvestigation of the Chemistry of Me_2AlPPh_2 and Et_2AlPPh_2", Organometallics 1983, 2, 796.

Papers Presented at Chemical Meetings

1. O. T. Beachley, Jr. and L. Victoriano, Inorganic Polymers and the Elimination-Condensation Reaction 186th National ACS Meeting, Washington, D.C. August 28-September 2, 1983.

End of Year Report 1983-84

Inorganic Polymers and the Elimination-Condensation Reaction

Task No. NR-053-686

Contract N00014-78-C-0562

Principal Investigator: O. T. Beachley, Jr.
Department of Chemistry
State University of New York at Buffalo
716-831-3266

Funding History:		
	March 1, 1984 - February 28, 1985	$50,000
	March 1, 1983 - February 28, 1984	$47,000

CONFIDENTIAL

Description of the Project

The elimination-condensation reaction which occurs between Group 3 Lewis acids and Lewis bases having an acidic proton is of fundamental importance to main-group organometallic chemistry and for the production of materials for the electronics industry. The nature of the elimination-condensation reaction is being investigated by synthetic reactions and kinetics studies in order to suggest new reagents and/or better experimental conditions. A second aspect of the research employs the product of the initial elimination reaction, an amphoteric species, as a reagent in transition metal organometallic chemistry. This research using amphoteric ligands is designed to determine the effects of the transition complex, the specific amphoteric ligand and the reaction conditions on the detailed nature of the reaction chemistry.

Significant Results

Some very interesting results have been achieved during the past year. The most important feature is the synthesis and characterization of a new series of organometallic reagents for possible semi-conductor synthesis and/or metal deposition. The new compounds include $Al(CH_2CMe_3)_3$, $Al(CH_2CMe_3)_2H$, $(CMe_3CH_2)_2AlPPh_2$, and $In(CH_2CMe_3)_3$. Disclosure statements for possible patents have been sent to the Research Foundation of SUNY and one chemical company has shown potential commercial interest in the new compounds. At the present time a screening agreement to test the usefulness of the compounds for the electronics industry is being finalized. Consequently, publication of this work has been delayed and this report must be considered confidential.

Our research on the reaction chemistry of the amphoteric ligands $(Me_3SiCH_2)_2GaPPh_2$ and $(Me_3SiCH_2)_2InPPh_2$ is continuing. Our studies of the products from the reaction of $NEt_4{}^+M_T(CO)_5Cl^-$ (M_T = Cr, Mo, W) are complete except for an X-ray structural study of $Et_4N^+Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]$. The X-ray data has been collected but the structure has not been solved. This study is necessary in order to determine whether the product involves a seven-coordinate chromium species with a four membered Cr-P-In-Cl ring (as suggested by spectroscopic data) or is a six-coordinate chromium species with a liner Cr-P-In-Cl atom sequence. Our investigation of the product from a $Mn(CO)_5Br$ and $(Me_3SiCH_2)_2GaPPh_2$ reaction suggests the formulation $Ga[Mn(CO)_4(Br)(PPh_2)]_3$. However, the solution of the X-ray data is also necessary for confirmation. Data has been collected but the structure has not been solved.

In a third area of research the solution chemistry of $(C_5H_5)_{3-n}GaMe_n$ (n

= 1,2) has been investigated. These compounds are of interest because they are useful cyclopentadienyl transfer reagents, deprotonating reagents and potential amphoteric ligands. The compound $C_5H_5GaMe_2$ reacts readily with $FeCl_2$ to form ferrocene and with $Fe_2(CO)_9$ to form $[(C_5H_5)Fe(CO)_2]_3Ga$. As a deprotonating reagent, $C_5H_5GaMe_2$ reacts at room temperature with $(C_6H_5NMeH)Cr(CO)_3$ to form $[C_6H_5NMe(GaMe_2)]Cr(CO)_3$ and C_5H_6.

A great variety of interesting chemistry has been developed but much work remains in these novel areas. The chemistry of amphoteric ligands is a new area of organometallic chemistry whose limitations are controlled only by the researcher's imagination.

Plan for Next Year's Work

During the next year our plans are to continue our research on the reaction chemistry of amphoteric ligands. Our immediate goals are to complete our studies on the structures of $NEt_4^+Cr(CO)_5[PPh_2In(CH_2SiMe_3)_2Cl]^-$ and $Ga[Ph_2PMn(CO)_4Br]_3$. We also will study the reaction between $NiBr_2$ and $(Me_3SiCH_2)_2GaPPh_2$ because the product will be an interesting molecule. Two structural possibilities exist for the product $NiBr_2[Ph_2PGa(CH_2SiMe_3)_2]_2$, either paramagnetic with tetrahedral coordination around nickel or diamagnetic with square planar coordination. It is also of interest to note that four membered Ni-Cl-P-Ga chelate rings are possible, even probable for this compound. In the project of another student, the syntheses of organogallium derivatives of ferrocene $Fe(C_5H_4GaR_2)_2$ are being investigated by studying the reactions of $Li_2(C_5H_4)_2Fe$ with two moles of $GaMe_2Cl$ or $Ga(CH_2SiMe_3)_2Cl$. If well characterized products are obtained from these reactions, the reaction of one mole of $GaRCl_2$ with one mole of $Li_2(C_5H_4)_2Fe$ will be studied to determine whether a GaR unit can bridge the two cyclopentadienyl rings bound to one iron (II) atom. All new compounds will be completely characterized incuding X-ray structural studies, if possible.

The second area of new research will require the synthesis and characterization of $R_2MCH_2PPh_2$ (M = Al, Ga, In; R = Me, CH_2SiMe_3, CH_2CMe_3) derivatives. These new compounds will enable us to compare the relative acidity, basicity and reactivity of $R_2MCH_2PPh_2$ with R_2MPPh_2. For example $Cr(CO)_5NMe_3$ reacted readily with $(Me_3SiCH_2)_2AlPPh_2$ but was unreactive to $(Me_3SiCH_2)_2GaPPh_2$. Will $(Me_3SiCH_2)_2GaCH_2PPh_2$ be a sufficiently strong acid/base to react? In additional studies, we will compare the reactivity of

$(Me_3SiCH_2)_2AlPPh_2$ with $(CMe_3CH_2)_2AlPPh_2$, which appears to be a significantly stronger acid/base.

Lastly, larger quantities of $Al(CH_2CMe_3)_3$, $Al(CH_2CMe_3)_2H$ and $In(CH_2CMe_3)_3$ will be synthesized for use in screening experiments in order to test these compounds usefulness for semiconductor synthesis and/or metal deposition. (See Significant Results).

Graduate Students and Post-doctoral Associates

Working on the Project

1. Luis Victoriano - Postdoctoral associate
2. John P. Kopasz - Graduate Assistant
3. Tommie L. Royster - Graduate Assistant
4. Michael A. Banks - Graduate Assistant

List of Technical Reports, Publication, Dissertation

and Manuscripts Issued During Last 12 Months

Publications

1. C. Tessier-Youngs, W. Youngs, O. T. Beachley, Jr. and M. R. Churchill, "The Reaction Chemistry of Transition Metal Diphenylphosphorous Complexes with Organoaluminum Compounds. The Synthesis, Characterization and Crystal and Molecular Structure of $Cr(CO)_5[PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2]$, An Example of THF Cleavage". Organometallics 1983, 2, 1128.

Manuscripts Issued for Review

1. Preparation and Properties of Cyclopentadienyl gallium(III) Compounds". O. T. Beachley, Jr. T. D. Getman, R. U. Kirss, R. B. Hallock, W. E. Hunter and J. L. Atwood, Organometallics.

Papers Presented at Chemical Meetings

1. Synthesis and Reaction Chemistry of Amphoteric Ligands. $(Me_3SiCH_2)_2MPPh_2$ (M = Ga, In).
National ACS Meeting, St. Louis, MO April 1984.

OFFICE OF NAVAL RESEARCH

PUBLICATIONS / PATENTS / PRESENTATIONS / HONORS REPORT

for

1 October 1984 through 30 September 1985

for

Contract N00014-78-C-0562

Task No. NR 053-686

Inorganic Polymers and the Elimination-Condensation Reaction

O. T. Beachley, Jr.

Department of Chemistry

State University of New York at Buffalo

Buffalo, New York 14214

Part I

a) Papers Submitted to Refereed Journals (and not yet published)

1) O. T. Beachley, Jr., R. U. Kirss, R. J. Bianchini and T. L. Royster
"Methylgallium(III) Compounds in Protic Solvents"
Organometallics

2) O. T. Beachley, Jr. and L. Victoriano
"The Elimination-Condensation Reaction Between Dimethylaluminum Hydride and Methylphenylphosphine"
Inorganic Chemistry

b) Papers Published in Refereed Journals

1) R. B. Hallock, W. E. Hunter, J. L. Atwood and O. T. Beachley, Jr.
"Synthesis, Characterization and Crystal and Molecular Structure of $Ga(CH_2SiMe_3)_3 \cdot Me_2NC_2H_4NMe_2 \cdot Ga(CH_2SiMe_3)_3$"
Organometallics 1985, 4, 547
Other support: National Science Foundation (JLA)

2) O. T. Beachley, Jr., T. D. Getman, R. U. Kirss, R. B. Hallock, W. E. Hunter and J. L. Atwood
"Synthesis, Characterization and Crystal and Molecular Structure of Tricyclopentadienylgallium(III)"
Organometallics 1985, 4, 751
Other support: National Science Foundation (JLA)

c) Sections of Books Submitted for Publication

1) O. T. Beachley, Jr. and C. Tessier-Youngs
"Trimethylsilylmethyl Lithium"
Inorganic Syntheses - Volume 24

2) O. T. Beachley, Jr. and C. Tessier-Youngs
"Tris(trimethylsilylmethyl)aluminum"
Inorganic Syntheses - Volume 24

3) O. T. Beachley, Jr. and C. Tessier-Youngs
"Bromo-bis(trimethylsilylmethyl)aluminum"
Inorganic Syntheses - Volume 24

4) O. T. Beachley, Jr. and J. P. Kopasz
"Indium Triiodide"
Inorganic Syntheses - Volume 24

5) O. T. Beachley, Jr., J. P. Kopasz and R. B. Hallock
"Tris(trimethylsilylmethyl)indium"
Inorganic Syntheses - Volume 24

d) Invited Presentations at Topical or Scientific Society Conferences

1) O. T. Beachley, Jr.
"The Effects of Bulky Ligands in Main-Group Organometallic Chemistry"
Gordon Conference on Organometallic Chemistry
Andover, N.H., August 13-17, 1984

2) O. T. Beachley, Jr.
"Approaches to Low Oxidation Organogallium Compounds"
IUPAC Congress
Manchester, England, United Kingdom
September 9-13, 1985

e) Honors/Awards/Prizes/Promotions

1) O. T. Beachley, Jr. - Promoted to full professor, State University of New York at Buffalo, Effective September 1, 1985

Part II

a) Complete Funding History

March 1, 1984 - February 28, 1985	$50,000
March 1, 1985 - February 28, 1986	$52,000
March 1, 1986 - February 28, 1987	$54,000

b) Current Telephone Number - 716-831-3266

c) Description of Project

The elimination-condensation reaction which occurs between Group 3 Lewis acids and Lewis bases having an acidic proton is of fundamental importance to main-group organometallic chemistry and for the production of materials for the electronics industry. The nature of the elimination-condensation reaction is being investigated by synthetic reactions and kinetics studies in order to suggest new reagents and/or better experimental conditions. The synthetic studies are designed to prepare typical organo - Group 3 compounds of aluminum, gallium and indium as well as novel organogallium and organoindium compounds in oxidation states less than the group number, 3. A second aspect of the research employs the product of the initial elimination reaction, an amphoteric species, as a reagent in transition metal organometallic chemistry. This research using amphoteric ligands is designed to determine the effects of the transition complex, the specific amphoteric ligand and the reaction conditions on the detailed nature of the reaction chemistry.

d) Significant Results During Last Year

Significant results have been realized in three areas of our research - (1) syntheses of new organometallic derivatives, (2) syntheses of novel low oxidation state organogallium and organoindium compounds, (3) reactions of amphoteric ligands.

(1) Synthesis of new compounds. The following new compounds have been synthesized and fully characterized - $(Me_3CCH_2)_2AlBr$, $[(Me_3CCH_2)_2AlNMeH]_2$, $Ga(mesityl)_3$, $Ga(mesityl)_2Cl$, $Ga(CH_2CMe_3)_2Cl$, $Ga(CH_2CMe_3)Cl_2$.

(2) Synthesis of new low oxidation state compounds. The first example of an organogallium(I) compound $Ga(CH_2CMe_3)$ has been synthesized. The new compound is believed to exist as a gallium cage because cryoscopic molecular weight studies in benzene suggest nine monomer units in the molecular species. Since the compound is not a crystalline solid, conformation of the molecular species is being sought by mass spectroscopic studies in collaboration with Joseph E. Campana at the Naval Research Laboratories.

The organoindium(I) compound, In(C_5Me_5), has also been recently prepared. An X-ray structural study reveals an association of six pentahaptocyclopentadienylindium(I) units in the form of a weakly bonded octahedral cluster. Future research will be designed to look for more examples of main-group metal clusters.

(3) Reactions of amphoteric ligands. The reactions of (Me_3CCH_2)$_2$InPPh$_2$ and (Me_3SiCH_2)$_2$InPPh$_2$ with Cr(CO)$_5$NMe$_3$ reveal that the neopentyl derivative is the more reactive amphoteric ligand. These observations have been interpreted to originate with the increased Lewis acidity of (Me_3CCH_2)$_2$InPPh$_2$ compared to (Me_3SiCH_2)$_2$InPPh$_2$. Similarly (Me_3SiCH_2)$_2$GaPPh$_2$ is unreactive towards Cr(CO)$_5$NMe$_3$. Our first example of another class of amphoteric ligands, (Me_3SiCH_2)$_2$GaCH$_2$PPh$_2$, has also been recently prepared.

e) Brief Summary of Plans for Next Year's Work

Our plans for this next year are designed to prepare new "simple" Group 3 compounds, to prepare new amphoteric ligands, to study the reaction chemistry of amphoteric ligands and to prepare and characterize novel low oxidation state organogallium and indium compounds.

The synthetic studies will lead to new organo - Group 3 compounds with bulky ligands such as In(CH_2CMe_3)$_2$Cl, In(CH_2CMe_3)Cl$_2$, Ga(mesityl)Cl$_2$ and In(mesityl)$_3$. These compounds as well as our previous ones with bulky ligands will enable us to prepare new amphoteric ligands such as (Me_3CCH_2)(Cl)InPPh$_2$, (Mesityl)$_2$InPEt$_2$, (Me_3CCH_2)$_2$GaCH$_2$PPh$_2$ and possibly (Me_3CCH_2)$_2$AlCH$_2$PMe$_2$. As we prepare these new amphoteric ligands, we will be looking for a system that will be amenable to kinetic studies. Our goal is to understand the elimination-condensation reaction in indium-phosphorus chemistry.

Amphoteric ligand such as (Me_3SiCH_2)$_2$GaCH$_2$PPh$_2$ will be first reacted with Cr(CO)$_5$NMe$_3$ in order to compare its reaction chemistry with (Me_3SiCH_2)$_2$GaPPh$_2$. It has been surprising but the most dominant property of the amphoteric ligand which influences its reaction chemistry appears to be the Lewis acidity. Additional experiments with this ligand will involve Fe$_2$(CO)$_9$ in an attempt to prepare Fe(CO)$_4$[PPh$_2$CH$_2$Ga(CH_2SiMe_3)$_2$]. Another class of amphoteric ligands, Ga(mesityl)$_3$, will make use of the potential basicity of the aromatic rings toward M(CO)$_3$(M=Co,Mo,W) moieties. The resulting compounds should have increased acidic properties at the gallium atom.

Our experiments in low oxidation state chemistry will be used to further characterize [Ga(CH_2CMe_3)]$_9$ by oxidation experiments with HgCl$_2$, AgOAc and I$_2$. The unusual property of In(C_5Me_5) that dissolution in benzene leads to the formation of indium metal and (C_5Me_5)$_2$ will be studied more completely. Lastly, new compounds such as In(C_5H_4Me), In[C_5H_2(SiMe$_3$)$_3$] and In(C_5H_5) will be synthesized and fully characterized. Our goal is to determine whether organoindium clusters exist according to the crystal structures of these compounds.

f) <u>Graduate students currently working on project</u>

J. P. Kopasz
J. C. Pazik
T. L. Royster
M. A. Banks
E. F. Spiegel

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

Contract N00014-78-C-0562

Task No. NR 053-686

Inorganic Polymers and the Elimination-Condensation Reaction

O. T. Beachley, Jr.

Department of Chemistry

State University of New York at Buffalo

Buffalo, New York 14214

(1 October 1985 through 30 September 1986)

Part I.

a. Papers Submitted to Refereed Journals (and not yet published)

1. O. T. Beachley, Jr., J. P. Kopasz; H. Zhang; W. E. Hunter; J. L. Atwood, "Synthesis and Characterization of Amphoteric Ligands Including the Crystal and Molecular Structure of $[(Me_3SiCH_2)_2InPPh_2]_2$", J. Organometallic Chemistry, NSF (J. L. Atwood) (accepted for publication).

2. O. T. Beachley, Jr.; M. R. Churchill; J. C. Pazik; J. W. Ziller, "Synthesis, Characterization and Crystal and Molecular Structure of Trimesitylgallium(III)", Organometallics (accepted for publication).

3. O. T. Beachley, Jr.; R. B. Hallock, "The Synthesis of Tris(pentamethylcyclopentadienyl)gallium(III)", Organometallics (accepted for publication).

b. Papers Published in Refereed Journals

1. O. T. Beachley, Jr.; M. R. Churchill; J. C. Fettinger; J. C. Pazik; L. Victoriano, "Synthesis and Crystal and Molecular Structure of $In(C_5Me_5)$-An Apparent Octahedral Cluster", J. Am. Chem. Soc. 1986, 108, 4666.

2. O. T. Beachley, Jr.; L. Victoriano, "The Elimination-Condensation Reaction Between Dimethylaluminum Hydride and Methylphenylphosphine" Inorg. Chem. 1986, 25, 1948.

c. Books (and sections thereof) Published

1. O. T. Beachley, Jr.; C. Tessier-Youngs, "Trimethylsitylmethyl Lithium", Inorganic Syntheses 1986, 24, 95.

2. O. T. Beachley, Jr.; C. Tessier-Youngs, "Tris(trimethylsilylmethyl)aluminum", Inorganic Syntheses 1986, 24, 92.

3. O. T. Beachley, Jr.; C. Tessier-Youngs, "Bromo-bis(trimethylsilylmethyl)aluminum", Inorganic Syntheses 1986, 24, 94.

4. O. T. Beachley, Jr.; J. P. Kopasz; R. B. Hallock, "Tris(trimethylsilylmethyl) indium", Inorganic Syntheses 1986, 24, 89.

5. O. T. Beachley, Jr.; J. P. Kopasz, "Indium Triiodide", Inorganic Syntheses 1986, 24, 87.

d. Invited Presentations at Topical or Scientific/Technical Society Conferences

1. O. T. Beachley, Jr.; "Low Oxidation State Main-Group Organometallic Chemistry"; Central Regional ACS Meeting, Bowling Green University, June 3, 1986.

e. Contributed Presentations at Topical or Scientific/Technical Society Conferences

1. O. T. Beachley, Jr.; J. C. Pazik; L. Victoriano; "Pentamethylcyclopentadienyl Indium Chemistry", National ACS Meeting, New York, April 1986.

2. O. T. Beachley, Jr.; T. L. Royster; "Trimesitylgallium(III)-A New Amphoteric Ligand to Some Transition Metal Carbonyls", National ACS Meeting, New York, April 1986.

f. Graduate Students Receiving Full or Partial Support on ONR Contract - 5

1. T. L. Royster
2. M. A. Banks
3. J. C. Pazik
4. J. D. Maloney
5. J. P. Kopasz

Part II.

a. Principal Investigator: O. T. Beachley, Jr.

b. Cognizant ONR Scientific Officer: Harold E. Guard

c. Current Telephone Number: 716-831-3266

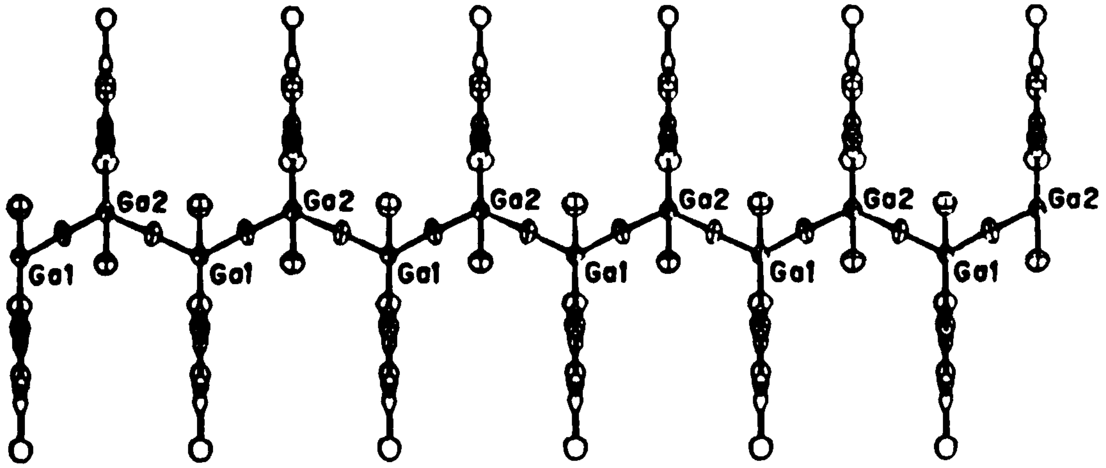
d. Brief Description of Project:

The elimination-condensation reaction which occurs between group 3 Lewis acids and Lewis bases having an acidic proton is of fundamental importance to main-group organometallic chemistry and for the production of materials for the electronics industry. The nature of the elimination-condensation reaction is being investigated by synthetic reactions and kinetics studies in order to suggest new reagents and/or better experimental conditions. The synthetic studies are designed to prepare typical organo-group 3 compounds of aluminum, gallium and indium as well as novel organogallium and organoindium compounds in oxidation states less than the group number, 3. A second aspect of the research employs the product of the initial elimination reaction, an amphoteric species, as a reagent in transition metal organometallic chemistry. This research using amphoteric ligands is designed to determine the effects of the transition metal, the specific amphoteric ligand and the reaction conditions on the detailed nature of the reaction chemistry.

e. Significant Results of Last Year:

Significant results have been realized in three areas of our research - (1) synthesis and characterization of new simple organometallic compounds, (2) synthesis of new amphoteric ligands, (3) synthesis of new transition metal derivatives of amphoteric ligands.

(1) Synthesis and characterization of new compounds. The following new compounds have been synthesized-$In(C_5Me_5)_2Cl$, $In(C_5Me_5)Cl_2$, $Ga(mesityl)Cl_2$ and $In(C_5H_4Me)$. An X-ray structural study of $Ga(mesityl)Cl_2$ reveals the existence an extended polymer with a gallium-chlorine background. This structure represents the first example of its type in group 3 chemistry.



$Ga(mesityl)Cl_2$

(2) Synthesis of new amphoteric ligands. The new compounds of the type $R_2MCH_2PPh_2$ (M=Ga, In; R=CH_2SiMe_3, CH_2CMe_3) have been prepared and characterized. These new compounds exist as dimers with six-membered rings and interact readily with NMe_3 in benzene as indicated by ^1H NMR spectra.

(3) Synthesis of new transition metal derivatives of amphoteric ligands. Compounds such as Ga(mesityl)$_3$ have the potential to act as amphoteric ligands to transition metals.[3] The mesityl ligand acts as a pi-electron donor and the gallium atom can be a Lewis acid. This amphoteric ligand potential has been realized by the synthesis and X-ray structural study of mesitylGa[mesityl-Mo(CO)$_3$]$_2$. The compound (mesityl)$_2$Ga[mesityl-Mo(CO)$_3$] has also been prepared.[3] In addition the chloro derivatives ClGa[MesMo(CO)$_3$]$_2$ and Cl$_2$Ga[MesMo(CO)$_3$] have been prepared and characterized.[3]

The new amphoteric ligand $R_2MCH_2PPh_2$(M=Ga, In; R=CH_2SiMe_3, Ch_2CMe_3) has been observed to react readily with $Cr(CO)_5NMe_3$ according to ^{31}P and ^1H NMR spectra. These observations suggest that $R_2MCH_2PPh_2$ is a much more reactive ligand than the related ligand R_2MPPh_2.

f. Summary of Plans for Next Year's Work:

Our plans for this next year are designed to continue the progress which we have made this year and to initiate some new projects.

1) Synthesis and characterization of new compounds. Attempts will be initiated to prepare a variety of new organoindium compounds including In(mesityl)$_3$, In(mesityl)$_2$Cl and In(mesityl)Cl$_2$, In($C_5H_4SiMe_3$), (Me_3CCH_2)InPMePh and (mesityl)$_2$GaPPh$_2$. One reason for preparing (mesityl)$_2$GaPPh$_2$ originates with our hypothesis that the gallium-phosphorus bond should be stabilized by pi-bonding. Our hypothesis of pi-bonding stems from our kinetic observations and the reduced reactivity of R_2MPPh_2 as an amphoteric ligand toward transition metals.

The compounds [(Me_3CCH_2)$_2$InPPh$_2$] and [(Me_3CCH_2)$_2$InCH$_2$PPh$_2$]$_2$ will be characterized by X-ray structural studies. Our goal in these studies will be to compare indium-phosphorus bond lengths. If (Me_3CCH_2)$_2$InPPh$_2$ has some pi-bonding, the In-P bond lengths in the corresponding dimer might be different than those in [(Me_3CCH_2)$_2$InCH$_2$PPh$_2$]$_2$, a molecule which will have only donor-acceptor bonds.

Our chemistry of amphoteric ligands will continue with the complete synthesis and characterization, including X-ray structural studies, of $Cr(CO)_5[PPh_2CH_2MR_2\cdot NMe_3]$ (M=Ga, In; R=CH_2SiMe_3, CH_2CMe_3). The potential of the ligand $R_2MCH_2PPh_2$ for novel compounds will be pursued by studying its reactions with $Fe_2(CO)_9$ and $Fe(CO)_5$. Our goal is to prepare a five coordinate transition metal derivative of an amphoteric ligand.

Our understanding of the chemistry of amphoteric ligands will be enhanced by X-ray structural studies of Me$_2$GaNMe[(phenyl)Cr(CO)$_3$] and (mesityl)$_2$Ga[mesitylMo(CO)$_3$]. The compound Me$_2$GaN(Me)[(phenyl)Cr(CO)$_3$] might exist as a dimer with gallium-nitrogen bonds, a polymer or a monomer with gallium-nitrogen pi-bonding. This insoluble compound is resistent to characterization by typical laboratory methods. Attempts will also be made to prepare and fully characterize Ph$_2$P-Ga[mesitylMo(CO)$_3$]$_2$, a compound with possible gallium-phosphorus pi-bonding.

g. Graduate Students Currently Working on Project:

John C. Pazik
Tommie L. Royster
Michael A. Banks
John D. Maloney

h. Technical Reports Submitted to ONR During Past Year:

(1) O. T. Beachley, Jr.; L. Victoriano, "The Elimination-Condensation Reaction Between Dimethylaluminum Hydride and Methylphenylphosphine".

(2) O. T. Beachley, Jr.; M. R. Churchill; J. C. Fettinger; J. C. Pazik; L. Victoriano, "Synthesis and Crystal and Molecular Structure of $In(C_5Me_5)$-An Apparent Octahedral Cluster".

(3) O. T. Beachley, Jr.; R. B. Hallock, "The Synthesis of Tris(pentamethylcyclopentadienyl)gallium(III)".

(4) O. T. Beachley, Jr.; M. R. Churchill; J. C. Pazik; J. W. Ziller, "Synthesis, Characterization and Crystal and Molecular Structure of Trimesitylgallium(III)".

(5) O. T. Beachley, Jr.; J. P. Kopasz; H. Zhang; W. E. Hunter; J. L. Atwood, "Synthesis and Charaterization of Amphoteric Ligands Including the Crystal and Molecular Structure of $[(Me_3SiCH_2)_2InPPh_2]_2$".

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